

SYMPOSIUM H

Functional and Multifunctional Oxide Films

November 29 - December 3, 2004

Chairs

Chang-Beom Eom

Dept. of Materials Science & Engineering
University of Wisconsin-Madison
Rm. 2164 ECB
1550 Engineering Dr.
Madison, WI 53706
608-263-6305

Darrell G. Schlom

Dept. of Materials Science & Engineering
Pennsylvania State University
108 Materials Research Inst. Bldg
University Park, PA 16802-6602
814-863-8579

Jean-Marc Triscone

DPMC
University of Geneva
24 Quai E.-Ansermet
1211 Geneva, 4 Switzerland
41-22-379-6827

David Norton

Dept. of Materials Science & Engineering
University of Florida
106 Rhines Hall
Gainesville, FL 32611-6400
352-846-0525

Symposium Support

Swiss National Centre of Competence in Research
Materials with Novel Electronic Properties - MaNEP

* Invited paper

8:15 AM *H1.1

Computational Design of Multifunctional Oxides.

Nicola A. Spaldin, Pio Baettig and Claude Ederer; Materials Department, University of California, Santa Barbara, California.

In this talk we show how modern theoretical and computational methods can be used to design technologically relevant oxides with dual- or multi-functionality. We choose multiferroic magnetoelectrics as an example; these are materials that are both ferromagnetic and ferroelectric in the same phase, and therefore have a spontaneous magnetization which can be switched by an applied magnetic field, a spontaneous polarization which can be switched by an applied electric field, and often some coupling between the two. Very few exist in nature, or have been synthesized in the laboratory, so we begin by determining the reason for the scarcity of ferromagnetic ferroelectric coexistence. Then we identify the chemistry behind the additional electronic or structural driving forces that must be present for ferromagnetism and ferroelectricity to occur simultaneously. Finally we describe the successful prediction and subsequent synthesis of new multiferroics and discuss the limitations that fundamental physics imposes on their potential applications.

8:45 AM *H1.2

Nonlinear Optical Probing of Ferroic and Multiferroic Complex Oxide Thin Films. Venkatraman Gopalan¹, Alok

Sharan¹, Aravind Vasudevarao¹, Yulan Li¹, Long-qing Chen¹, Darrell Schlom¹, J. Schubert³, K. J. Choi², Chang-Beom Eom², R. Uecker⁴ and P. Reiche⁴; ¹Materials Science and Engineering, Penn State University, University Park, Pennsylvania; ²Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; ³Institut für Schichten und Grenzflächen ISG1-IT, Forschungszentrum Jülich GmbH, Jülich, Germany; ⁴Institute of Crystal Growth, Berlin, Germany.

Ferroic and multiferroic materials have a rich array of cross-coupled phenomena ranging from ferroelectricity, ferromagnetism, ferroelasticity, piezoelectricity, pyroelectricity, magnetoelectricity, piezomagnetism, electro-optic, magneto-optic, elasto-optic and nonlinear optical effects. In thin film form, complex domain microstructures, their dynamics, and phase transitions can be a challenge to study, particularly when direct electrical measurements are not feasible due to dielectric losses, and structural distinctions between domain variants is too small to detect through conventional means. This talk presents nonlinear optical probing, particularly through second harmonic generation, as a powerful quantitative means of probing complex domain dynamics in real time under external influences such as electric fields and temperature. Specific example systems of epitaxially strained ferroelectric systems of BaTiO₃ and SrTiO₃ with giant ferroelectric enhancement, and ferroelectricity in multiferroic system of BiMnO₃ will be discussed. Large enhancements in higher order nonlinear optical effects such as nonlinear absorption and nonlinear refraction in Bi-based ferroics will also be presented.

9:15 AM H1.3

Large Second Harmonic Generation (SHG) in GaFeO₃ pulsed laser deposited thin films on YSZ buffered silicon.

Darshan C. Kundaliya¹, S. B. Ogale¹, S. E. Lofland², Keith McDonald², Ernst Knoesel², S. R. Shinde¹ and T. Venkatesan¹; ¹Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland; ²Department of Chemistry and Physics, Rowan University, Glassboro, New Jersey.

Gallium Iron Oxide (GaFeO₃) is a compound which exhibits ferromagnetic and piezoelectric properties simultaneously. This kind of non-centrosymmetric polar ferromagnet also produces giant magneto-optical Kerr effect (MOKE) as reported recently in a single crystal [1]. We report the epitaxial growth of GaFeO₃ thin films on silicon with a Y-ZrO₂ (YSZ) buffer layer and without chemical removal of the surface oxygen on silicon. The X-ray diffraction pattern shows c-axis orientation of YSZ and b-axis orientation of GaFeO₃ on Si (100) substrate. Ferromagnetic transition temperature (T_C 220 K) is in good agreement with the bulk data. We performed the analyzer angle dependence of second harmonic light at room temperature (above T_C) and at 150K (below T_C) to explore the nonlinear Kerr rotation. The nonlinear Kerr rotation angle (ϕ) is large (17 degree) below T_C . Above T_C , the second harmonic light is completely polarized from vanishing magnetic component. Work supported under DARPA (# N000140210962) and NSF-MRSEC (# DMR-00-80008) [1]Y. Ogawa, Y. Kaneko, J.P. He, Z.Z. Yu, T. Arima and Y. Tokura, PRL 92, 047401 (2004)

9:30 AM H1.4

Multiferroic BiFeO₃ Thin Films. Junling Wang¹, Haimei Zheng¹, Manfred Wuttig¹, Jiefang Li², Feiming Bai², Dwight Viehland² and R. Ramesh³; ¹Department of Materials Science and Engineering, University of Maryland, College Park, Maryland; ²Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia; ³Department of Materials Science and Engineering, University of California, Berkeley, California.

Multiferroic materials have attracted many research activities recently. Among all the choices, BiFeO₃ is of particular interests because of its simple structure and the coexistence of ferroelectric (T_C 1100K) and antiferromagnetic (T_N 640K) orders at room temperature. Properties of BiFeO₃ have been puzzling. (1) Reported polarization value ($< 10 \mu\text{C}/\text{cm}^2$) is very small for a ferroelectric material with such a high Curie temperature. (2) Its G-type antiferromagnetic spin configuration is subjected to a spiral modulation. We have successfully deposited highly resistive BiFeO₃ thin films using pulsed laser deposition. (001), (110) and (111) cut SrTiO₃ substrates were used to control the film orientation. Much larger polarizations were observed for all three orientations (55 $\mu\text{C}/\text{cm}^2$ for (001) films, 80 $\mu\text{C}/\text{cm}^2$ for (101) films, and 100 $\mu\text{C}/\text{cm}^2$ for (111) films). We will also report our results on the dielectric and piezoelectric responses along the different crystallographic directions, as well as the field and temperature dependence magnetic property characterized by SQUID. This work is supported by the Office of Naval Research (grant #s, MURI N000140110761, N000140210340, N000140210126) and the National Science Foundation (grant #s MRSEC DMR-00-80008).

10:15 AM H1.5

Giant Ferroelectric Polarization in Multiferroic BiFeO₃ Thin Films. Kwi-Young Yun¹, Dan Ricinchi¹, Minoru Noda¹, Saburo

Nasu² and Masanori Okuyama¹; ¹Department of Systems Innovation, Osaka University, Osaka, Japan; ²Department of Physical Science, Osaka University, Osaka, Japan.

Bismuth ferrite (BiFeO₃, BFO) has attracted considerable interest recently due to its giant ferroelectric polarization (GFP) and multiferroic properties (simultaneously exhibiting ferroelectric and magnetic ordering). Prepared in thin film form, it has shown a much larger remanent polarization than that in bulk. This was attributed to the high sensitivity of polarization to small changes of the crystalline structure and lattice parameters of the film heteroepitaxially constrained to the single crystal substrate. The 300nm-thick BFO thin films have been deposited on Pt/TiO₂/SiO₂/Si substrates by PLD. The oxygen pressure was 0.05 Torr and the deposition temperature was fixed at 450°C. Pt top electrodes with 240 μm diameter have been formed by rf-sputtering. The room-temperature (RT) X-ray diffraction measurement indicates that the BFO thin films grown on Pt/TiO₂/SiO₂/Si substrate consist of polycrystalline perovskite of single-phase with the lattice parameters of $a = 0.393$ and $c = 0.400$ nm. Ferroelectric polarization vs. electric field ($P - E$) hysteresis loop of BFO thin film was measured in 1 kHz triangular waveform at various temperatures of 90 K to RT. The remanent polarization (P_r) at RT is 102 $\mu\text{C}/\text{cm}^2$, which is considerably higher than previously reported for BFO. Moreover, decreasing the temperature down to 90 K allowed us to obtain GFP such as P_r of 146 $\mu\text{C}/\text{cm}^2$ and a saturation polarization (P_s) of 158 $\mu\text{C}/\text{cm}^2$ with a coercive field of 120 kV/cm at 20 V maximum applied voltage. These values are the highest in ferroelectric materials ever-measured so far. We obtained good reproducibility of these values of polarization when changing the measured capacitor. The hysteresis loops at 90 K have a saturated rectangular shape and do not show evidence of large leakage current when measured at 1 kHz frequency. The memorized polarization during a standard retention measurement of our BFO thin films has been well maintained. In addition, the BFO thin films have shown good multiferroic properties. The magnetization-magnetic field ($M - H$) loops of the films measured at RT show a well-saturated weak ferromagnetic hysteresis characteristic with saturation magnetization M_s of 40 emu/cm³ for a maximum magnetic field of 10 kOe. The piezoelectric hysteresis loop of the films measured by AFM also show a piezoelectricity of 66 pm/V, which is comparable to the value obtained from epitaxial BFO thin films on STO single crystal substrate.

10:30 AM H1.6

Systematic investigation of multiferroic properties in the Bi(Fe,Sc)O₃ system using thin film composition spreads.

Makoto Murakami¹, Maria A. Aronova¹, Toyohiro Chikyow², Susan Trolier-McKinstry³, S. E. Lofland⁴, K. McDonald⁴, E. Knoesel⁴ and Ichiro Takeuchi¹; ¹Materials Science & Engineering, University of Maryland, College Park, Maryland; ²NIMS, Tsukuba, Ibaraki, Japan; ³Ceramic Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; ⁴Physics and Astronomy, Rowan University, Glassboro, New Jersey.

BiFeO₃ (BFO) is known to be a multiferroic material where ferroelectric and ferromagnetic properties coexist. We are systematically exploring properties of solid solutions where the B-site of BFO is continuously substituted. In particular, we have fabricated BFO - BiScO₃ (BSO) composition spreads in order to investigate their properties as a function of continuously changing composition. The composition spreads were fabricated using our combinatorial pulsed-laser deposition technique. We have found that BFO can be grown epitaxially on SrTiO₃ (001) (STO) and on epitaxial SrRuO₃ (SRO) on STO (001) [SRO/STO] which is used as a bottom electrode for capacitance measurements. In comparison, BSO does not grow on STO (001) directly, but it grows on BFO buffered STO (001). Thus, in order to obtain epitaxial BFO - BSO composition-spread thin films, BFO buffer layer is necessary. Crystal structure of the composition spread thin films was characterized by micro x-ray diffraction. The lattice constant was found to increase as one approach the pure BFO end of the spread. We observed a sudden change in the lattice constant at the BSO composition of 40-60% characteristic of a structural phase transition. Dielectric constant and loss tangent delta were found to continuously increase as the BFO concentration was increased. Second harmonic generation (SHG) was used to investigate the ferroic properties of the spread. The largest SHG was observed at pure BFO and decreased continuously with the addition of BSO, for both the S and P polarizations, suggesting that the ferroic properties degrade with BSO, in agreement with the dielectric measurements.

10:45 AM H1.7

Artificial Magnetolectric Multiferroic Superstructures.

Arjen Molag, Guus Rijnders and Dave H. A. Blank; Fac. of Science & Technology and MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands.

Multiferroic materials exhibit two or more of ferroelectricity, ferromagnetism and ferroelasticity. Materials that exhibit both ferroelasticity and ferroelectricity or ferromagnetism are relatively well known. However, only a limited number of materials are both ferroelectric and ferromagnetic. These magnetolectric multiferroic materials are both of theoretical interest, in elucidating just why they are so scarce, and of practical interest, in for example the application in memory devices or actuators/transducers. The synthesis of magnetolectric multiferroics, such as BiMnO₃ and YMnO₃, is complicated, especially in thin film form. Artificial heterostructures, such as alternating layers of ferromagnetic and ferroelectric materials, are useful to understand the nature of the interactions between them. In our study, we constructed artificial heterostructures of the ferromagnetic SrRuO₃ and the ferroelectric SrTiO₃ with individual layer thicknesses ranging from 1 to 10 unit-cell layers. We present structural, electrical and magnetic measurements of this model system for an artificial multiferroic compound.

11:00 AM *H1.8

Multifunctional Complex Oxide Heterostructures. R. Ramesh, Department of Materials Science & Engineering and Department of Physics, University of California-Berkeley, Berkeley, California.

In this talk, I would like to describe to you some of the recent developments in the field of complex oxide materials. These materials, such as perovskites, exhibit a rich spectrum of functional responses, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc. The functional responses can typically be described (in thermodynamics terms) through the conjugate pair (strain and stress; polarization and electric field, magnetization and magnetic field). There exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics. Using our work in the field of ferroelectrics and ferromagnetics as the background, we are now exploring such materials, as epitaxial thin films as well as nanocomposites. Specifically, we are studying the role of thin film growth, heteroepitaxy and processing on the magnitude of the coupling between the order parameters. A very exciting new development has been the discovery of the formation of spontaneously assembled nanostructures consisting of a ferromagnetic phase embedded in a ferroelectric matrix that exhibit very strong coupling between the two order parameters. This involves 3-dimensional heteroepitaxy between the substrate, the matrix perovskite phase and spinel phase that is embedded as single crystalline pillars in this matrix. This epitaxial coupling is critical and is responsible for the significantly higher magnetolectric coupling and magnetic anisotropy in such vertical heterostructures compared to a conventional heterostructure. This work is supported by the UMD-MRSEC and by the ONR under a MURI program.

11:30 AM H1.9

Multiferroic Perovskite-Spinel Oxide Nanostructures.

Haimei Zheng¹, Junling Wang¹, F. Zvaliche¹, L.

Mohaddes-Ardabili¹, D. G. Schlom² and R. Ramesh³; ¹Department of Materials Science and Engineering, University of Maryland, College

Park, College Park, Maryland; ²Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; ³Department of Materials Science and Engineering and Department of Physics, University of California, Berkeley, California.

Ferroelectric/ferrimagnetic perovskite-spinel oxide nanostructures have been synthesized by pulsed laser deposition. Spinel phase i.e. CoFe₂O₄, or NiFe₂O₄ and perovskite phase i.e. BaTiO₃, BiFeO₃ spontaneously separated during heteroepitaxial growth on single crystal SrTiO₃ (001) substrates with or without bottom SrRuO₃ electrodes. The ferrimagnetic phase forms nano-pillar arrays embedded in a ferroelectric matrix. The growth of the nanostructures is a process directed by both thermodynamic equilibrium and kinetic diffusion. Magnetic measurements exhibit that all the films have a large uniaxial magnetic anisotropy with an easy axis normal to the film plane. It is calculated that stress anisotropy is the main contribution to the anisotropy field. We measured the ferroelectric and piezoelectric properties of the films, which correspond to the perovskite phase. The coupling between the two order parameters of polarization and magnetization was illustrated in the BaTiO₃-CoFe₂O₄ system by a change in magnetization at the ferroelectric Curie temperature. This work is supported by the NSF-MRSEC under contract No. DMR-00-80008.

SESSION H2: Strain Engineering of Ferroics

Chairs: Long-Qing Chen and R. Ramesh

Monday Afternoon, November 29, 2004

Grand Ballroom (Sheraton)

1:30 PM *H2.1

Microscopic and "Macroscopic" First-Principles Modeling of Functional Oxide Thin Films and Superlattices. Karin M. Rabe, Physics and Astronomy, Rutgers University, Piscataway, New Jersey.

With continuing advances in computational algorithms and hardware, it is now possible to carry out first-principles density-functional-theory calculations of the structure and electrical and magnetic properties of structurally and chemically complex systems, including superlattices and thin films of perovskite oxides. Despite some limitations in the types of systems that can be studied and in the accuracy in the prediction of certain quantities, an active theoretical-experimental dialogue is underway. Modeling based on the first-principles results has emerged as the key to making the bridge between theory and experiment. Our first-principles models include both "macroscopic" and microscopic atomic-scale effects. The former involve coupling of the film and substrate (or layers in a superlattice) through macroscopic electric fields and epitaxial strain, with the effects of applied fields and stresses being taken to be those of the bulk, computed from first principles. Strain enhancement of the spontaneous polarization, epitaxial stabilization of non-bulk phases, thickness dependence of the ferroelectric instability via incomplete compensation of the depolarization field, formation of dipolar layers by charge transfer, band bending, and ferroelectric field effects on the conductivity and optical properties of the substrate can all be described, at least semi-quantitatively, in this framework. For a fuller understanding, especially for systems with unlike constituents, it is important also to characterize the microscopic atomic-scale effects at the interface and surfaces: surface and interface reconstructions, changes in stoichiometry, and the crystal and electronic structures of buffer layers introduced to facilitate epitaxy. These modifications at the interface can give rise to properties completely distinct from those of the constituents, and offer rich opportunities for multifunctional materials design. Illustrations drawn from recent first-principles work at Rutgers on BaTiO₃ and PbTiO₃ ultrathin films on SrTiO₃, BiFeO₃ thin films, layered perovskites, BaTiO₃/SrTiO₃ superlattices and other prototypical systems, and connections to relevant experimental studies, will be presented.

2:00 PM H2.2

Structure of SrTiO₃ Films on DyScO₃ (110) Substrates.

D. D. Fong¹, M. D. Biegalski², M. A. Zurbuchen¹, J. A. Eastman¹, P. H. Fuoss¹, S. K. Streiffer¹, S. Trolier-McKinstry², D. G. Schlom², R. Uecker³ and P. Reiche³; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania; ³Institute of Crystal Growth, Berlin, Germany.

Due to the structural nature of the ferroelectric instability, the ferroelectric transition is highly sensitive to the mechanical boundary conditions placed on a material. By tuning the amount of misfit strain in epitaxial thin films, it is possible to elevate the transition temperature hundreds of degrees above its unstrained value [1, 2], or even to induce a ferroelectric transition in what is normally a non-ferroelectric material, as recently demonstrated for the case of SrTiO₃ films grown on DyScO₃ substrates [3]. In this study, we use in

situ synchrotron x-ray scattering at the Advanced Photon Source to characterize the strain state of SrTiO₃ epitaxial films grown on DyScO₃ (110) substrates by MBE, as a function of film thickness at various temperatures and oxygen partial pressures. The films range from 5 to 100 nm in thickness. We find that the critical thickness lies between 25 and 50 nm, in agreement with RHEED performed in situ during MBE growth. Films both below and above the critical thickness display extremely high structural quality, with rocking curve widths less than 20 arcseconds in all cases, the best ever reported for perovskite films. Interestingly, films above the critical thickness show only small amounts of strain relaxation, even after high temperature annealing. These results will be discussed in the context of models for strain relaxation in epitaxial films and in the light of previous work on dislocations formed in SrTiO₃. We will discuss the implications of these results on optimizing the material properties of SrTiO₃ by strain variation. 1. S. K. Streiffer et al., Observation of Nanoscale 180° Stripe Domains in Ferroelectric PbTiO₃ Thin Films Phys. Rev. Lett. **89**, 067601 (2002). 2. D. D. Fong et al., Ferroelectricity in Ultrathin Perovskite Films Science **304**, 1650 (2004). 3. J. H. Haeni et al., Room-Temperature Ferroelectricity in Strained SrTiO₃ (to be published in Nature).

2:15 PM H2.3

Giant Enhancement of Ferroelectricity in Strained BaTiO₃ Thin Films. K. J. Choi¹, C. B. Eom¹, M. Biegalski², Y. L. Li², A. Sharan², Long-qing Chen², V. Gopalan² and D. G. Schlom²; ¹Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; ²Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

Epitaxial ferroelectric thin films have different properties from the bulk single crystals due to epitaxial and thermal strain and substrate constraints and it offers opportunity to modify the various ferroelectric properties. We deposited fully commensurate BaTiO₃ (a = 3.992 Å) ferroelectric thin films on novel substrates including (110) DyScO₃ (a = 3.944 Å) and (110) GdScO₃ (a = 3.97 Å) by pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) and observed ferroelectric transition using temperature dependent (room temperature to 900 oC) four-circle x-ray diffraction and second harmonic generation measurements. Biaxial compressive strain dramatically enhanced the ferroelectric properties-both the ferroelectric transition temperature (T_c) and remnant polarization (Pr)-of BaTiO₃ thin films. This strain, imposed by commensurate epitaxy, can result in a T_c nearly 500 K higher and a Pr at least 250% higher than BaTiO₃ single crystals. This is the largest increase in T_c ever reported for a ferroelectric. These giant property enhancements are consistent with thermodynamic predictions. This work demonstrates a route to a lead-free ferroelectric with the high T_c and high Pr needed for ferroelectric memories, and also a general means for achieving extraordinary physical properties in thin films through strain engineering.

2:30 PM H2.4

Non-Linear Optical Probing of Enhanced Ferroelectricity in Strained SrTiO₃ and BaTiO₃ Epitaxial Films. Alok Sharan¹, Aravind Vasudeva Rao¹, Mike Biegalski¹, Yulan L. Li², Long Qing Chen², Darrell G. Schlom^{1,2}, Venkatraman Gopalan^{1,2}, Kyoung Jin Choi³ and Chang Beom Eom³; ¹Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; ²Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; ³Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Second Harmonic Generation is used for *in-situ* probing of ferroelectric domain reversal and phase transitions in strained SrTiO₃ and BaTiO₃ thin films on unique scandate substrates. Recently we have grown commensurately strained structures of epitaxial SrTiO₃ and BaTiO₃ thin films using unique scandate substrates, such as GdScO₃ and DyScO₃. Enormous compressive strains (up to 1.5%) have been imparted to thin films to shift the Curie temperature, T_c by hundreds of degrees. This can produce room-temperature ferroelectricity in strontium titanate, a material that normally is not ferroelectric at any temperature. In BaTiO₃, the T_c is shifted from 120C for bulk crystals to 650C for thin films on DyScO₃. This talk will present real-time second harmonic generation experiments and modeling to probe these dramatic changes the Curie temperature, and to probe the real-time dynamics of domain reversal under external fields in these strained films beyond their normal Curie temperatures where domains are not expected at all.

2:45 PM H2.5

Effect of Strain and Heterointerfaces on Polarization Enhancement in Atomic-Scale Three-Component Perovskite Superlattices. Ho Nyung Lee, Matthew F. Chisholm, Hans M. Christen, Christopher M. Rouleau and Douglas H. Lowndes; Condensed Matter Sciences Division, Oak Ridge National Laboratory,

Oak Ridge, Tennessee.

Epitaxial perovskite superlattices provide an effective platform to combine, modify, and improve the physical properties of complex materials. In particular, theoretical considerations indicate that significant strain-enhancement of the ferroelectric polarization is to be expected under the appropriate circumstances. While pulsed laser deposition (PLD) has previously been shown to yield perovskites with excellent physical properties without the requirement for post-treatment, there has been only limited success in applying PLD to the formation of superlattices in which each constituent layer is controlled with atomic precision. The challenge lies both in producing lattice-matched conducting electrodes with sufficient quality and in appropriately choosing the deposition parameters. To this end, we have established a PLD synthesis regime to produce atomically-flat SrRuO₃ bottom electrodes on single-stepped (001) SrTiO₃ single crystals, onto which nearly perfect heterostructures can be grown. Perovskite-type oxide heterostructures with atomically-flat interfaces, and single unit-cell steps on the surface, have been grown on such substrates by PLD at 700 °C in 10 mTorr O₂. The heterostructures were atomic-scale asymmetric three-component superlattices (TCSs) comprised of BaTiO₃, SrTiO₃, and CaTiO₃ layers. Well-pronounced, regular oscillations of the reflection-high energy electron diffraction (RHEED) specular spot were recorded over the entire growth of TCS structures, even for those having total thicknesses in excess of 1000 nm (2500 individually controlled layers)! For those structures having an in-plane lattice constant equal to that of the substrate we recorded increased ferroelectric polarization – one TCS, for example, having a BaTiO₃ layer fraction as little as 50%, had $2P_r \approx 33 \mu\text{C}/\text{cm}^2$, an increase of almost 50% as compared to a BaTiO₃ single film! Most strikingly, however, was the effect of heterointerfacial strain on polarization enhancement. This type of enhancement was present only if the in-plane lattice parameter of the TCS was *locked* to that of the substrate, thereby yielding a stronger tetragonal distortion of BaTiO₃. This was seen to occur only if the BaTiO₃ thickness did not exceed the combined value for the SrTiO₃ and CaTiO₃ layers. Furthermore, we found strong evidence of compositionally-broken inversion symmetry within the TCSs as evidenced by a distinct asymmetry in the measured ferroelectric hysteresis curves. In addition to presenting the synthesis and structure-property relationship of such atomic-scale three-component perovskite superlattices, we will thus also discuss potential enhancements to the ferroelectric polarization due to the local asymmetry. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, as part of a BES NSET initiative.

3:30 PM H2.6

Contribution of Strain Gradients to the Size Effect in Ferroelectric Thin Films. Gustau Catalan¹, Marty Gregg² and Lesley Sinnamon²; ¹Materials Science Center, University of Groningen, Groningen, Netherlands; ²Department of Pure and Applied Physics, Queen's University of Belfast, Belfast, Northern Ireland, United Kingdom.

We have identified strain gradients as one of the key contributing factors to the so-called size effect (the decrease of permittivity of ferroelectric thin films relative to bulk). Strain gradients may couple to ferroelectric polarisation through the flexoelectric effect. By including flexoelectricity in the phenomenological Landau-Ginzburg-Devonshire description of the ferroelectric transition, it is shown that strain gradients have the effect of suppressing the dielectric singularity at the Curie temperature, thereby reducing the dielectric constant. This reduction is shown to be more pronounced for the thinner films, and, importantly, it is independent of the sign of the strain or the strain gradient, consistent with universally observed features of the size effect. Other consequences of the flexoelectric contribution, such as the changes on the polarisation, or the splitting of the Curie temperature into three significant transition temperatures, will also be discussed, and contrasted with the predictions from the homogeneous-strain case.

3:45 PM H2.7

Strain-Mediated Enhancement of Polarization in an Epitaxial PZT: LSMO Heterostructure at the Paramagnet-Ferromagnet Transition. Tom Wu, M. Zurbuchen, S. Saha, J. F. Mitchell and S. K. Streiffer; Materials Science Department, Argonne National Laboratory, Argonne, Illinois.

Materials with complimentary coupling between the electric, magnetic and structural order parameters are of fundamental and technological importance. Such a magnetoelectric (ME) effect has been realized in both single-phase materials such as YMnO₃ and composites of bonded thick piezoelectric/ferromagnetic layers. Attempts to harness this effect in epitaxial heterostructures grown on substrates such as SrTiO₃ show little effect because of the clamping effect of the substrate. Here, we report a unique heterostructure composed of a

tetragonal composition lead zirconate titanate (PZT) layer epitaxially deposited on a layered manganese single crystal of composition $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. We find a strong strain-mediated coupling between the ferromagnet and the ferroelectric due to the epitaxial nature of the interface and the bulk mechanical distortions of the single-crystal substrate. The manganite crystal has been shown by neutron diffraction to exhibit a strong, anisotropic lattice anomaly at T_C , with an expansion of the in-plane axis $\Delta a/a = 0.1\%$. This tensile strain induces an approximate 20% enhancement of the out-of-plane polarization of the PZT layer as temperature is reduced across T_C . We will discuss results on various combinations of ferroelectric and ferromagnetic materials that vary the sign of the coupling across T_C . The known magnetic field dependence of the lattice anomaly in the manganite system suggests that a large magneto-electric effect should be possible in these structures.

4:00 PM H2.8

Tunable anisotropic in-plane strain relaxation in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ epitaxial thin films. Ingrid C. Infante, Florencio Sanchez and Josep Fontcuberta; Institut de Ciencia de Materials - CSIC, Bellaterra, Spain.

Magnetotransport properties of epitaxial thin films of manganites are known to depend sensitively on substrate induced strains. Indeed, it has been claimed that stress-induced structural elastic deformations are at the origin of the commonly observed depression of the Curie temperature of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (LCMO) nanometric films when grown, fully strained, on (001)-oriented SrTiO_3 (STO) substrates. For many applications, knowledge and control of the in-plane magnetic anisotropy would be highly desirable as it may allow, for instance, coherent magnetic switching. However, in-plane magnetic anisotropy of (001)-LCMO films is moderate and improvements and alternatives would be required for some applications. In this paper we shall report on the growth and characterization of (110)-LCMO on (110)-STO substrates. Epitaxial films with thicknesses (t) varying from 10 to 110nm were grown by rf magnetron sputtering and structural, morphological and magnetic properties were exhaustively investigated. For comparison purposes, (001)-LCMO films were grown simultaneously on (001)-STO substrates. The magnetic characterization revealed that films on (110)-STO substrates have -indefectively- a higher Curie temperature and larger saturation magnetization than (001) films. X-ray reciprocal space mapping was done to accurately evaluate in-plane and out-of-plane lattice parameters as a function of film thickness. It turned out that (110) films relaxed faster than (001) films. More remarkably, we found that in (110) films, there is a huge in-plane anisotropic strain and anisotropic strain relaxation that reduces as film thickness increases. It is found that films are strained along the [001] direction but gradually more relaxed along [1-10]. Observation of in-plane anisotropic strain relaxation is not without surprise, and it shall enlighten the mechanisms of epitaxy formation in complex oxides. Accompanying the anisotropic strain, the (110) films display prominent in-plane magnetic anisotropic properties: the magnetic hard axis is always aligned along the more relaxed ([1-10]) direction, whereas the more strained direction ([001]) remains the easy magnetization axis. We will discuss on the origin of structural anisotropic relaxation in this system and its impact on the properties of the films. The observation that the in-plane magnetic anisotropy is controlled by the anisotropic film strain, which itself can be modified by the film thickness, clearly indicates the magnetoelastic origin of the anisotropy in (110) films. This contrasts with the magneto-crystalline dominated anisotropy in (001) films. Perspectives for exploiting the tunable in-plane anisotropy and extension of these findings to other functional oxidic materials will be also addresses.

4:15 PM H2.9

Investigation on Room Temperature Operation of Resistive Bolometer with Strain Induced Thin Film of $\text{La}_0.8\text{Ba}_0.2\text{MnO}_3$. Hideaki Touyama, Hidekazu Tanaka and Tomoji Kawai; The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan.

The strain induced perovskite-type manganese oxide of $\text{La}_0.8\text{Ba}_0.2\text{MnO}_3$ (LBMO) thin film deposited on $\text{SrTiO}_3(001)$ substrate is studied from the view point of application for uncooled resistive bolometer. We previously found that the tensile strain can increase Curie temperature up to 320K with film thickness of around 20nm [1], and we can tune the metal-insulator transition temperature, where temperature coefficient of resistivity (TCR) become large, around room temperature. The thin film was grown by pulsed laser deposition technique at the substrate temperature of 730C in oxygen atmosphere of 0.1 Pa, followed by post-annealing at 850C for 7 hours in oxygen flowing. The maximum value of temperature coefficient of resistivity of epitaxial film can be more than 4 % - 6 %/K at room temperature (300K) with relatively low resistivity of 0.005 Ωcm . The minimal sensor structure was constructed and the fundamental sensor performance was investigated. Uncooled operation of the

bolometer was confirmed by irradiating IR from a heat source. The achieved responsivity and response time can be around 0.7 V/W and 180 msec, respectively. At room temperature, it was shown that the prosperous sensor could successfully detect the IR from human body. We will also discuss the low frequency noise (1/f noise) which gives influence on sensor performance. [1] T. Kanki et al. Phys. Rev. B64, 184404 (2001)

4:30 PM H2.10

Evidence for Strain Induced Phase Separation in Ultrathin $\text{La}_{0.8}\text{MnO}_{3-\delta}$ Films. Michael A. DeLeon¹, Trevor Tyson¹, Catherine Dubourdieu², Joseph Dvorak³ and Dario Arena⁴; ¹Applied Physics, New Jersey Institute of Technology, Newark, New Jersey; ²Physics, CNRS, Grenoble, France; ³NLSL, Brookhaven National Labs, Upton, New York; ⁴Physics, Rutgers University, New Brunswick, New Jersey.

The magnetic and transport studies have been conducted on $\text{La}_{0.8}\text{MnO}_{3-\delta}$ films of thickness varying from 60 to 1600Å. While all films show metal-like behavior in transport measurements, the magnetic studies show a strong thickness variation- depending on the length scale probed. Bulk magnetization measured with a SQUID magnetization reveal that films with thickness 1600, 300 and 60Å have magnetization ratios of 1:0.75:0.57. Measurement of the top 60 Å of the films measured by XMCD reveals that the ferromagnetic components of the films are similar. Hence, the low total moment found in the films by SQUID measurements suggest the existence of another non-magnetic component in the thin films - which increases with reduced film thickness. Structural measurements on multiple length scales will be combined the transport and magnetic measurements to ascertain the nature of the insulating phase and determine the relative volume.

4:45 PM H2.11

Effect of Three Dimensional Strain States on Magnetoelectric Properties of BiFeO_3 Thin Films. Rasmi R. Das, Dong Min Kim and Chang-Beom Eom; Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Multifunctional oxides have drawn considerably attention due to the flexibility of using the same material for variety of functional devices. The coupling of different order parameters and their control to design a specific material system is crucial and need to be understood. BiFeO_3 has been reported to have both ferroelectric, with saturated polarization of 6 $\mu\text{C}/\text{cm}^2$, and weak magnetic behavior in the bulk form. However, thin films (<100 nm) of BiFeO_3 showed an order of magnitude higher value of remanent polarization (60 $\mu\text{C}/\text{cm}^2$) and saturated magnetization, which believed to be due to the substrate induced strain states in the lattice. In order to understand the three dimensional strain states, we have studied the thickness dependant magnetoelectric properties of BiFeO_3 thin films on various perovskite substrates. Structural and microstructural characterization of the films was carried out using x-ray diffraction and atomic force microscopy. The electrical properties and magnetic properties of the films were correlated to the thickness dependant strain states. The detailed epitaxial film fabrication and magnetoelectric properties of BiFeO_3 will be presented with close correlation to the film thicknesses and the three dimensional strain states.

SESSION H3: Poster Session: Multiferroics, Strain Engineering of Ferroics, Ferroelectrics/Piezoelectrics
Chairs: Simon Phillpot and Nicola Spaldin
Monday Evening, November 29, 2004
8:00 PM
Exhibition Hall D (Hynes)

H3.1

Effect of BaTiO_3 on Electrical and Structural Properties of BiFeO_3 Thin Films. Rajasekarakumar Vadapoo, Pijush Bhattacharya and Ram S. Katiyar; Physics, University of Puerto Rico, San Juan, Puerto Rico.

The multiferroic BiFeO_3 (BFO) perovskite exhibits both ferroelectricity and magnetism. This unique property makes it attractive for a variety of technological applications like tunable sensors and memory devices. It is difficult to synthesize phase pure BiFeO_3 by conventional calcinations process. It was reported that calcinations using rapid thermal processing produced single phase BFO. In this work, a series of calcination was carried out at different temperatures from 800°C to 880°C in steps of 20°C for 8 minutes. The XRD analysis showed that the formation of secondary phases is highly dependent upon the processing parameters and almost phase pure BFO formed at the calcination temperature of 860°C. It is well known that BFO usually has high dc leakage current. To reduce the leakage current, 0.7 BiFeO_3 -0.3 BaTiO_3 (BFO-BT) solid solutions

were synthesized. The calcination temperatures were varied from 800°C to 920°C in steps of 20°C for 8 to 20 minutes. XRD analysis confirmed that the phase pure material has synthesized at the calcinations temperature of 900°C for 20 minutes. The sintered BFO pellets have been used as a target for the preparation of thin films on platinum coated silicon substrates using pulsed laser deposition at various O₂ pressures and substrate temperatures. The room temperature dielectric constant and the loss tangent are 111.2 and 0.08 respectively at 100 kHz for the BFO thin films deposited on the platinum coated silicon substrate with a thickness of 600 nm. However, no saturated ferroelectric hysteresis was obtained in thin films due to the high dc leakage current. The detailed electrical characterization of these thin films and the effect of BT incorporation in BFO will be presented in correlation with deposition parameters.

H3.2
Magneto-Electric Effect in Composites of Fe_{1-x}Gax/Pb (Zr_{1-x}Tix)O₃. Shuxiang Dong, Jiefang Li and Dwight Viehland; Materials Science & Engineering, Virginia Tech, Blacksburg, Virginia.

Piezomagnetic /piezoelectric laminate composites of Gafenol (Fe_{1-x}Gax) and PZT (Pb(Zr_{1-x}Tix)O₃) operating in a longitudinal magnetized and longitudinal or transverse polarized (L-L or L-T) modes have been experimentally investigated and modeled using an equivalent circuit. Experimental results revealed that there is a large magneto-electric effect in this laminate composite. Our composites are meaningful as a magnetic field or current sensors, because of high sensitivity and low-cost. Key words: piezoelectric, piezomagnetism, Gafenol, magneto-electric, magnetic sensor

H3.3
Electromechanical Probing of BiFeO₃ Films. Catalin Harnagea, Cristian Victor Cojocaru and Alain Pignolet; University of Quebec, INRS-EMT, Varennes, Quebec, Canada.

Bismuth ferrite BiFeO₃ (BFO) is a multiferroic material which has recently attracted some attention due to its ferroelectric properties which are very much enhanced in the thin film form. For example, epitaxial films a few hundreds nm thick (therefore strained by the substrate) exhibit a spontaneous polarization of the order of 100 μC/cm², more than one order of magnitude higher than that of BFO bulk single crystal. This enhanced ferroelectricity, together with the multiferroic character of BFO (it is also antiferromagnetic at room temperature), have opened perspectives for novel applications. For real device fabrication, however, a very good understanding of the basic ferroelectric - electromechanical properties, as well as their coupling with the magnetic order parameter is necessary. We have used the well-known piezoresponse force microscopy technique to study the domain structure and local switching in BFO films grown by pulsed laser deposition. A distinct ferroelectric behavior was found for films of different thickness, ranging from 500 nm down to 20 nm. The interpretation of experimental data, however, is more difficult than in traditional films with tetragonal symmetry (such as PZT and BaTiO₃). This is caused by the fact that, the crystal symmetry of BiFeO₃ is rhombohedral and therefore the piezoelectric response is not related to the components of spontaneous polarization in a simple way. Nevertheless, the magnitude of the piezoresponse is comparable to that of PZT films, in agreement with macroscopic piezoelectric measurements from literature.

H3.4
Engineering of Multiferroic PbTiO₃-CoFe₂O₄ Nanostructure in Constrained Films on SrTiO₃ Substrate. Jianhua Li^{1,2}, R. Ramesh^{3,1}, Alexander L. Roytburd^{1,2}, Igor Levin², Peter Schenck² and Martin Green²; ¹Materials Science and Engineering, University of Maryland, College Park, College Park, Maryland; ²Ceramics Division, National Institute of Standards and Technologies, Gaithersburg, Maryland; ³Materials Science and Engineering, University of California, Berkeley, California.

Ferroelectromagnetic PbTiO₃-CoFe₂O₄ thin film nanostructures on SrTiO₃ substrate has been developed by pulsed laser deposition. The different composition and orientation of substrate are studied with film thickness close to 350nm. X-ray and TEM studies show that the films consist of CoFe₂O₄ nano-pillars embedded in the PbTiO₃ matrix. There are epitaxial relation between the phases as well as between each phase and the substrate. The diameter of the pillars increases from 10nm at the composition 1/3CoFe₂O₄-2/3PbTiO₃ till 50nm at the composition 2/3CoFe₂O₄-1/3PbTiO₃. For (100), (110), and (111) film orientations, the pillars are normal to the substrates. The nanostructures demonstrate rectangle shape of ferromagnetic and ferroelectric hysteresis loops. The magnetization and polarization are decreased due to constraints between the two phases. Theory estimation of these parameters is in good agreement with the experiment. The possibilities to engineer the nanostructure with optimum properties are discussed. This work is supported by the NSF under contract No. DMR-00-80008 and NSF-MRSEC under contract

No. DMR-02-10512.

H3.5
Theory and Modeling of Multiferroic Heterostructures. Julia Slutsker¹, Alexander Roytburd² and Andrei Artemev³; ¹NIST, Gaithersburg, Maryland; ²Materials Science and Engineering, University of Maryland, College Park, Maryland; ³Mechanical and Aerospace, Carleton University, Ottawa, Ontario, Canada.

We present thermodynamic theory and phase field modeling of the formation and performance of heterostructures consisting of a ferroelectric and ferroelastic films. The elastic interactions between the phases dictate the domain architecture of the heterostructures and control their response to electrical field. For ferroelectric-ferroelastic multilayer it is shown that it is possible to obtain the giant converse piezoresponse for single domain layers as well as for polydomain ones. Phase-field modeling demonstrate the piezoresponse of the heterostructure which is in good agreement with an analytical estimation.

H3.6
Self-organized growth of pyramidal nanoclusters in ferrimagnetic CoCr₂O₄(001) epitaxial thin films. Ulrike Luders, Florencio Sanchez and Josep Fontcuberta; Institut de Ciencia de Materials - CSIC, Bellaterra, Spain.

The extremely rich variety of functional properties of complex oxides, and the excellent crystal matching they can present, allows the design of a new electronics involving only oxides. Common device architectures are based in epitaxial multilayers, in which the properties of the films can depend greatly on the lattice strain, and the complexity of the crystal structures favours the formation of defects. Also, some devices require defining geometries at a level not easily attainable with standard lithographic processes. For these reasons, self-assembly techniques are alternatives to be considered. New behaviors can be obtained with these new technologies, as was shown with the recent findings of Zheng et al. [1]. The authors fabricated arrays of ferrimagnetic CoFe₂O₄ nanopillars embedded in a ferroelectric BaTiO₃ by a self-assembly technique, and observed a remarkable coupling of magnetic and ferroelectric properties not found in ordinary multilayer structures. In this presentation we shall overview our recent research [2-4] on the heteroepitaxial growth of nanometric pyramidal objects (quadratic or hut cluster type) of the insulating ferrimagnetic spinel CoCr₂O₄ (CCO) on MgAl₂O₄(001). The surfaces of the structures are {111} facets, which form an angle >50 degrees with the (001) surface, so the pyramids can be considered as true three-dimensional objects. Important characteristics, as the size and the density of the structures, can be tuned by varying the deposition time and/or growth temperature. It allows one to obtain isolated {111} pyramids self-ordered in arrays along <110> directions or fully {111} faceted surfaces. The size-distribution of the objects can be controlled by varying the fabrication conditions: the observed bimodal distribution obtained at low temperatures transforms into a single modal one in films grown at high temperature. Moreover, the equilibrium shape of CCO islands is pyramidal for any object size, which is a key feature for the controlled fabrication of nanoobjects. The driving forces for the observed {111} faceted objects and surfaces, and bimodal size distributions are discussed. We discuss on the (dis)similarities of the growth of the spinel CCO structures with that of the widely studied of SiGe semiconductor dots. These findings illustrate that the growth of complex oxides can promote a variety of novel self-organized morphologies, and suggest original strategies to fabricate templates or hybrid structures of oxides combining different functionalities. References [1] Zheng et al., Science **303**, 601 (2004). [2] Luders et al., Appl. Phys. A **79**, 93 (2004). [3] Luders et al., Phys. Rev. B **69** (24), in press. [4] Luders et al., submitted

H3.7
Large Nonlinear Optical responses in Bismuth-based Perovskite Oxides. Alok Sharan, Yunfa Jia, James Lettieri, Darrell G. Schlom and Venkatraman Gopalan; Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania.

We have discovered unusually large nonlinear optical responses in a number of Bismuth perovskite oxides: Bismuth Manganite, Bismuth Titanate and Strontium Bismuth Niobate. For example, BiMnO₃ exhibits a large third order nonlinear optical response (with nonlinear absorption coefficient α_I -0.08 cm/kW and nonlinear refractive index n_I -0.53 x 10⁻⁹ cm²/W. A second harmonic generation coefficient d_{eff} 193pm/V is also measured. These large nonlinear optical responses open up possibilities for all-optical modulation devices Using femtosecond and nanosecond laser pulses, we present detailed studies of spectral and temporal response of these nonlinearities, using four-wave mixing, and z-scan studies. We also report the results of optical SHG near band edge, coupled with the dielectric studies to probe the origin of the giant enhancement of SHG signals in this material. BiMnO₃ is also a multiferroic, possessing

both ferroelectricity and ferromagnetism. We will also present *in situ* nonlinear optical studies of domain dynamics in ferroelectrics under external fields.

H3.8

Investigations on Sol-Gel Derived Multiferroic Lead Iron

Niobate Thin Films. Rajasekarakumar Vadapoo¹, Sudipta Bhattacharyya¹, Subhashish Basu Majumder¹, Ram S. Katiyar¹, Prasanta Dutta², Mohindar S. Seehra² and Ayyakkannu Mani Manivannan²; ¹Physics, University of Puerto Rico, San Juan, Puerto Rico; ²Physics, West Virginia University, Morgantown, Virginia.

Multiferroic ceramics have been attracting considerable attention in the recent times owing to their interesting ferroelectric and magnetic properties in a common material platform. There have been significant achievements in the synthesis and understanding of byfunctional behavior in phase pure ferroelectromagnets with potential applications in tunable sensors and spintronic devices. Among several material candidates possessing multiferroic nature, lead iron niobate stands out because of its unique electrical properties, which also shows a coupling with the magnetic properties. Despite the distinct structural similarities with typical relaxors, this material possesses some characteristics, which does not fall under the wings of a pure relaxor, instead it follows the behavior of normal ferroelectrics. Very interestingly, the isovalent replacement of tantalum shifts the properties of this system towards a pure relaxor. This material also possesses a high dielectric constant and a diffused phase transition, which is very much welcome for energy storage applications which is insensitive to thermal fluctuations. There had been very little work performed on this extremely interesting material in the thin film form. There are a number of open issues, which should be addressed while working with this system. There are, the formation of secondary phases during the synthesis, and the role of any seeding material on the phase formation kinetics. In this report, we have tried to tackle this problem by depositing thin films of lead iron niobate on several substrates by a modified sol-gel route. The substrate was found to drastically affect the formation of secondary phases. We have measured the electrical properties through temperature dependent dielectric, ferroelectric and leakage current measurements. The impedance measurements were employed to understand the role of the microscopic relaxation mechanisms that resulted in a high dielectric constant in this material across the phase transition temperature. The magnetic properties have been studied using a squid magnetometer and the magnetic hysteresis and susceptibility measurements as a function of temperature has been performed. Also room temperature EMR (electron magnetic resonance) studies have been carried out. We made a systematic attempt to understand the origin of magnetic properties from a compositional point of view. Finally, we have tried to understand the coupling between the magnetic properties with the electrical properties in this interesting material system.

H3.9

Multi-ferroic Properties of YMnO₃ Epitaxial Films.

Norifumi Fujimura, Norimichi Shigemitsu, Takeshi Yoshimura and Atsushi Ashida; School of Applied Materials Science, Osaka Prefecture University, Osaka, Japan.

The magnetoelectric effect presumed to exist by Pierre Curie [1] - i.e. the induction of a magnetization by means of an electric field and induction of a polarization by means of a magnetic field - attracted a great deal of interest in 1960s-70s. In recent years, relevant studies on magnetic ferroelectrics have come to the fore again [2-6]. From a technological point of view, the mutual control of electric and magnetic properties is an intriguing feature, though the number of candidate materials is limited and the effects are typically too small to be useful in applications. RMnO₃ (R is rare earth) crystallizes in a hexagonal structure when the ionic radius of R is small (R=Ho-Lu, Y, and Sc). In this hexagonal structure, each Mn³⁺ ion with S=2 is surrounded by three in-plane and two apical oxygen ions, and thus is subject to a trigonal crystal field. These MnO₅ blocks are two-dimensionally connected with each other on their corners, and the triangular lattice of the Mn³⁺ ions is formed. Based on such a triangular lattice, these compounds experience several characteristic distortions. One is Mn "trimers" (i.e., $\sqrt{3}\times\sqrt{3}$ ordering), which are characterized by the shift of three Mn³⁺ ions surrounding one oxygen ion toward the oxygen. Another one is the displacement of ions along the c axis (perpendicular to the triangular-lattice plane) causing a ferroelectric polarization. Since the ferroelectric transition temperature of these compounds is fairly high (>900 K), they have potential use for application, for example, ferroelectric gate FETs [7]. Here, we show the dielectric anomalies at around Neel point of YMnO₃ epitaxial films deposited by pulsed laser deposition method. The relationship between the magnetic structure and the dielectric properties are discussed in terms of the temperature dependences of magnetization and dielectric permittivity. Eventually, the control of ferroelectric domain switching by applying external magnetic field is

presented. REFERENCES [1] Curie, P., J. Physique 3 Serie, III, 393 (1894), [2] Katsufuji, T. et al., Phys. Rev. B 64, 104419 (2001), [3] Fiebig, M. et al., Nature 419, 818 (2002), [4] Wang, J. et al., Science 299,1719 (2003), [5] Kimura, T. et al. Nature 426,140 (2003), [6] Fujimura, N, et al. J. Appl. Phys. 93 (2003) 6990, [7] Ito, D. and Fujimura, N. et al. J. Appl. Phys. 94 (2003) 4036

H3.10

Study of Highly Oriented ZT and ZTS Multifunctional Oxides for Satellite Communications. Marco Viticoli¹,

Giuseppina Padeletti¹, Saulis Kaciulis¹, Gabriel Ingo¹, Luca Pandolfi¹ and Carlos Zaldo²; ¹Istituto per lo Studio dei Materiali Nanostrutturati-CNR, Monterotondo (Rome), Italy; ²Instituto de Ciencia de Materiales de Madrid-CSIC, Cantoblanco (Madrid), Spain.

Functional and multifunctional oxides have been studied for decades due to both their application in important technologies and the fundamentally interesting relationship among their crystal chemistry, crystal structure and physical properties. Zirconium titanate based ceramics have attracted large interest because they have been used in a wide range of applications (Catalysis, Humidity Sensors, Industrial Chemistry, Composite Materials, Optical devices and Telecommunications). In latest years, recent dramatic changes in satellite communications have made the importance of these materials with the unusual combination of high permittivity (ϵ_r), low dielectric loss ($\tan\delta$) and low temperature dependence of permittivity (Tcc) of great interest. The basic compound, ZrTiO₄, has long been known to have a relatively low temperature coefficient of the dielectric constant, but the compound Zr_{0.8}Sn_{0.2}TiO₄, has been found to have optimal properties at microwave frequencies (ϵ_r 38, Tcc = 0 ppm °C⁻¹ and $\tan\delta \approx 1 \times 10^{-4}$). In this work we report the study on the chemical, physical and functional properties of Zirconium Titanate thin films prepared by MOCVD and PLD techniques. Surface roughness, chemical composition and microstructural features of the films were controlled by varying the deposition conditions in order to achieve the most suitable dielectric properties. Substrate temperature of 500-600 °C and deposition pressure of 5×10^{-2} mbar are required for the formation of highly oriented crystalline films. Changes of substrate temperature in the range 500–600 °C cause variations on films stoichiometry, microstructure and residual strains. The realization of crystalline and single phase thin films having a high dense columnar structure and low residual strains revealed to be the fundamental requirement for achieving high permittivity and low loss dielectric films.

H3.11

Leakage Current Behavior of PbZr_{0.4}Ti_{0.6}O₃ Film Spin-Coated on Pt Bottom Electrode Buffered with Thin La_{0.5}Sr_{0.5}CoO₃ Layer. Jai-Hyun Kim and Woong Kil Choo; Material Science and Engineering, KAIST, Taejeon, South Korea.

For high 32M FRAM density, to defend the electrical shorting problem which often results from the etching process between the capacitors, it is desirable to reduce the current 400 500nm capacitor thickness of top electrode-ferroelectric layer-bottom electrode to a lower thickness smaller than 300nm. For this reason along, both Pt and buffer LSCO layer thickness should be reduced. In this study, we limited the thickness of LSCO buffer layer at 5nm. Subsequently, we have checked the capacitor performance measuring electrical properties. We have studied ferroelectric properties of PbZr_{0.4}Ti_{0.6}O₃ (PZT 40/60) film grown on Pt(111)/TiO₂/SiO₂/Si(100) bottom electrode buffered La_{0.5}Sr_{0.5}CoO₃ (LSCO) layer. Conductive perovskite LSCO thin films (about 5nm thick) of fine grain size (less than 20nm) are grown on Pt/TiO₂/SiO₂/Si substrate at relatively low temperature (450°C) by rf magnetron sputtering. Pt-LSCO interface shows ohmic contact. In order to investigate the ferroelectric properties of spin-coated PZT 40/60 film, we have measured the P-V hysteresis curve vs. temperature. The coercive voltage of the capacitor decreased with temperature as usual, but the remanent polarization unusually increased with temperature up to 375K. It then decreased with temperature increase above 375K. We measured the J-V curve vs. temperature. Different from the general increase of leakage current with temperature in the schottky or ohmic contact, it shows a very small increase up to 373K. However, above 373K, the increase of leakage current density appears in different aspect. This space charge limited conduction shows two scopes of leakage current density with temperature from the existence of thin LSCO buffer layer.

H3.12

The Ab Initio Atomic and Electronic Structure Calculations for ABO₃ Perovskite Polar Surfaces. Eugene Heifets¹, Eugene A. Kotomin², Yuri Mastrokov², Robert A. Evarestov³ and Joachim Maier²; ¹Materials and Process Simulation Center, Beckman Institute (139-74), California Institute of Technology, Pasadena, 91125, California; ²Max Planck Institut fur Festkorperforschung, Stuttgart, D-70195, Germany; ³Department of Quantum Chemistry, St. Petersburg University, St. Peterhof, 198904, Russian Federation.

Results of ab initio calculations of the atomic and electronic structure of the SrTiO₃ and LaMnO₃ perovskite surfaces are presented and discussed. Calculations are performed using 6 different exchange-correlation functionals varied between Hartree-Fock and DFT-LDA, and including hybrid DFT-HF functionals. Both localized atomic orbitals and plane wave basis sets were used as implemented into the Crystal and VASP computer codes, respectively. We discuss the surface relaxation, surface polarization, surface energy, the electron density redistribution, and covalent bonding on the neutral and polar (001), (110), and (111) surfaces with different terminations using 2D slabs of different thickness (varied between 4 crystalline planes and 20 planes). We demonstrate an importance of oxygen vacancy formation on polar surfaces as the most efficient way to eliminate their macroscopic dipole moment perpendicular to the surface. The polar surfaces in general are much more perturbed as compared to neutral surfaces, with the O-termination revealing typically the lowest surface energy of all possible terminations. We show also that the covalent component in the B-O chemical bonding on the (110) SrTiO₃ surface with Ti-termination exceeds twice that in the bulk, and by 50 per cent that on the neutral surfaces. In conclusion, we discuss the ferroelectricity in strained thin SrTiO₃ films.

H3.13

Meta-Stability of Barium Strontium Titanate in Thin Film Capacitor Structures. Akeela Lookman¹, Jonny McAneney¹, Robert M. Bowman¹, Marty J. Gregg¹, John Kut², Susana Rios², Andreas Ruediger³, Matt Dawber³ and James F. Scott²; ¹Department of Pure & Applied Physics, Queen's University Belfast, Belfast, United Kingdom; ²Department of Earth Science, University of Cambridge, Cambridge, United Kingdom; ³DPMC, University of Geneva, Geneva 4, Switzerland; ⁴Centre of Nanoelectronics for Information Technology, Institute of Solid State Research, Juelich, Germany.

Barium strontium titanate (BST) thin film capacitors, with varying thickness of dielectric layer, have been fabricated using pulsed laser deposition (PLD). The dielectric properties of these capacitors have been studied as a function of temperature (from 80K to 400K) and frequency (10²Hz to 10⁵Hz). Our results indicate three major features that have not been observed in the literature to date: (i) T_m^c (the temperature at maximum dielectric constant) measured from unpoled BST capacitors is NOT fundamentally related to the Curie Temperature, as is widely assumed. Hence, care needs to be taken when interpreting changes in T_m^c as illustrative of alterations in thermodynamics with reduced thickness of BST; (ii) Dielectric anomalies that DO relate to fundamental phase transitions can be seen after BST has been poled at low temperature, delineating temperature regions which appear to correspond to cubic, tetragonal, orthorhombic and rhombohedral symmetries; (iii) Ferroelectric poling, within the orthorhombic phase regime, appears to prevent the phase transition to rhombohedral on cooling; similarly poling treatment within the tetragonal phase field appears to suppress phase transitions to either orthorhombic or rhombohedral. It therefore seems that metastability of symmetry states can readily occur in these ferroelectric thin film systems.

H3.14

2D Planar Size Effects in Epitaxial PZT Thin Films. Kilho Lee, Keewon Kim, Soon Ju Kwon and Sunggi Baik; MSE, Pohang University of Science and Technology (POSTECH), Pohang, South Korea.

Significant modification of domain structure has been observed as the thickness of PZT thin films is reduced below a certain critical thickness.[1,2] In order to test a critical lateral dimension in 2D planar ferroelectrics, PZT thin films are patterned into discrete islands lithographically with different lateral sizes. As the pattern size decreases, the substrate clamping effect is significantly reduced and thus the misfit strain in the films could be relaxed further. Evolution of 90° domain structures as a function of lateral dimensions was characterized extensively by reciprocal space mapping using synchrotron x-ray. As the lateral 2D planar size decreases in PbTiO₃ patterns on MgO(001), some of the *a*-domains turned into *c*-domains due to the relaxed *tensile* strain. In the PbTiO₃ patterns on Pt(001) / MgO(001), on the other hand, the formation of 90° domains is enhanced by reduction in *compressive* misfit strain. Equilibrium domain structures in the continuous PZT thin films and discrete islands are also analyzed respectively by the finite element simulation and found to be consistent with the experimental observation. [1] K. S. Lee and S. Baik, J. Appl. Phys., **87** 8035 (2000) [2] Y. K. Kim, K. Lee, and S. Baik, J. Appl. Phys., **95** 236 (2004)

H3.15

High Quality Screen Printed PZT Thick Films Using Modified Chemical Solution for Piezo-MEMS Devices. Seung-Hyun Kim, Chang Young Koo, Jung-Hoon Yeom, Jong-Hyeon

Cheon and Jowoong Ha; R&D Center, INOSTEK Inc., Ansan, Gyeonggi, South Korea.

There is a strong interest in introducing ferroelectric films for applications in microelectromechanical systems (MEMS) since they have large piezoelectric coefficients and electromechanical coupling coefficients. Among ferroelectrics, PZT films are considered the most promising candidates for these applications since they can produce high mechanical strain under applied electric field. However, stress induced in PZT thin films due to clamping of the films by the substrates and other degradation parameters such as low breakdown strength, reduced extrinsic domain wall contribution and insufficient poling have limited these thin films to be used in some MEMS applications. To develop PZT films for MEMS devices, it is necessary to fabricate high quality PZT thick films over 10 micrometer. Some deposition techniques such as screen printing and hydrothermal depositions have been used for preparing PZT thick films, but in general PZT thick films by these methods have showed insufficient film quality for MEMS devices due to porous or low film density, poor surface morphology and bad electrical properties. In the case of CSD method, it can produce relatively high quality PZT films, but it has serious thickness limitation over 5 micrometer and many multiple process steps for achieving high quality thick films. To solve these drawbacks, we have performed an extensive experiment for optimized chemical solution modified hybrid deposition techniques. Based on the experimental results of the piezoelectric and dielectric properties of PZT films with these techniques, we introduce simple process design for high quality thick films for MEMS devices. Here, we also describe the property relationships between the effects of film composition and thickness on the piezoelectric and dielectric properties of high quality PZT thick films and applications in MEMS devices in detail. *This work was supported by National Research Laboratory Program (NRL)

H3.16

Microstructure and Stress Evolution of Reactively Sputtered RuOx Thin Films. Junxia Shi¹, Feng Huang², Mark L. Weaver² and Tonya M. Klein¹; ¹Chemical Engineering, The University of Alabama, Tuscaloosa, Alabama; ²Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama.

Conducting RuOx thin films are promising for applications such as electrodes for ferroelectric devices and electrochemical reactions. In this study, RuOx thin films were deposited at room temperature by reactive rf magnetron-sputtering using Ar/O₂ discharge of varying ratios of O₂/Ar+O₂ over the range from 10% to 50%. With increasing oxygen content in the chamber, the film microstructure undergoes a transition from metal-rich nanocrystalline at 10% O₂ to nanocrystalline (amorphous) oxide at 20% O₂ and then to polycrystalline oxide films at oxygen contents higher than 20%. Texture changes continuously from (110) at 25% O₂ to (101) at 50% O₂. Film thickness, roughness and density are determined using x-ray reflectivity, topography is studied using atomic force microscopy and composition is measured using x-ray photoelectron spectroscopy. The stress-temperature measurements using an in-situ curvature measurement technique shows the films with oxygen contents from 25% to 50% are almost stress-free after annealing in air up to 500°C for 1 hour.

H3.17 TRANSFERRED TO H11.56

H3.18

Effect of Ozone Annealing on the Electrical Properties of CSD Derived BST Thin Films. Sandip Halder¹, Theodor Schneller¹ and Rainer Waser^{1,2}; ¹Institut für Werkstoffe der Elektrotechnik, RWTH -Aachen, Aachen, NRW, Germany; ²Institute für Festkörperforschung, Forschungszentrum Juelich, Juelich, Germany.

(Ba,Sr)TiO₃ (BST) thin films have shown great promise for use as a capacitor dielectric with existing CMOS technology. The dielectric constants of the BST films are much higher than the current dielectrics in use. However due to the continuous scaling of the devices the thickness of the capacitor dielectric is also being reduced and in such a scenario the leakage is often quite high. Hence the need for improvement in processing of thin films. Thin films of BST were deposited by CSD on Pt coated Si wafers. On changing the ambient atmosphere from oxygen to the strongly oxidizing ozone during crystallization it was noticed that the films crystallized at lower temperatures. The crystallization temperature was lowered to 600oC by using an ozone environment. In addition the leakage in the thin films reduced by three orders of magnitude when a post deposition anneal was carried out for 30 minutes at 400oC. The post annealing in ozone was carried out at various temperatures between 300 and 450oC. It was noticed that post annealing at temperatures lower than 300oC did not produce any noticeable change in the leakage. In addition microstructural studies involving XRD and SEM were also performed.

H3.19

Development of TiO₂ Thick Film Capacitors for use as Strain Gauge Sensors. Khalil Ibrahim Arshak¹, Arousian Arshak², Deirdre Mary Morris², Olga Korostynska¹, Essa Jafer¹, John Harris¹ and Seamus Clifford¹; ¹Computer and Electronic Engineering, University of Limerick, Limerick, Ireland; ²Physics, University of Limerick, Limerick, Ireland.

Strain gauges are commonly used in automotive and aerospace applications and of the various types available, thick film technology is the best equipped to provide highly sensitive, robust and cost effective transducers. However, many materials used in the development of high sensitivity gauges are toxic in nature and working with such materials has become a serious concern. For example, strict legislation regarding the use of lead has been introduced due to its toxic effects. With this in mind, a highly sensitive strain gauge has been fabricated from relatively non-toxic materials. An oxide is preferred as polymer thick films are prone to slippage of the molecular chains, resulting in poor linearity and large hysteresis [1]. TiO₂ was chosen, as it has been used in medical applications [2]. To form the paste, TiO₂ powder was mechanically milled for 24 hours, then pressed to form a pellet, which as fired at 1250 °C for five hours. After cooling the pellet was crushed to a fine powder, which was combined with PVB and a suitable solvent to make the thick film paste. Using this fabrication method, the need for surfactant and ruthenium oxide to make sensitive films is avoided. Two capacitor designs were then fabricated, a single plate capacitor using interdigitated electrodes and a sandwich structure (Metal-Insulator-Metal), which can yield a higher sensitivity than planar designs [1]. The sensors were placed in a cantilever beam arrangement so that the change in capacitance with strain, or piezocapacitive effect could be measured. The gauge factor, which demonstrates the sensitivity to strain, can be found by dividing the fractional change in capacitance by the strain. For oxide sensors, the gauge factor is usually less than 20. During this study, gauge factors exceeding 30 have been recorded. In addition, the sensors showed a high degree of linearity with low hysteresis, this is attributed to the materials high Youngs modulus, allowing it to withstand large strains. It is thought that the improved sensitivity is related to the small particle size achieved by mechanically milling the TiO₂ powder. By using SEM to examine the particle size and the effect of applied strain on films microstructure sensitivity of the films can be further optimized. The effect of firing TiO₂ at elevated temperatures is also under investigation using XRD. An examination of the sensors AC electrical properties has shown TiO₂ thick films to be extremely stable at high frequencies and that tunnelling is the dominating conduction mechanism. The temperature coefficient of capacitance has also been measured and is in good agreement with typical values for thick film capacitive devices. From the results, it can be seen that TiO₂ thick film capacitors can provide highly sensitive and stable strain gauges capable of competing with existing compositions. 1. Arshak, K.I. et. al, (1995), Sensors and Actuators A, 49, p. 41-45 2. Brunette, D.M., Titanium in Medicine, Springer, 2001

H3.20

Electrical and Structural Characterization of Laser Ablated Ca Doped Barium Titanate Thin Films on Different Substrates. Victor Pushpara^{1,2} and S. B. Krupanidhi¹; ¹Materials Research Center, Indian Institute of Science, Bangalore, Bangalore, India; ²Materials Science Engg., Rensselaer Polytechnic Institute, Troy, New York.

The doping of Ca in the BaTiO₃ ceramics showed a remarkable improvement in the electromechanical behavior, increase in temperature range of stability of tetragonal phase and inhibited formation of unwanted hexagonal phase of BaTiO₃. Ca doped BaTiO₃ is a promising photorefractive materials with larger electro optic coefficients (r₁₃ and r₃₃) compared to other conventional materials. Ba_{1-x}Ca_xTiO₃ (at. % Ca x = 0.05, 0.1, 0.13 and 0.18 at%) and La_{0.5}Sr_{0.5}CoO₃ targets were prepared by solid state reaction technique and the BCT and LSCO thin films were deposited on Pt coated Si substrates and Si(100) substrates by pulsed excimer laser ablation technique. The dielectric constant and phase transition temperature in both the bulk and the thin films were found to decrease with the increase of Calcium content in Barium titanate matrix. The dielectric phase transition was studied for the BCT thin films deposited on the Pt coated Si, LSCO/PT and Si substrates. Calcium doped BaTiO₃ properties are highly dependent on the processing parameters. There is a strong anomaly observed in the decrease of phase transition and could be tailored accordingly to the processing parameters. The decrease in the phase transition was analysed in terms of the size dependence of ferroelectric domains, intergranular stresses and strain existing at the film/substrate interface. XRD, XPS, SIMS and Micro Raman analysis on these thin films, were carried out for the structural characterization. SIMS analysis carried on the BCT thin films on Si showed a sharp interface existing at the substrate/thin films without any interdiffusion of the elements. The possibility of the Ca occupancy in the Ba or Ti site has

been extensively investigated through this structural characterization and their extensive correlation with the electrical properties are also dealt.

H3.21

The Unusual Behaviour of Ferroelectric Polarization in PbTiO₃/SrTiO₃ Superlattices. Matthew Dawber¹, Celine Lichtensteiger¹, Jean-Marc Triscone¹ and Philippe Ghosez²; ¹DPMC, University of Geneva, Geneva, Switzerland; ²Dept of Physics, University of Liege, Liege, Belgium.

We have fabricated 20 bi-layer PbTiO₃/SrTiO₃ superlattices with extremely fine periodicity (layers as thin as 1 unit cell) using off axis RF sputtering. Using x-ray diffraction to measure the tetragonality we have studied the change in the ferroelectric polarization in the PbTiO₃ layers as a function of their thickness. Intuitively one expects that as the ferroelectric layer thickness is decreased the polarization should decrease, and indeed we observe this as the initial behaviour as the PbTiO₃ layer thickness is reduced. However in the thinnest PbTiO₃ layers we observe an intriguing increase of the polarization to near bulk values, a finding we confirm by AFM piezoresponse measurements. First principles studies have recently shown that the essential physics of the problem of critical thicknesses in ferroelectric thin films (J. Junquera and P. Ghosez, *Nature* **422**, 506(2003)) and of interactions between ferroelectric and non-ferroelectric layers in multilayer structures (J.B Neaton and K.M. Rabe, *Appl.Phys.Lett.* **82** 1586 (2003)) can be understood on the basis of simple electrostatics. We show that an electrostatic model is also able to explain the initially surprising result obtained here.

H3.22

Non-Linear Dielectric Response in {111} and {100} Oriented 0.5Pb(Yb_{1/2}Nb_{1/2})O₃-0.5PbTiO₃ Thin Films.

Nazanin Bassiri Gharb and Susan Trolier-McKinstry; Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania.

The effective dielectric and piezoelectric coefficients of piezoelectric films depend on the applied electric field strength and frequency. The application of these films in microelectromechanical systems (MEMS) requires an understanding of these nonlinearities for prediction of the device behavior. The AC electric field dependence of the permittivity and piezoelectric response of ferroelectric thin films in sub-switching conditions can be modeled using Rayleigh-type behavior. (1-x)Pb(Yb_{1/2}Nb_{1/2})O₃-xPbTiO₃ (PYbN-PT) presents one of the highest Curie temperatures (360°C) near the morphotropic phase boundary (x0.5) among the relaxor-PT solid solution systems, which makes it a very good candidate for devices with good temperature stability and wide working temperature range. The highest piezoelectric responses in this material are observed for the {100} orientation. In this work, the nonlinear dielectric response of {111} and {100} oriented thin films of 0.5PYbN-0.5PT are reported as a function of AC electric field and frequency. The responses are modeled with a frequency-dependent modification of Rayleigh law as $\epsilon'_{r,init} = \epsilon'_{r,init}(\omega) + \alpha'(\omega)E$ where $E_{AC} = E \cdot \sin(\omega t)$ is the AC driving field and $\epsilon'_{r,init}$ and α' are the reversible and irreversible Rayleigh coefficients. This modified model predicts the dielectric properties of the PYbN-PT films in the intermediate AC field and frequency regions relatively well. Furthermore, {100} oriented films show higher irreversible Rayleigh coefficients than {111} oriented films. The ratio of the irreversible to reversible coefficients is also higher in the {100} oriented films, showing a higher contribution to the dielectric constant due to the irreversible component (movement of the domain walls) in these films with respect to the {111} oriented films. Work on the piezoelectric nonlinearity for these films will also be described.

H3.23

Pulsed Laser Deposition of NaxCoO₂ Thin Films. Weidong Si, Sang-moon Park and Peter Johnson; Physics, Brookhaven National Laboratory, Upton, New York.

NaxCoO₂ has been discovered to have very large thermoelectric power, which shows that it may be used in potential integrated heating spreading solution. Recently it was also found to be superconducting at certain sodium concentration after intercalated with water. It has a layered structure similar to the cuprates and considered to be helpful to the understanding of the mechanism of the high temperature superconductor. We have successfully grown c-axis oriented thin films of NaxCoO₂ on substrates of polycrystalline sapphire and (0001) sapphire by pulsed laser deposition. The in-plane transport and magnetic measurements has been performed in the NaxCoO₂ films and show similar behaviors as in the single crystal samples. Their structure properties as well as physical properties will be discussed.

H3.24

Strong Degradation of Physical Properties and Formation of

a Dead Layer in Ferroelectric Films due to Interfacial Misfit Dislocations. Ibrahim Burc Misirliglu¹, S. Pamir Alpay¹, A. L. Vasiliev¹, Mark Aindow¹, Valanoor Nagarajan² and R. Ramesh³; ¹Materials Engineering, University of Connecticut, Storrs, Connecticut; ²Institute for Electronic Materials, Department IFF Forschungszentrum, Juelich, Germany; ³Department of Materials Science and Engineering and Department of Physics, University of California, Berkeley, California.

Structural defects like atomic vacancies, twins and dislocations have been observed in ferroelectric crystals as in many other crystalline materials. The effect of these defects on the physical properties in ferroelectrics has to be seriously considered since these crystals are of interest for potential device applications. Although there have been extensive studies on vacancies and twins in ferroelectric thin films, the research conducted on effects of dislocations in ferroelectrics has been limited. Dislocations are the most common type of defects and are unavoidably present in all crystalline materials. Experiments have shown that they drastically degrade the electrical properties and change phase transition characteristics. Dislocations form in large numbers when the ferroelectric crystal is grown in thin film form on a substrate with a similar lattice configuration. Thus, different from those observed in bulk, they form to relax the internal stresses resulting from the mismatch between the substrate and the film. In this study, we investigate both experimentally and theoretically the effect of dislocations on the physical and structural characteristics of lead-zirconium-titanate (PZT) and barium-strontium-titanate (BST) ferroelectric thin films of various stoichiometry. Due to the coupling of the stress field of the dislocation and the polarization, there is a drastic variation in the polarization near the dislocation. These polarization gradients result in strong depoling fields that suppress the polarization in a region that extends over several nanometers. In epitaxial ferroelectric films, these polarization gradients should result in the formation of dead layers that severely degrade ferroelectric properties. The detrimental effect of such regions will be enhanced in ultra-thin ferroelectric thin films, and hence play a critical extrinsic role in size effect studies of ferroelectrics. This work is supported by the NSF-MRSEC under contract No. DMR-00-80008 and by NSF DMR-0132918.

H3.25
Correlation of Microscopic and Macroscopic Piezoelectric Displacement via 90° Domain Switching in Active Lead Barium Titanate Films for MEMS Applications.

Jennifer Lynn Ruglovsky¹, Matthew Dicken¹, Youngbae Park¹, Stacey Boland¹, Mohammed El-Naggar¹, David Boyd¹, Alexandros Papavasiliou², Sossina M. Haile¹, David Goodwin¹, Kaushik Bhattacharya¹ and Harry A. Atwater¹; ¹California Institute of Technology, Pasadena, California; ²Lawrence Livermore National Laboratory, Livermore, California.

Ferroelectric thin films grown via deposition on amorphous substrates typically have polycrystalline microstructures, but control of grain texture is possible by incorporating a template layer. This presents an opportunity to compare the piezoelectric properties of biaxially-textured and randomly ferroelectric thin films at similar grain size. We have produced high quality, textured $Pb_xBa_{1-x}TiO_3$ films formed via epitaxy on IBAD MgO template on amorphous Si_3N_4 . Thin films of $Pb_xBa_{1-x}TiO_3$ were fabricated by two growth methods: metallorganic chemical vapor deposition ($x=0.9$) and sol-gel ($x=0.5$) film synthesis. For both methods, the $Pb_xBa_{1-x}TiO_3$ inherits the texture of the MgO template, showing out-of-plane and in-plane orientation distributions about [001] and [100] of 8 and 15 degrees, respectively. Free-standing cantilever and membrane structures were patterned via deep reactive ion etching the backside of the silicon wafer. Electrodes were defined by lift-off. Several devices are accessible on each chip, including cantilevers activated in-plane by interdigitated electrodes at several spacings and membranes of various sizes for capacitance measurements. We find that the mechanism for piezoelectric displacement in these films is via 90° domain wall switching. The presence and switching behavior of 90° domains is confirmed by x-ray diffraction (XRD) and piezoresponse force microscopy (PFM) measurements. The films exhibit grain-scale domain morphology and microstructure-dependent domain switching. Piezoelectric performance of the $Pb_xBa_{1-x}TiO_3$ is also explored with PFM. As an example, a single sol-gel grain, constrained by its neighboring grains in the polycrystalline film in a 1 micron/50 nm/200 nm/200 nm $Pb_{0.5}Ba_{0.5}TiO_3/MgO/We$ have produced high quality, textured $Pb_xBa_{1-x}TiO_3$ films formed via epitaxy on IBAD MgO template on amorphous Si_3N_4/Al membrane exhibits a piezoelectric coefficient $d_{33} = 40$ pm/V. Ultimately, this work fundamental relationships between the microscopic properties and macroscopic behavior of active ferroelectric films. We will discuss limits to theoretically attainable values for actuation displacements of randomly-oriented and textured films due to grain misorientation and elastic constraints, and compare with macroscopic displacement measurements for devices with both randomly-oriented

($Pb_xBa_{1-x}TiO_3$ on amorphous Si_3N_4). We have produced high quality, textured $Pb_xBa_{1-x}TiO_3$ films formed via epitaxy on IBAD MgO template on amorphous Si_3N_4) and textured active layer films (textured $Pb_xBa_{1-x}TiO_3$ on MgO). We have produced high quality, textured $Pb_xBa_{1-x}TiO_3$ films formed via epitaxy on IBAD MgO template on amorphous Si_3N_4).

H3.26
Composition and Dielectric Properties of Cosputtered Ba1-xSrxTiO3 Thin Films by Continuous Composition Spread Technique. Yuqing Yu, Ji-Won Choi and Bruce van Dover; Materials Science and Engineering, Cornell University, Ithaca, New York.

Ba1-xSrxTiO3 thin films were prepared by 90 off-axis cosputtering using separate targets of BaTiO3 and SrTiO3. Films were deposited directly on (100) silicon as well as Pt/Ti coated Si substrates. Codeposition spreads prepared at room temperature were annealed ex situ at temperatures in the range of 350-950C for 30 min, while other spreads were deposited at substrate temperatures from 300C to 600C. X-ray diffraction was used to compare the crystallinity of the various films. Codeposition results in films that are intimately mixed and have a natural composition gradient. The composition was inferred as a function of position using Rutherford backscattering spectroscopy together with calibrations based on the measured position-dependent deposition rate from each target. The dielectric loss and tunability observed in these films will be discussed along with preliminary results obtained for pseudo-ternary (BaTi, SrTi along with dopants such as W and Ta) composition spreads. This work confirms that the composition spread technique is particularly well suited for explanation of novel ferroelectric materials that are process-compatible with Si IC technology.

H3.27
Nanoscale Ninety Degree Domain Switching Characteristics in Polycrystalline Pb1-xBaxTiO3 Thin Films by Piezoresponse Force Microscopy. Youngbae Park¹, J. L.

Ruglovsky¹, M. J. Dicken¹, Harry A. Atwater¹, S. W. Boland², Sossina M. Haile² and K. Bhattacharyac³; ¹Thomas J. Watson Lab. of Applied Physics, California Institute of Technology, Pasadena, California; ²Department of Material Science, California Institute of Technology, Pasadena, California; ³Department of Mechanical Engineering, California Institute of Technology, Pasadena, California.

We have investigated nano-domain switching in $Pb_{1-x}Ba_xTiO_3$ thin films grown on Pt substrates using atomic force microscopy (AFM) and piezoresponse force microscopy (PFM). Piezoresponse images, in combination with in-plane (IPP) and out-of-plane (OPP) polarization measurements, allow differentiation between 90° and 180° domains and reconstruction of the three-dimensional polarization arrangement. Using this approach, we have obtained clear evidence of 90° domain switching in the $Pb_{1-x}Ba_xTiO_3$ thin films with randomly oriented texture. Sol-gel synthesis was used to prepare sols suitable for the deposition of ferroelectric lead barium titanate ($Pb_{1-x}Ba_xTiO_3$) thin films using lead nitrate, barium acetate, and titanium isopropoxide as metal sources, ethylene glycol as a solvent, and diethanolamine as a chelating agent. Sols were prepared with varied Ba content (x) with $x = 0.2$ and 0.5 . The Pt/ Si_3N_4 /Si substrate was used to provide a bottom electrode for the ferroelectric material. The edges of the substrate were masked to provide easy access to the bottom metal electrode for PFM measurement. Three layers of PBT sol were deposited on masked substrates via spin coating (3000 rpm, 40 seconds), with a five minute drying step (200°C) between each layer. The edge masks were then removed, and the samples were calcined in air at 600°C for two hours with a heating rate of 5°C/min and cooling rate of 20°C/min. In PFM experiments, a dc-bias above coercive field (10 Vdc) was applied by a conducting probe tip on the whole scanned area to investigate the domain polarization vector rearrangement and switching mechanism. An effective piezoelectric coefficient (d_{33}) and strain behavior are obtained in the nanoscale-subgrain region by calibrating force-distance (F-d) curves using a scanning probe microscope and in lock-in amplification technique. Micro-Raman spectroscopy was used to characterize local vibrational structure and chemical disorder. Microstructural analysis was performed using X-ray diffraction and transmission electron microscopy. The film composition was determined by Rutherford backscattering spectrometry. The effect of composition and orientation on the domain switching mechanism, and connection to continuum electromechanical modeling will be discussed.

H3.28
FIB Processing of Ferroelectric Single Crystal Nano-Capacitors: Nanoscale Studies of Dielectric Phenomena in Perovskite Single Crystals. Mohamed Mohamed Saad¹, Paul S. Baxter¹, Robert M. Bowman¹, Marty J. Gregg¹, Finlay D. Morrison² and James F. Scott²; ¹Condensed Matter Physics and Material Science, Queen's University Belfast, Belfast, Antirum, United Kingdom; ²Earth Sciences, University of Cambridge, Cambridge,

United Kingdom.

The focused ion beam microscope (FIB) has been used to fabricate parallel-plate capacitor structures from single crystal BaTiO₃, in which the thickness of ferroelectric lamellae was varied between 450nm and 75nm. The dielectric properties of these capacitors were investigated as a function of temperature. It was observed that the behaviour of the dielectric constant of the single crystal thin film lamellae was extremely similar to that of bulk single crystal material: There is a notable absence of any broadening or temperature shift of the dielectric peak or loss tangent. Peak dielectric constants of 25,000 are obtained, and Curie-Weiss analysis demonstrates 1st order transformation behavior. This is in surprising contrast to results on conventionally deposited thin film capacitor heterostructures, which show large dielectric peak broadening and temperature shifts [e.g. C. B. Parker *et al.*], as well as an apparent change in the nature of the paraelectric-ferroelectric transition from 1st to 2nd order. Our data are compatible with the recent model by Bratkovsky and Levanyuk, which attributes dielectric peak broadening to gradient terms that will exist in any thin film capacitor heterostructure, either through defect profiles introduced during growth, or through subtle asymmetry between top and bottom electrodes. The observed recovery of 1st order transformation behavior is consistent with the absence of significant substrate clamping in our experiment, as modeled by Pertsev *et al.*, and illustrates that the 2nd order behavior seen in conventionally deposited thin films cannot be attributed to the effects of reduced dimensionality e.g. size effects in the system, nor on the influence of an intrinsic universal interfacial capacitance associated with the electrode-ferroelectric interface. - C. B. Parker, J.-P. Maria, and A. I. Kingon, Appl. Phys. Lett. 81, 340 (2002) - A. M. Bratkovsky and A. P. Levanyuk, cond-mat/0402100 (2004) - N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett., 80, 1988(1998) - M. M. Saad, R. M. Bowman and J. M. Gregg, Appl. Phys. Lett., 84, 1159 (2004)

H3.29

Orientation dependence of the converse piezoelectric constants for epitaxial single domain ferroelectric films.

Jun Ouyang¹, S.-Y. Yang^{2,1}, Lang Chen¹, Ramamoorth Ramesh^{2,1} and Alexander Roytburd¹, ¹Materials Research Science and Engineering Center, Department of Materials Science and Engineering, University of Maryland, College Park, Maryland; ²Dept. of Materials Science and Engineering, University of California at Berkeley, Berkeley, California.

The orientation dependence of the converse piezoelectric constants in epitaxial single domain piezoelectric films constrained by substrate is calculated. The calculations are supported by the experimental measuring results of longitudinal piezoelectric constants (d_{33}) of epitaxial ferroelectric films in pseudo cubic (001), (110) and (111) orientations, which include tetragonal Pb(Zr_{0.2}Ti_{0.8})O₃ and rhombohedral 0.67Pb(Mg_{1/3}Nb_{2/3})O₃-0.33PbTiO₃. Based on available experiment data, 3-D orientation dependences of d_{33} are predicted for epitaxial films of Pb (Zr_{1-x}Ti_x) O₃ and x Pb (Mg_{1/3}Nb_{2/3}) O₃-(1-x) PbTiO₃ solid solutions with various compositions. This work is supported by the NSF under contract No. DMR-02-10512 and NSF-MRSEC under contract No. DMR-00-80008.

H3.30

Reversible Ultrahigh Piezoelectric Response in Epitaxial PbZr_{0.52}Ti_{0.48}O₃ Ferroelectric Thin Films.

Jun Ouyang¹, Dong Min Kim², Valanoor Nagarajan^{3,1}, S. Trolier-McKinstry⁶, Igor Levin⁴, Zhengkun Ma¹, S.-Y. Yang^{5,1}, Darrel Schlom⁵, C.-B. Eom², J. Melngailis¹, A.L. Roytburd¹ and R. Ramesh^{5,1}, ¹Materials Research Science and Engineering Center, Department of Materials Science and Engineering, University of Maryland, College Park, Maryland; ²Dept. of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin; ³Institute for Electronic Materials, IFF, Forschungszentrum, Germany; ⁴National Institute of Standards and Technologies, Gaithersburg, Maryland; ⁵Dept. of Materials Science and Engineering, University of California, Berkeley, California; ⁶Dept. of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

Due to the substrate clamping the effective piezoelectric constants of ferroelectric films are on the order of 100 pm/V. We report the observation of reversible piezoelectric strains 0.3% in (011) oriented epitaxial PbZr_{0.52}Ti_{0.48}O₃ films under applied AC electric fields less than 30kV/cm, which correspond to effective piezoelectric constants 1000 pm/V. High-resolution X-ray analysis and TEM pictures demonstrate that the (011) films contain domains of tetragonal and rhombohedral phases. Theoretical interpretation of these results on the basis of a field induced phase transition is presented. This work is supported by the NSF under contract No. DMR-02-10512 and NSF-MRSEC under contract No. DMR-00-80008.

H3.31

Capacitance Temperature Sensors using Oxygen Isotope Exchanged Strontium Titanate Single Crystal.

Hiroshi Takashima¹, Ruiping Wang¹, Naoki Shirakawa¹, Bambang Prijamboedi¹, Akira Shoji¹ and Mitsuru Itoh², ¹National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; ²Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Capacitance temperature sensors are useful tools for monitoring cryogenic temperatures under magnetic fields. Strontium titanate, SrTi¹⁶O₃, shows dielectric constant (ϵ) of more than 20,000 at ~2K. Unfortunately, the temperature gradient of ϵ , $d\epsilon/dT$, decreases sharply at $T < 10$ K due to the quantum effect and the practical application of the pure SrTiO₃ as capacitance temperature sensor materials is greatly limited. Recently, it is found that for partially oxygen isotope exchanged strontium titanate, SrTi(¹⁸O_{x¹⁶O_{1-x})₃, if the exchange rate x is less than 0.30 and the quantum paraelectric state is preserved, $d\epsilon/dT$ at cryogenic temperatures is increased, a trend that is favorable for the capacitance thermometer. In this report, characteristics of (110)- and (100)-oriented SrTi(¹⁸O_{x¹⁶O_{1-x})₃ single crystals as capacitance thermometers are investigated and compared with those of the commercially available capacitance thermometers. It is found that temperature sensitivity and dimensionless temperature sensitivity of the $x = 0.24$ and (110)-oriented SrTi(¹⁸O_{x¹⁶O_{1-x})₃ are 176 pF/K and 0.012 at 2.2 K, respectively. These values are the same order as these of commercially available bulk doped-SrTiO₃ capacitance temperature sensors. In comparison, the temperature sensitivity and dimensionless temperature sensitivity of SrTi¹⁶O₃ are 70 pF/K and 0.007 at 2.2 K, respectively. The above results reveal that the parallel capacitor with partially oxygen isotope exchanged quantum paraelectric strontium titanate is promising for capacitance thermometer that monitors cryogenic temperature under high magnetic fields. For practical application, the advantages of our capacitance thermometer using quantum paraelectric strontium titanate are obvious. Firstly, the size of devices can be greatly miniaturized because of the high dielectric constant of strontium titanate. Secondly, at cryogenic temperature below 1 K, the thermometer element will prevent from increasing temperature due to smaller Joule's heat of I^2R , where R and I are resistance and current of thermometer, respectively. A thermometer element with smaller joule's heat can guarantee a ³He refrigerator to reach a lower temperature.}}}

H3.32

Dielectric Phase Transition and Microstructural Studies of Functionally Graded PMN-PT Thin Films.

R. Ranjith¹, Apurba Laha¹, Victor Pushparaj² and S.B. Krupanidhi¹, ¹Materials Research Centre, Indian Institute of Science, Bangalore, Karnataka, India; ²Rensselaer Nanotechnology Centre, Rensselaer Polytechnic Institute, Troy, New York.

Compositionally graded (1-x)PMN-(x)PT thin films were prepared with a compositional variation of PT (PbTiO₃) across the film. The fabricated films were found to possess an enhanced diffusiveness in the phase transition, which actually seemed to be an envelope of the phase transition of the single layer relaxor ferroelectrics of a fixed composition within the limits of variation of x . These functionally graded films showed a very high nonlinear dielectric response and hence a high tunability near about 65%, which is nearly, double the times of what has been observed in any of the individual PMNPT compositions. The saturation polarization and remanent polarization of these films were found to be 32 $\mu\text{C}/\text{cm}^2$ and 20 $\mu\text{C}/\text{cm}^2$ respectively at 300°C. The hysteresis of these films showed a slim vertical loop characteristic even at temperatures well above the transition temperature. This could be attributed to thermal activation of the polar clusters, which might have been clamped due to the stress gradient present across the film at low temperatures.

H3.33

Assessment of Materials and Processes for Resonant Electromechanical Devices.

J. McPhillips¹, N.J. Donnelly^{3,1}, J. M. Gregg¹, R.M. Bowman¹, G. McRobbie², K.J. Kirk² and S. Cochran²; ¹Department of Pure and Applied Physics, Queen's University Belfast, Belfast, United Kingdom; ²Microscale Sensors, School of ICT (EEP), University of Paisley, Paisley, United Kingdom; ³Material Research Lab., Penn State University, University Park, Pennsylvania.

We describe the characterisation of electromechanical and acoustic behaviour of thin film structures of Au/(1-x)Pb(Mg_{1/3}, Nb_{2/3})O₃-xPbTiO₃ (PMN-PT)/La_{1/2}Sr_{1/2}CoO₃ grown by pulsed laser deposition onto LaAlO₃ single crystal substrates. Using conventional methods, we have characterised the relaxor ferroelectric PMN-PT thin film system and determined a dielectric constant of up to 2000, d_{33} of 100 pmV⁻¹ and Q_{33} of 1.9 x 10⁻² C⁻⁴cm² [1]. To further characterise the electromechanical coefficients of the material the composite resonator technique of Zhang et al [2] has been explored. This method

takes into account the fact that the films are not self supported and that their properties are dependent upon the substrate. It allows the direct determination of the electromechanical coupling coefficient, the density and the elastic constant of the film from the parallel and series resonant spectra of the composite resonator. Reverberations induced in the substrate are characterised by a frequency inversely proportional to its thickness. To facilitate this, we have developed a novel method of increasing the bulk acoustic wave frequency travelling in the substrate by lapping, whilst ensuring its robustness and acoustic isolation by encasing in microballoon-filled epoxy. To correlate experimental data with modelling we use software based on a frequency-domain matrix formulation of solutions of the one-dimensional wave equation [3]. The lapping process makes the substrate more compliant, and this behaviour has been modelled by Finite Element Analysis (FEA), with experimental measurement of the deflections by laser interferometric probing. [1] N.J. Donnelly et al, *J. Appl. Phys.* 93, 9924-9 (2003) [2] Y. Zhang et al, *IEEE Trans. Ultrason., Ferroelect., Freq., Contr.*, 50, 321-333 (2003). [3] G.K. Lewis, A matrix technique for analyzing the performance of multilayered front matched and backed piezoelectric ceramic transducers, *Acoust. Imaging* 8 (1978) 395-416.

H3.34

X-ray Determination of Room Temperature Symmetry States in Ferroelectric Thin Films Under Differing Conditions of Substrate Clamping. Jonny McAnaney¹, Lesley J. Sinnamon¹, Akeela Lookman¹, Robert M. Bowman¹, Marty Gregg¹, Gustau Catalan², Beatriz Noheda², Susana Rios³ and Jim F. Scott³; ¹Department of Pure and Applied Physics, Queen's University Belfast, Belfast, United Kingdom; ²Material Science Centre, University of Groningen, Groningen, Netherlands; ³Department of Earth Science, University of Cambridge, Cambridge, United Kingdom.

There is currently a great deal of interest on the degree to which homogeneous misfit strain, induced at the interface between the film and substrate, changes the sequence of phase transitions that occurs in ferroelectric thin films with temperature. Recent modelling by Pertsev *et al* [*Phys. Rev. Lett.* 80, 1988 (1998)], Ban *et al* [*J. Appl. Phys.* 91, 9288 (2002)], and Dieguez *et al* [arXiv:con-mat/0402101 (2004)] imply that homogeneous strain can alter the thermodynamics of the system to such an extent that phases inherently forbidden in bulk systems may be stabilised. Of equal current interest is the potential influence of gradients in inhomogeneous strain associated with an uneven distribution of defects (both chemical and structural) through the film thickness. However, there has been little experimental work to verify the validity of models used to date. Here we experimentally investigate the impact of mismatch strain between thin film, lower electrode and substrate, on the symmetry of phases in ferroelectric thin films that exist at room temperature. Crystallographic studies identifying both homogeneous and inhomogeneous strains in both Ba_{0.5}Sr_{0.5}TiO₃ / SrRuO₃ / MgO and Ba_{0.5}Sr_{0.5}TiO₃ / (La,Sr)CoO₃ / MgO will be discussed, and the influence of strain state on symmetry will be compared to that theoretically predicted in literature.

H3.35

Micro-Fabrication of Ferroelectric bilayers, using Aurivillius SBT with in-plane polarisation, as an analogous system to spin-valves. Stephen Campbell, Marty Gregg and Robert M. Bowman, Queens University Belfast, Belfast, United Kingdom.

Since its discovery in 1988, Giant Magneto Resistance (GMR) has led to huge development in magnetic recording, storage and sensor industries. While work has been performed on ferroelectric/ferromagnetic superlattices, and ferroelectric/ferroelectric superlattices, little is published on attempting in-plane coupling of the ferroelectric dipole, in a system analogous to those of ferromagnetic Spin-valves. Theory suggests that coupling between alternative layers of ferroelectric materials could result in novel hysteresis behaviour [K. H. Chew et al. *Appl. Phys. Lett.* 77, 2755 (2000)], with potential applications as high density non-volatile memory. The theory was presented without any reference to how such a system might be practically realised, as the direction of polarisation would necessarily be in-plane, contrary to most commonly grown perovskite ferroelectrics. Recently Aurivillius SBT, has been examined as a potential material for ferroelectric memory due to its apparently fatigue free nature with commercial platinum electrodes. The polarisation is in the **a**-axis, and it proves difficult to fabricate with **a**-axis out of plane, however, this apparent disadvantage can be harnessed in the realisation of structures comparable to ferromagnetic spin-valves. **c**-axis SBT thin films are deposited on {001} MgO by Pulsed Laser Deposition (PLD). Optimised films, prepared at 725°C and 0.4 mbar, were characterised to confirm single phase SBT. The optimised films are demonstrated to be epitaxial with the MgO substrate, with the orientation relation, SBT[110] // MgO[100]. This is evident from Φ -scans of the SBT(115) and MgO{100} reflections. Films deposited at 725°C display the smallest FWHM for the SBT

(208) reflections. To access the in-plane functional properties test capacitors have been micro-fabricated using conventional photolithographic processing, Ar⁺ ion milling and focussed ion beam processing. The in-plane polarisation is probed using opposed inter-digital electrodes, and other novel electrode configurations. A series of polarisation measurements taken on films fabricated with varying layer thicknesses of both the SBT and the dielectric spacer layer are presented. Measurements will also be presented on films with variations in spacing layer composition and dielectric behaviour, thus demonstrating the validity of the theory.

H3.36

Correlation of Structure and Electronic Properties for Zr_{0.2}Sn_{0.2}Ti_{0.6}O₂, a High Performance Dielectric.

S. C. Barron¹, L. Fitting², David A. Muller² and R. B. van Dover¹; ¹Materials science and engineering, Cornell University, Ithaca, New York; ²Applied and engineering physics, Cornell University, Ithaca, New York.

The amorphous dielectric Zr_{0.2}Sn_{0.2}Ti_{0.6}O₂ (a-ZTT) has been found to have a dielectric constant $\epsilon = 62$ and breakdown field $E_{br} = 4$ MV/cm. For injecting charge into today's smaller electronics, a critical parameter is $\epsilon E_{br} = Q_{max}/A$, the maximum areal charge induced on the electrodes. For a-ZTT deposited at 200 C, this parameter is $35 \mu C/cm^2$, compared to $3.7 \mu C/cm^2$ for SiO₂ and $8 \mu C/cm^2$ for optimized Al₂O₃. We have examined the correlation between dielectric properties and atomic structure by varying the processing temperatures for Zr_{0.2}Sn_{0.2}Ti_{0.6}O₂. Samples are rf-sputter deposited at substrate temperatures from room temperature to 400 C and subjected to post-deposition anneals up to 400 C. The dielectric constant and leakage current are determined from capacitance and current-voltage measurements, and properties are found to be optimized at 200 C deposition temperature with no post anneal. Structural characterization by XRD indicates that processing at 400 C gives a crystalline material, while the optimal material and depositions at less than 200 C are amorphous at the sensitivity of the XRD (25 Angstroms). STEM analysis, sensitive to smaller length scales, is used to probe for grains and short to intermediate range order in the x-ray amorphous materials. We will present systematic data of the structure/processing/property relationships for this dielectric and interpret their apparent dependence on both short- and intermediate-range order.

H3.37

Domain Stability Diagram and Ferroelectric Properties of Epitaxial BaTiO₃ Thin Films: Thermodynamic Analysis and Phase-Field Simulations. Yulan Li¹, Long-qing Chen¹, M.

Biegalski¹, D. G. Schlom¹, A. Sharan¹, V. Gopalan¹, K. J. Choi² and C. B. Eom²; ¹Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; ²Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Domain structures and ferroelectric properties of epitaxial thin films could be dramatically different from the corresponding unconstrained bulk single crystals. In this work, BaTiO₃ ferroelectric thin films are studied using thermodynamic theories based on the phenomenological Landau theories and phase-field simulations. Since existing phenomenological coefficients developed for BaTiO₃ systems are only applicable to small compressive strains (< 0.4%), a new set of coefficients were obtained for the Landau-Ginsburg-Devonshire thermodynamic potential with up to eighth-order terms. It is shown that ferroelectric transition temperatures can be shifted by about 300°C with about 1% compressive strain and about 450°C with 1.6% compressive strain as compared to the bulk ferroelectric transition temperature. The predictions are confirmed by experimental measurements of lattice parameters and second-harmonic generation on fully coherent (001) BaTiO₃ thin films epitaxially grown on (110) GdScO₃ and DyScO₃ substrates as a function of temperature. The phase-field approach was employed to simulate the domain structures of the BaTiO₃ films under biaxial substrate constraints. Based on the phase-field simulations, a domain stability diagram was constructed, which displays the stability of various ferroelectric phases and their stability as a function of temperature and magnitude of substrate constraint.

H3.38

Aging Effect in Sol Gel Derived Lead Zirconate Titanate Thin Films. Subhashish Basu Majumder¹, Anju Dixit¹ and Ram S.

Katihar¹; ¹Physics, University of Puerto Rico, San Juan, Puerto Rico; ²University of Puerto Rico, San Juan, Puerto Rico.

In order to the study the aging effect of the precursor sol, we have prepared Pb_{1.10}Zr_{0.53}Ti_{0.47}O₃ (PZT) thin films on platinized silicon substrates using sols aged for 650, 500, 400, 275, and 200 days. All these films crystallized into rhombohedral perovskite structure and the surface roughness and grain size of PZT films increased with aging

time. Appreciable changes in the electrical properties are apparent and it was found that (i) the dielectric constant reduced and the loss tangent increased systematically with aging time, (ii) the polarization and coercive field increased with sol-aging, and (iii) the leakage current densities reduced at high field regime and also the breakdown strength is increased with sol-aging. AC electric field dependence of the permittivity at sub-switching fields in terms of Rayleigh law was investigated for both freshly prepared and aged films. The estimated irreversible domain wall displacement contribution to the dielectric permittivity was found to be systematically increased with aging time. Domain vibration and reversal at sub-switching and switching fields respectively were found to control the observed dielectric and ferroelectric properties of aged PZT films.

H3.39

Steady State Leakage Currents in Ferroelectric Thin Films. Herbert Schroeder, EEM, IFF, FZ Juelich GmbH, Juelich, Germany.

Ferroelectric thin films are the main ingredient of non-volatile memory devices such as ferroelectric random access memory (FeRAM) and ferroelectric field effect transistor (FeFET). In order to guarantee the correct function of these devices the leakage current should be smaller than a certain limit. Although there are numerous studies of leakage current in ferroelectric thin film capacitors the understanding as well as the theoretical description of the effects are still unsatisfactory. We have applied a recently developed model for leakage currents in high permittivity dielectric capacitors to the case of ferroelectric thin films. In this model the carrier injection /ejection at the electrode interfaces is described by thermionic emission and is combined with the band conduction properties of the thin ferroelectric film, which is assumed as mono-domain with respect to the polarization state and modelled as wide band gap semiconductor. Numerical simulation studies have been performed for this system calculating the steady state leakage current density. Simulation data will be presented in dependence on several extrinsic and intrinsic parameters (polarization, applied voltage, temperature, film thickness, electrode barrier height, dead layer properties, etc.) for symmetrical and asymmetrical electrodes. The trends of the simulation results will be compared to experimental leakage data of materials such as PZT and BTO, to which the input parameters were adjusted.

H3.40

Dielectric Response of Epitaxial Compositionally Graded Ferroelectric Thin Films. Shan Zhong¹, Pamir Alpay¹ and Joseph Mantese²; ¹Metallurgy and Materials Engineering and Institute of Materials Science, University of Connecticut, Storrs, Connecticut; ²Delphi Research Laboratories, Delphi Research Laboratories, Shelby Township, Michigan.

In recent years, polarization graded ferroelectrics became an object of intensive research because of their unique behavior and properties that are not observed from homogenous bulk or thin film ferroelectrics. Polarization graded ferroelectrics are distinguished from homogenous ferroelectrics by a spatial systematic variation of the electric dipole moment which can be accomplished by systematic variations in the composition. Unlike homogenous ferroelectrics which are characterized by a symmetric hysteresis loop with respect to the polarization and applied field axes, graded ferroelectric systems display strikingly new behavior, the most notable being a translation of the hysteresis loop along the polarization axis and a built-in potential associated with this translation. In this presentation, a thermodynamic model is developed to analyze the dielectric properties of compositionally graded epitaxial ferroelectric films. The dielectric properties of such films display a broadening in the temperature response as compared to a single peak for homogenous bulk ferroelectrics. The dielectric maximum and the extent of the temperature broadening of the dielectric response can be controlled by the strength of the compositional gradient as well as by tailoring the internal stresses. Numerical results are presented for various compositionally graded BaTiO₃-SrTiO₃ and PbTiO₃-PbZrO₃ epitaxial films as a function of the average strain in the film and the film thickness. This work is supported by the National Science Foundation under Grant No. DMR-0132918.

H3.41

Low Temperature Transport and Grain Boundary Induced Phase Transition in SrTiO₃. Rui Shao¹, Dawn A. Bonnell¹ and Gerd Duscher^{2,3}; ¹Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ³Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Recent studies have revealed strong correlations between electrical field effects and the structure of functional oxide interfaces. Atomically abrupt SrTiO₃ grain boundaries, which is often used as a model, have shown to cause sufficient disruption of local potential to

alter dielectric properties many tens of nanometers from the interface. Here we show that these boundaries induce a phase transition at low temperatures. The electrical properties of 0.05wt% Nb-doped SrTiO₃ bicrystals with misorientation angles of 36.8° and 24° have been determined by four point I-V and capacitance measurements. The GBs in these samples were found to be atomically sharp by STEM. In addition we have developed a new scanning probe approach for determining surface potential in UHV and determined the temperature dependence of potential. In both types of GBs, the resistance exhibits a complex temperature dependence, similar to the positive temperature coefficient effect in doped polycrystalline BaTiO₃. The maxima of resistance for 36.8° and 24° GBs are 163K and 147K respectively. The grain boundary capacitance significantly deviates from Curie-Weiss law below the temperatures for the maximum resistance. This discovery is a direct evidence of the appearance of grain boundary polar states at low temperatures. The possible mechanism is ascribed to the stabilization of a ferroelectric phase in SrTiO₃, which is a quantum paraelectric material, due to a large built-in electric field at the grain boundaries. In addition, after annealing in vacuum (p 4x10⁻¹⁰ mbar) at 500-600°C, the temperature dependence of the GB resistance becomes metallic showing no maximum. This work is supported by DOE research funding DE-FG02-00ER45813-A001.

H3.42

Phase-Field Simulation of Ferroelectric Domain Switching in Polycrystals. Samrat Choudhury, Yulan Li and Long-qing Chen; Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

The effects of grain boundaries on ferroelectric domain structures and polarization switching in polycrystals are studied. A phase-field model is developed, taking into account the polycrystalline grain structure as well as the various energetic contributions including elastic energy, electrostatic energy, and domain wall energy. It is shown that grain boundaries have a significant effect on the shape and size of ferroelectric domains. Based on the observation of ferroelectric domain evolution, it is found that domain switching involves the nucleation of 90° domains through the formation of twin boundaries, resulting in a reduction of the coercive field as compared to direct 180° switching. The dependencies of the remnant polarization and coercive field on grain sizes are studied. It is found that the coercive field increases with a decrease in grain size and with an increase in speed of electric field loading. The results will be compared with experimental measurements of single crystals and polycrystals.

H3.43

Investigation of Niobium Oxide Thin Film Deposition for Biomedical Applications. James Groves¹, Robin Catalano¹, Michael Gorman², Igor Lyubinetzky³ and Suntharampillai Thevuthasan³; ¹Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; ²Science, Technology, and Society, University of Virginia, Charlottesville, Virginia; ³Pacific Northwest National Laboratory, Richland, Washington.

Within the Center for Nanoscopic Materials Design, biomedical engineering researchers are developing research tools that facilitate laboratory studies of wound healing, the progression of atherosclerosis in arteries, and tumor cell invasion. For a portion of their research they would like to have access to diffuse arrays of cell adhesion sites on surfaces. By studying the interaction of cells with these nanoscale adhesion site arrays, they hope to generate insight into various biological processes. In the literature, researchers suggest that nanoscale metal oxide islands on metal oxide substrates could constitute the foundation of these cell adhesion site arrays. With colleagues, we have recently demonstrated the ability to guide the growth of Cu₂O quantum dots on SrTiO₃ (100) substrates, using focused ion beam substrate surface prepatterning to define quantum dot growth location. For the biomedical applications described above, a different metal oxide material system combination has been identified as potentially useful - NbO₂ on TiO₂. This paper will present the results of initial molecular beam epitaxy (MBE) experiments designed to map the relationship between MBE growth conditions and niobium oxide phase formation, a critical step towards formation of NbO₂ quantum dots on TiO₂ single crystal surfaces. The experiments described here varied substrate temperature (in the range of 500 - 1000°C) and oxygen partial pressure in the growth chamber (in the range of 5x10⁻⁸ Torr and 5x10⁻⁵ Torr). The results show a broad process space in which multiphase niobium oxides were created with only select conditions generating single niobium oxide films. Characterization results from atomic force microscopy, x-ray photoelectron spectroscopy, and reflected high energy electron diffraction will be presented. These results will be placed in the context of the limited literature available describing niobium oxide synthesis.

H3.44

Epitaxial Mixed Ruthenium Oxide Films: Tunable Lattice-Matched Bottom Electrodes for Complex Ferroelectric Oxides. Olivier Gautreau¹, Catalin Harnagea¹, Alexandre Dube¹, Alain Pignolet¹ and Teodor Veres²; ¹INRS-Energie et Materiaux, Varennes, Quebec, Canada; ²Industrial Material Institute / National Research Council Canada - Conseil National de Recherches Canada, Boucherville, Quebec, Canada.

SrRuO₃ (SRO) is a conductive perovskite, which is currently being tested as a bottom electrode for epitaxial ferroelectric thin films. It possesses a low resistivity and a good lattice match with some ferroelectric perovskites (BaTiO₃, PZT 20/80, BLT, SBT), for which it promotes the epitaxial growth. In order to obtain a better lattice match for a variety of materials, we propose the use of a solid solution of SrRuO₃ and CaRuO₃ (CRO) as a conductive electrode and buffer layer for the epitaxial growth of ferroelectric thin films for device applications. Its resistivity is comparable to that of SRO but, have a smaller lattice parameter, depending on the concentration of CRO. It enables therefore to grow epitaxial ferroelectric films with lower strains, which in turn leads to higher quality films with better properties. We report here the growth and characterization of SRO and CRO films, as well as solid solution thereof, by pulsed laser deposition on both silicon and strontium titanate substrates. Their structural and microstructural properties, investigated by XRD and AFM, as well as their transport properties will be presented and discussed.

H3.45

Strained SrTiO₃ Films on DyScO₃ Substrates.

Michael D. Biegalski¹, D. D. Fong², Y. Li¹, Y. Jia¹, J. H. Haeni¹, Long-qing Chen¹, M. A. Zurbuchen², J. A. Eastman², P. A. Fuoss², C. Thompson^{3,2}, W. Chang⁴, S. W. Kirchoefer⁴, P. Irving⁵, J. Levy⁵, R. Uecker⁶, P. Reiche⁶, S. K. Streiffer², S. Trolier-McKinstry¹ and D. G. Schlom¹; ¹Material Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; ²Materials Science Division, Argonne National Laboratory, 60439, Illinois; ³Department of Physics, Northern Illinois University, DeKalb, Illinois; ⁴Navy Research Labs, Washington, District of Columbia; ⁵Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania; ⁶Institute of Crystal Growth, Berlin, Germany.

Using reactive MBE, strained epitaxial SrTiO₃ films were grown on DyScO₃ substrates. Films with thicknesses ranging from 50 Å to 1000 Å were grown to establish the critical thickness in this 1% mismatched system, and to investigate properties as a function of film thickness. These films have excellent crystalline quality with rocking curve full widths at half maxima (FWHM) of 10-18 arc-sec. (0.003-0.005°), which is narrower than any previously report for epitaxial perovskite films and is comparable to the structural perfection observed in heteroepitaxial films of conventional semiconductors produced by MBE. Strain has been predicted to have a large effect on the properties of SrTiO₃. Although unstrained SrTiO₃ is not ferroelectric at any temperature, we observe these strained SrTiO₃ films to be ferroelectric and to have extremely high dielectric constants in the vicinity of room temperature. In contrast to unstrained SrTiO₃, which shows a monotonic increase in dielectric constant with decreasing temperature, reaching 20,000 near 4 K, these strained SrTiO₃ films show a peak in their dielectric constant near 250 K that exceeds 15,000 at low measurement frequencies. The dielectric data shows frequency relaxation that is well fit by a Vogel-Fulcher equation over six orders of magnitude in frequency. The Vogel-Fulcher fitting indicates a freezing temperature of 204 K, which agreed with measurements of remanent polarization as a function of temperature. This dielectric dispersion will be discussed in terms of models for disorder in ferroelectrics and relaxor behavior. These films also exhibit clear hysteresis loops below the T_{max} with an in-plane remanent polarization up to 10 μC/cm² at 77 K.

H3.46

Growth and Characterization of Multilayer SrBi₂Ta₂O₉/SrBi₂Nb₂O₉ Thin Films using Pulsed Laser Deposition Technique. Nora P. Ortega, Pijush Bhattacharya, Rasmi R. Das and Ram S. Katiyar, Physics Department, University of Puerto Rico, San Juan, Puerto Rico.

Among the bismuth layer perovskites, SrBi₂Ta₂O₉ (SBT) and SrBi₂Nb₂O₉ (SBN) have been extensively studied for non-volatile random access memory applications. Previously we have observed a dramatic increase in the remanent polarization (Pr 25 mc/cm²) of laser ablated SBN films using suitable deposition parameters. However, the dc leakage current of SBN films was relatively higher in comparison to SBT thin films. In order to suppress the dc-leakage current of SBN capacitors, in this work, we have fabricated multilayer thin films (SBT/SBN) on Pt/TiO₂/SiO₂/Si substrates. The thickness of all these films are 400 nm with a stacking periodicity of SBT(50 nm)/SBN(50 nm) is 100 nm. X-ray diffraction studies showed that the

peak positions of multilayer SBT/SBN thin films were nearly in the same positions as of SBN. Raman scattering studies on the films were carried out in order to understand the lattice vibrational characteristics. The X-ray photoelectron spectroscopy was used to analyze the composition and oxidation states of the multilayer films. The dielectric constant of the films was found to be lower (150) than the single layer SBN films of similar thicknesses. The leakage current behavior of the single layer and multilayer films was studied with different temperatures ranging from 100-650 K. The observed data were fitted to the interfacial dominated Schottky mechanisms. The switching polarization of multilayers was in the range of 10-15 mC/cm². The leakage current density of multilayer films was found to be lower (10-7 A/cm²) than SBN films (10-5 A/cm²). The detailed structural and electrical characterizations of the multilayer thin films will be presented along with a comparison to single layer SBT and SBN thin films.

H3.47

Microstructural and Electrical Characterization of PZT Thick Films on Metal Foils. Aiyong Wu¹, Paula Maria Vilarinho¹, Sudarsan Srinivasan², Angus Ian Kingon² and Ian Michael Reaney³; ¹Ceramics and Glass Engineering Department, University of Aveiro, Aveiro, Portugal; ²Materials Research Center, North Carolina State University, Raleigh, North Carolina; ³Department of Engineering Materials, University of Sheffield, Sheffield, United Kingdom.

Functional ferroelectric oxide thick-films are of particular interest for microelectronics applications, in which high applied voltages are necessary. Furthermore, the fabrication of ferroelectric films on metal foils is of interest for devices integrated into the electronic package, an approach which is currently receiving much attention due to the cost and space advantages. The fabrication of thick functional oxide layers requires modified deposition techniques, such as Electrophoretic Deposition (EPD). EPD is quite well suited for the preparation of thick layers on metal foils due to the high deposition rates and to the possibility of using nanosized powder suspensions with a controlled degree of agglomeration, which permits lower sintering temperatures for the thick films. However, the utilization of metal foils as substrates for thick films raises important problems of compatibility between the high sintering temperature required to crystallize the ceramic film and the refractoriness of the substrate. An investigation of the ferroelectric-foil compatibility issues is an important part of this presentation. In this work ferroelectric PZT thick films in the thickness range from 5 to 20 micron were deposited on metal foils by EPD. Flexible copper and platinum foils were used as substrates. The deposited films were sintered at different temperatures from 900 to 1030C. The effect of adding a PbO coating on the film surface was studied with the aim of improving the sintering, and to produce dense films. The phase purity was analysed by x-ray diffraction (XRD). The microstructure of the deposited films and the interface reaction region were inspected by transmission electron microscopy (TEM) and Rutherford backscattering (RBS). The electrical properties were improved in the films with PbO coatings. The electrical properties of the films were correlated with the reaction region and the density of the films.

H3.48

Electronic Structure of KDP and DKDP Hydrogen-Bonded Ferroelectric Oxides. Sergei O. Kucheyev¹, C. Bostedt^{1,2}, T. van Buuren¹, T. M. Willey¹, T. E. Felter¹, S. G. Demos¹, T. A. Land¹, L. J. Terminello¹, A. J. Nelson¹ and A. V. Hamza¹; ¹Lawrence Livermore National Laboratory, Livermore, California; ²HASYLAB at DESY, Hamburg, Germany.

Single crystals of normal and deuterated KD_{2x}H_{2(1-x)}PO₄, often called KDP (x = 0) and DKDP (x > 0), are perhaps the best studied hydrogen-bonded ferroelectric oxides. They are also important (non)linear optical materials widely used for frequency conversion and optoelectrical switching in laser systems. What makes these materials unique is that single-crystal KDP and DKDP can be conveniently grown with linear dimensions in the range of 50-100 cm, as required for large-aperture high-power lasers. Despite excellent optical characteristics and rather mature crystal growth methods, KDP and DKDP are also notoriously known for their complex fundamental materials properties, resulting in a range of challenging problems. In this presentation, we discuss how the electronic structure of KDP and DKDP is affected by radiation damage and complex deuterium-hydrogen exchange in crystals stored at ambient conditions. The electronic structure is studied by synchrotron-based soft x-ray absorption near-edge structure (XANES) and x-ray emission (XES) spectroscopies, while H and D depth profiles are measured by elastic recoil detection analysis (ERDA). In particular, we study the dependence of the element-specific partial density of states in the conduction and valence bands on (i) deuteration, (ii) the crystallographic phase (tetragonal and orthorhombic), (iii) sample temperature, and (iv) dose of ionizing radiation. We also compare our experimental results with previous molecular orbital and band

structure calculations. This study fills some gaps in the current understanding of the fundamental materials properties of KDP and DKDP ferroelectrics. This work was performed under the auspices of the U.S. DOE by the University of California, LLNL under Contract No. W-7405-Eng-48.

H3.49

Structural and Electrical Characterization of Sputtered $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ Thin Films for Tunable Microwave Devices. Sriraj Manavalan¹, Ashok Kumar² and Thomas Weller¹; ¹Electrical Engineering, University of South Florida, Tampa, Florida; ²Mechanical Engineering, University of South Florida, Tampa, Florida.

The dependence of dielectric permittivity on the applied electric field and high dielectric constant makes barium strontium titanate (BST) as a promising ferroelectric material for applications in tunable microwave devices like filters, phase shifters and resonators. High tunability and low dielectric loss are desired for tunable microwave devices. The objective of this research is to optimize the tunability and dielectric loss of sputtered BST thin films at microwave frequencies with different deposition and annealing conditions. The optimization of tunability and dielectric loss of pulsed laser deposited BST thin films at microwave frequencies with different deposition conditions has been performed and the tunability of 3:1:1 and loss tangent of 0.0121 was achieved at 0.4 – 0.6 GHz. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin films were deposited on Pt/TiO₂/SiO₂/Si substrates by sputtering technique. BST was etched selectively using buffered HF and platinum was deposited using e-beam evaporation in order to make the coplanar waveguide electrode structure. The electrical measurements were achieved in the parallel plate capacitor configuration with platinum as the top and bottom electrode. The microstructural and phase analysis of the BST films were performed using X-ray diffraction (XRD) method. XRD results show that the BST (110), (100), (200) and (211) and films were crystalline. The diffraction patterns are attributed to cubic (perovskite) crystal system. After the deposition of BST thin films, hillock formation was observed in platinum and led to shorted devices and measures to avoid hillock formation will be investigated. The analysis of surface morphology is done using atomic force and scanning electron microscopy. Results of structural and surface analysis, tunability and loss tangent as a function of deposition temperature, oxygen pressure and annealing temperature for the films deposited using sputtering technique will be discussed. The optimized structural and dielectric properties of thin films deposited using both sputtering and PLD will be compared.

H3.50

Formation of Patterned Crystalline Oxide Structures using Photosensitive Metal-Organics and Hydrothermal Processing. Clifford L. Henderson, Paul J. Roman, Augustin Jeyakumar and Abimbola Balogun; School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia.

There is a growing need for high dielectric constant films and structures in electronics applications ranging from IC transistor gates to capacitive RF MEMS switches. For example, low cost MEMS switches are prime candidates to replace conventional GaAs FET and p-i-n diode switches used in RF and microwave communication systems. In most capacitive MEMS switches reported so far, the dielectric layer has been silicon nitride (SiN) deposited via CVD methods. Likewise, simple silicon dioxide layers have been the material of choice for transistor gate oxides in ICs. In order to improve device performance there is a need to move to higher dielectric constant oxides. However, these and many other similar applications require the formation of patterned oxide structures. This can be difficult with many desirable oxides such as the perovskite family of materials (e.g. BST). Also, for many MEMS applications, low cost and mild processing conditions will be required for large scale implementation of such materials. No previous methods that we are aware of can easily meet these demands for production of patterned oxides at low cost using mild conditions. This paper presents an update concerning our ongoing work to develop novel methods for directly depositing patterned metal oxide dielectrics. Our basic approach uses photosensitive metal-organic precursor films that can be selectively converted to the desired metal oxide by patterned exposure to ultraviolet light. In this process, a photosensitive metal-organic precursor solution is used to coat the substrate and form a solid precursor thin film. Upon UV exposure, the organic ligands of the precursor molecules are cleaved which results in the formation of an amorphous metal oxide in the exposed areas while the unexposed precursor material is later washed away using a developer solvent. Thus, these photosensitive materials allow the selective deposition of oxide structures without requiring the deposition of blanket oxides using vacuum methods or subtractive plasma or wet etching. A summary of our work to date in this area will be presented along with highlights of the amorphous oxides that have been deposited and their resulting physical and electrical properties. In many applications

however, the production of higher dielectric constant crystalline oxide structures may be desirable. Our recent work has focused on developing a method to produce directly patterned crystalline oxides. We have succeeded in developing a method for producing patterned crystalline oxide dielectrics without the need for etching processes or high temperatures by using a combination of the photodefinable metal-organic systems and subsequent low temperature hydrothermal treatment. This paper will discuss our recent results in this area including physical and electrical characterization of the patterned crystalline oxides and results from the use of these materials in actual devices such as MEMS microwave switches.

H3.51

Abstract Withdrawn

SESSION H4: Ferroelectrics/Piezoelectrics I
Chairs: A. Roytburd and Jean-Marc Triscone
Tuesday Morning, November 30, 2004
Grand Ballroom (Sheraton)

8:15 AM *H4.1

Effect of Electrical Boundary Conditions on Ferroelectric Behavior in Epitaxial PbTiO_3 Thin Films. S. K. Streiffer¹, D. D. Fong¹, G. B. Stephenson¹, J. A. Eastman¹, P. H. Fuoss¹, S. Mallu², Carol Thompson², O. Auciello¹, D. M. Kim³, K. J. Choi³, C. B. Eom³, M. D. Biegalski⁴, S. Trolier-McKinstry⁴ and D. G. Schlom⁴; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Department of Physics, Northern Illinois University, De Kalb, Illinois; ³Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin; ⁴Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

Ferroelectric behavior is strongly dependent on the degree to which the spontaneous polarization is compensated by charge at interfaces. As examples, incomplete charge compensation for electroded ferroelectrics, arising from finite carrier densities in the electrodes, has been identified as one possible origin of size effects in ferroelectric thin films; alternately, ferroelectric thin films on insulating substrates form an equilibrium 180° domain pattern to minimize depolarization energy. However, little experimental data exists that directly compares ferroelectric behavior in thin films with different degrees of polarization compensation or different interface structures. Here we report synchrotron x-ray scattering studies of the ferroelectric phase transition in epitaxial thin films of the prototypical perovskite PbTiO_3 , for films under different electrical boundary conditions: chamber ambient / ferroelectric / insulator, chamber ambient / ferroelectric / electrode, and electrode / ferroelectric / insulator. The impact of the different interface electrical conditions on phase transition temperature will be discussed in terms of models for T_C suppression in thin films. Changes in the depolarization domain phase diagram for the two PbTiO_3 /insulator cases also indicate an evolution in top interface electrical behavior with temperature, that yields insight into ferroelectric behavior for samples deposited in typical growth systems. Finally, efforts to probe symmetric insulator / ferroelectric / insulator heterostructures will also be described.

8:45 AM *H4.2

Photoelectron diffraction studies of ultra-thin PbTiO_3 films. L. Despont¹, C. Lichtensteiger², J.-M. Triscone² and P. Aebi¹; ¹Institut de Physique, Université de Neuchâtel, Neuchâtel, Switzerland; ²DPMC, University of Geneva, Geneva, Switzerland.

Ferroelectricity in ultra-thin films has been investigated in epitaxial c-axis PbTiO_3 films prepared by off-axis magnetron sputtering onto (001) Nb-SrTiO₃ metallic substrates. Finite size effects were probed by measuring angle-scanned X-ray photoelectron diffraction (XPD) patterns in a series of c-axis oriented PbTiO_3 perovskite films with thicknesses ranging from 500 Å down to 20 Å. Angle-scanned XPD, based on photoelectron spectroscopy, measures the angular distribution of photoelectrons emitted from a selected atomic species or site. Due to the finite mean free path of the photoelectrons, XPD provides local, real-space information on the atomic arrangement around a selected site. It is therefore a truly atomic-scale probe of the ferroelectric, broken symmetry state. As a main result we find that, within the precision of our measurements, films as thin as 20 Å still exhibit a single polarization state over a macroscopic sample area. This thickness is well below any prediction for the ferroelectric state to persist.

9:15 AM H4.3

Ferroelectricity and Tetragonality in Ultrathin PbTiO_3 Films. Céline Lichtensteiger¹, Javier Junquera^{2,3}, Philippe Ghosez² and Jean-Marc Triscone¹; ¹DPMC, University of Geneva, Geneva, Switzerland; ²Dept. de Physique, University of Liege, Sart-tilman

It has been argued for many years that, as the physical dimensions of a ferroelectric material are made smaller, the stability of the ferroelectric phase is altered, leading to a minimum critical thickness required for ferroelectricity. Recently, local probe experiments have however allowed the detection of ferroelectricity in perovskite $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ films down to a thickness of 40\AA (10 unit cells)[1], and ab-initio calculations identified a critical thickness valued at 24\AA (6 unit cells) for BaTiO_3 [2], much smaller than what was previously thought. In this study, a series of epitaxial perovskite films of c-axis oriented PbTiO_3 ranging from 500 down to 24\AA (6 unit cells) were grown using off-axis RF magnetron sputtering onto metallic (001) Nb-SrTiO_3 substrates. Topographic measurements using atomic force microscopy showed that these films were essentially atomically smooth with RMS roughness of about 3\AA . The thickness of the films, the c-axis length, and the epitaxial growth were studied using high resolution x-ray diffraction measurements. It is shown that the c-axis parameter systematically decreases with decreasing film thickness below 200\AA . Using a first-principles model Hamiltonian approach, the decrease in tetragonality is related to the reduction of polarization. The analyses demonstrate that films well below 100\AA are ferroelectric and that the progressive polarization reduction is due to the depolarizing field resulting from imperfect screening [3]. Because of the crucial role played by imperfect screening, we are currently studying the effect of using a SrRuO_3 epitaxial film instead of an Nb-SrTiO_3 metallic substrate as a bottom electrode. An additional step will be to study the strain effect due to lattice mismatch by using other substrates with different lattice parameters. [1] Tybell et al., *Appl. Phys. Lett.* **75**, 856 (1999). [2] Junquera et al., *Nature* **422**, 506 (2003). [3] Lichtensteiger et al., *condmat/0404228*.

9:30 AM H4.4

Surface and Interface Characterization of Epitaxial PbTiO_3 Grown on SrTiO_3 . Masaki Kurasawa and Paul C. McIntyre; Materials Science and Engineering, Stanford University, Stanford, California.

For ferroelectric random access memory (FeRAM) capacitors, reliability phenomena, such as fatigue and imprint failures, are of great importance. These failures may result in part from interfacial defects present between the ferroelectric film and the electrode material. However, the microscopic origins of these failures are still uncertain. It is very important to comprehend the overall interface behavior for overcoming these failures as well as for realizing a thinner ferroelectric capacitor for a future low voltage-operated FeRAM. As a first step toward understanding interface behavior in greater detail, we have investigated the interaction of Pt with high quality PbTiO_3 epitaxial thin films using X-ray photoemission spectroscopy (XPS) and electrical characterization. PbTiO_3 thin films were grown on single-crystal SrTiO_3 (100) substrates at 600°C by metal organic chemical vapor deposition. The films have been confirmed to be nearly coherently grown with (001) orientation on the SrTiO_3 substrates by X-ray diffraction reciprocal space mapping. The full width at half maximum of diffracted peak for the PbTiO_3 (002) plane is 0.06° as observed in X-ray diffraction rocking curve measurements, comparable to that of the single crystal substrate. Finite thickness oscillations observed in X-ray diffraction indicate the films have a smooth surface. Angle resolved XPS (ARXPS) was measured for the determination of the surface structure of PbTiO_3 . In-situ XPS measurements during Pt deposition were carried out to investigate interface behavior and band structure between Pt and PbTiO_3 . ARXPS indicated that 10\AA thick surface mixed layer of lead carbonate and lead oxide exists on the stoichiometric PbTiO_3 film. However, it is found that the surface layer can be completely removed by HNO_3 treatment. During in-situ XPS measurement as a function of Pt deposition onto HNO_3 treated films, all $\text{Pb}4f$, $\text{Ti}2p$ and $\text{O}1s$ core-level peaks shift by up to 0.9 eV toward higher binding energy as a result of metallization-induced electron energy band bending. Furthermore, we extract an energy off-set is 2.4 eV between the Fermi edge of Pt and valence band maximum of PbTiO_3 at the interface. Our results suggest that the Fermi energy is pinned 2.4 eV above valence band maximum, because this offset energy is not consistent with the ideal value derived from the reported work function of Pt (5.3 eV), the electron affinity and the forbidden gap of PbTiO_3 (3.5 eV and 3.4 eV). We have also observed that Pb metal diffuses from PbTiO_3 into the Pt layer during room temperature Pt deposition. Based on the band structure as determined by photoelectron spectroscopy, the measured leakage conduction properties of $\text{Pt/PbTiO}_3/\text{SrTiO}_3$ thin film capacitors will be discussed.

10:15 AM H4.5

Microstructure and Ferroelectric Properties of Self-Assembled PbTiO_3 Nanostructures Prepared by MOCVD. Hajime Nonomura¹, Hironori Fujisawa^{1,2}, Masaru Shimizu^{1,2}, Hirohiko Niu^{1,2} and Koichiro Honda³; ¹Dept.

In the past several years, interest in ferroelectric nanostructures has increased greatly not only from the point of view of application but also from that of ultimate potential for ferroelectricity. We already reported on the preparation and ferroelectricity of self-assembled PbTiO_3 and PZT nanostructures grown on various substrates by MOCVD. However, structural control of PbTiO_3 nanostructures, microstructures and their crystalline and ferroelectric properties were not well understood. In this paper, structural control using epitaxial relation and microstructures of self-assembled PbTiO_3 nanostructures were studied. Piezo- and ferroelectric properties were also discussed. In our experiments, PbTiO_3 nanostructures were fabricated self-assembled on Pt/SrTiO_3 and Pt/MgO by MOCVD. Using epitaxial relation, structural control such as shape, size and arrangement was performed. Pyramidal-shaped, triangular-prism-shaped and square-shaped PbTiO_3 nanostructures were successfully prepared on $\text{Pt/SrTiO}_3(111)$, (110) and (100) substrates, respectively. TEM observation and SEAD (selected area electron diffraction) showed that nanostructures had a tetragonal structure and 90° domain structure in some cases. From high temperature X-ray diffraction measurement, nanostructures were found to have the same phase transition temperature as the bulk PbTiO_3 . PFM (piezoresponse force microscopy) measurement revealed that PbTiO_3 nanostructures on various substrates had piezo- and ferroelectricity. Raman spectroscopy results will also be discussed.

10:30 AM H4.6

Artificially Induced Cation Disorder by Composition Modulation in Multilayer PZT. Arjen Janssens¹, Guus Rijnders¹, Dave H. A. Blank¹ and Beatriz Noheda²; ¹Fac. of Science & Technology and MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; ²Materials Science Center, University of Groningen, Groningen, Netherlands.

PZT, a well known ferroelectric material, is due to its strong piezoelectric-effect already used in many applications. The maximum piezoelectric effect is found close to the morphotropic phase boundary (MPB) due to the presence of a lower symmetry (monoclinic) phase providing an extra degree of freedom for the polarization. Through unit-cell layer-by-layer growth we are able to investigate the influence of cation ordering on the piezoelectric properties of this phase with lower symmetry. Pulsed laser interval deposition, controlled by reflection high-energy electron diffraction (RHEED), is used for the monolayer growth with different compositions of $\text{PZ}(x)\text{T}(1-x)$. Alternating deposition of unit-cell layers, using two targets with slightly off-stoichiometric compositions, on both sides of the MPB, is used to construct the artificial structures. In this contribution the interval deposition of the artificial structures as well as their properties will be presented.

10:45 AM H4.7

High-Resolution TEM Study of Ion Slicing of Single-Crystal Ferroelectric Thin Films. Sasha Bakhr¹, Djordje Djukic¹, Ryan Roth¹, Bryan Lulicht², Kathleen Dunn², Jonathan Rullan², Tomoyuki Izuhara¹, Hassaram Bakhr² and Richard M. Osgood¹; ¹Columbia University, New York, New York; ²SUNY Albany, New York, New York.

Single-crystal thin films of many ferroelectric materials can now be fabricated from bulk crystals by deep ion implantation followed by ion-induced-strain-selective etching of the implanted region [1,2]. Despite the success of this technique there have been relatively few studies of the materials physics of this process. In this paper, we report the use of high-resolution TEM and X-ray scattering to examine the implanted region and to relate the structure and properties of the implanted region to its selective etching and internal lattice distortion. Our studies use z-cut LiNbO_3 implanted with $1-4.3\text{ MeV He}^+$ ions to form a $0.25\text{ }\mu\text{m}$ wide implanted region beneath the surface of the crystal. Our TEM studies show that, after implantation and low-temperature (200°) annealing for 30s, He bubbles form in the crystalline lattice. The coalescence of these bubbles is known to result from the low solid solubility of He in the lattice and result in local stain in the crystal. These nanobubbles are concentrated in the heavily implanted area and decrease rapidly away from the interface. The average diameter of these bubbles is approximately 5 nm and scale in size with the local concentration of the He implant dose. A comparison with the recent micromechanical theory of He bubble growth by Varma, which was developed for light-ion implanted regions in Si illustrates the importance of the different materials properties in Si and LiNbO_3 . X-ray studies of shallow implanted crystals have enabled us to determine the degree of strain in the implanted crystal as a function of implantation dose and heat treatment. I. M. Levy, R.M. Osgood, Jr., R. Liu, E. Cross, G.S. Cargill III, A. Kumar and H. Bakhr, "Fabrication of Single-Crystal

Lithium Niobate Films by Crystal Ion Slicing." Appl. Phys. Lett. 73, 2293 (1998) 2. T. Izuhara, R. M. Osgood, Jr., M. Levy, M.E. Reeves, Y.G. Wang, A. N. Roy, and H. Bakhru, "Low-Loss Crystal Ion Sliced Single-Crystal Potassium Tantalate Films." Appl. Phys. Lett. 80, (2002)

11:00 AM H4.8

MOCVD Growth and Ferroelectric Properties of PZT Ultrathin Films with Thicknesses below 10nm.

Hironori Fujisawa^{1,2}, Hajime Nonomura², Masaru Shimizu^{1,2}, Hirohiko Niu^{1,2} and Koichiro Honda³; ¹Dept. of Elect. Eng. & Comp. Sci., University of Hyogo, Himeji, Hyogo, Japan; ²Dept. of Elect. Eng. & Comp. Sci., Himeji Inst. Tech., Himeji, Hyogo, Japan; ³Fujitsu Lab. Ltd., Atsugi, Kanagawa, Japan.

The critical thickness in ferroelectric thin films has long been studied because it will limit a minimum operation voltage in ferroelectric memories and also because it is closely related to the origin of ferroelectricity. Recently, there have been several reports on ferroelectric ultrathin films with a well-refined microstructure and ferroelectricity. For example, T. Tybell et al. reported that ferroelectricity was observed in 4nm-thick PZT films. On the other hand, several theoretical studies demonstrated that ferroelectricity was stable down to several unit cells for lead titanate (PbTiO₃). Therefore, the minimum thickness in which stable ferroelectric polarization has been experimentally observed is seems to be larger than theoretically predicted values. One of reasons for this is difficulty in detecting ferroelectric state due to an increase in leakage and a decrease in ferroelectric signal. In this study, PbTiO₃ and PZT ultrathin films with thicknesses less than 10nm were epitaxially grown on SrRuO₃/SrTiO₃(100) and SrTiO₃(100) substrates by MOCVD (metalorganic chemical vapor deposition). Ferroelectric properties were investigated by contact-resonance piezoresponse force microscopy (CR-PFM) with a higher sensitivity than that of conventional PFM. Thicknesses of PZT thin films were obtained from cross-sectional TEM observations and X-ray reflectivity measurements. PZT films thinner than 10nm with a very smooth surface were successfully grown on SrRuO₃/SrTiO₃ by MOCVD because PZT showed the Stranski-Krastanov (S-K) growth mode. Island formation subsequent to the 2-dimensional layer growth was observed when thicknesses were over 7-10nm. Using CR-PFM, in 1.6-5nm thick PZT films, we can observe antiparallel domains with upward and downward polarizations which were formed by applying DC voltages of $\pm 2V$. Switched domains were stable for at least 24 hours in 1.6nm thick PZT films. Therefore, it can be concluded that the 1.6nm-thick PZT thin films had stable ferroelectric polarizations. Current-sensitive AFM observations of local leakage currents in PZT ultrathin films will be also discussed.

11:15 AM H4.9

Dielectric Behaviour of Sub-100nm Single Crystal 'Thin Films' of BaTiO₃ Made Using FIB, and Associated Implications for the Origins of Ferroelectric 'Size Effects'.

Marty Gregg¹, Mohammed Saad¹, Paul Baxter¹, Robert M. Bowman¹, Finlay Morrison² and Jim Scott²; ¹Pure and Applied Physics, Queens University Belfast, Belfast, United Kingdom; ²Department of Earth Sciences, University of Cambridge, Cambridge, United Kingdom.

Measurements on free-standing single-crystal barium titanate capacitors made using a Focused Ion Beam Microscope, with thicknesses down to 75 nm, show a dielectric response typical of large single crystals, rather than conventional thin films. There is a notable absence of any broadening or temperature shift of the dielectric peak or loss tangent. Peak dielectric constants of ca. 25,000 are obtained, and Curie-Weiss analysis demonstrates 1st order transformation behavior. This is in surprising contrast to results on conventionally deposited thin film capacitor heterostructures, which show large dielectric peak broadening and temperature shifts, as well as an apparent change in the nature of the paraelectric-ferroelectric transition from 1st to 2nd order. Our data are compatible with recent models, which attribute dielectric peak broadening to gradient terms that will exist in any thin film capacitor heterostructure, either through defect profiles introduced during growth, or through subtle asymmetry between top and bottom electrodes. The observed recovery of 1st order transformation behavior is consistent with the absence of significant substrate clamping in our experiment, and illustrates that the 2nd order behavior seen in conventionally deposited thin films cannot be attributed to the effects of reduced dimensionality in the system, nor to the influence of an intrinsic universal interfacial capacitance associated with the electrode-ferroelectric interface.

11:30 AM H4.10

Dielectric and Mechanical Properties of Self-Supported Ferroelectric Films. Vera Lyahovitsky¹, Mark Greenberg¹, Ilya Zon¹, Ellen Wachtel² and Igor Lubomirsky¹; ¹Materials & Interfaces,

Weizmann Institute of Science, Rehovot, Israel; ²Chemical Support Unit, Weizmann Institute of Science, Rehovot, Israel.

Nanocrystalline self-supported ferroelectric films are very promising for a large variety of devices ranging from infrared detectors to microwave resonators. We have investigated the mechanical stability and dielectric properties of self-supported ferroelectric films of BaTiO₃ (200-600 nm thick, 100-300 μ m lateral dimensions). The shape of the ferroelectric films undergoes an abrupt reversible change from predominantly cylindrical curvature to a dome-like shape between 130 and 160 °C. Below the transition temperature, regions with strong birefringence appear suggesting that the change in shape is associated with the para- to ferroelectric phase transition. Despite the relatively small grain size of 40-80 nm, the films possess a dielectric constant of more than 2500 and, after poling, a pyroelectric coefficient comparable with that of a single BaTiO₃ crystal is achieved at room temperature. The phase of the pyroelectric effect can be reversed by application of external bias proving that the films are ferroelectric. Although the pyroelectric effect disappears abruptly at ≈ 130 °C, no maximum in the temperature dependence of the dielectric constant versus temperature was observed. Instead, the first derivative of the dielectric constant versus temperature shows a break point at ≈ 130 °C. The dielectric constant shows strong dispersion within the frequency range of 300-1200 Hz. The relaxation time decreases linearly with temperature and has an inflection point at 130 °C, which suggests that electromechanical resonance is responsible for the observed dielectric relaxation. The experimental data indicate that the dielectric and mechanical properties of the self-supported ferroelectric films are substantially different from their substrate-supported counterparts and consequently will require thorough, independent theoretical consideration.

SESSION H5: Ferroelectrics/Piezoelectrics II

Chairs: Paul McIntyre and Stephen Streiffer

Tuesday Afternoon, November 30, 2004

Grand Ballroom (Sheraton)

1:30 PM *H5.1

Ferroelectricity in Perovskite Materials by Molecular-Dynamics Simulation. Simon R. Phillpot, Department of Materials Science & Engineering, University of Florida, Gainesville, Florida.

We show how traditional atomic-level simulation methods can provide atomic-level insights into ferroelectric behavior in oxides and can reproduce the complex phase behavior of perovskite ferroelectrics. In particular KNbO₃ and BaTiO₃ each show a sequence of phase transitions from the high-temperature non-ferroelectric cubic phase through tetragonal, orthorhombic and rhombohedral ferroelectric phases. We explore the interaction of the ferroelectric behavior with strain in solid solutions and superlattices of a ferroelectric and a paraelectric with a very high dielectric constant. We expose the complex dynamical behavior associated with the phase transitions and compare it with that of the structurally very different ferroelectric LiNbO₃.

2:00 PM H5.2

Interlayer Coupling and Stability of Single Domain State in a Ferroelectric Bilayer. S. Pamir Alpay¹, Zhigang Ban¹, Joseph Mantese² and Alexander Roytburd³; ¹Metallurgy and Materials

Engineering, Univ. of Connecticut, Storrs, Connecticut; ²Delphi Research Laboratories, Shelby Township, Michigan; ³Department of Materials and Nuclear Engineering, University of Maryland, College Park, Maryland.

Ferroelectric multilayers and superlattices have gained considerable interest due to their dramatically different behavior from their constituents in bulk form and many unique properties. In this presentation, we analyze the interlayer coupling between two ferroelectric materials and the possibility of stabilization of single domain states in the bilayer. Basic electrostatic considerations show that the different levels of polarization in the bilayer result in a built-in internal electric field. The onset of the instability of single domain state occurs when this depolarization field is larger than the theoretical coercive field of the layer having the larger polarization. On the other hand, single domain state may be retained in the presence of an external electric field that opposes the depolarization field in this layer. It is also shown that the single domain state can be stabilized if there are free charge carriers in both layers to compensate for the bound charges at the bilayer interface or by internal stresses as it may be the case in an epitaxial ferroelectric bilayer. The theoretical model is applied to epitaxial BaTiO₃/SrTiO₃ and BaTiO₃/PbTiO₃ bilayers and compared to experimental results from the literature. The work at UConn is supported by the National Science Foundation under Grant No. DMR-0132918.

2:15 PM **H5.3**

Nanoscale Studies of Disorder-controlled Domain Wall Creep in Epitaxial Pb(Zr_{0.2}Ti_{0.8})O₃ Thin Films.

Patrycja Paruch¹, Thomas Tybell², Thierry Giamarchi¹ and

Jean-Marc Triscone¹; ¹DPMC, University of Geneva, Geneva, Switzerland; ²DPE, Norwegian University of Science and Technology, Trondheim, Norway.

We have applied the general framework of elastic systems in a pinning potential to the study of ferroelectric domain walls, elastic objects separating regions with opposite polarization states, embedded in a crystalline film with random defects. The behaviour (both static and dynamic) of an elastic object in a disorder potential is governed by the competition between elasticity and pinning. A static manifold in equilibrium exhibits a roughness characterized by the exponent ζ . In the presence of a weak driving force, F , the manifold moves with a velocity $v \propto \exp[-(F_c/F)^\mu]$, a motion known as creep. The dynamical exponent $\mu = (d-2+2\zeta)/(2-\zeta)$ is a function of both the dimensionality, d , of the system and the nature of the disorder potential, via ζ . Using atomic force microscopy (AFM) and epitaxial ferroelectric Pb(Zr_{0.2}Ti_{0.8})O₃ thin films we have investigated individually written nanoscopic domains, showing a two-step switching process. After initial nucleation under the AFM tip, domains grow by radial domain wall motion, perpendicular to the polarization direction. We have demonstrated this motion to be a creep process with the characteristic electric field dependence of the velocity $v \propto \exp[-(R/k_B T)(E_c/E)^\mu]$, where R is an energy, T the temperature and E_c a critical field. The dynamical exponent μ , was found to be between 0.6 and 1.0. Our analysis shows that the previously proposed bulk nucleation model of domain growth (3) cannot explain the behavior observed in thin films, but rather, that disorder is at the origin of ferroelectric domain wall creep. One way to probe the disorder in the films, and to independently verify the observed creep behavior, is to directly access the static exponent ζ by measuring the equilibrium roughness of the domain wall. We will present results of AFM studies of domain wall roughness in ferroelectric Pb(Zr_{0.2}Ti_{0.8})O₃ thin films, and compare them with the dynamical exponents obtained for the films in our previous studies. Another approach is to alter the intrinsic disorder in the film, and observe the effect on domain wall dynamics. We have introduced two kinds of macroscopic defects, columnar (by heavy ion irradiation) and planar (by a-axis inclusions) and observe a noticeable decrease in the dynamical exponent μ in the presence of these defects. We will also present results of studies on films on pure PbTiO₃ films, in which the presence of Zr ions cannot contribute to a disorder potential. (1) P. Paruch, et al., *Appl. Phys. Lett.* **79**, 530 (2001). (2) T. Tybell et al., *Phys. Rev. Lett.* **89**, 097601 (2002). (3) R. C. Miller et al., *Phys. Rev.* **117**, 1460 (1960)

2:30 PM **H5.4**

Piezoresponse Force Microscopy: Quantitative Analysis of Nanoscale Ferroelectric Hysteresis Loops. Alexei Gruverman²,

Brian J. Rodriguez¹, Dawn A. Bonnell³ and Sergei V. Kalinin⁴;
¹Physics, North Carolina State University, Raleigh, North Carolina;
²Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ³Materials Science and Engineering, The University of Pennsylvania, Philadelphia, Pennsylvania; ⁴Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

In the last several years, Piezoresponse Force Microscopy has established itself as one of the primary techniques for the nanoscale characterization of ferroelectric materials. The applications of PFM include vertical and lateral polarization imaging, tip-induced polarization switching, nanodomain patterning and nanoscale hysteresis loop measurements. While the shape of the macroscopic hysteresis loops is determined by the time-dependent nucleation of multiple domains at the defect sites in the weak uniform field as described by Kolmogorov-Avrami and Ishibashi theories, the mechanism for hysteresis loop formation in PFM is fundamentally different. Here we analyze the mechanism for hysteresis loop formation in the PFM. It is shown that the high concentration of electric field below the tip results in the domain nucleation irrespectively of the presence of defects sites. The hysteresis loop shape is determined by the formation of the transient domain below the tip, the size of which increases with the tip bias. This allows quantitative description of the hysteresis loop shape. This analysis is applied to investigation of the local switching properties in SrBi₂Ta₂O₉ (SBT) thin films. Variations in PFM contrast of individual grains due to their random crystallographic orientation are consistent with the grain switching behavior examined via vertical and lateral hysteresis loops. Dependence of the hysteresis loop parameters on the grain crystallographic orientation is analyzed. It has been found that grain deviation from the ideal (010) orientation when the polar axis is normal to the film plane results in the decrease of the PFM signal and increase of the coercive voltage in agreement with theoretical predictions. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with

UT-Battelle, LLC. Research performed as a Eugene P. Wigner Fellow (SVK). AG acknowledges financial support of the National Science Foundation (Grant No. DMR02-35632).

2:45 PM **H5.5**

Bit Error Evaluation of Tbit/inch² Ferroelectric Data Storage. Yoshiomi Hiranaga and Yasuo Cho; Research Institute of Electrical Communication, Tohoku University, Sendai, Japan.

Ferroelectric ultrahigh-density data storage based on scanning probe microscopy has generated considerable interest as a next-generation storage method replacing the current magnetic storage devices. This method enables writing to be performed by applying a voltage pulse to a ferroelectric medium and locally switching the polarization direction. Although several reading methods using piezoelectric or nonlinear dielectric responses have been proposed, read/write technique based on scanning nonlinear dielectric microscopy (SNDM)[1-2] is especially superior to other methods in terms of bit detection resolution and processing speed of read signal. Using this technique, up to now, artificial nanodomain formation in lithium tantalate (LiTaO₃) single crystal has been studied in detail. In a series of the studies, 1.5 Tbit/inch² data writing were demonstrated.[1] Additionally, data transfer rate were also examined employing the prototype of data storage system.[2] Concerning reliability test, however, there have been few reports. In particular bit error rate (BER) should be evaluated urgently, because the performances of storage devices are often discussed in terms of BER dependence on recording density and data transfer rate. Thus, a large recording medium are prepared to write relatively large bit data, and BER evaluation are conducted herein. In general, it is desirable to make a medium as thin as possible in order to write nanodomain with high density, because when a pulse voltage is applied to a sample using the sharp-pointed tip, the electric field is highly concentrated in the vicinity of the tip. Additionally, high homogeneity in thickness over a large area is required for the recording medium. In order to preparing the medium meeting such requirements, both polarization controlled wet etching (PCWE)[3] and dry etching process was employed. Using these processes, 120-nm-thick LiTaO₃ single-crystal recording medium with a diameter of 3 mm was prepared. The standard deviation of 5.1 nm in the thickness was too small to cause scatter in the domain writing characteristics. 256x256 bit data was recorded on the medium using SNDM domain engineering system. The data bits of '1' and '0' were recorded as +z and -z domains, respectively. Data bits were written by applying 21 V, 5 μ s voltage pulses. The bit spacing was 50 nm, which is equivalent to the areal data storage density of 0.258 Tbit/inch². By distinguishing the data bits visually from the SNDM image and counting up the number of bit errors, the bit data was evaluated to be 1.2×10^{-3} . Additionally, 0.403 and 0.717 Tbit/inch² data bit pattern was also recorded, and the tendencies of bit errors were compared. [1] Y. Cho, K. Fujimoto, Y. Hiranaga, Y. Wagatsuma, A. Onoe, K. Terabe and K. Kitamura: *Appl. Phys. Lett.* **81** (2002) 4401. [2] Y. Hiranaga, Y. Cho, K. Fujimoto, Y. Wagatsuma and A. Onoe: *Jpn. J. Appl. Phys.* **42** (2003) 6050. [3] Y. Hiranaga, Y. Wagatsuma and Y. Cho: *Jpn. J. Appl. Phys.* **43** (2004) L569

3:30 PM ***H5.6**

Medical Ultrasound Transducers and Imaging: 1-D to 4-D. Stephen W. Smith, Department of Biomedical Engineering, Duke University, Durham, North Carolina.

The progress of medical ultrasound imaging and its associated transducers over the last fifty years has been a fascinating interplay as new clinical niches demanded technological innovations and scientific advances produced new medical applications. The technology of medical ultrasound transducers has progressed from simple 1MHz piston transducers translated in a water bath to produce a tomographic image (2-D) over many minutes to today's real time linear and curvilinear phased array scanners to the real time three dimensional scanners (4-D) using matrix array transducers which will soon be the standard of medical practice. Clinical usage includes every medical specialty especially obstetrics, cardiology and radiology with increasing endoscopic and interventional applications such as esophageal, vaginal, rectal, intraoperative, intracardiac and intravascular scanning. This overview of ultrasound imaging will discuss scanning modalities highlighting array transducers, associated beam forming technology and their clinical impact. Our own recent work has been concentrated in the field of real time 3-D ultrasound scanning where we have developed matrix phased array transducers with as many as 65,000 elements operating at frequencies up to 10 MHz for cardiac, intracardiac and radiological applications. These were used in a commercial version of our Duke 3-D system developed by Volumetrics Medical Imaging for cardiac applications. The system scans a 65 degree 3-D pyramid at up to 30 volumes/sec and features five simultaneous slice images at any desired angle and depth as well as real time 3-D rendering, 3-D pulsed and color flow Doppler. We have also modified this scanner to produce the first real time 3-D rectilinear and curvilinear images using arrays of $256 \times 256 = 65,536$

elements operating at 5 MHz for vascular and small parts applications. Finally, we have developed catheter 2-D arrays for intra-cardiac 3-D ultrasound including 112 channels in a 2.2 mm lumen (7 French) operating at 5-7 MHz. In animal studies, these transducers have been applied to the guidance of cardiac interventional procedures including RF ablation, ECG mapping, surgical biopsy and atrial septal puncture.

4:00 PM *H5.7

Functional Oxides in MEMS. Paul Murlat, Ceramics Laboratory, EPFL, Lausanne, Switzerland.

The earliest functional oxides investigated in MEMS were probably ZnO films in Lambwave devices during the mid 80's. Polar thin films have always been considered as potentially interesting to build miniaturized sensors, actuators, and transducers. Quite a number of piezoelectric MEMS devices have been demonstrated such as linear actuators, strain, motion and pressure sensors, microphones, ultrasound actuators, micromotors and imaging devices. Pyroelectric films have been used to demonstrate IR detectors for IR imaging, gas spectroscopy and air condition control. Generally one can say that thin film devices are good for applications and device principles that still work well after downscaling. In resonant applications this is equivalent to a frequency increase. An ideal situation is met for bulk acoustic wave resonators. Whereas the bulk device is good for ultrasonic imaging in the 3 to 10 MHz range, the thin film device is good for microwave signal filtering in the 2 to 10 GHz frequency range. In both cases, the device principle exploits the maximal possible piezoelectric coupling of the material. In this talk it is attempted to give an overview of past achievements and to discuss strength and weakness in view of physical principles, materials and process limitations, as well as industrial constraints of MEMS solutions based on functional oxides. Some examples will be presented in more detail. The problem of downscaling bulk applications is treated by means of piezoelectric micromachined ultrasonic transducers (pMUT). A different resonating structure needs to be applied in pMUT's as compared to bulk transducers in order to be compatible with the thin film thickness range. Instead of a bulk wave one uses a deflection wave in a plate. A unique application for piezoelectric thin films can be identified in nanoprobe technologies. AFM scanning speeds as well as non-contact excitation frequencies could be increased by means of Pb(Zr,Ti)O₃ thin film cantilevers. Major problem is the realization of an integration process that is compatible with tip fabrication. Gas detection is an interesting sensor application. Pyroelectric thin film arrays allow for sampling of complete infrared spectra in a wavelength interval defined by the optics. In simple sensors, the photoacoustic signal can be measured by means of a Pb(Zr,Ti)O₃ thin film microphone. Speaking about processes, improvements are still possible. One usual constraint is the fact that thin films are mostly deposited on flat surfaces. In piezoelectric applications it could be advantageous to work with curved structures, or to deposit into cavities. Some preliminary results on 3-d structures with PZT films will be presented showing possibilities to overcome this problem.

4:30 PM H5.8

Giant Piezoelectric Response in Epitaxial Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ on Silicon for High-Performance Electromechanical Systems. Dong Min Kim¹, Chang Beom Eom¹, June Ouyang², V. Nagarajan², R. Ramesh³, V. Vaithyanathan⁴, D. G. Schlom⁴, W. Tian⁵ and X. Q. Pan⁶; ¹Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin; ²Materials Science and Engineering, University of Maryland, College Park, Maryland; ³Materials Science and Engineering, University of California, Berkeley, California; ⁴University of Wisconsin, Madison, Wisconsin; ⁵Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; ⁶Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan.

Smart materials that can sense, manipulate, and position are crucial to the functionality of micro and nano-machines. Most microelectromechanical systems (MEMS) are silicon-based, but increasingly make use of more active piezoelectric materials that are integrated with the silicon. We have fabricated heterostructures with the highest longitudinal piezoelectric coefficient ever realized on silicon substrates by (1) synthesizing optimally-oriented, epitaxial thin films of Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) on miscut (001) Si wafer with epitaxial (001) SrTiO₃ template layer, a material which in single crystal form is known for its giant piezoelectric response, and (2) structuring it to reduce the constraint imposed by the underlying silicon substrate. When subdivided into 1 μ m² capacitors by focused ion beam processing, a 4 μ m thick film shows a low-field d₃₃ of 800 pm/V that increases to over 1200 pm/V under bias. These epitaxial heterostructures can be used for multilayered MEMS devices that function with low driving voltage, high frequency ultrasound transducer arrays for medical imaging, and capacitors for charge and energy storage. Since these PMN-PT films are epitaxially integrated with the silicon, they can make use of the well-developed fabrication process for patterning/micromachining of this large-area,

cost-effective substrate.

4:45 PM H5.9

Integration of Piezoelectric Pb(Zr_xTi_{1-x})O₃ with Ultrananocrystalline Diamond for High-Performance MEMS Applications. Wei Fan, Guoren Bai, James Birrell, Jian Wang, John A. Carlisle and Orlando Auciello; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Ultrananocrystalline diamond (UNCD) with exceptional mechanical strength, chemical inertness and tribological performance exhibits great potential for a new generation of high-performance MEMS devices. Meanwhile, ferroelectric/piezoelectric Pb(Zr_xTi_{1-x})O₃ (PZT) thin films has attracted much attention due to projected applications for intelligent MEMS based on its outstanding piezoelectric and electromechanical coupling coefficients, easy dipole reorientation and high remnant polarization. Successful integration of PZT films with UNCD layers provides the platform for producing reliable MEMS structures (e.g., cantilever and membrane) actuated by the piezoelectric PZT film and strengthened by the mechanically robust UNCD base. However, integration of piezoelectric films with diamond turns out to be quite challenging. Direct deposition of PZT by sputtering or CVD with O₂ presence results into chemical etching of the underlying UNCD layer even at relatively low temperatures. Another critical challenge lies in the huge thermal stress between PZT layer, Pt electrode and UNCD base, causing film delamination in the deposition and annealing processes. In this study, a bi-functional TiAl alloy is investigated and used as an oxidation barrier and adhesion layer interposed between the PZT and UNCD layer to achieve integration of these dissimilar materials. A thin amorphous TiAl barrier with thickness less than 20 nm successfully protected the integrity of the UNCD substrate up to 600 °C in O₂ and significantly improved the adhesion between Pt and UNCD. In order to lower the risk of UNCD oxidation and to control the PZT crystallography, low temperature PZT growth (450 °C) by MOCVD was also developed to produce highly (001)/(100)-oriented PZT films on annealed Pt/TiAl/UNCD substrates. Extensive chemical and structural analyses revealed that the sharp interfaces in the layered structure of Pt/PZT/Pt/TiAl/UNCD without interdiffusion or delamination through the oxide growth and post-deposition annealing, due to the formation of a thin amorphous TiAlO_x layer. As a result, promising ferroelectric/piezoelectric properties have been obtained for PZT films grown on UNCD substrates. The PZT-UNCD capacitor structure exhibited permittivity $\epsilon_r = 600$ 700, remnant polarization $P_r = 25$ μ C/cm² and coercive field $E_c = 80$ kV/cm. Piezoelectric performance of the PZT-UNCD based cantilever and membrane will be discussed in this report as well. This work was supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

SESSION H6: Magnetic Oxide

Chairs: David P. Norton and Mark Rzchowski
Wednesday Morning, December 1, 2004
Grand Ballroom (Sheraton)

8:15 AM *H6.1

Half-Metallic Oxides for Magnetic Tunnel Junction and Spin Valve Devices. Arunava Gupta, Center for Materials for Information Technology, Department of Chemistry, Chemical and Biological Engineering, University of Alabama, Tuscaloosa, Alabama.

The emerging field of spintronics aims to exploit the electron spin, in addition to its charge, to create a new class of devices that scale down to much smaller dimensions with added functionalities. Of particular relevance are magnetic tunnel junctions (MTJs) and spin valves (SVs), consisting of two ferromagnetic electrodes separated by an insulating barrier or conducting spacer layer, that exhibit large magnetoresistance (MR) at relatively low fields. Half-metallic systems, which contain a gap in one spin band at the Fermi level and no gap in the other spin band, are expected to have a spin polarization value approaching 100%. Band structure calculations have shown that a number of magnetic oxide materials, such as the mixed-valence manganites (La_{1-x}A_xMnO₃, A=Ba, Sr, or Ca), magnetite (Fe₃O₄), and chromium dioxide (CrO₂), are half-metallic. We have used chemical vapor deposition to grow heterostructures of CrO₂ with lattice-matched semiconducting barrier (SnO₂, VO₂) and conducting spacer (RuO₂) materials. These are then patterned to fabricate MTJ and SV devices with CPP geometry. The structural and magnetic properties of the heterostructures and the magnetoresistance properties of the patterned devices will be reported.

8:45 AM H6.2

Current-Induced First-Order Transition in Epitaxial Manganite Thin Films. Atsunobu Masuno, Takahito Terashima, Yuichi Shimakawa and Mikio Takano; Institute for Chemical Research, Kyoto University, Kyoto, Japan.

We examined electroresistive effects of epitaxial $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) thin films deposited on $\text{LaAlO}_3(100)$ (LAO) substrates. The films are under compressive strain due to lattice mismatch between LCMO ($a \approx 3.86 \text{ \AA}$) and LAO ($a \approx 3.79 \text{ \AA}$). To relax this strain, our films appear to consist of regions of high-strained charge-ordered insulator (COI) and low-strained ferromagnetic metal (FMM) at low temperatures. The transport properties of these inhomogeneous samples showed non-ohmic current-voltage characteristics and large magnetoresistance effect below the insulator-metal transition temperature of 150 K. These mixed-phase inhomogeneous thin films also showed an interesting current-induced first-order transition from COI to FMM. By using a microfabricating process to the samples, high electric field or large current density can be applied effectively. The resistivity at $1 \mu\text{A}$ did not coincide with that after applying them at large enough current density. This non-reversible behavior is pronounced with increasing maximum applied current. These results strongly suggest that spin-polarized electrons in FMM are injected into COI; as a result, antiferromagnetic localized electron spins are forced to align ferromagnetically. Parts of the COI regions in our microfabricated thin film sample are thus changed to FMM by means of electrical current.

9:00 AM H6.3

Structural, transport and magnetic properties of $\text{R}_{1-x}\text{AxMnO}_3$ ($\text{R}=\text{La, Nd, A}=\text{Ce}$) thin films fabricated by laser MBE method. Takeshi Yanagida¹, Teruo Kanki¹, Bertrand Vilquin¹, Hidekazu Tanaka^{1,2} and Tomoji Kawai¹; ¹ISIR, Osaka University, Osaka, Japan; ²PRESTO, Kawaguchi, Japan.

The perovskite type manganese oxides ($\text{R}_{1-x}\text{AxMnO}_3$) have attracted much attention of many researchers due to their fascinating physical properties including colossal magnetoresistance phenomena. Although the major interest of research in this field has been directed at hole-doped systems with doping a divalent cation (e.g. Ca, Sr and Ba), it has been recently reported that electron doped manganese oxide systems would be also feasible by doping a tetravalent cation (e.g. Ce and Sn). If such electron doped systems were available, the p-n homo-junctions of both hole and electron doped manganese oxides would be possible and promising for spintronics applications in future. Although previous experimental investigations as to this family of manganites consistently showed the presence of metal-insulator transition, ferromagnetic transition and colossal magnetoresistance effect, the physical origin is not fully understood. Since the ionic radius of cation in this family affects significantly the physical properties as seen in hole doped systems, it would be interesting to investigate such effects by changing A site cation including La and Nd, whose 3+ ions have 1.16Å and 0.98Å of the ionic radius, respectively. $\text{R}_{1-x}\text{AxMnO}_3$ ($\text{R}=\text{La, Nd, A}=\text{Ce}$) thin films were fabricated via a PLD method. Note that the single phase of these bulk materials were found to be not feasible by solid state reaction method due to CeO_2 segregation phases. XRD measurements of these films showed the single phase of these films and did not show the impurity peaks of CeO_2 segregation phases within the films. For $\text{La}_{0.9}\text{Ce}_{0.1}\text{MnO}_3$ (LCeMO) film systems, there was significant effect of oxygen partial pressure during film deposition upon the structural, transport and magnetic properties. As the oxygen partial pressure increased from 10-3Pa to 1Pa, the electrical resistivity was found to drastically decrease. In addition the metal-insulator-like transition peak emerged around 200K when the oxygen partial pressure was set to be 1Pa. The magnetization showed weak ferromagnetism and the Curie temperature increased with increasing the oxygen partial pressure. In fact, these trends on transport and magnetic properties are not consistent with general trends for an electron doped system, because in general decreasing oxygen composition for electron doped systems gives electron carriers. Furthermore, thermopower measurement identified the major carriers within the films to be holes, indicating cation vacancies due to over-oxidization are essential. In addition, this study first successfully fabricated $\text{Nd}_{1-x}\text{Ce}_x\text{MnO}_3$ (NCeMO) thin films by PLD technique without CeO_2 impurity on the XRD data. In the similar manner to LCeMO film systems, there was significant effect of oxygen partial pressure upon the film properties. The structural, transport and magnetic properties of NCeMO films will be discussed.

9:15 AM H6.4

Colossal Magnetoresistance Based Tunnel Junctions with Magnetic and Nonmagnetic Insulating Barriers.

Lisa Alldredge¹, Rajesh Chopdekar¹ and Yuri Suzuki²; ¹Applied & Engineering Physics, Cornell University, Ithaca, New York; ²Materials Science & Engineering, UC Berkeley, Berkeley, California.

We have studied both magnetic and nonmagnetic insulating barrier layers in magnetic tunnel junctions in order to determine the effect of having magnetic moments in the barrier as well as to increase our understanding of junction behavior at electrode/barrier interfaces. We have fabricated epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

(LSMO)/ $\text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3$ /LSMO trilayer junctions in order to produce high quality interfaces through the use of an isostructural barrier layer. The insulating $\text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3$ barrier layer becomes antiferromagnetic below 160K. The large energy cost to flip a spin in an antiferromagnet may preserve spin orientation during transport through the junctions. We observed junction magnetoresistances (JMRs) of up to 4% at 5K, with hysteretic peaks that correspond well with magnetization data. Magnetization measurements of unpatterned trilayer films show the separate coercive fields of the top and bottom LSMO layers as well as exchange biasing of the LSMO layers by the antiferromagnetic barrier after field cooling. Junction resistance and magnetization measurements suggest interdiffusion at the interfaces between the barrier layer and the magnetic layers, perhaps resulting in a graded composition and a reduced effective barrier thickness. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interdiffusion, the JMR is not completely suppressed. We have previously demonstrated successful junctions using a paramagnetic barrier, CoCr_2O_4 . We observed JMRs of 20% at 80K in junctions with LSMO and Fe_3O_4 electrodes. Although the junction barriers were too thick for direct tunneling, these junctions exhibited a spin-conserving inelastic hopping behavior at low biases. Having shown that magnetic barrier layers do not prohibit JMR, we characterized a nonmagnetic barrier, Mg_2TiO_4 (MTO), with the expectation of separating out the effects on the JMR of having magnetic moments in the barrier and examining further the conduction mechanism of the spin-polarized current. We have grown MTO on (110) SrTiO_3 substrates with pulsed laser deposition in various atmospheres: (i) vacuum ($<10^5$ Torr), (ii) 7 mTorr of a N_2/O_2 mixture (99% and 1%, respectively), and (iii) 7 mTorr of O_2 . Films grown in oxygen poorer atmospheres have lower resistivities than films grown in 7 mTorr of O_2 , which exhibit highly insulating behavior. MTO grown in the N_2/O_2 mixture shows a variable range hopping behavior below 400K. Magnetization measurements of trilayer films with Fe_3O_4 /MTO/LSMO layers display the expected switching of the two magnetic layers at coercive fields comparable to those of single layer LSMO and Fe_3O_4 films. We will discuss transport properties of these trilayers.

9:30 AM H6.5

Structural, Magnetic and Electronic Properties of Epitaxial Thin Films of the Bilayer Manganite $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$.

Yayoi Takamura¹, Jostein K. Grepstad^{3,1}, Hong Zheng², John F.

Mitchell² and Yuri Suzuki¹; ¹Department of Materials Science and Engineering, UC-Berkeley, Berkeley, California; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ³Department of Electronics and Telecommunication, Norwegian University of Science and Technology, Trondheim, Norway.

The doped rare-earth manganites, $(\text{R}_{1-x}\text{A}_x)_{n+1}\text{Mn}_n\text{O}_{3n+1}$, where R=trivalent lanthanide, and A=divalent alkaline earth, have received increased interest in recent years due to the discovery of their colossal magnetoresistance (CMR). In particular, the $n=2$, $x=0.4$ version of the Ruddlesden-Popper series, $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, which consists of interleaved double blocks of rock-salt (La,SrO) and metallic-ferromagnetic MnO_2 bilayers, has been shown to possess anisotropic properties depending on whether transport occurs along the MnO_2 sheets or by tunneling across the insulating (La,SrO) layers. We have grown 150-200nm thick epitaxial thin films of the bilayer manganite $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ on LaAlO_3 and SrTiO_3 substrates by pulsed laser deposition. The epitaxial quality of the films depends strongly on the deposition conditions, including the substrate temperature and the oxygen partial pressure. We have successfully grown films with the MnO_2 sheets oriented both parallel and perpendicular to the substrate surface with either compressive or tensile strain, as verified by x-ray diffraction analysis. Rutherford backscattering spectrometry confirms the stoichiometry and the epitaxial relationship of these films with the substrate, while atomic force microscopy shows that smooth films with less than 0.5nm rms surface roughness can be grown. Magnetic measurements of the films performed with a SQUID magnetometer demonstrate that a ferromagnetic to paramagnetic transition occurs at a Curie temperature in approximate agreement with the value measured for the bulk target ($T_c=120\text{K}$). For all current and magnetic field configurations, magnetotransport measurements reveal a large negative magnetoresistance (MR) at high fields indicative of the CMR effect. MR measurements with current perpendicular and parallel to the applied field direction suggest that anisotropic MR effects (i.e., MR associated with the relative orientation of the current and the magnetization) are dominant. We will discuss the anisotropic transport properties parallel and perpendicular to the MnO_2 sheets.

10:15 AM *H6.6

Fundamental Investigations of Magnetically Doped Oxides.

Scott A. Chambers, Pacific Northwest National Laboratory, Richland, Washington.

Metal oxides such as TiO₂ and SrTiO₃ exhibit fascinating properties when doped with a few to several atomic percent of some magnetic dopant. We have explored the synthesis and properties of these oxides doped with several candidate magnetic dopants using molecular beam epitaxy and ion implantation as the growth methods. Our dopant set includes Co, Cr, Fe and Ni. We find that room temperature ferromagnetism is a common occurrence, despite the absence of any measurable dopant metal inclusions, and the absence of free carriers. In this talk, I will give an overview of our work in this area and discuss progress in understanding the mechanism(s) of magnetism is (are) operative.

10:45 AM H6.7

Ferroelectric Field Effect on Ferromagnetism in Diluted Magnetic Insulator Anatase Co:TiO₂. T. Zhao¹, S. R. Shinde², S. B. Ogale^{1,2}, H. Zheng¹, T. Venkatesan², R. Ramesh³, S. Das Sarma⁴ and J. Misewich⁵, ¹Materials Research Science and Engineering Center, Department of Materials Science and Engineering, Univ. of Maryland, College Park, Maryland; ²Center for Superconductivity Research, Department of Physics, Univ. of Maryland, College Park, Maryland; ³Department of Physics and Department of Materials Science and Engineering, Univ. of California, Berkeley, California; ⁴Condensed Matter Theory Center, Department of Physics, Univ. of Maryland, College Park, Maryland; ⁵Materials Science Department, Brookhaven National Laboratory, Upton, New York.

Recently considerable success is reported in making a non-magnetic semiconductor ferromagnetic by dilute doping of magnetic impurities. However it has not always been clear that the reported DMS ferromagnetism is indeed induced by the carriers. In this work we report the first successful implementation of an external electric field modulation of ferromagnetism in an oxide-based DMS. An anatase TiO₂ layer with 7% Co doping and a ferroelectric PbZr_{0.2}Ti_{0.8}O₃ (PZT) layer were epitaxially grown on a conducting SrRuO₃ buffered LaAlO₃ substrate by pulsed laser deposition. The high-quality of epitaxy and uniform distribution of Co were confirmed by X-Ray diffraction and transmission electron microscopy. The Co:TiO₂ channel grown in this case at a high temperature of 875 °C is insulating in nature. The magnetic hysteresis loops of the Co:TiO₂ were measured by superconducting quantum interference device after positive or negative electric poling on PZT. A 15% difference in the room temperature saturated magnetic moment of Co:TiO₂ is observed according to the two polarization states of PZT, which can be modulated over several cycles. This first demonstration of electric field effect in an oxide based diluted ferromagnetic insulator system provides evidence of its intrinsic nature. Furthermore, the ability of electric field modulation of ferromagnetism is very promising for next-generation multi-functional electronic devices. Possible mechanisms for electric field induced modulation of insulating ferromagnetism are discussed. This work was supported by DARPA SpinS program (through US-ONR) and the NSF-MRSEC (DMR 00-80008) at Maryland and by a grant from Brookhaven National Laboratory. The PLD and RBS facilities used in this work are shared experimental facilities (SEF) supported in part under NSF-MRSEC.

11:00 AM H6.8

Magnetic Properties of EuO Thin Films for Ferromagnetic Barrier Layer. Matsumoto Tetsuro^{1,2}, Kawaguchi Kenji², Kirihara Kazuhiro², Koshizaki Naoto², Kashiwaya Satoshi³, Tani Kiyoe³, Yamaguchi Katsuhiko⁴ and Yamada Koji¹, ¹Saitama University, Saitama, Japan; ²Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan; ³Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan; ⁴Fukushima University, Fukushima, Japan.

Recently, spintronics devices, which utilize both carrier and spin of electron, have been studied attractively as next generation devices. A magnetic tunnel junction (MTJ) is well known for tunnel magnetoresistance (TMR) effect and as a promising advanced device for high sensitive hard disk reading head and magnetic random access memory (MRAM). Most of MTJ's consist of ferromagnetic metallic electrodes and insulative barrier layer. On the other hand, some researchers pay attention to ferromagnetic barrier MTJ (FM/TJ) as spin filter device and p-junction device. Ferromagnetic insulator or semiconductor is essential to realize this device. Europium monoxide (EuO) is a well-known ferromagnetic semiconductor with 1.12 eV energy gap. The crystal structure is a simple NaCl structure and the Curie temperature is rather high (70 K) in ferromagnetic semiconductors. And various physical properties such as Curie temperature and carrier concentration are controllable by changing oxygen stoichiometry or third element doping. Thus, we consider EuO a good barrier material for the trial study of FM/TJ. Metal niobium (Nb) is employed as electrodes because non-magnetic electrodes are suitable to examine the ferromagnetic barrier effect and Josephson junction with ferromagnetic barrier is our next subject. Since there have been very few nano-layer studies about ferromagnetic

semiconductors, we have started to investigate the magnetic and transport properties of EuO nano-layer. A molecular beam epitaxy system equipped with an XPS spectrometer is used for the sample preparation. First, EuO nano-layers with various thicknesses (2.5 - 10.0 nm) were deposited on thick Nb layer (50 nm) and the oxidation condition was examined by in-situ XPS. The deposition rate of EuO is fixed to 0.05 nm/sec. and oxygen partial pressure (P_{O₂}) is ranged from 2.0 × 10⁻⁶ Pa to 1.0 × 10⁻⁵ Pa. In XPS spectra, both Eu²⁺ and Eu³⁺ 3d_{5/2} peaks were observed around 1126 and 1135 eV for P_{O₂} > 6.0 × 10⁻⁶ Pa samples. It means that EuO layer is over oxidized. For P_{O₂} is 2.0 and 4.0 × 10⁻⁶ Pa samples, Eu³⁺ peaks disappeared. It is considered that P_{O₂} of 6.0 × 10⁻⁶ Pa is over oxidation condition to prepare nano-layer EuO. The optimum P_{O₂} decreases as the EuO layer thickness is decreased. Thus, we have to change P_{O₂} according to the thickness of EuO layer. Thick Nb protecting layer was deposited before the sample was taken out. The thinnest EuO (2.5 nm) measured by SQUID magnetometer shows the similar ferromagnetic hysteresis curve and Curie temperatures around 70 K as other thicker EuO samples. No superparamagnetic behavior has been observed. These results suggest that the 2.5 nm EuO is a continuous layered structure rather than an island structure. The thickest EuO (10 nm) layer shows a little smaller MS (5.32 μB/atom) than ideal value (7.0 μB/atom) and MS decreases significantly with decreasing EuO thickness. The reasons for the reduced MS of thinner EuO layers are not elucidated.

11:15 AM *H6.9

2D carrier confinement in bilayer manganites. Ch. Renner, London Centre for Nanotechnology, Department of Physics and Astronomy, University College London, London, United Kingdom.

Layered transition metal perovskite oxides, including high temperature cuprate superconductors and colossal magnetoresistive manganites, exhibit very anisotropic transport properties. The in-plane resistivity is metallic, whereas it is non metallic perpendicular to the layers. We present a new insight on this issue using scanning tunneling microscopy (STM) on La_{1.4}Sr_{1.6}Mn₂O₇ single crystals cleaved in ultra high vacuum. STM spectroscopy reveals a gap E_g associated with the room temperature c-axis resistivity, which remarkably does not vanish when the temperature is lowered through the metal-insulator transition. This striking result suggests that the carriers are confined to the perovskite layers, where the intrinsic transport between adjacent layers is thermally activated at all temperatures, with a characteristic activation energy E_g. Furthermore, E_g is spatially homogeneous at all temperatures, excluding electronic phase separation in this compound. We shall discuss these spectroscopy data and atomically resolved STM micrographs in the context of colossal magnetoresistance (CMR), and their contribution to our understanding of CMR perovskites. Work done in collaboration with H.M.Ronnnow and G.Aeppli.

SESSION H7: Oxide on Si/Gate Oxide
Chairs: Charles Ahn and Darrell G. Schlom
Wednesday Afternoon, December 1, 2004
Grand Ballroom (Sheraton)

1:30 PM H7.1

MBE-Grown HfO₂ Gate Dielectrics for Si Nano CMOS and III-V Semiconductor MOSFETs. J. Kwo¹, M. Hong², J. P. Mannaerts², W. J. Lee², H. P. Chang², Y. J. Lee², C. H. Chu², K. L. Jaw², Y. L. Hsu¹, K. Y. Lee², C. H. Pan², C. C. Huang³, Y. L. Huang², T. Gustafsson⁴ and E. Garfunkel⁵; ¹Physics, National Tsing-Hua University, Hsinchu, Taiwan; ²Materials Science & Engineering, National Tsing-Hua University, Hsinchu, Taiwan; ³Institute of Electronics Engineering, National Tsing-Hua University, Hsinchu, Taiwan; ⁴Physics and Astronomy, Rutgers, The State University of New Jersey, Piscataway, New Jersey; ⁵Chemistry, Rutgers, The State University of New Jersey, Piscataway, New Jersey.

The adoption of alternative high κ gate dielectric candidate in the time frame required by the Si industry roadmap for CMOS scaling in the next 5-6 years is a great challenge for both scientific and engineering community as a whole. The world wide research thrust also represents an exciting opportunity for advancing new frontiers in the nanoscience and nanotechnology. However, the progress toward attaining high performance high κ CMOSFET has been hampered due to the lack of good thermodynamic stability of the high κ dielectrics in contact with Si at both lower and upper interfaces in MOS gate stacks. The preferred materials choice like HfO₂ for 45 nm CMOS in year 2007 deposited by common thin film deposition techniques inevitably formed interfacial layer at least 1.0 nm thick containing SiO₂ and Hf-silicates. Following our previous work on high κ rare earth oxides using advanced molecular beam epitaxy, we have recently undertaken studies of the high κ dielectrics HfO₂ films with additions of Al. Based on extensive characterizations using RHEED,

ellipsometry, x-ray reflectivity, TEM, XPS, and MEIS, we have demonstrated for the first time an atomically abrupt HfO_2/Si interface free of SiO_2 or silicate formation, thus achieving a significant saving of the equivalent oxide thickness (EOT) to be less than 1.0 nm. The stability of this HfO_2/Si interface at high temperature is also examined by in-situ annealing tests during MEIS, and rapid thermal anneals under a variety of atmosphere. Studies are currently applied to HfO_2 growth on strained Si layer to improve electron mobility of the CMOSFET, along with the integration with dual metal gates. Furthermore, a key challenge in developing compound semiconductor MOSFET technology is to identify thermodynamically stable insulators on the compound semiconductors that provide a low density of interfacial states (D_{it}) and low electrical leakage. Following our previous discovery of novel $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ oxides for effective GaAs passivation, we have recently extended the investigations to several high κ dielectrics including HfO_2 ($\kappa = 20$) and Sc_2O_3 ($\kappa = 12$) to passivate the compound semiconductor surface. Low electrical leakage films have been obtained for both HfO_2 and Sc_2O_3 films deposited on GaAs (100) at room temperature by UHV evaporation. Interfacial structures have been analyzed by MEIS, XPS, and TEM to establish growth procedures to avoid the formation of unwanted As-containing oxides causing Fermi level pinning.

1:45 PM H7.2

Oxide Screening Effects in HfO_2 High-k Gate Stacks.

Jeff J. Peterson¹, Joel Barnett¹, Chadwin D. Young¹, George A. Brown¹, Jim Gutt¹, Sundar Gopalan¹, Paul D. Kirsch^{1,2}, Hong-Jyh Li^{1,3}, Naim Mouden^{1,2}, Byoung-Hun Lee^{1,2}, Pat Lysaght¹, Gennadi Bersuker¹, Peter M. Zeitzoff¹, Mark I. Gardner^{1,4}, Robert W. Murto^{1,5} and Howard R. Huff¹; ¹International SEMATECH, Austin, Texas; ²IBM, Hopewell Junction, New York; ³Infineon, Munich, Germany; ⁴AMD, Sunnyvale, California; ⁵Texas Instruments, Dallas, Texas.

The presence of fixed charge in high-k dielectrics is known to have a negative effect on the mobility of high-k gate stacks through carrier scattering. Additionally, charge trapping in the high-k dielectric has been shown to contribute to inversion charge loss in the channel, giving the appearance of a mobility degradation. Soft optical phonons are also believed to have a scattering role, reducing the mobility of high-k gate stacks. These mechanisms may be mitigated through the introduction of a bottom interfacial screening oxide between the high-k gate dielectric and the transistor channel. In relation to the fixed high-k charge, the screening oxide increases the distance between the fixed charge in the high-k dielectric and the carriers, thereby reducing the scattering effect of the fixed charge. In the case of soft optical phonons, the screening oxide acts as a barrier to dampen the phonon penetration and likewise reduce the scattering effect of the soft optical phonons. However, since the screening oxide forms a significant portion of the HfO_2 high-k gate stack EOT, it is critical to understand the role and relative contributions of the screening oxide in achieving high-k gate stacks with optimal mobility. This work presents an evaluation of the screening effects of the oxide bottom interface layer in HfO_2 high-k gate stacks. We have fabricated HfO_2 high-k gate dielectric transistors and capacitor structures on 200 mm Si <100> wafers using a conventional CMOS process with a 1000C/10s final anneal. In order to evaluate the oxide thickness screening effect on transistor mobility, several bottom interface oxides are compared: a 1 nm ozonated oxide, a 1.2 nm thermal oxide, and a standard 1.6 nm rapid thermal nitrided oxide. After completion of CMOS processing, standard C-V and I-V analysis was done to evaluate EOT, CET, Vfb, Jg, and Vt. Mobility was extracted using the mob2d methodology. These data demonstrate both peak and high-field mobilities are increased through the incorporation of thicker screening oxides. While the 1 nm ozonated oxide achieves a peak mobility of 216 cm²/Vs (62.5% of the SiO₂ universal mobility), the 1.2 nm thermal oxide achieves even higher peak mobilities of 250 cm²/Vs (77.5% of SiO₂). Finally, the thickest screening oxide, the 1.6 nm rapid thermal nitrided oxide, achieves a peak mobility of 312 cm²/Vs (81.6% of SiO₂). Similarly, analysis of the high-field mobility in the region dominated by acoustic phonon and surface roughness scattering also shows improved mobilities with thicker screening oxides. In the high-field case, the 1 nm ozonated oxide gate stack (EOT 1.1 nm) achieves high-field mobility of 63.9% of the SiO₂ universal mobility, the 1.2 nm thermal oxide gate stack (EOT 1.1 nm) achieves high-field mobility of 72.5% of the SiO₂ universal mobility, and the 1.6 nm rapid thermal nitrided oxide gate stacks (EOT 1.8 nm) achieves high-field mobility of 89.1% of the SiO₂ universal mobility.

2:00 PM *H7.3

Calculations of Band Gaps and Defect Levels in Functional Oxides. John Robertson¹, Ka Xiong¹ and Stewart J. Clark²;

¹Engineering, Cambridge University, Cambridge, United Kingdom; ²Physics, Durham University, Durham, United Kingdom.

It is well known that first principles calculation of electronic structures of semiconductors and insulators using the local density

approximation (LDA) gives good structures but leads to severe under-estimate of the band gap. This can be corrected empirically by the "scissors approximation" of rigidly raising conduction bands to get the experimental band gap, but this loses any predictive power. It can be corrected by methods such as the GW approximation, but this computationally expensive. It can be corrected by lower cost methods such as the screened exchange (sX) method, which we and others [1] have found to be quite accurate and reliable. However, for oxides, sX has the disadvantage of requiring the use of norm-conserving pseudopotentials. These require a cutoff energy of up to 1000 eV for oxygen, whereas the smoother ultra-soft pseudopotentials of Vanderbilt need only a cutoff of 350 eV. We present calculations of the band gaps of oxides using a new method, the weighted density approximation (WDA)[2], implemented within the CASTEP code. This allows use of ultra-soft pseudopotentials and has a computer time which scales as the number of plane waves to power 3, compared to power 4 for sX and power 5 for GW. A further advantage of WDA (and sX) is that it is a density functional, not a perturbative method like GW, so that the structural energy can be minimised within WDA itself. This is important in defect calculations where the defect level could be in the conduction band in the LDA, so that LDA could actually find the wrong structure for some charge states. Thus the WDA method opens up many opportunities for supercell calculations of surfaces, interfaces and defects. As examples, we calculate the minimum band gaps as SiO₂ 9.2 eV, Al₂O₃ 9.3 eV, MgO 7.7 eV, LaAlO₃ 6.7 eV, LaScO₃ 6.3 eV, SrTiO₃ 3.0 eV, c-ZrO₂ 6.0 eV, HfO₂ 6.1 eV, ZrSiO₄ 7.0 eV, SrCu₂O₂ 4.1 eV. Calculations of vacancy energy levels are also given. [1] C B Geller, A J Freeman et al, App Phys Lett 79 368 (2001) [2] P P Rushton, D J Tozer, S J Clark, Phys Rev B 65 235203 (2002)

2:30 PM H7.4

Physical and electrical properties of LaAlO₃, potential candidate for high K gate dielectric. Marie-Christine Hugon¹,

Bernard Agius¹, Olivier Voltaire¹, Israel Baumvol², Karen Paz Bastos², Leonardo Miotti², Camille Cohen³ and Christophe Cardinaud⁴; ¹Universite Paris Sud, Orsay, France; ²Instituto de Fisica, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil; ³Universite Paris 6 et 7, Paris, France; ⁴IMN, Nantes, France.

There is currently an extensive research effort to find an alternative gate dielectric to replace SiO_2 in metal oxide semiconductor field effect transistors (MOSFETs). LaAlO_3 is a promising material: it has a dielectric constant in the range 20-27, an optical bandgap of 5.6eV and large band offsets with Si substrate ($1.8 \pm 0.2\text{eV}$ for electrons and $3.2 \pm 0.1\text{eV}$ for holes). RuO_2 is proposed as a gate electrode. LaAlO_3 films were deposited directly onto silicon substrates by rf magnetron sputtering of a LaAlO_3 target in argon atmosphere. Thin film properties are studied as a function of deposition parameters (rf power, process pressure) and thermal annealings (in $^{16}\text{O}_2$ or $^{18}\text{O}_2$ atmospheres, pressures in the range 10^{-5} and 10^5 Pa, and temperatures from 450 to 1000°C). Physical properties of as deposited material (composition, density), as determined by Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Analysis (NRA) and X-ray reflectometry, are seen to depend only slightly on deposition parameters. The films are stoichiometric and present a density of $5.5 \pm 0.5\text{g}\cdot\text{cm}^{-3}$ close to the bulk material one ($6.5\text{g}\cdot\text{cm}^{-3}$). The thermal stability of LaAlO_3 has been investigated under typical conditions of a MOSFET processing. O and Al transport during annealing are investigated with sub-nanometric depth resolution via the narrow resonances of $^{18}\text{O}(p,\alpha)^{15}\text{N}$ at 151 keV (fwhm=100eV) and $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ at 404.9keV (fwhm=40eV) respectively. After a thermal treatment at 1000°C for 20s under 10 Pa and 10^3 Pa of oxygen, Al diffusion has been only observed for a oxygen pressure of 10^3 Pa. The interfacial characteristics of LaAlO_3/Si were measured by spectroscopic ellipsometry, X-ray reflectometry, XPS and RBS in channelling mode. The initial measurements subject the presence of an interfacial layer whatever the deposition pressure. We have performed high frequency (1MHz, 100kHz, 1kHz) C-V and I-V characteristics on $\text{RuO}_2/\text{LaAlO}_3/\text{Si}$ MIS structure. After a thermal treatment at 600°C, the C-V curves exhibit well defined accumulation, depletion and inversion regimes which indicate a low interface state density. With the device biased in accumulation regime, a permittivity of 15 was deduced. Low leakage current is detected for films deposited at 0.5Pa or 5Pa and annealed at 600°C under 1 atm of oxygen.

2:45 PM H7.5

Physical properties and crystallization temperature of rare earth scandate films. Isao Ohkubo^{1,2}, Hans Christen¹, Gerald

Jellison¹, Christopher Rouleau¹, Mark Reeves³, Shuang Huang³, Junhui Jia⁴ and Darrell Schlom⁴; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Department of Applied Chemistry, School of Engineering, University of Tokyo, Tokyo, Japan; ³Department of Physics, George Washington University, Washington, District of Columbia; ⁴Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

The crystallization temperature of materials is a critical parameter to be considered when selecting high-k dielectrics for transistor gate applications. A low crystallization temperature is clearly required for crystalline films (to allow deposition onto partially formed device structures), whereas applications of amorphous layers rely on the opposite condition such as to avoid unintended crystallization during further processing. The great recent interest in rare earth scandates (ReScO_3 , where $\text{Re} = \text{La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y}$) has motivated us to investigate crystallization temperatures systematically, by employing a temperature-gradient deposition method. In this approach, pulsed laser deposition is used to grow ReScO_3 films simultaneously on 15 LaAlO_3 substrates held at different temperatures in the range of 200 - 800 °C. Subsequent analysis by X-ray diffraction allows us to determine the crystallization temperature for each of these materials. The obtained epitaxial films are then analyzed by 2-modulator generalized ellipsometry for their optical properties (in particular the refractive index in the range $\lambda = 300 - 800 \text{ nm}$) and by scanning microwave microscopy for their dielectric permittivity (at $f = 1.6 \text{ GHz}$). The resulting phase map of dielectric constant, lattice parameter, and crystallization temperature, provides valuable guidance in the selection of these materials for specific applications. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

3:30 PM H7.6

Atomic Layer Deposition of Y_2O_3 Thin Film. Jin-Seong Park, Philippe De Rouffinac and Roy G. Gordon; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Y_2O_3 thin films were deposited with yttrium tri(*N,N*-diisopropylacetamidate) and water by atomic layer deposition (ALD) at 295°C. The self-limiting surface reaction yielded a growth rate of 1.1 Å/cycle. The growth rate was linear with the number of cycles and nucleation was fast on hydrogen terminated Si. The film was highly conformal in deep holes and trenches (more than 40:1 aspect ratio). The deposited film was shown to be the cubic structure of Y_2O_3 , with the (222) and (400) peaks reflected by X-ray diffraction (XRD). The composition of yttrium oxide was $\text{O/Y} \approx 1.9$ by Rutherford backscattering spectroscopy (RBS) after air exposure. Oxygen rich phase might come from adsorbed hydroxyl groups during air exposure because X-ray photoelectron spectroscopy (XPS) showed the peak intensity of OH bonding was decreased after annealing. The Y_2O_3 thin films had a high dielectric constant (≈ 15) and low leakage current ($10^{-6} \text{ A/cm}^2 @ 1 \text{ MV/cm}$).

3:45 PM H7.7

The atomic structure of epitaxial $\text{Sc}_2\text{O}_3/\text{Si}$ interfaces.

Dmitri O. Klenov¹, Lisa F. Edge², V. Vaitnyanathan², Darrell Schlom² and Susanne Stemmer¹; ¹Materials, University of California, Santa Barbara, California; ²Materials Science and Engineering, Penn State University, University Park, Pennsylvania.

The performance of novel field-effect transistors that employ epitaxial oxides as gate dielectrics as a replacement for SiO_2 is determined by the atomic structure of the interface between the oxide and Si. Scandium oxide (Sc_2O_3) is a promising gate dielectric because it has a high dielectric constant (13) and large bandgap of 6.3 eV. Sc_2O_3 has a bixbyite crystal structure with a lattice parameter of 0.985 nm. We present investigations of the atomic structure of interfaces between epitaxial Sc_2O_3 thin films grown by molecular beam epitaxy and (111) silicon substrates, and of defects in the films. Despite the large lattice mismatch (9.8 %), films grew epitaxially with a cube-on-cube orientation relationship, as confirmed by both x-ray and selected area electron diffraction. Planar defects spaced 20 nm apart parallel to $\{12\bar{1}\}_{\text{Sc}_2\text{O}_3}$ were observed. Their origin will be discussed based on symmetry considerations and their atomic structure will be determined using high resolution transmission electron microscopy (HRTEM) exit wave reconstruction. HRTEM showed an abrupt interface along both $[-112]_{\text{Si}}$ and $[1\bar{1}0]_{\text{Si}}$ directions. No reaction layer was observed between the film and the substrate. The large misfit between the two lattices was relieved by an interfacial misfit dislocation network. The Burgers vector of the dislocations was found to be $1/4[1\bar{1}0]_{\text{Sc}_2\text{O}_3}$ with a spacing of about 2 nm. The formation of this dislocation network is discussed using near coincidence site lattice (NCSL) concepts.

4:00 PM H7.8

MBE Growth and Characterization of High-Quality Single Crystal Sc_2O_3 Films on Si (111). M. Hong¹, H. Y. Lee², A. R. Kortan¹, J. Kwo³, C. P. Chen¹, Y. F. Hsieh⁴, H. M. Cheng⁵, Y. L. Hwang¹ and J. P. Mannaerts¹; ¹Materials Science & Engineering, National Tsing-Hua University, Hsinchu, Taiwan; ²National Synchrotron Radiation Res. Center, Hsinchu, Taiwan; ³Physics, National Tsing-Hua University, Hsinchu, Taiwan; ⁴Materials Analysis Technology Inc., Hsinchu, Taiwan; ⁵Industrial Technology Res. Inst.,

The hetero-epitaxial growth of insulators on semiconductors (or vice-versa) is of great importance in electronic industry. Typical examples include GaN on sapphire for blue, green lasers and LED's, and single crystal oxide films epitaxially grown on Si. The latter may allow us to grow GaN or GaAs indirectly on Si. Here, we report the MBE growth and single-crystal synchrotron x-ray characterization of very high quality Sc_2O_3 films grown on Si (111). The Sc_2O_3 films of 4 and 18 nm thickness were deposited by e-beam evaporation on Si in a multi-chamber MBE/UHV system. Substrate surface was prepared by the RCA method, followed by an HF dip, heated to 800°C and an Si buffer layer growth. The films were protected from ambient exposure by a 4 nm thick layer of amorphous silicon cap. Streaky RHEED patterns along the in-plane axes of Si were observed after an oxide growth of 1 nm thickness, indicative of an in-plane alignment between the oxide film and the Si substrate. High resolution x-ray diffraction measurements find that Sc_2O_3 films grow epitaxially in Bixbyite structure with (111) axis oriented parallel to the substrate (111) normal and an in-plane rotation of 60 degree with respect to the substrate surface. The 4 nm film yields a mosaic scan width of 0.044 degrees (158 arc-seconds) for the Sc_2O_3 (444) peak, that is remarkably sharp, and suggests a defect free structure for the epi-layer. The 18 nm thick film, however yields an 319 arc-second mosaic width for the Sc_2O_3 (222) peak, suggesting that, this film thickness exceeds the critical thickness, and the film is partially relaxed. The bulk lattice constants of Si 0.543 nm and Sc_2O_3 0.986 nm are mismatched by 9.2 %, if we match the double Si unit cell dimension. The observed perfection in the film structure is very unusual, in light of the large lattice mismatch. The Bixbyite structure consists of a defective fluorite structure with oxygen vacancies. The role of this open structure and the exact nature of the interfacial structure will be discussed. Electrical properties and cross section TEM studies on the hetero-structure of $\text{Sc}_2\text{O}_3/\text{Si}$ will also be presented.

4:15 PM H7.9

Effects of High-Temperature Annealing on $\text{SrTiO}_3/\text{Si}(100)$ and Applications for Frequency-Agile Devices. Yong Liang¹,

Hao Li², Jeff Finder², Corey Overgaard², Joe Kulik¹, Dave McCreedy³ and Shuttha Shutthanandan³; ¹APRDL, Freescale Inc, Tempe, Arizona; ²MPSL, Motorola Inc, Tempe, Arizona; ³EMSL, Pacific Northwest National Lab, Richland, Washington.

Epitaxial $\text{SrTiO}_3/\text{Si}(100)$ shows promise as a virtual substrate for integration of various functional oxides in RF and optoelectronics applications. However, there are three fundamental problems with the $\text{SrTiO}_3/\text{Si}(100)$ system: [i] the substrate-film interface is chemically unstable at high temperatures, [ii] the high dielectric loss of Si hinders its use for RF applications, and [iii] the 2% lattice mismatch between SrTiO_3 and Si results in films with high defect densities. In this study, we show that annealing $\text{SrTiO}_3/\text{Si}(100)$ at high temperature in oxygen introduces a thick (2000 Å), amorphous SiO_2 layer at the substrate-film interface, and that growth of this interfacial layer prevents SrTiO_3 from reacting with Si. The SiO_2 layer also dielectrically decouples the SrTiO_3 film from the Si substrate, while the annealing process improves the crystalline quality of the SrTiO_3 epilayer. In conjunction with the annealing process, expansion of the SrTiO_3 lattice was measured by variable-temperature (25 C-1000 C), in-situ x-ray diffraction. Strongly non-linear changes in the SrTiO_3 lattice parameter were observed above 800 C, at which temperatures the films were mostly relaxed. However, upon slow cooling to room temperature, the SrTiO_3 films returned to a partially strained state. Ex-situ cross-section transmission electron microscopy imaging and ion channeling measurements revealed improvements in the crystallinity of the SrTiO_3 epilayer after annealing. The combined effects of the Si(100) substrate and activities at the SiO_2/Si interface on the strain state of the SrTiO_3 films will be discussed. In addition, we show that epitaxial (Ba,Sr)TiO₃-based capacitors with 66% tunability and 1.6% dielectric loss were successfully fabricated on SOI substrates using this approach.

4:30 PM H7.10

Linear Ferroelectricity in Artificial Superlattices of $\text{PbZrO}_3 / \text{BaZrO}_3$ Deposited on Si for Ferroelectric Memory Application. Cheng-Lung Hung and Tai-Bor Wu; Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan.

Artificial superlattice is a structure with arbitrarily engineered stacking sequence fabricated by layer-by-layer growth technique. Giant dielectric constant or anomalous properties different from those of ordinary ferroelectric films can be obtained from the ferroelectric superlattices. Therefore, artificial layered-perovskite composed of alternating layers of antiferroelectric PbZrO_3 (PZO) and paraelectric BaZrO_3 (BZO) was fabricated on $\text{LaNiO}_3/\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates at 475 °C by radio frequency magnetron sputtering with dual cathodes. It had an (001)-oriented superlattice structure with an average composition of $(\text{Pb}_{0.75}\text{Ba}_{0.25})\text{ZrO}_3$ (PBZ). X-ray diffraction

and transmission electron microscopy confirmed the formation of superlattice structure with designed composition modulation. The dielectric property was enhanced from the strain manipulation of the superlattice with decreasing the stacking periodicity. The ferroelectricity also increases and a linear ferroelectricity is found in the PZO/BZO superlattices which are denoted by the linear dependence of remanent polarization (Pr) and coercive field (Ec) on the applied voltage. Furthermore, the PZO/BZO superlattices also showed good fatigue resistance and low leakage current characteristics as those of natural layered-perovskites.

4:45 PM H7.11

Epitaxial La_{0.67}Ca_{0.33}MnO₃ and La_{0.67}Sr_{0.33}MnO₃ Films on GaAs. Sergey I. Khartsev, Joo-Hyung Kim and Alexander M. Grishin; Condensed Matter Physics, Royal Institute of Technology, Stockholm-Kista, Sweden.

Colossal magnetoresistive (CMR) La_{0.67}Ca_{0.33}MnO₃ (LCMO) and La_{0.67}Sr_{0.33}MnO₃ (LSMO) films have been grown by pulsed laser deposition technique on GaAs(001) substrates buffered with epitaxial MgO layer. X-ray diffraction revealed strong c-axis out-of-plane orientation and strong in-plane texture of CMR/MgO bilayers on GaAs single crystal. The maximum temperature coefficient of resistivity TCR = 9.0%/K @ 223K and 2.0%/K @ 327K and differential magnetoresistance $d\rho/dH$ = -7.3%/kOe and -1.4%/kOe have been achieved for LCMO/MgO/GaAs and LSMO/MgO/GaAs heteroepitaxial structures, respectively. Comparison with the test LCMO and LSMO films grown directly onto the bulk MgO(001) single crystal demonstrates the identity of LSMO/MgO/GaAs and LSMO/MgO films properties whereas the LCMO films grown on MgO buffered GaAs show lower transition temperature $T_c = 242$ K compared to 253K in LCMO/MgO.

SESSION H8: Poster Session: Magnetic Oxide, Oxide on Si/Gate Oxide

Chairs: Arunava Gupta and John Robertson

Wednesday Evening, December 1, 2004

8:00 PM

Exhibition Hall D (Hynes)

H8.1

High-Performance Gate Dielectric Compositions in the Ternary Y₂O₃-HfO₂-Al₂O₃ System.

Dmitry Anatolyevich Kukuruznyak¹, Ken Hasegawa², Parhat

Ahmet¹, Takahiro Nagata¹ and Toyohiro Chikyow¹; ¹Nano-materials Assembly, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; ²Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Performance of Y₂O₃-HfO₂-Al₂O₃ oxides as gate dielectric materials was investigated. Complete continuous ternary spreads were deposited onto a single bare silicon substrate using combinatorial pulsed laser deposition technique. In all situations the fabrication technique achieved atomically mixed compounds. Crystal structure phase diagram was established with combinatorial XRD (Rigaku, Bruker). In the range between Hf_{1.65}Y_{2.35}O_{7.15+x} and Hf_{2.95}Y_{1.05}O_{6.5+y} binary Y₂O₃-HfO₂ alloys form a single fluorite phase. Chemical composition - lattice parameter dependence suggests that the strong deviation from the standard fluorite stoichiometry was facilitated by forming of oxygen vacancies. Addition of Al₂O₃ to Y₂O₃-HfO₂ alloys results in the development of amorphous compounds. Dielectric constant and electrical characteristics such as flatband voltage shifts and leakage currents were measured at each point in the ternary diagram. It was found that particular single compounds and tie lines in the ternary spreads exhibit advantageous electric properties. For example the tie line connecting compounds Y_{2.24}Hf_{1.76}O₇ and Al_{0.16}Hf_{0.84}O_x exhibits zero fixed charge and low leakage current. The tie line compositions correspond to particular ordered atomic arrangements at the interface with silicon. In such highly ordered arrangements each cation has a whole number of oxygen nearest neighbors. Atomic mixing in arbitrary proportions yields local spatial fluctuations of the number of nearest neighbors, dangling bonds, and electronic defects. Discovered composition-dependent atomic arrangements correspond to both well-known crystalline phases and amorphous-like materials lacking long-range order. Moreover, the favorable tie line compositions includes both thermodynamically stable phases and metastable arrangements. Locally-ordered metastable compounds, fabricated by vacuum deposition techniques maintain defect-free characteristics after annealing at moderate temperatures. This information gives new insight on the formulation of prospective gate dielectric materials.

H8.2

Diffusion Barrier Properties of Hf-based Gate Dielectrics Between Si and Silicide-forming Gate Metals.

Katherine L. Saenger, Cyril Cabral, Paul C. Jamison, Roy A.

Carruthers and Rajarao Jammy; Semiconductor R&D Center, IBM TJ Watson Research Center, Yorktown Heights, New York.

Advanced complementary metal oxide semiconductor (CMOS) devices will increasingly be relying on metal gate materials and high-k dielectrics. Pt, a potential gate material for nFETs (due to its high work function), is known to be thermodynamically stable on both HfO₂ and SiO₂. However, system failures can result not only from a reaction between the gate metal and gate dielectric, but from reaction of the gate metal and the underlying semiconductor if the gate dielectric is an insufficiently robust diffusion barrier. Here we probe the diffusion barrier properties of various Hf-based gate dielectrics by examining PtSix formation in Si(substrate)/HF-based gate dielectric/Pt samples as a function of gate dielectric type, thickness, and crystallinity. We attribute the better diffusion barrier properties of HfSiO_x (vs. HfO₂) in the temperature range 650-750C to the fact that HfO₂ is typically crystalline as-deposited whereas HfSiO_x remains amorphous (and free of grain boundaries) up to its 800-850C crystallization temperature.

H8.3

Transport and Thermoelectric Properties of Ca₃Co₄O₉ Thin Films. Yufeng Hu¹, Qiang Li¹ and Weidong Si²; ¹Materials Science

Department, Brookhaven National Laboratory, Upton, New York; ²Physics Department, Brookhaven National Laboratory, Upton, New York.

It has been discovered recently that cobaltates have very large thermoelectric power, which shows that cobaltates hold great promise to be potential integrated heating spreading solution, such as thermal management of microprocessors. Among the layered cobaltates, Ca₃Co₄O₉ has been shown to have one of the highest thermoelectric power in single crystal form. The purpose of this work is to study the transport and thermoelectric properties of Ca₃Co₄O₉ thin films. We have successfully grown the c-axis orientated Ca₃Co₄O₉ thin films using Pulsed Laser Deposition (PLD) technique on various substrates, including Si, LaAlO₃, Al₂O₃. The in-plane transport and magnetization measurements have been performed in the Ca₃Co₄O₉ films and show similar behaviors as in the single crystal samples. The detailed transport and thermoelectric properties of Ca₃Co₄O₉ thin films will be discussed. This work was supported by the U. S. Dept. of Energy, Office of Basic Energy Science, under contract No. DE-AC-02-98CH10886.

H8.4

Growth and Characterization of Pulsed Laser Deposited Rare Earth-Based Manganites onto Si(100) Semiconductor using SrTiO₃ Template Layer. A. K. Pradhan, S. Mohanty, Kai Zhang, J. Dadson, D. Hunter and G. B. Loutts; Center for Materials Research, Norfolk State University, Norfolk, Virginia.

Integrating the rare earth-based manganites onto the semiconducting materials such as Si, GaAs, GaN remains a challenging task for potential device applications that utilize both information processing and data storage in the same device. The recent progresses on the direct integration of SrTiO₃ (STO) onto Si have opened a possibility to integrate both STO and R_{1-x}BxMnO₃ into this technologically important semiconductor. In order to obtain a highly epitaxial manganite film, a substrate should meet at least three major requirements, such as minimization of the film and substrate lattice mismatch, matching of the film and substrate thermal expansion coefficients, and elimination of the chemical reaction between the substrate and deposited film. It is well known that silicon does not comply with all these requirements thus a template layers must be introduced to accommodate mechanical and chemical dissonances. In order to explore this possibility, we have successfully fabricated R_{1-x}BxMnO₃/STO/Si heterostructures using multitarget pulsed laser deposition system. We demonstrate the growth of La_{1-x}BaxMnO₃ (LBMO) and La_{1-x}SrxMnO₃ (LSMO) epitaxial films on Si (100) substrates buffered by heteroepitaxially grown STO. The growth conditions for the heterostructures are optimized. The films grown under optimum conditions show remarkable epitaxy, surface morphology, and ferromagnetic properties above room temperature. This will produce many generic approaches to the integration of multicomponent oxide thin films on semiconducting surfaces, which can impact a variety of technologies. Apart from IR imaging, epitaxial perovskite heterostructures can be fabricated for photosensitive and field effect transistors (FET), and other room temperature spintronic devices, controlling ferromagnetism both by light and electric fields.

H8.5

Fabrication of Epitaxial PZT/Pt/ γ -Al₂O₃/Si Structure and its Ferroelectric Characteristics. Daisuke Akai¹, Mikako Yokawa², Keisuke Hirabayashi², Koji Matsushita², Kazuaki Sawada² and Makoto Ishida²; ¹Venture Business Laboratory, Toyohashi University of Technology, Toyohashi, Japan; ²Department of Electrical and Electronic Engineering, Toyohashi University of Technology,

In this paper, we proposed epitaxial γ -Al₂O₃ films on Si substrates to control the orientation of Pt and PZT films, and investigated ferroelectric properties of epitaxial PZT films with various compositions on those substrates. This is the first report to grow epitaxial Pt and PZT/Pt films on single crystal γ -Al₂O₃/Si substrates. Pb(Zr_xTi_{1-x})O₃ (PZT) thin films have been extensively investigated for potential applications in nonvolatile memory devices and infrared sensors. The electrical properties of PZT are well known to strongly depend on crystalline orientation and the Zr/Ti ratio. Crystallinity and orientation of substrates are very important to control orientation of bottom electrode (i.e. Pt) and PZT films. MgO single crystal and SrTiO₃ single crystal substrates were reported. Epitaxial Pt and PZT/Pt films were grown on those substrates and the orientation of these films were well controlled. However, these single crystal substrates are very expensive and not suitable for monolithic integration of the ferroelectric films and signal processing circuits. Previously, we have been studied epitaxial γ -Al₂O₃ films on Si substrates using chemical vapor deposition (CVD). The γ -Al₂O₃ films have been applied for an insulator for SOI substrates [1] and buffer layers for heteroepitaxial growth [2]. The fabrication of the epitaxial γ -Al₂O₃ films on Si substrates was carried out using a CVD method. γ -Al₂O₃ (001) and γ -Al₂O₃ (111) films 60 nm thick were epitaxially grown on Si(001) and Si(111) substrates, respectively. Epitaxial Pt thin films were prepared by rf sputtering system at various temperature. The 240-nm-thick PZT films with various compositions were prepared by sol-gel method. X-ray diffraction and reflection high-energy electron diffraction shows (001) and (111) epitaxial Pt films on (001) and (111) γ -Al₂O₃/Si substrates sputtered above 600 °C, respectively. At room temperature, polycrystalline Pt films were obtained on substrates. Epitaxial PZT(001) films with various components were obtained on the Pt(001)/ γ -Al₂O₃(001)/Si(001) substrates. PZT(111) films were also fabricated on the Pt(111)/ γ -Al₂O₃(111)/Si(111) substrates. Epitaxial PZT films showed better ferroelectric properties and pyroelectric properties than polycrystalline PZT films. The P-E hysteresis loop of epitaxial PZT films were observed with remnant polarization of 14.3 μ C/cm² and coercive field of 50 kV/cm. Especially, maximum pyroelectric coefficients of epitaxial films appeared and values were 1.8 μ C/cm²K and 1.4 μ C/cm²K on Zr/Ti ratio of 40/60 for the PZT(001) film and the ratio of 52/48 for the PZT(111) film, respectively. These pyroelectric coefficients are the same as the PZT ceramics. We expect that this epitaxial PZT/Pt/ γ -Al₂O₃/Si structure can be applied to Si integrated ferroelectric sensor devices. Refs. [1] M. Ishida et al., Jpn. J. Appl. Phys. 39, 2078 (2000). [2] D. Akai et al., J. Cryst. Growth 259, 90 (2003).

H8.6

Etching of Heteroepitaxial

La_{0.67}(Sr,Ca)_{0.33}MnO₃/Bi₄Ti₃O₁₂/CeO₂/YSZ/Si Film

Structures for IR Bolometer Applications. Joo-Hyung Kim,

Sergey I. Khartsev and Alexander M. Grishin; Condensed Matter Physics, Royal Institute of Technology, Stockholm-Kista, Sweden.

La_{0.67}(Sr,Ca)_{0.33}MnO₃ (LSCMO) films have been grown by a pulsed laser deposition technique on Si(001) substrates buffered with Bi₄Ti₃O₁₂/CeO₂/YSZ heteroepitaxial layers. X-ray diffraction showed cube-on-cube growth of an epitaxial Bi₄Ti₃O₁₂/CeO₂/YSZ heterostructure on Si whereas the LSCMO layer grows in the "diagonal-on-side" manner on top of the Bi₄Ti₃O₁₂ template. LSCMO composition has been optimized to get the maximum of temperature coefficient of resistivity TCR = 4.4%/K at 294 K. As a prototype of an uncooled bolometer, heteroepitaxial CMR structure on Si demonstrates the noise equivalent temperature difference NETD = 1.2 uK/(Hz)^{1/2}@30Hz at 294 K. We develop an adhesive wafer-level bonding technique to make an array of micromachined uncooled IR CMR bolometers. For this purpose, we studied wet KOH and Ar ion beam dry etching (IBE) of heteroepitaxial CMR structures on Si. LSCMO film was found to be highly chemically resistive against 23% of KOH at 80 °C with the etching rate is less than 0.2 nm/min. The etching rate of Ar-IBE was 16 nm/min and 14-17 nm/min for LSCMO and buffer oxide layers correspondingly. This is a lower than 24 nm/min for Si at the same etching conditions. We present x-ray diffraction patterns, scanning electron micrographs, AFM and Scanning Spreading Resistance Microscopy (SSRM) images of oxide films at different stages of the etching process.

H8.7

Elaboration and Characterization of Y-Doped HfO₂ Thin Films Grown by MOCVD. Erwanl Rauwel¹,

Catherine Dubourdieu¹, Frederique Ducroquet², Nevine Rochat³, Bernd Hollaender⁴ and Cyril Millon¹; ¹Laboratoire des Matériaux et du Génie Physique, CNRS / INPG, St Martin d'Heres, France; ²Laboratoire de Physique de la Matière, CNRS / INSA Lyon, Villeurbanne, France; ³DRT/DTS-LET/SCPC, CEA Grenoble, Grenoble, France; ⁴Forschungszentrum, Juelich, Germany.

Extensive miniaturization of integrated circuits and their demand for increased performance has spurred on the search for dielectric oxides to replace SiO₂ in future Si-based microelectronic applications. HfO₂ has been extensively studied as it has a medium permittivity of 20-25 for the monoclinic phase and is stable with silicon. In fact HfO₂ may also crystallize in a cubic or tetragonal structures, which should exhibit a higher permittivity than the monoclinic phase. We have studied the possible stabilization of HfO₂ in a cubic phase using yttrium as a dopant. Thin films were grown on (001) Si by liquid injection Metal Organic Chemical Vapor Deposition. Hf and Y precursors were dissolved in octane with varying Y precursor content (from 0 to 100 % with step of 10 %). These films were then characterized by X-ray diffraction, X-ray reflectometry, infrared spectroscopy (in the total reflection mode), ellipsometry, Rutherford backscattering spectrometry and atomic force microscopy. Electrical measurement C-V and I-V were carried out on MOS structures after evaporation of gold electrodes. The equivalent oxide thickness was calculated from the capacitance in the charge accumulation mode. The X-ray diffraction diagrams show a clear transition from the monoclinic to a cubic structure (HfO₂-Y₂O₃ or Hf₂Y₂O₇) with a possible coexistence of the two structures. This result is confirmed by attenuated total reflection infrared spectra. The density of the films decreases when the yttrium concentration increases. Equivalent oxide thickness evolves linearly with films thickness. An effective permittivity of 17 is found for optimized doping. Comparison of electrical properties of doped and undoped films will be discussed.

H8.8

Abstract Withdrawn

H8.9

Experimental Study and Modeling of Nanopatterning Effect on 90° Domain Behavior in PbZr_{0.2}Ti_{0.8}O₃ Film on Si

Substrate. Zhengkun Ma¹, Lang Chen¹, Jun Ouyang¹, R. Ramesh³,

John Menlgaillis² and Alex Roytburd¹; ¹Department of Materials Science and Engineering, University of Maryland at College Park, College Park, Maryland; ²Department of Electrical Engineering, University of Maryland, College Park, Maryland; ³Department of Materials Science and Engineering, University of California, Berkeley, California.

Focus ion beam milling has been used to pattern and characterize sub-micron ferroelectric devices (capacitor islands) on epitaxial PbZr_{0.2}Ti_{0.8}O₃/SrRuO₃/SrTiO₃/Si heterostructures to reduce the substrate clamping. The effects of geometry of island on 90° domain configuration and properties are investigated. The configuration of 90° domain and corresponding piezoelectric properties are shown to be able to manipulated by the geometry of the island. Piezoresponse, d₃₃ and polarization under electric field is significantly enhanced due to 90° domain movement. The intrinsic piezoelectric response of 90° domain are simulated by the finite element analysis. Comparison with experimental data allows us to estimate, the extrinsic contribution of 90° domain movement to piezoeffect. Piezoelectric force microscopy study reveals that stripe-shape islands has two-domain plane-parallel structure in agreement with phase field modeling [1]. These structures demonstrate enhanced piezoresponse. This work is supported by NSF-MRSEC under grant DMR-00-80008.

H8.10

Characterization of HfO₂ and HfxSiyOz Gate Dielectric Films Grown by Chemical Vapor Deposition using TEMAH

Precursor and Oxygen. Sug Hun Hong, Suk Woo Lee, Jaehoo

Park, Moonju Cho, Seong Keun Kim and Cheol Seong Hwang; School of Materials Science and Engineering and Inter-university Semiconductor Research Center, Seoul National University, Seoul 151-742, Korea, Seoul, South Korea.

HfO₂ gate dielectric films were deposited on SC1 and HF-cleaned Si wafers by chemical vapor deposition (CVD) method using [Tetrakis(Tetra-Ethyl-Methyl-Amino) Hafnium, Hf[N(CH₃)(C₂H₅)₄]₄] and O₂ or N₂O, as the precursor and oxidant, respectively. The deposition temperatures were varied from 280 to 420 °C and characteristics of the films were evaluated. The as-deposited films were partially crystallized and became fully crystallized after post-deposition annealing (PDA) at 800 °C. Interfacial layer (IL) thickness between HfO₂ and Si substrate was increased by 50% by the PDA. AFM results showed that the HfO₂ film deposited at higher temperature showed the smaller RMS roughness values. Therefore, the HfO₂ film deposited at 420 °C showed the lowest leakage current density. The leakage current largely increases by the PDA. Therefore, it was found that the inhibition of crystallization and obtaining smallest surface roughness are the most important factors for obtaining the small leakage current. The flat-band voltage remained at the ideal value and the hysteresis in the capacitance-voltage plots was minimized (80mV). For HfxSiyOz film deposition, various Si precursor vapor was introduced simultaneously with the TEMAH.

The Si-precursors show a rather high deposition temperature window (> 400°C). Therefore, only a high deposition temperature window was available for the silicate film growth. Detailed electrical properties of the MOSCAP and MOSFET devices using poly-Si and metal (Pt) gate electrodes will be presented.

HS.11
Improvements in Electrical and Structural Properties of CVD Hf_xAl_yO_z Gate Dielectric Films Grown with N₂O Oxidant. Suk Woo Lee, Jaehoo Park, Moonju Cho, Sug Hun Hong, Tae Joo Park and Cheol Seong Hwang; Seoul National University, Seoul, South Korea.

Hf_xAl_yO_z gate dielectric films were deposited on RCA cleaned Si wafers by chemical vapor deposition (CVD) method using HF-Al single molecular precursor [HfAl(OC₃H₇)₅(OC₄H₈OCH₃)₂]. N₂O and O₂ were used as the oxidants during the deposition process and the comparisons of the electrical and structural properties were performed. The as-grown films have a Hf-rich composition (Hf : Al : O = 2.16 : 1 : 4) as confirmed by Rutherford Backscattering Spectroscopy and a dielectric constant of 16-17. The Hf_xAl_yO_z films maintained amorphous structure up to a rapid thermal annealing temperature of 800°C under a N₂ atmosphere, but showed two-phase microstructure composed of crystallized monoclinic HfO₂ and amorphous interfacial layer after the annealing at 1000°C. Capacitance Equivalent Thickness (CET) of the O₂-Hf_xAl_yO_z films increased monotonously with the increasing annealing temperature. However, CET of the N₂O-Hf_xAl_yO_z decreased up to 700°C due to densification (confirmed by Transmission Electron Microscopy and Spectroscopic Ellipsometry) and nitrogen incorporation (confirmed by Secondary Ion Mass Spectroscopy) and increases with a smaller rate. The incorporated nitrogen at the film/Si interface of the N₂O-Hf_xAl_yO_z film improved the thermal stability of flat band voltage and reduced the C-V hysteresis compared to those of the O₂-Hf_xAl_yO_z. Furthermore, XPS (X-ray Photoemission Spectroscopy) analysis showed that the use of N₂O oxidant reduced non-oxidized Hf bonding, such as Hf-Hf, Hf-Si, and Hf-Al. The Si-O (or Silicate) peak position of the Si 2p shifts toward a high binding energy by the N-incorporation.

HS.12
Optical, Electronic, and Interface studies on ZrO₂ and HfO₂ thin films grown on Si and amorphous SiO₂ by RF reactive sputtering and metal oxidation. Ciro Manuel Lopez¹, N. A. Suvorova¹, A. A. Suvorova², M. Saunders² and E. A. Irene¹; ¹Chemistry, University of North Carolina-Chapel Hill, Chapel Hill, North Carolina; ²Centre for Microscopy and Microanalysis, University of Western Australia, Crawley, Western Australia, Australia.

Zirconia, ZrO₂, and Hafnia, HfO₂, thin films have been deposited on single crystal MgO (100), Si (100), and amorphous SiO₂ by both ion-beam sputter deposition of the parent metal and subsequent oxidation as well as reactive-sputtering. The optical properties of the films deposited by both techniques have been determined by *in-situ* spectroscopic ellipsometry (SE) in the photon energy range of 1.5-4.5 eV. The temperature dependence of the optical properties has also been studied. It has been determined that the oxidation of Zr can occur at temperatures as low as 250°C. Further oxidation, up to 700°C, did not significantly change the optical properties of the dielectric. Morphology studies have shown hillock formation for metal deposition on Si with subsequent oxidation, though this was not the case for depositions on SiO₂. Time of flight mass spectrometry of recoiled ions (TOF-MSRI) and SE performed *in-situ*, along with analytical electron microscopy were used to investigate the extent and composition of the interface formed with Si and amorphous SiO₂. The optical properties of the interface layers have been determined and modeled using Lorentz oscillators. It has been found that for ZrO₂ the nature of the interface is optically different for depositions on Si than for those on SiO₂, even after complete oxidation. Electrical measurements were performed on fabricated Pt/ZrO₂/Si and Pt/HfO₂/Si capacitors (prepared *in vacuo*) with and without a purposely grown SiO₂ interlayer. Effective dielectric constants (K_{eff}) for the films stacks as well as density of interface traps (D_{it}) were studied. Both dielectrics were also deposited on thin SiO₂ layers (2-7 nm), in order to both minimize the SiO₂ thickness and D_{it} while maximizing K_{eff} .

HS.13
In situ XPS/LEIS Characterisation of ALD Grown HfO₂/Si Decomposition Kinetics during Vacuum Annealing. Andrei Zenkevich¹, Yuri Lebedinskii¹, Giovanna Scarel² and Marco Fanciulli²; ¹Solid State Physics, Moscow Engineering Physics Institute, Moscow, Russian Federation; ²National Laboratory MDM-INFN, Agrate Brianza (MI), Italy.

Metal-oxide-semiconductor field-effect transistor (MOSFET) devices have been aggressively scaled to improve performance, but some of

the physical properties of SiO₂ gate dielectric limit further decreasing of feature size. Hf based dielectrics have been evaluated as the most promising candidates to replace silicon dioxide as gate dielectric. Since the technology includes post annealing of the grown MOS structures, the issue of HfO₂ thermal stability in contact with Si has recently received much attention. It is established that, depending upon the annealing environment (vacuum, N₂, O₂), the Hf oxide layer degradation may occur in the temperature range 800-950 C with the formation of Hf silicide on the Si surface. However, the exact mechanism of HfO₂ degradation is still not clear. In this work, we present the experimental results on the chemical composition and diffusion in HfO₂ thin films on Si obtained during vacuum (10⁻⁹ Torr) annealing with the combination of two techniques, x-ray photoelectron spectroscopy (XPS) and low energy ion spectroscopy (LEIS). HfO₂ thin layers were grown on Si using Atomic Layer Deposition (ALD). The measurements were performed in situ in the temperature range 800-950 C and reveal that the temperature at which degradation starts (determined from the appearance of the silicide peak in the Hf 4f XPS spectrum) depends on film thickness. For a HfO₂ (4nm) / SiO₂ (1nm)/Si stack annealed in vacuum, Si emerges on the surface at T = 900 C, as established with LEIS. Moreover, XPS shows that Si is in the metallic form. No silicide is seen with XPS at this temperature. Ex situ AFM and SEM analyses of the sample surface upon this stage of annealing reveal no voids down to a 10 nm scale. Judging from the Hf4f spectra, Hf silicide starts to form at T = 930 C. XPS spectra recorded at different take-off angles indicate that Hf silicide formation starts on the surface of the oxide. The set of experimental data support the model according which enhanced Si diffusion through HfO₂ at certain temperatures is likely to occur due to oxygen vacancies while Si segregating at the surface may facilitate Hf silicide formation.

HS.14
A Novel Epitaxial Growth Technique of Ultrathin Single Crystalline γ -Al₂O₃ Films with Very Smooth Surface on Si substrates. Takayuki Okada¹, Mohammad Shahjahan², Kazuaki Sawada¹ and Makoto Ishida¹; ¹Electrical and Electronic Engineering, Toyohashi University of Technology, Toyohashi, Japan; ²Physics, Rajshahi University, Rajshahi, Bangladesh.

1. Introduction Single-crystalline g-Al₂O₃ films are quite attractive in the microelectronics and thin-film-device applications as an insulator, ion barrier and protective coating, because the crystalline films provide higher device performances and better chemical and thermal stability than that of amorphous ones. We have established the two-step growth method of the ultrathin single-crystalline g-Al₂O₃ films on Si substrates with very smooth surface, and the several device applications have been reported [1] [2] [3]. However, it is required to control some parameters precisely at the first growth step. In this paper, we propose a novel growth method of ultrathin crystalline g-Al₂O₃ films with very smooth surface on Si substrates without precise controlling. 2. Experiments Si(111) and Si(100) substrates were primary cleaned with a modified RCA process. Then, a chemical oxide layer was formed on the surface with the thickness of 10-15 Å. The substrates were inserted into a vacuum system that provides a mixed source molecular beam epitaxy (MBE) for the crystalline g-Al₂O₃ growth using solid Al as aluminum source and N₂O gas as oxygen source. During the epitaxial growth, the substrates temperature, the Al-Knudsen cell temperature and N₂O gas pressure were maintained at 750 °C, 1120 °C and 3.2 × 10⁻² Pa, respectively. 3. Results and discussions As a result, the epitaxial g-Al₂O₃ films and a c-axis oriented g-Al₂O₃ films were formed on the Si(111) and Si(100) substrates respectively, which were confirmed by streaky reflection high-energy electron diffraction (RHEED) patterns. Furthermore, the smooth surface morphologies were confirmed by atomic force microscope (AFM) images that show the typical root mean square (RMS) values are 0.25-0.30 nm for the 2.5 nm² thick-films. The in-situ X-ray photoelectron spectroscopy (XPS) spectra taken before and after growth showed that Al₂O₃ films were formed (i.e. Al2p peaks were shifted toward to higher binding energy) and chemical oxide layers disappeared (i.e. Only Si2p peaks were observed after growth) due to the growth. This fabrication mechanism may be considered as evaporated Al atoms react with oxygen derived from chemical oxides at the initial stage of Al₂O₃ growth. Consequently, initial Al₂O₃ films are epitaxially formed due to the thinness. After the initial Al₂O₃ film formation, the epitaxial growth can continuous by MBE. 4. Conclusions In this study, we proposed a novel growth method of ultrathin crystalline g-Al₂O₃ films. This method provides epitaxial g-Al₂O₃ films and a c-axis oriented g-Al₂O₃ films on Si(111) and Si(100) substrates respectively with smooth surface. This new technique will be technologically important due to its simplicity. References [1] Y. C. Jung et al., Jpn. J. Appl. Phys 38 (1999) 2333 [2] M. Shahjahan et al, Jpn. J. Appl. Phys 41 (2002) 2602 [3] M. Shahjahan et al, Jpn. J. Appl. Phys 41(2002) 1474

HS.15
Comparative Study of Post-Deposition Plasma Treatments on

HfO₂ Layers in Cylindrical DRAM Capacitors.

Thomas J. Kwon, J. C. Lee, K. J. Nam, Y. G. Park, J. H. Choi, Y. S. Kim, C. Y. Yoo, S. T. Kim and U. I. Chung; Process Development Team, Semiconductor R&D center, Samsung Electronics, Youngin-City, Gyeonggi-Do, South Korea.

HfO₂ has widely been evaluated for DRAM capacitor dielectric because of its high permittivity and wide band gap. It has been reported that leakage current of HfO₂ is increased due to both residual carbons in HfO₂ film, originated from its own deposition process and crystallization of HfO₂ film. In order to suppress the leakage current by removing the residual carbons, low temperature post treatment is required and therefore plasma treatment would be the most promising technology. However, step coverage of plasma treatment would be the major concern because the HfO₂ film deposited on the bottom of cylindrical capacitor in aspect ratio of about 40:1. In this study, post plasma treatments using high density RF source on TIT capacitor was performed. At first, to confirm "step coverage" of plasma treatment on cylindrical structures of DRAM capacitor, we applied plasma treatments using oxygen and nitrogen on cylindrical-shape poly-silicon with high aspect ratio of 40: 1 and measured the thickness of oxide and nitride grown by plasma treatment by TEM. Up to 90% of plasma step coverage was observed under optimal plasma condition at relatively low temperature, 250C. In this article, optimal conditions of plasma treatments will be discussed in detail. These plasma conditions were implemented to reduce the leakage currents on TIT capacitor. ALD HfO₂ was used as dielectrics layer in this application. It was demonstrated that leakage current of TIT capacitors with plasma-treated HfO₂ thin layer decreased about 1 order at $\pm 1.5V$ compared to that of TIT capacitor without plasma treatment. In summary, the leakage current of cylindrical capacitor is effectively reduced by the post plasma treatment with high step coverage. It is concluded that TIT capacitor with HfO₂ thin film can be applied to DRAM device with 70nm Design Rule and beyond.

H8.16

Changes in the Chemical State of N-incorporated HfO₂ Thin Films. Kwun Bum Chung^{1,2}, Mann-Ho Cho², Chung Nam Whang¹, Dae Won Moon², Dong Won Lee³ and Dae-Hong Ko³; ¹Institute of Physics and Applied Physics, Yonsei University, Seoul, South Korea; ²Nano Surface Group, Korea Research Institute of Standards and Science, Daejeon, South Korea; ³Ceramic Engineering, Yonsei University, Seoul, South Korea.

The changes in the chemical state of HfO₂ related to N incorporation via NH₃ ambient post-annealing treatment were investigated by using synchrotron radiation x-ray photoelectron spectroscopy (SRXPS), near edge x-ray absorption fine structure (NEXAFS) analysis, and medium energy ion scattering spectroscopy (MEIS). The core-level energy states, Hf4f peak showed a shift to higher binding energy, indicating that a silicate layer is formed, until the NH₃ annealing temperature reaches 700°C. The data obtained using various tools showed that a small quantity of N was incorporated in the film below the annealing temperature at 700°C, and the effect caused by N incorporation was negligible. However, SRXPS spectra revealed the lower binding energy shift at annealing temperature above 800°C, resulting from the incorporation of nitrogen into HfO₂ films. In addition, absorption spectra of N-K edge also showed the dramatic chemical state changes at annealing temperature above 800°C: i.e., the N was incorporated in the film over the annealing temperature at 800°C, while it was dominantly observed in the interfacial region below the annealing temperature. Moreover, the incorporation of nitrogen drastically changed the chemical bonding properties of HfO₂ films at the annealing temperature of 900°C and critically affected the electrical characteristics.

H8.17

Low Temperature Growth of (Pb,Ba)(Zr,Ti)O₃ Thin Films by Sol-Gel Method Followed by Hydrothermal Treatment Compatible with Si ULSI Process. Minoru Noda, Youji Sakioka, Nobuaki Edokoro, Takuji Naoyama and Masanori Okuyama; Department of Systems Innovation, Graduate School of Engineering Science, Osaka Univ., Toyonaka Osaka, Japan.

Recently low temperature preparation of ferroelectric thin films has been required for the development of highly integrated ferroelectric memory. It is reported that PZT thin films were prepared at low temperature so far by sol-gel method followed by hydrothermal treatment with KOH solution, and confirmed to have good electrical properties. However, the KOH is impossible to be applied to a conventional Si ULSI process since potassium ion in the KOH is well-known as a notorious mobile-impurity ion and also the KOH etches off the Si substrate seriously. Therefore, in this work we have newly prepared (Pb,Ba)(Zr,Ti)O₃ (PBZT) thin films by hydrothermal treatment using Ba(OH)₂ related solution as alkali mineralizer other than KOH. After sol-gel solution of PZT was spin-coated on Pt/Ti/SiO₂/Si wafer, the films were dried at 150°C for 10 min. and

pre-baked at 300 °C for 30 min. Thickness increase of the gel film for one coating was about 50nm. Hydrothermal treatment was carried out in an autoclave by submerging the sample in 30ml Ba(OH)₂ solution. A part of Ba ions are substituted for Pb ions during the hydrothermal treatment and the film becomes (Pb,Ba)(Zr,Ti)O₃ (PBZT). A PBZT thin films with 100-200nm thickness were finally produced by repeating a series of process of a spin-coating and hydrothermal treatment several times. A perovskite PBZT film with (111) preferred orientation is clearly obtained after the hydrothermal treatment, although the PZT gel film is amorphous before the hydrothermal treatment. When the first spin-coated layer was thicker than 80nm, it was hardly crystallized by the hydrothermal treatment using the Ba(OH)₂ solution. We have found in this work that it is essential to make each spin-coated gel film as thin as possible in order to improve the crystallinity in the PBZT thin film. Moreover, we have also applied the method to produce BaTiO₃ and (Pb,Ba)TiO₃ (PBT) thin films from TiO₂ gel films by sol-gel method followed by hydrothermal treatment at the temperature of 300°C or less. After sol-gel solution of TiO₂ was spin-coated on Pt/Ti/SiO₂/Si wafer, the films were dried at 150°C for 10 min. and pre-baked at 300 °C for 30 min. Hydrothermal treatment was carried out in an autoclave by submerging the sample in 35 ml Ba(OH)₂ and Pb(OH)₂ mixed solution. The TiO₂ gel films in an autoclave were heated to 140-240 °C and the system was held for 60 to 180min. After the hydrothermal treatment, a perovskite phase with (110) preferred orientation was clearly observed. Pb/Ba ratio in the film was obtained as about 0.5 from XRF analysis. The ratio is controllable by changing the ratio of Ba(OH)₂ and Pb(OH)₂ in the solution. *P-E* hysteresis shows good shape and twofold *P_r* is about 22μC/cm². Finally, we expect that the low-temperature hydrothermal treatment using Ba(OH)₂ solution becomes an effective approach for application to back-end ferroelectric capacitor process in the next-generation Si ULSI process.

H8.18

Effect on Ferroelectric Properties of Internal Stress Controlled by Buffer Layers in PZT Thin Film on Si Substrate.

Keisuke Fujito¹, Naoki Wakiya¹, Kazuo Shinozaki¹, Nobuyasu Mizutani¹ and Koichi Seo²; ¹Metallurgy and Ceramics, Tokyo Institute of Technology, Tokyo, Japan; ²PANalitical, Tokyo, Japan.

Recently, epitaxial multiple oxide layers on Si have been widely studied due to future Si-based electronics devices. Lead zirconate titanate (PZT) thin films have been well known to realizing ferroelectric random access memory (FeRAM) material. PZT thin films were grown on Si substrate with epitaxial relationship by introducing Yttria stabilized zirconia (YSZ) and CeO₂ buffer layers. However, PZT thin films must have larger tensile internal stresses compared with oxide substrate along film plane that might depress the remanent polarization (Pr). The tensile stress in PZT films were occurred by the thermal expansion coefficient (TEC) difference between thin film and substrate (Si: 4x10⁻⁶, PZT: 16.7x10⁻⁶). In this paper, we introduced buffer layers to control the internal stress of PZT thin film, and investigated the relation between internal stresses and ferroelectric properties of PZT thin films. To clarify the effect of TEC difference between PZT film and the substrate, SrTiO₃ and Si were used to compare the absolute value of internal stresses. Effects of PZT thickness on the internal stresses and the electrical properties of PZT/buffer/SrTiO₃ system are examined. Also the effects of thickness of the buffer layer in the epitaxial multilayer structure, PZT/LSCO/buffer/CeO₂/YSZ/Si was discussed. YSZ and CeO₂ and bottom electrode (La, Sr)CoO₃ (LSCO) were epitaxially grown on Si with perovskite structure by pulsed laser deposition (PLD). Buffer layers for stress control were deposited by metalorganic chemical vapor deposition (MOCVD) as PZT, PT, and compositional gradient PZT (gradually changed from PT to PZT with growing direction) films. Ferroelectric Pb(Zr_{0.5}Ti_{0.5}) thin film was also deposited by MOCVD. The internal stress in ferroelectric PZT thin films was measured by thin film X-ray diffractometer using sin²ψ method. The internal stresses of PZT thin films with and without 25nm PT buffer layer on ST substrate were 0.47GPa and 0.87GPa, respectively. The internal stress in PZT/LSCO/CeO₂/YSZ/Si structure (without stress control-buffer layer) was 2.22GPa. As the results, without the PT buffer layer, the internal stress in PZT film was enhanced. The internal stress of the PZT thin film deposited on Si substrate was larger than that of the oxide substrate. Based on these results, it suggests that the internal stress was controlled by introducing buffer layers and ferroelectric property was improved.

H8.19

Alternative Gate Insulators for Organic Field-effect Transistors. Leszek A. Majewski, Raoul Schroeder and Martin Grell; Department of Physics and Astronomy, University of Sheffield, Sheffield, United Kingdom.

Field-effect transistors manufactured with organic semiconductors (OFETs) promise cheap, flexible and disposable "plastic" electronics. Although numerous high-performance OFETs and their integrated

circuits (IC) were presented [1, 2], there are still some unresolved problems which have to be addressed. Besides the organic semiconductor itself, and the metal/semiconductor contact, there still is a need for a high-quality, high-permittivity (k) gate insulators. While polymeric OFET insulators work in principle, they often have low capacitance C_i , which leads to transistors that require high switching voltages that are much larger than what realistically will be available for disposable electronics applications. A better choice for low-voltage operated transistors are metal oxide gate insulators. As the most suitable technique of oxide formation for disposable electronics, we have proposed anodisation (electrochemical oxidation) [3]. Anodized films are pinhole-free, homogenous and dense oxide layers of precisely controlled thickness. Anodisation does not require any vacuum steps and anodised metal oxides are not soluble in organic solvents. The most promising metal oxides seem to be aluminium oxide (Al₂O₃) and titanium oxide (TiO₂). Sputtered Aluminium on plastic film is cheaply available commercially, and its oxide is characterized by high electric breakdown (7.7 MV/cm) and relatively high k . TiO₂ has exceptionally high k , which should enable very low voltage operation. Here, we present our recent work [4-6] on low-voltage, high-capacitance, flexible OFETs using anodised Al₂O₃ and TiO₂ as gate insulators in conjunction with commercially available organic semiconductors, namely regioregular poly(3-hexyl thiophene) and pentacene. The presentation includes an OFET with 130 mV/dec inverse subthreshold slope and threshold voltage -0.49 V, that switches 'on' with less than 1 Volt. References [1] T W Kelly, D W Muyres, P F Baude, T P Smith, T D Jones, *Mat. Res. Soc. Symp. Proc.*, 771, L6.5.1 (2003) [2] G Wang, J Swensen, D Moses, A J Heeger, *J. Appl. Phys.*, 93, 6137 (2003) [3] L A Majewski, M Grell, S D Ogier, J Veres, *Organic Electronics* 4, 27 (2003) [4] L A Majewski, R Schroeder, M Grell, *J. Phys. D.: Appl. Phys.* 37, 21 (2004) [5] L A Majewski, R Schroeder, M Grell, *Synth. Met.* 144, 97 (2004) [6] L A Majewski, R Schroeder, M Grell, submitted to *Adv. Mater.*

H8.20

Integration of Yttrium Oxide Films in MIM Capacitors. Christophe Durand¹, Catherine Dubourdieu², Christophe Vallee¹, Serge Blonkowski³, Mickael Derivaz¹, Maurice Kahn¹ and Marceline Bonvalot¹; ¹Laboratoire des Technologies de la Microelectronique, CNRS, Grenoble, France; ²Laboratoire des Matériaux et du Genie Physique, CNRS/INPG, St Martin d' Heres, France; ³STMicroelectronics, Crolles, France.

High-K materials are extensively studied for the replacement of SiO₂ in future silicon-based microelectronic applications. Among these applications are the metal-insulator-metal (MIM) structures, which are present in the upper levels of integrated circuits. Since MIM capacitors are integrated in the back-end process, their preparation requires low thermal budget deposition (<450°C). We report on the integration of Y₂O₃ in MIM structures. The films were grown by plasma-enhanced metalorganic chemical vapor deposition using a liquid injection delivery scheme. The substrates were TiSi₂ (60 nm)/TiN (30 nm) stacks prepared on p-type 200 mm Si (100) standard substrates. The deposition temperature was limited to 380°C. Different films thicknesses were prepared, ranging from 8 to 35 nm. Low temperature annealings (450°C) were performed in order to investigate their effect on the electrical properties. X-ray photoelectron spectroscopy was used to identify the nature of chemical bonds in the films. The microstructure was studied by X-ray diffraction and SIMS. Gold electrodes were evaporated as top electrodes for the C(V) and I(V) measurements. We find capacitance up to 10 fF/μm² with electrical breakdown fields E_{bd} of 5-6 MV/cm for the thinnest annealed samples of 8 nm (however, when considering the breakdown voltage, it is only 1 V and the linearity is not satisfactory). Optimized devices exhibit capacitance as high as 6 fF/μm² with a breakdown voltage of 5 V. The effect of films thickness on the device performance (capacitance, E_{bd} , linear and quadratic parameters) will be discussed. It is found that the linearity is degraded when decreasing films thickness.

H8.21

Magneto-Impedance Measurements at High Frequencies ($f > 100$ kHz) in Polycrystalline La_{0.7}Sr_{0.3}MnO₃ Films. Dana Stanescu¹, Yannich Plancher¹, Pascal Xavier¹, Luana Fratila², Catherine Dubourdieu² and Jacques Richard³; ¹IMEP ENSERG, 23 avenue des Martyrs, BP257 38016, Grenoble, France; ²LMGP ENSPG, UMR CNRS 5628, ENSPG BP 46 38402, Saint Martin Heres, France; ³CRTBT CNRS, 25 avenue des Martyrs, 38042, Grenoble, France.

Until now the majority of magnetotransport studies performed on manganite oxides such as La_{1-x}A_xMnO₃ (A = Ca, Sr, Ba) were realized in static region. The characterization of these oxides in dynamic region (for frequencies varying from 0 up to some GHz) is of interest both from theoretical and application point of views. Such a study could answer to questions such as: i) Does the colossal magnetoresistive effect still exist at high-frequencies? ii) What is the difference between the magneto-impedance of a polycrystalline and of

an epitaxial film? We present original measurements of the magneto-impedance of polycrystalline La_{0.7}Sr_{0.3}MnO₃ films grown on silicon as a function of the frequency (from 100 kHz to 20 GHz), of the temperature (from 4 K to 300 K) and of the external magnetic field (from 0 to 6 T). The films were patterned using UV lithography, argon ion beam etching and sputtering of the metallic contacts. The measurements were realized using an impedance analyzer (for frequencies between 100 kHz and 200 MHz) and a network analyzer (for frequencies between 140 MHz and 20 GHz). A very sharp decrease of the magneto-impedance is observed when increasing the frequency. To analyze this result we have to consider the microscopic granular structure of the polycrystalline film that will result in a macroscopic equivalent capacitive and resistive behavior of the film in the presence of high-frequency signals. It is shown that when increasing the magnetic field from 0 to 6 T the values of the magnitude of the impedance decrease. Consequently, the magneto-resistive effect still exists even at high frequencies up to 200 MHz. The decrease of the impedance values is also observed when decreasing the temperature. Except for the capacitive behavior already mentioned due to the polycrystalline nature of the films, it seems that there is no phenomenological difference in the variation of the magnetotransport in the DC and AC region up to 200 MHz. Results at frequencies up to 20 GHz will be presented.

H8.22

Production of Silicon Amides for ALD/CVD of Next-Generation Silicates and the Development of Ultra-High Purity (<10 ppm Zr) Hafnium Precursors. Scott H. Meiere, John Peck, Jim P. Natwora, Michael M. Litwin, Michael T. Mosscrop, Delong Zhang and Cynthia A. Hoover; Electronics, Praxair, Tonawanda, New York.

In recent years there has been increasing interest in the development and utilization of silicates for next-generation dielectrics, electrodes, and barriers. Some of the integration difficulties identified for simple binary oxides (e.g., HfO₂) have been assuaged by incorporating silicon into deposited films (e.g., HfSiON). As ALD/CVD processes continue to gain momentum in the industry due to the demand for thinner, more uniform/conformal films onto more complex topographies, the interest and demand for suitable precursors has increased as well. Although many studies concerning the advantages and disadvantages of a number of precursors for the aforementioned binary oxides have been completed, there have not been extensive publications on appropriate compounds for silicon components. Although some of the most widely recognized ALD/CVD precursors contain silicon (e.g., SiH₄, HSiCl₃, TEOS), their utility for deposition with next-generation materials requires further analysis. Not only must the newly proposed precursors be studied on an individual basis for satisfactory safety, stability, volatility, etc., but they must be evaluated further in tandem with the complimentary precursor (e.g., hafnium amides) to determine compatibility and reactivity. Some precursors which produce outstanding films on their own may not be useful for ternary systems and vice versa. We have synthesized and purified a number of silicon amide compounds to incorporate with our previously developed precursors (e.g., hafnium, tantalum). Rational ligand design and chemical properties (e.g., vapor pressure, melting point, thermal stability) will be presented, as well as some deposition conditions and film characteristics of ternary systems. Furthermore, compatibility with common hafnium precursors (e.g., HfCl₄, hafnium amides) will be discussed. Additionally, we have developed a methodology for purifying hafnium precursors to a remarkably high level, including the reduction of zirconium content to < 10 ppm. These ultra-high purity hafnium precursors will allow the industry to determine if zirconium impurities are detrimental to device performance, and what level of purity is necessary for production.

H8.23

Photoemission Perspective on Interfacial Properties of HfO₂/SiO₂/Si. Yong Liang¹, Jimmy Yu¹, Jay Curless¹, Karen Moore¹, Clarence Tracy¹, Dina Triyoso², Leo Fonseca¹, Alex Demkov² and Phil Tobin²; ¹APRDL, Freescale Inc, Tempe, Arizona; ²APRDL, Freescale Inc, Austin, Texas.

The continuing size reduction of CMOS devices requires an alternative gate oxide with higher dielectric-constant as the conventional SiO₂ gate oxide will soon reach its fundamental limits. Among many high-k dielectrics, HfO₂ is a promising candidate because of its good dielectric properties and superior chemical and thermal stabilities. In this presentation, we will show interfacial properties of an ALD grown HfO₂/SiO₂/Si stack studied by photoemission (XPS and UPS). Specifically, we will discuss the effects of oxygen and ultra-high vacuum annealing on band bending in Si, SiO₂, and HfO₂ and the implication of the results on interfacial stability. Our photoemission results show that low temperature annealing in oxygen results in negligible amount of band bending in Si and SiO₂ on both HfO₂/SiO₂/n-Si and HfO₂/SiO₂/p-Si, indicating well-behaved Si/SiO₂ and SiO₂/HfO₂ interfaces. However, a

considerable amount of band bending takes place in Si and SiO₂ when the HfO₂/SiO₂/Si stack is subjected to an UHV annealing at 450 to 500 °C, suggesting that degradation of the two interfaces occurs. Detailed analysis of XPS and UPS spectra indicates that the HfO₂/SiO₂ interface is vulnerable to UHV annealing. In addition to photoemission, electrical results on HfO₂/SiO₂/Si will also be presented to compare and contrast with the photoemission data.

H8.24

Lanthana-Based Oxides as High- κ Gate Dielectrics: Processing Issues for MIS Devices with EOT < 1.0 nanometer. Daniel J. Lichtenwalner and Angus I. Kingon; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Lanthana and lanthanum silicate dielectrics have been investigated for use as high- κ gate dielectrics due to their promising bulk properties such as a large bandgap, high dielectric constant ($\kappa \approx 28$), and stability of the amorphous phase. Of particular interest is lanthana's reactivity with SiO₂ to form a silicate, providing a possible route towards eliminating interfacial silica, and obtaining MIS devices having an equivalent oxide thickness (EOT) of less than 1 nm. It is only in this regime that high- κ gate dielectrics can competitively replace conventional silica or silicon oxy-nitride dielectrics, and meet future ITRS goals. Using UHV reactive evaporation to deposit the lanthana-based dielectric, we have fabricated 50 x 50 μm^2 MIS device stacks having an EOT of 0.70 nm, corresponding leakage current $J(V_{fb}+1V)$ of 7.0×10^{-1} A/cm², and breakdown fields >14 MV/cm, for post-processing temperatures up to 700°C. The lanthanum silicate dielectric is found to be more stable than the lanthanum oxide w/r to atmospheric exposure and post-processing. Gate metal (Ta) capping in-situ is crucial for maintaining low EOT for all processing conditions examined. The effects of the substrate - dielectric interface, post-metallization annealing up to 1000°C, and forming gas anneals on MIS devices having EOT of < 1.0 nm will be presented.

H8.25

The characterization of HfSiO films by atomic layer deposition. Dongwon Lee¹, Dongchan Suh¹, Yong Seok Kim¹, Dae-Hong Ko¹ and Mann-Ho Cho²; ¹Department of Ceramic Engineering, Yonsei university, Seoul, South Korea; ²Nano Surface Group, Korea Research Institute of Standards and Science, Daejeon, South Korea.

Sub 1.5nm thick SiO₂ gate dielectric will be required for application of the Sub 0.1 μm CMOS devices, but the direct tunneling through SiO₂ gate dielectric increases abruptly and leads to leakage current. Because of the limitations of SiO₂, high permittivity materials have been currently studied such as HfO₂, ZrO₂, Al₂O₃, etc. Especially, HfO₂ is nominated as a permissive candidate. However HfO₂ for application of the gate dielectric has demerits, crystallization at annealing temperature below 600°C and low mobility of electron and hole in the channel region. In this study, in order to maintain the high mobility and low leakage current, we investigated the formation of HfSiO films grown by ALD (atomic layer deposition) using HfCl₄ and tris(dimethylamino)silane ((CH₃)₂N)₃SiH) as Hf and Si sources, respectively, and H₂O as an oxygen source. Also the annealing of the HfSiO films were performed by RTP in a N₂ ambient at 700, 800, 900 and 1000°C for 1min. We observed their physical properties as well as electrical characteristics using TEM, XRD, and XPS as well as C-V and I-V measurements. To grow the HfSiO films, 2Å thick monolayer of the HfO₂ film is pre-deposited between Si substrate and the HfSiO film by ALD. According to XPS depth profile analyses, the silicon content of the HfSiO films is varied up to 24 at.% as relative cycle ratio between Si oxidation step and Hf oxidation step increase in turns with ALD method. And the HfSiO films are thermally stable, maintaining their amorphous phase even after RTP annealing at 1000°C. Pt/HfSiO/p-type Si. structure were fabricated the MOSCAP structures, in order to investigate the C-V and I-V characterization of the HfSiO films as annealing temperature increase up to 1000°C. The CET values of the HfSiO films slightly increased with annealing temperature up to 900°C. Especially, Vt values of the HfSiO films annealed at 1000°C shifted positively due to the separation of the HfSiO films.

H8.26

Thermal Stability of Ru and RuO₂/ HfSiO/Si Structures. M. El Bouanani¹, V. Ukirde², C. Duk Lim², M. Quevedo-Lopez² and M. El Bouanani²; ¹Materials Science and Engineering, University of North Texas, Denton, Texas; ²Laboratory for Electronic Materials and Devices, Dept. of Material Science & Engineering, University of North Texas, Denton, Texas.

Alternative metal-based gate electrodes are currently under consideration as a replacement of Poly-Si gates. Metal gates are required to maintain scaling and performance of future CMOS devices. Ru based compounds are potential gate electrode candidates

for future metal-oxide-semiconductor (MOS) devices. Ru and RuO₂, with thickness of 500Å were deposited on HfSiO/Si structures by DC sputtering. These structures were annealed in flowing N₂ atmosphere at temperatures ranging from 500C to 900C. The thermal stability and interfacial diffusion and reaction of both Ru and RuO₂ on HfSiO/Si gate dielectric were investigated using Rutherford Backscattering Spectrometry (RBS), SEM and AFM. An overview of Ru and RuO₂/ HfSiO/Si interface integrity and pinhole formation issues will be presented. This work was supported by the Texas Advanced Technology Program.

H8.27

Hydrogen Incorporation and Release in CVD HfSiO/Si Structures. M. El Bouanani, V. Ukirde, C. Duk Lim, J. Feng and M. Quevedo-Lopez; Materials Science and Engineering, University of North Texas, Denton, Texas.

Hydrogen is of paramount importance in semiconductor technology due to its prevalence in various deposition processes and post processing of electronic structures. Understanding the effects of hydrogen in semiconductors and its behavior such as incorporation, diffusion, trapping and release is of great importance in view of its role in defects passivation as well as degradation of electronic structures. Trap transformations under annealing treatments in hydrogen ambient are known to involve passivation of traps at thermal SiO₂/Si interfaces. Similar behavior is observed for highk dielectrics based Metal-Oxide-Semiconductor (MOS) structures and is indirectly confirmed by low interfacial state density traps from electrical characterization of MOS structures. However, little or no studies giving direct information on the location and concentration of hydrogen in high-k based MOS interface regions and how it is affected by hydrogen annealing treatments is available. Elastic Recoil Detection Analysis data are used to characterize the evolution of hydrogen in the bulk and the interface of HfSiO/Si structures during annealing in hydrogen ambient in combination with preprocessing in oxygen. Strong correlation between processing conditions and hydrogen incorporation and release are probed. This work was supported by the Texas Advanced Technology Program.

H8.28

Thermal Response of Ru Electrodes in Contact with SiO₂ and HfSiOx Gate Dielectrics. Huang-Chun Wen¹, Patrick

Lysaght¹, Michael Campin¹, Brendan Foran¹ and Prashant Majhi²; ¹International SEMATECH, Austin, Texas; ²Phillips Assignee to International SEMATECH, Austin, Texas.

Integration of metal electrode materials and high-k gate dielectrics into CMOS device fabrication has emerged as a requirement to meet stringent performance targets of devices scaled beyond the 100-nm node. Elemental Ru metal has been identified as a promising gate electrode candidate for PMOSFET devices due to its appropriate work function and predicted stability as bulk material. However, integration of metal gates requires process compatibility and thermal stability in direct contact with novel underlying dielectric films. High-Resolution Transmission Electron Microscopy (HRTEM) and High-Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) using Energy Dispersive X-ray Spectra (EDXS) and Electron Energy Loss Spectra (EELS) have been utilized to produce elemental profiles of silicon, oxygen, nitrogen, hafnium, ruthenium, and tantalum to provide interfacial chemical information and to convey changes in concentration across the gate stack system as a function of temperature. Blanket films of 10 nm thick Ru have been deposited on both SiO₂ (2 nm) and metal organic chemical vapor deposited hafnium silicate (HfO₂)_x(SiO₂)_{1-x}, x = 0.8 (4.5 nm) and capped with TaN (200 nm). Both film systems have been annealed by rapid thermal annealing over a temperature range of 500 to 1000°C in nitrogen ambient. HRTEM cross-sectional analysis indicates distinctly different interfacial reactions corresponding to the Ru/SiO₂ and Ru/HfSiOx film systems. The onset of interfacial reaction of Ru/SiO₂ has been identified by the detection of Si substrate pitting associated with 900°C annealing with evidence of Ru in the dielectric and in the Si substrate as observed in EELS chemical scan profiles. HRTEM and EDXS analysis of the Ru/SiO₂ sample exposed to 1000°C indicate extreme up-diffusion of Si into the Ru layer characterized by voiding along the Si substrate interface and Ru conversion to RuSi, which is consistent with the diffusion mechanism for ruthenium silicide formation. In contrast, Ru films in contact with Hf-rich HfSiOx appear stable up to 1000°C. In this work, we present high-resolution chemical analysis of the Ru/HfSiOx interface stability over a broad temperature range as a function of Si composition, and the impact on device characteristics will be addressed.

H8.29

Preparation and Properties of La_{1-x}Ag_yMnO_{3+z} Thin Epitaxial Films. Oleg Gorbenko¹, Oleg Melnikov¹, Andrey Kaul¹, Alexander Taldenkov², Natalia Babushkina², Rita Szymczak³, Ljudmila Koroleva⁴, Yuri Suhorukov⁴ and Natalia Loshkareva⁴;

¹Chemistry, Lomonosov Moscow State University, Moscow, Russian Federation; ²Research Center Kurchatov Institute, Moscow, Russian Federation; ³Institute of Physics, Polish Academy of Sciences, Warsaw, Poland; ⁴Institute of Metal Physics, Ekaterinburg, Russian Federation.

We report here for the first time the preparation and properties of $\text{La}_{1-x}\text{Ag}_y\text{MnO}_{3+z}$ thin epitaxial films. The original two-step preparation procedure was developed. At the first step $\text{La}_{1-x}\text{MnO}_{3+z}$ were grown epitaxially by MOCVD on the single-crystal substrates (001) and (110) SrTiO_3 , (111) and (001) $\text{ZrO}_2(\text{Y}_2\text{O}_3)$. Treatment in the vapor of the metallic silver in oxygen atmosphere (at 1 bar or 20 bar) at the second step resulted in the selective absorption of silver by $\text{La}_{1-x}\text{MnO}_{3+z}$ phase. The value of y depended on the process conditions and revealed different kinetics of the silver saturation for (001) and (110) orientation of the $\text{La}_{1-x}\text{MnO}_{3+z}$ films. The films prepared were characterized by XRD, SEM with EDX, high resolution TEM, XPS, magnetization, electrical resistivity and magnetoresistance measurements in a four-probe configuration. We have found that resistivity peak temperature (T_p) possessed a maximum of 380 K at $x = 0.15$ in the series with $x = y$ ($\text{La}_{1-x}\text{Ag}_x\text{MnO}_{3+z}$). At the same time T_p was significantly higher than magnetoresistance peak temperature, the latter being close to Curie temperature. The remarkably high intrinsic magnetoresistance was measured in the magnetic field of 1T near the room temperature in the series of $\text{La}_{1-x}\text{Ag}_x\text{MnO}_{3+z}$ epitaxial films 22% at 310 K and 50% at 280 K. The room temperature IR-optical magnetotransmission as high as 16% (1T) was found. The properties make the new materials interesting for magnetic sensor and magneto-optic modulator applications.

H8.30

Growth Orientation Control and Anisotropic Thermoelectric Properties of New Cobalt Oxides A_xCoO_2 ($\text{A}=\text{Sr}$ and Ca) Thin Films. Satoshi Yotsuhashi, Tsutomu Kanno and Hideaki Adachi; Advanced Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd., Soraku-gun, Kyoto, Japan.

Epitaxial thin films of new layered cobalt oxides A_xCoO_2 ($\text{A}=\text{Sr}$ and Ca) are fabricated on sapphire substrates by radio-frequency (rf) magnetron sputtering. We find that the epitaxial orientation of the film can be controlled by the surface plane of the substrates and the grown phase in the A_xCoO_2 films is a monoclinic β -phase of primitive layered cobalt oxides in both cases. For the a -axis oriented thin films, not only resistivity parallel to the CoO_2 plane ρ_{\parallel} for A_xCoO_2 but also that perpendicular to the CoO_2 plane can be measured. The resistivity parallel to the CoO_2 plane ρ_{\parallel} for the β - Sr_xCoO_2 is as low as 2 m Ωcm at room temperature and shows metallic behavior. The ratio of perpendicular resistivity and parallel one $\rho_{\perp}/\rho_{\parallel}$ increases from 20 at room temperature to 90 at 30K. More isotropic nature was observed in the Seebeck coefficient. Parallel Seebeck coefficients S_{\parallel} of A_xCoO_2 are approximately 60 $\mu\text{V}/\text{K}$ at room temperature and the perpendicular one S_{\perp} is about a half of S_{\parallel} .

H8.31

Microstructure of $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_4$ thin films of n-type thermoelectric material. Mika Ueno, Tomoki Yoshikawa, Yusuke Ichino, Yutaka Yoshida and Yoshiaki Takai; Energy Engineering and Science, Nagoya University, Nagoya, Japan.

The Co-based oxides such as NaCo_2O_4 and $\text{Ca}_3\text{Co}_4\text{O}_9$ have been reported to be thermoelectric materials with high electrical conductivity and large thermopower. However, their carrier type is p-type and there are few n-type oxide materials showing high thermoelectric properties. $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_4$ (SCCO) material is known as the electron doped superconductor and it has strong electric anisotropy. We have tried to control crystallographic orientation of SCCO material by thin film technique based on the study of oxide superconducting thin film. The SCCO thin films were deposited on MgO (100) and SrTiO_3 (100) substrates by the pulsed laser deposition (PLD) method. As the results, the SCCO with the substitution of Sm-Ce, $x = 0.02$ deposited on SrTiO_3 substrate showed the power factor of 1.14 mW/mK² at 323K, as an n-type thermoelectric material. The value of the power factor in SCCO films is as high as that in Bi_2Te_3 material. In this study, we discuss the microstructures of SCCO thin films measured by transmission electron microscopy (TEM). Furthermore, we discussed the relationship between microstructure and thermoelectric properties of the films. The cross-sectional TEM images of the SCCO ($x = 0.1$) thin film grown on the MgO showed that the c -axis direction in each grain tilted to various angles and the grain size was as small as 100nm. The Hall mobility of the SCCO thin film grown was 0.172 cm²/Vs and 6.22 cm²/Vs, respectively on MgO and SrTiO_3 substrates. So, the low Hall mobility of the SCCO thin film on the MgO was caused by the inclination of the c -axis direction and the small grain size. However, the low thermal conductivity may be expected by the enhancement of phonon scattering at grain boundaries. Therefore both high electrical

conductivity and low thermal conductivity are expected by optimizing the grain size in oxide thin films. This research was partially supported by the Thermal & Electric Energy Technology Foundation and the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (B), 16360479, 2004.

H8.32

Thermoelectric Properties of $\text{RE}_{2-x}\text{M}_x\text{CuO}_4$ Thin Films Deposited by the PLD Method. Tomoki Yoshikawa, Mika Ueno, Tomoki Nonoyama, Yusuke Ichino, Yutaka Yoshida and Yoshiaki Takai; Nagoya University, Nagoya, Japan.

In order to adapt thermoelectric material to practical use in the future, oxide materials of which the thermoelectric properties does not deteriorate in the high temperature atmosphere are expected. Although the p-type oxide materials which show the figure of merit of $ZT=1$ around 1000 K are reported, there are few oxide materials which show the excellent thermoelectric properties in the middle temperature range (300 - 800 K). Therefore we studied the RE_2CuO_4 (RECO) as the high-performance oxide thermoelectric materials in the middle temperature range. It is well known that carrier doped $\text{RE}_{2-x}\text{M}_x\text{CuO}_4$ (REMCO) becomes a superconductor. The crystal structure of RECO is almost similar to that of K_2NiF_4 , and RECO has strong electric anisotropy. In this study, we prepared $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_4$ (SCCO) as the n-type film and $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (LMCO: $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) as p-type one, and evaluated the thermoelectric properties. The REMCO thin films ($x = 0.01 - 0.15$) were deposited on the MgO (100) and SrTiO_3 (100) substrate by the pulsed laser deposition (PLD) method. X-ray diffraction (XRD) was used to determine the crystallographic, and the orientation, both perpendicular to the surface and in plane. From the XRD patterns, the SCCO thin films were confirmed that c -axis was parallel to the substrate normal and in-plane alignment was cube-on-cube for the substrate. The Seebeck coefficient and electrical resistivity decreased with the increasing amount of Ce^{4+} substitution. And the electrical resistivity showed the metallic temperature dependences. We calculated the power factor from those values and found that the highest value of 1.14 mW/mK² at 323 K was achieved by the SCCO thin film with $x = 0.02$. This value is about ten times higher than that in $\text{Nd}_{1.95}\text{Ce}_{0.05}\text{CuO}_4$ bulk at 320 K. Also, as a result of repeated measurements of the thermoelectric properties in the high temperature more than 800 K, the high stability of the SCCO thin films was confirmed. We will also report the changes of the Seebeck coefficient, electric resistivity and thermal conductivity for M^{4+} substitution in LMCO in symposium. This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (B), 16360479, 2004 and the Thermal & Electric Energy Technology Foundation.

H8.33

Interplay between A-site and B-site Driven Instabilities in Perovskite Alloys. Marco Fornari¹, Monica Ghita¹, Samed H. Halilov^{2,3} and David J. Singh²; ¹Dept. of Physics, Central Michigan University, Mt. Pleasant, Michigan; ²Center for Computational Materials Science, Naval Research Laboratory, Washington, District of Columbia; ³Dept. of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

The formation of a morphotropic phase boundary between tetragonal and rhombohedral phases is crucial to obtain good piezoelectric performances in PZT and perovskite relaxors. In these systems the A-site motion drives the ferroelectric instabilities but, as we will show, it is the energetics of the B-site displacement that tips the balance between rhombohedral and tetragonal ground states. We have analyzed several perovskitic compounds and classified them according to four different classes: (1) stable cubic, e.g. BaZrO_3 , (2) B-site active, e.g. BaTiO_3 , (3) purely A-site active, e.g. PbZrO_3 , and (4) cooperative systems, e.g. PbTiO_3 . The expected ground state for class 1 to 3 is rhombohedral whereas for class 4 the ground state is tetragonal. In addition we have looked at the role of zone boundary instabilities. We will show results from first principles calculations on titanates, zirconates, and scandates that elucidate the effect of chemical substitution and its role on the anisotropy of the cation-cation interaction. In addition we will propose qualitative strategies to predict novel ferroelectric and piezoelectric compounds.

H8.34

Electronic Structure and Large Faraday Effect for Ferrimagnetic Zinc Ferrite Thin Film Prepared By a Sputtering Method. Seisuke Nakashima¹, Koji Fujita¹, Katsuhisa Tanaka¹, Kazuyuki Hirao^{1,2}, Tomoyuki Yamamoto² and Isao Tanaka^{3,2}; ¹Material Chemistry, Kyoto University, Kyoto, Japan; ²Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, Japan; ³Materials Science and Engineering, Kyoto University, Kyoto, Japan.

As is well known, the stable phase of zinc ferrite (ZnFe_2O_4) crystal

possesses the normal spinel structure, in which the nonmagnetic Zn^{2+} ions and the magnetic Fe^{3+} ions occupy octahedral (A) and tetrahedral (B) sites, respectively. Due to the weak and negative superexchange interaction among Fe^{3+} ions only on B sites, the stable phase of $ZnFe_2O_4$ is an antiferromagnet with Néel temperature as low as 10 K and is paramagnetic at room temperature. Recently, we fabricated $ZnFe_2O_4$ thin films by using a sputtering method, and showed that the thin film exhibits ferrimagnetic behavior even at room temperature. X-ray diffraction analysis and energy dispersive X-ray spectroscopy indicated that the thin film is composed of nanocrystalline $ZnFe_2O_4$ whose composition is almost stoichiometric. The static and dynamic magnetic responses, such as the discrepancy between zero-field-cooled and field-cooled dc magnetizations, the frequency dependence of linear ac susceptibility, and the temperature dependence of nonlinear ac susceptibility, demonstrated that the present thin film is superparamagnetic with the interaction among magnetic clusters or particles. It is considered that the curious magnetic state in the $ZnFe_2O_4$ thin film is caused by highly disordered arrangements of Zn^{2+} and Fe^{3+} in the spinel structure, because the preparation of thin film by the sputtering method involves very rapid cooling of vapor to form solid-state phase. In this study, we present the analysis of Zn K-edge X-ray absorption fine structure (XAFS) to clarify the cationic distribution in the $ZnFe_2O_4$ thin film. The extended X-ray absorption fine structure (EXAFS) measurements revealed that the distribution of Zn^{2+} and Fe^{3+} ions in the spinel structure is almost completely random. The comparison between the experimental data of X-ray absorption near-edge structure (XANES) and the theoretical spectra based on the first principles calculations (FLAPW) also gave the evidence for the random distribution of Zn^{2+} and Fe^{3+} ions. As a result of the disordered arrangements of Zn^{2+} and Fe^{3+} ions in $ZnFe_2O_4$ thin film, Fe^{3+} ions occupy both A and B sites, and the strong superexchange interaction among them gives rise to ferromagnetic properties. We have also measured Faraday effect in the wavelength range of 350-800 nm for the $ZnFe_2O_4$ thin film. A maximum of absolute value of Faraday rotation angle is observed at around 380, 470, and 530 nm. In particular, the absolute value of Faraday rotation angle is rather large at around 380 nm which corresponds to the emission wavelength of the (Ga, In) N laser diode: the absolute value of Faraday rotation angle is 2.85×10^4 deg/cm under an external magnetic field of 15 kOe. In addition, the thin film is extremely transparent at wavelengths longer than 450 nm. Consequently, we propose that the $ZnFe_2O_4$ thin films are very promising materials for the application to magneto-optical devices which operate in visible to ultraviolet regions.

H8.35

FMR studies in Colossal Magnetoresistance Films.

Natalia Noginova, R. Bah, D. Bitok and A. Pradhan; NSU, Norfolk, Virginia.

Ferromagnetic resonance (FMR) in both in-plane and out-of-plane magnetic field orientations, and effect of the laser light on the magnetic ordering were studied in series of colossal magnetoresistance films, $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ba_xMnO_3$. The FMR line width increased with decrease in temperature in $La_{1-x}Sr_xMnO_3$ films and was practically independent on temperature in $La_{1-x}Ba_xMnO_3$, that can be attributed to the different degree of magnetic homogeneity of the films. Novel layered structures $La_{1-x}Ba_xMnO_3$ on silicon with intermediate layer of $SrTiO_3$ were characterized by FMR as highly homogeneous with T_c above 300 K. From the shape and temperature dependence of the FMR spectra, the effective magnetization was estimated. The laser light illumination resulted in change of FMR line shape; this effect was interpreted in terms of optically induced magnetic disordering and photoinduced transition.

H8.36

Effects of Ca-Doping on the Artificial Grain Boundary in Epitaxial $YBa_2Cu_3O_{7-\delta}$ Thin Film. Henrik Pettersson and Eva Olsson; Experimental Physics, Chalmers University of Technology, Gothenburg, Sweden.

The critical current density, J_c , is suppressed at grain boundaries in the high T_c -superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO). Effects such as interface charging and electronic band structure bending are believed to reduce the J_c . A partial substitution of Y^{3+} with Ca^{2+} can create an over doped grain boundary and thus increase J_c , by reducing the interface charges. However, the Ca is also affecting the J_c of the YBCO grains of either side of the boundary. In this work a grain boundary in a 20% Ca-doped (001) $YBa_2Cu_3O_{7-\delta}$ epitaxial thin film, grown on a 24° symmetric (001) $SrTiO_3$ bicrystal is investigated. The aim is to find out whether the calcium segregates to the grain boundary or not. We pay particular attention to the structure of the YBCO grain boundary and also the film substrate interfaces. The evolution of the YBCO grain interfacial atomic arrangement and distribution of Ca in the grain boundary area have been studied. The microstructural investigation has been performed with high-resolution transmission electron microscopy (HRTEM), electron energy loss

spectroscopy (EELS), energy filtered TEM (EFTEM) and energy dispersive x-ray spectroscopy (EDX). To obtain a cross-section TEM-specimen of the grain boundary an *in situ* lift-out technique, using a FEI Strata DualBeam 235M, was applied. The specimen was first milled out, and then a needle was attached for the lift-out procedure, subsequently the specimen was welded onto a TEM Cu-grid and finally thinned down to less than 100nm.

H8.37

Anomalous Hall Effect and Hall Angle Measurements on $Ca_xSr_{1-x}RuO_3$ Thin Films. Peter Khalifah¹, Isao Ohkubo¹, Hans Christen¹, John Cerne², David Mandrus¹ and Brian Sales¹; ¹Condensed Matter Sciences Division, Oak Ridge Nat'l Laboratory, Oak Ridge, Tennessee; ²Dept. of Physics, University at Buffalo, Buffalo, New York.

Early measurements of the Hall effect in both $SrRuO_3$ and $SrRuO_3$ revealed an unexpected sign change. We have prepared and measured samples across the entire solid solution between these two end members to obtain insights into the origin of this sign change. The anomalous part ($\propto M$) and ordinary part ($\propto 1/ne$) of the Hall effect are found to have opposite signs, and the anomalous part is of larger magnitude at almost all temperatures and compositions (even in the paramagnetic regime). There is a systematic variation in R_s across the series, and our data unexpectedly support an extrinsic origin of the anomalous Hall effect. The cotangent of the Hall angle in this system scales as $(B + T^\alpha)$ with $\alpha \approx 2$ for samples near the ferromagnetic quantum phase transition at 70% Ca. This T^2 scaling of $\cot(\theta_H)$ holds over the entire temperature range measured (5-350K).

H8.38

Influence of Surface Morphological Evolution on Hyper-Thermal Processes during Pulsed Laser Deposition.

Aaron Fleet¹, Darren Dale², Y. Suzuki³ and J.D. Brock¹; ¹School of Applied & Engineering Physics, Cornell University, Ithaca, New York; ²Department of Materials Science & Engineering, Cornell University, Ithaca, New York; ³Department of Materials Science & Engineering, UC Berkeley, Berkeley, California.

Researchers have achieved excellent practical proficiency in the growth of high quality complex oxide thin films by Pulsed Laser Deposition (PLD). These materials exhibit a range of functional properties that may be incorporated into future microelectronics, storage and energy applications. However, few studies have advanced the fundamental understanding of plume-substrate interactions during the PLD process. We have found evidence suggesting that energetic species in the plume initiate rapid smoothing processes upon arrival at the substrate. Specifically, during PLD, we diffract synchrotron x-rays from the growing film, while observing the change in the normalized anti-Bragg intensity immediately following a laser pulse. In the limit where the pulse duration is much shorter than any other time scale (e.g. diffusion), $\Delta I/I$ is independent of the state of the surface during homoepitaxy. In contrast, our experimental measurements of $\Delta I/I$ during $SrTiO_3$ homoepitaxy do depend on the surface morphology. The correlation between $\Delta I/I$ and the cyclical variation of surface step-edge density during layer-by-layer growth suggests that the rapid smoothing process may consist of insertions near step edges. The activation of such mechanisms in PLD may present significant advantages in smooth film growth over traditional thermal techniques. Additionally, measurements of $\Delta I/I$ can be used to probe fundamental surface interactions in any pulsed growth experiment. This work is supported by the Cornell Center for Materials Research, under National Science Foundation Grant No. DMR-0079992, and uses facilities at the Cornell High Energy Synchrotron Source, NSF Grant No. DMR-0225180.

H8.39

Epitaxial Growth and Properties of Double Perovskite Thin Films. Hidefumi Asano, Norifumi Kozuka, Kazumasa Imaeda, Mikito Sugiyama and Masaaki Matsui; Crystalline Materials Science, Nagoya University, Nagoya, Japan.

Thin films of ordered double perovskite Sr_2FeMoO_6 and Sr_2CrReO_6 have been epitaxially grown on substrates with small lattice mismatch of -0.1% by sputtering. Their microstructural, magnetic and electrical properties have been investigated. Coherent growth without strain relaxation can be obtained for Sr_2FeMoO_6 thin films on $Ba_{0.6}Sr_{0.4}TiO_3$ -buffered $SrTiO_3$ and Sr_2CrReO_6 thin films on $SrTiO_3$. It is shown that these double perovskite films exhibit atomically flat surfaces and high magnetization values predicted for the fully ordered half-metallic materials.

H8.40

Interface Properties and Spin Polarization of $La_{0.7}Sr_{0.3}MnO_3$ in TMR Junctions. Hidefumi Asano, Mikito Sugiyama, Hirohisa Tanabe, Kazumasa Imaeda and Masaaki Matsui; Crystalline Materials Science, Nagoya University, Nagoya, Japan.

Tunneling magnetoresistance (TMR) junctions based on the doped manganites such as half-metallic $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) exhibit large TMR ratio. Many studies were made on junctions containing LSMO, and the point of discussion focused on interfaces between LSMO and the tunnel barrier. Some factors (oxygen defects, strain, phase separation, roughness) might affect physical properties of LSMO and the tunnel barrier at interface in a junction. However it is not clarified how each factor affects junction properties such as TMR ratio and its temperature dependence. In this study we investigated the spin polarization of LSMO through TMR effect and Andreev reflection (AR) in junction using LSMO. $\text{LSMO}/\text{SrTiO}_3$ (STO)/LSMO (for LSL junction), $\text{Co}/\text{STO}/\text{LSMO}$ (for CSL junction) and $\text{NbN}/\text{AlN}/\text{LSMO}$ (for NAL junction) multi layers were fabricated by the magnetron sputtering method on $\text{MgO}(001)$ substrate. CSL and LSL junctions were for tunnel junction and NAL junction for AR junction. CSL junction showed TMR ratio of 50%, which implies the high spin polarization of LSMO at the interface between STO barrier and bottom LSMO layers. On the other hand LSL junction showed TMR ratio of 4%. These two samples fabricated by same procedure except for top layer. If we assume that the properties of interfaces of between STO and bottom LSMO layers are equivalent in two types of junctions, small TMR ratio observed in LSL junction implies the drop of the spin polarization of LSMO at upper interface. We also investigated the barrier thickness dependence on junction resistance. The junction resistance-area product depended on barrier thickness weakly in LSL junctions, while that in CSL junctions increased exponentially with increase of barrier thickness. The difference was also observed in temperature dependence of junction resistance. In LSL junction, the junction resistance changed according to $T^{1/4}$ law in the region higher than 180 K. These junction resistance dependences on barrier thickness and temperature imply the existence of conduction through localized energy level caused by oxygen vacancies formed in the process of upper LSMO deposition at high temperature. As the result it is possible that the oxygen vacancy in the STO layer causes that in upper LSMO layer at the junction interface. From these results spin polarization estimated from TMR effect is affected by not only interface properties but also tunnel conductance mechanism. Moreover we will report the measurement of Spin polarization by AR. For AR junction we use amorphous AlN interlayer, which is different from that of TMR junctions, so we can distinguish the main factors that rule the spin polarization of LSMO by the comparison of results acquired from TMR effect and Andreev reflection.

H8.41

Growth Optimization and Magnetic Properties of R(Ba,Sr)MnO/STO/Si Heterostructures. Jacob Dadson, Kai Zhang, Somadatta Mohanthy and A. K. Pradhan; Center for Materials Research, Norfolk State University, Norfolk, Virginia.

We have demonstrated the successful fabrication and high performance of epitaxial $\text{R}(\text{Ba,Sr})\text{MnO}/\text{STO}/\text{Si}$ heterostructures with a T_c tuned to room temperature. The growth parameters are optimized. The surface morphology and X-ray diffraction studies show that the films are high quality. We have shown that $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ epitaxial films on SrTiO_3 buffered Si substrate display significantly improved transport and magnetization properties in the vicinity of room temperature. Our results suggest the scope of the integration of epitaxial manganite films on a semiconducting substrate, such as Si, using STO template/buffer layer. This will produce many generic approaches to the integration of multicomponent oxide thin films on semiconducting surfaces, which can impact a variety of technologies. Apart from IR imaging, epitaxial perovskite heterostructures can be fabricated for photosensitive and field effect transistors (FET), and other room temperature spintronic devices, controlling ferromagnetism both by light and electric fields.

H8.42

Room Temperature Ferromagnetism in Co doped ZnO Films. S. Ramachandran, Ashutosh Tiwari and J. Narayan; Materials Science & Engineering, North Carolina State University, Raleigh, North Carolina.

We have performed a systematic study of structural, optical, and magnetic properties of epitaxial $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ films grown on c-plane sapphire single crystal, using pulsed-laser deposition technique. The main emphasis in this work has been on the correlation of microstructure with properties, specifically with magnetic properties and the fate of cobalt ions into substitutional sites versus precipitates. The reasons for room-temperature ferromagnetism are explored, and convincingly proved to be one of the inherent properties of the material. Most importantly, the presence of nanoclusters of any magnetic phase was ruled out. This was determined by high-resolution transmission electron microscopy, coupled with electron energy loss spectroscopy and STEM-Z (scanning transmission electron

microscopy-atomic number) contrast studies.

H8.43

Ferromagnetic Properties of SrRuO₃ Thin Films Grown on Bi-axially Oriented Ion-Beam-Assisted-Deposited MgO Templates. Bo Soo Kang, Jang-Sik Lee, Liliana Stan, Leonardo Civalè, Raymond F. Depaula, Paul N. Arendt and Quan Xi Jia; Materials Science & Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

An itinerant ferromagnet SrRuO_3 (SRO) is widely used as an electrode or a buffer layer for various oxide epitaxial thin films and heterostructures for the application to many different types of devices. However, when made to epitaxial heterostructures, each layer is more or less liable to structural deformation such as strain, and subsequent change of physical properties is inevitable. Therefore, it is very important to investigate the influence of structural change on the properties of epitaxial oxide thin films. We have epitaxially deposited SRO thin films on SiO_2/Si substrates using pulsed laser deposition by introducing bi-axially oriented ion-beam-assisted-deposited MgO as templates with various degrees of in-plane texture. Interestingly, the SRO films grown on the templates with better in-plane texture were found to be subjected to more tensile stress, while the films on the templates with rather broad in-plane alignment tend to grow relatively loosely strained, with lattice parameters close to those of bulk material. The saturation magnetization in field-dependent magnetization hysteresis loop was $1.1 \mu_B$ per Ru atom, which agrees to the known value for bulk crystal. The magnetization measured with field-cooling-warming showed very good agreement with Bloch's $T^{3/2}$ law in low temperatures, which is well known as the result of spin-wave excitation: $M(T)/M(0) = 1 - AT^{3/2}$. The film with most bulk-like lattice parameters showed A value of $2.2 \times 10^{-4} \text{ K}^{-3/2}$ which is close to the theoretically estimated value ($1.6 \times 10^{-4} \text{ K}^{-3/2}$), while strained films showed larger A values, reflecting larger magnetization suppression. The suppression of magnetization moment in the strained thin films is believed to result from a change in the magnetic coupling since this coupling is very sensitive to inter-atomic distance.

H8.44

High-Throughput Characterization of Conductivity by the Low-Temperature Scanning Microwave Microscope.

Sohei Okazaki¹, Noriaki Okazaki², Sei-ichiro Yaginuma³, Ryuta Takahashi³, Yuji Matsumoto^{3,4}, Hideomi Koinuma³ and Tetsuya Hasegawa^{1,5}; ¹Department of Chemistry, The University of Tokyo, Tokyo, Japan; ²National Institute for Materials Science, Tsukuba, Japan; ³Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; ⁴Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan; ⁵Kanagawa Academy of Science and Technology, Kawasaki, Japan.

Scanning microwave microscope ($S\mu\text{M}$) has been attracting much attention as a high-throughput electric-property screening tool in the combinatorial materials science and technology. We have so far developed $S\mu\text{M}$ systems utilizing either a lumped-constant resonator or a coaxial cavity resonator as a sensor probe. The former probe has been shown to possess enough performance for dielectric-constant mapping of the combinatorial thin films, while the latter is advantageous in that one can evaluate dielectric loss / conductance from the measurement of Q-value shift. In this research, we report on the characterization of a Ca-doped $\text{NdBa}_2\text{Cu}_3\text{O}_7$ superconducting thin film by using a newly developed low-temperature $S\mu\text{M}$. We used a high-Q $\lambda/4$ coaxial cavity as a resonator probe, which was mounted on the motorized low-temperature XYZ stage. Resonance frequency and Q value were measured by a network analyzer. A single crystalline thin film of $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_7$ (NCBCO) was fabricated on a STO substrate by the tri-phase epitaxy method. First, we measured the temperature dependence of $\Delta(1/Q)$, which is considered as a measure of sample resistivity. With decreasing temperature from 300K to 80K, $\Delta(1/Q)$ decreased monotonously and showed sharp drop at around 80K. This behavior is in good agreement with the dc-resistivity curve obtained by the four-probe method. Next, the sample was annealed at temperatures gradient between 490C and 600C under the oxygen pressure of 1 Torr in order to induce local oxygen-content variation along the temperature-gradient axis. The line profiles of $\Delta(1/Q)$ measured at temperatures lower than 60K showed a stepwise change, where low $\Delta(1/Q)$ region at lower annealing-temperature side is considered to be in superconducting state. The results clearly indicate that superconducting transition is sensitively detectable by the present $S\mu\text{M}$ as a sharp jump in $\Delta(1/Q)$.

H8.45

Magnetic and Transport Properties of Transition Metal-Doped TiO₂ Thin Films Grown by Laser Molecular Beam Epitaxy. Taro Hitosugi^{1,2}, Go Kinoda², Yutaka Furubayashi², Yasushi Hirose², Yukio Yamamoto², Hidetaka Sugaya³, Kazuhisa Inaba³, Yuji Matsumoto³, Hideomi Koinuma⁴, Masashi Kawasaki⁵,

Toshihiro Shimada^{1,2} and Tetsuya Hasegawa^{1,2}; ¹Dept. of Chemistry, University of Tokyo, Bunkyo, Tokyo, Japan; ²Kanagawa Academy of Science and Technology (KAST), Kawasaki, Japan; ³Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan; ⁴Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; ⁵Institute for Materials Research, Tohoku University, Sendai, Japan.

Epitaxial TiO₂ films were fabricated on r-Al₂O₃ substrates by laser molecular beam epitaxy. Ablation with a Co-doped and Fe-doped TiO₂ target produced single phase of rutile films. Fe-doped films were prepared in vacuum at a substrate temperature of 920 K. The oxygen pressure during deposition was 10⁻⁶ Torr. The pulsed KrF excimer laser (248 nm) with a laser beam intensity of 1-2 J/cm² was used for deposition. The deposition rate was 0.02 nm/s, and the film thickness varied from 60 to 100 nm. Ferromagnetic properties were observed in both Co-doped and Fe-doped TiO₂ rutile films by magneto-optical studies carried out at room temperature. The magnetic hysteresis could also be observed even at room temperature. Scanning superconducting quantum interference device (SQUID) microscope observation revealed ferromagnetic domain structures at 3K. The ferromagnetic domain size was relatively smaller than the domains observed in GaMnAs diluted magnetic semiconductors.

H8.46

Organic Self Assembled Monolayers On Ferromagnetic Oxide Thin Films For Spin Transport. Scott J. Rutherford¹, Xianglin Ke², Dong Min Kim¹, Mark Rzczowski² and Chang-Beom Eom^{1,2}; ¹Materials Science and Engineering, University of Wisconsin - Madison, Madison, Wisconsin; ²Physics, University of Wisconsin - Madison, Madison, Wisconsin.

The inherent nanoscale structure of organic molecules permits assembly with atomic-scale precision, a feature that is being taken advantage of in forefront organic electronic devices. Engineering polymer chains with capabilities of attaching to ferromagnetic oxides could potentially lead to exciting advances in manipulation and control of carrier magnetic spin using heterostructures for applications as magnetoelectronic sensors and non-volatile memories. Self assembled monolayers (SAMs) can be specifically tailored to meet the desired needs of a material or device structure. The tunneling barrier length can be adjusted with atomic precision by changing the number of repeat units in a short organic chain. The covalent bond between the SAM endgroup and a ferromagnetic oxide electrode defines an atomically abrupt interface with no interdiffusion or mixing. The challenge we face with SAM deposition is creating a single monolayer that is free of any pinholes or other imperfections across the surface of the substrate. We have deposited two different types of organic layers, Octadecyltrichlorosilane and Dimethylhexadecylamine, onto epitaxial ferromagnetic oxide SrRuO₃ (SRO) thin films. The SRO films are deposited by 90 degree off-axis sputtering on single surface Ti-terminated SrTiO₃ (001) substrates. AFM and STM images verify the SRO is atomically smooth with unit-cell high steps (4 angstroms), therefore providing an excellent template for SAM attachment. The substrates are submerged in the SAM solution to allow the chains to gradually bond and align themselves on the surface of the SRO film. The SRO is chemically stable which allows us to preserve abrupt interfaces between the organic monolayer and SRO film. AFM images display steps heights ranging between 30 and 50 angstroms, which is consistent with the length of the deposited SAM chains. Using a STM measurement technique, smooth topography of SAM on SRO is confirmed along with thickness measurements consistent with AFM results. The mechanisms which govern the formation of these SAMs, I-V characteristics and spin dependent tunneling behavior will also be discussed.

H8.47

Metal-Insulator Transition of Sr_{2/3}Bi_{1/3}FeO₃ Epitaxial Film.

Naoaki Hayashi¹, Shigetoshi Muranaka¹, Takahito Terashima² and Mikio Takano²; ¹Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan; ²Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan.

It is known that perovskites containing high valence iron ions exhibit unique properties. In Sr_{2/3}R_{1/3}FeO₃ (R = La³⁺, Pr³⁺, Nd³⁺, Sm³⁺...), Fe ions result in average charge valence cations of Fe_{3.67+} at room temperature, whereas they align to Fe³⁺, Fe⁵⁺, Fe³⁺... in the [111] (cubic perovskite's) direction at low temperatures, leading to metal-insulator transition. For R = Bi³⁺, however, it is not clear due to the difficulty of the synthesis of a bulk sample. In this study, Sr_{2/3}Bi_{1/3}FeO₃ epitaxial film on SrTiO₃ (001) substrate was prepared by pulsed laser deposition blowing on it with partially ozonized oxygen. The film possessed excellent crystallinity, and its resistivity behavior rapidly increased below 200 K. Also, the resultant of Mössbauer spectroscopy will be reported.

H8.48

Field Effect Experiments in NdBa₂Cu₃O_{7-δ} Ultrathin Films using a SrTiO₃ Single Crystal Gate Insulator. Daniel Matthey, Stefano Gariglio and Jean-Marc Triscone; DPMC, University of Geneva, Geneva, Switzerland.

We report on the electrostatic modulation of superconductivity in ultrathin NdBa₂Cu₃O_{7-δ} films using a field effect device based on a SrTiO₃ single crystal gate insulator. To achieve large electric fields, the thickness of the commercial dielectric single crystal SrTiO₃ substrate (also used as the gate insulator) was reduced to about 100 microns. T_c modulations of several Kelvin have been measured in several devices. With this device, the polarization can be precisely measured allowing the dependence of the superconducting critical temperature on the carrier concentration in the underdoped region of the phase diagram to be determined. We analyse the change in the critical temperature and activation energy for vortex motion as a function of the applied polarization. We find that the relative change in the activation energy ΔU/U is almost constant as a function of the applied magnetic field and correlated to the relative change in the critical temperature (ΔT_c/T_c) through a relation derived from a vortex liquid resistivity based on thermally activated behaviour.

H8.49

Active Defects in La_{0.67}Sr_{0.33}MnO₃ Thin Films.

Tomas Liljenfors¹, Robert Gunnarsson² and Eva Olsson¹;

¹Microscopy and Microanalysis, Experimental Physics, Chalmers University of Technology, Goteborg, Sweden; ²Microelectronics and Nanoscience (MC2), Chalmers University of Technology, Goteborg, Sweden.

La_{1-x}Sr_xMnO₃ (LSMO) is a colossal magnetoresistance (CMR) compound that is characterized by a large change in resistance as the applied magnetic field is altered. LSMO attracts attention due to that it shows a magnetic transition temperature above room temperature. Depending on the doping (x), the crystal structure at room temperature is known to change between orthorhombic, rhombohedral, cubic and monoclinic. For x=0.3 the structure has been determined to be rhombohedral. However, in epitaxial thin films the structure is not only affected by the doping but also by the lattice mismatch between the substrate and the film. Several processes are known to relax the mismatch-induced strain in epitaxial films. For example, a phase transition in the crystalline structure can rearrange the atomic positions and thereby reduce the strain. As the film relaxes, the global CMR properties will change. The present work is concerned with the interfacial microstructure of LSMO thin films. Epitaxial thin films of (001)_{pseudocubic} La_{0.67}Sr_{0.33}MnO₃ have been deposited using a pulsed laser deposition method on (001) SrTiO₃ substrates. The films have been analysed using a Philips CM200 transmission electron microscope (TEM), equipped with a Gatan imaging filter and Link ISIS EDX spectrometer. The TEM investigation was performed on both cross sectional and plane sectional specimens. In the plane view specimens a cross pattern was observed. The pattern consisted of orthogonal lines oriented along the [100]_{STO} and [010]_{STO} directions. The origin of the cross pattern will be discussed. The microstructure will be correlated to magnetic and electric properties.

H8.50

HRTEM Investigation of the Atomic Structure of SrRuO₃ Thin Films on SrTiO₃ Substrate. Johan Borjesson¹, Khaled

Khamchane², Tomas Liljenfors¹ and Eva Olsson¹; ¹Dept. of Experimental Physics, Chalmers University of Technology, Gothenburg, Sweden; ²Dept. of Microtechnology and Nanoscience (MC2), Chalmers University of Technology, Gothenburg, Sweden.

SrRuO₃ is a ferromagnetic metallic perovskite with magnetical and mechanical properties that make it suitable for different device application. The physical properties are influenced by the atomic structure of the material. In thin films, new phenomena are observed, which can be due to the interfacial interaction between the film and the substrate. Therefore, substantial information about the atomic structure is needed to understand the thin film evolution during the growth. Bulk SrRuO₃ is known to have an orthorhombic, distorted, pseudo-cubic structure with the space group Pbnm (no. 62); however, there have also been reports of a tetragonal phase. We have studied the microstructure of epitaxial (001)_{pseudo-cubic} SrRuO₃ films grown on (001) SrTiO₃ substrates. The films were grown with pulsed laser deposition (PLD), with different growth parameters, such as substrate temperature and oxygen pressure. The investigation was performed with transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Standard TEM sample preparation techniques were used, involving grinding, polishing and ion etching. High-resolution data of the atomic structure in the SrRuO₃ films and film/substrate interface are presented, taken from planar and cross-section view respectively. Electron diffraction, EDS and energy filtered TEM data are also presented and discussed.

H8.51

Superconducting properties of oxygen post-annealed

PLD-ErBa₂Cu₃O_y films. Shigeru Horii^{1,6}, Masashi Mukaida^{2,6}, Yusuke Ichino^{3,6}, Kaname Matsumoto^{4,6}, Tohru Ohazama^{2,6}, Ataru Ichinose^{5,6}, Yutaka Yoshida^{3,6}, Jun-ichi Shimoyama^{1,7} and Kohji Kishio¹; ¹Dept. Superconductivity, Univ. of Tokyo, Tokyo, Japan; ²Yamagata Univ., Yonezawa, Japan; ³Nagoya Univ., Nagoya, Japan; ⁴Kyoto Univ., Kyoto, Japan; ⁵CRIEPI, Yokosuka, Japan; ⁶CREST, JST, Saitama, Japan; ⁷PRESTO, JST, Saitama, Japan.

We report superconducting properties of PLD - ErBa₂Cu₃O_y/SrTiO₃ (Er123/STO) thin films which were fabricated in the substrate temperature range from 720°C to 780°C and dramatic enhancement of J_c by an oxygen post-annealing process. Interestingly, in the temperature region below 760°C, in which T_cs before and after annealing are almost same and showed to be approximately 90K, J_cs were obviously enlarged to the order of 10⁶ A/cm⁻² by an oxygen post-annealing in comparison with those of the as-deposited films (0.3-0.6x10⁶ A/cm⁻²). On the other hand, in the 780°C-deposition film, clear enhancement of J_c was not observed. The PLD Er123/STO films were found to be crystallographically excellent and highly conductive in the temperature region below 770°C from x-ray diffraction measurement and normal state resistivities. In the 123 films fabricated through a non-equilibrium process such as the PLD method, even though the as-deposited film shows T_c 90K, a homogenization process of oxygen contents in a whole part of the grown 123 film is suggested to be important for enhancement of critical current properties. There is possibility that the oxygen annealing is recognized as one of the most effective processes for improvement of J_c in PLD-REBa₂Cu₃O_y (RE: rare earth elements) coated conductors and superconducting devices.

H8.52

Non-bolometric Radiation Response in Thin Films of

Mixed-phase Manganites. M. Raj Rajeswari, Mason A. Overby, Vera N. Smolyaninova, Adekunle Adeyinka and Eumin Kong; Physics, Astronomy and Geosciences, Towson University, Towson, Maryland.

Manganite materials of the composition La_{1-(x+y)}Pr_yCa_xMnO₃ are characterized by the coexistence of two or more phases with different magnetic and electrical properties as a result of the intrinsic phase separation. The phase separation in turn arises due to the local strain introduced by Pr substitution, leading to the presence of competing ground states which are identified as the charge ordered insulating phase and the ferromagnetic metallic phase. The multi-phase coexistence alters the characteristics of the insulator-metal transition, leading to percolative transitions as distinct from the insulator-metal transitions in the comparatively simpler manganite systems such as La_{1-x}Ca_xMnO₃. The resistivity change accompanying the percolative transition is very steep, making the Pr substituted materials interesting for bolometric detector applications. We have studied the photo response of epitaxial thin films of La_{0.37}Pr_{0.30}Ca_{0.33}MnO₃ using a phase-sensitive detection technique. In addition to the expected bolometric (thermal) response which is proportional to the temperature-derivative of the resistance (dR/dT), we observe a significant non-bolometric component. The temperature dependence of the non-bolometric response suggests a radiation induced decrease in the resistivity of the mixed phase which is non-thermal in origin. In contrast, we observe that the radiation response in the thin films of La_{0.67}Ca_{0.33}MnO₃ shows a purely bolometric response due to the thermal effect. We will discuss the details of the non-bolometric response including its dependence on temperature, radiation intensity and frequency, its relaxational dynamics and the possible correlation with magnetoresistance. This work is supported by the NSF grants DMR-0116619 and DMR-0348939 and an Undergraduate Research Grant from the College of Science and Mathematics, Towson University.

H8.53

The Effects of Substrate, Film Thickness and Deposition Parameters on the Charge Ordering in Bi_{0.6}Ca_{0.4}MnO₃ Thin Films Grown by Pulsed Laser Deposition. Mason A. Overby¹,

M. Raj Rajeswari¹, Vera N. Smolyaninova¹, Robert Kennedy¹, Bryce Taylor¹, Francesco Murphy¹, Luis C. Aldaco¹, David M. Schaefer¹, Samuel E. Lofland³, Z.Y. Li² and Richard L. Greene²; ¹Physics, Astronomy and Geosciences, Towson University, Towson, Maryland; ²Center for Superconductivity Research, University of Maryland, College Park, Maryland; ³Chemistry and Physics, Center for Materials Research and Education, Rowan University, Glassboro, New Jersey.

Materials of the composition Bi_{1-x}Ca_xMnO₃ are known to exhibit charge ordering, a phenomenon wherein, spatial ordering of the heterovalent cations (Mn³⁺ and Mn⁴⁺) leads to localization of the charge carriers. Charge ordering can be destroyed by a number of external perturbations such as magnetic field, electric field, and electromagnetic radiation over a range of wavelengths, making this

phenomenon interesting from the perspectives of both fundamental science and technological applications. While charge ordering in the bulk material is determined only by the material composition, we find that the charge ordering in epitaxial thin films is more complex, governed by a number of variables such as the substrate, film thickness and kinetics of film growth. The sensitivity to these variables in thin films arises mainly due to the influence of lattice mismatch strains and associated defects and disorder on the charge ordering phenomenon, as has been previously demonstrated in the case of charge ordering in thin films of alkaline earth -doped rare earth manganites. We will discuss our studies of charge ordering in epitaxial Bi_{0.6}Ca_{0.4}MnO₃ thin films on several lattice-mismatched substrates, with tensile or compressive bi-axial strain. We find that both types of strain fields suppress the charge ordering temperature below the bulk value of 340 K. We will discuss systematics of the dependence of charge ordering temperature on film thickness and other deposition parameters that influence the film growth kinetics and strain relaxation. This work is supported by NSF Grant No. DMR-0116619, and DMR-0348939 at Towson University.

H8.54

Abstract Withdrawn

H8.55

Fabrication of the Nano-Channel of Transition Metal Oxides with Room Temperature Ferromagnetism using Atomic Force Microscopy Lithography and their Electrical Transport Properties. Hidekazu Tanaka^{1,2}, Motoyuki Hirooka¹ and Tomoji Kawai¹; ¹ISIR-Sanken, Osaka University, Ibaraki, Osaka, Japan; ²PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama, Japan.

The magnetic materials in nanoscale has attracted much attention. Especially, in transition metal oxides with strongly correlated electrons, novel interesting phenomena can be expected in nano-scale, such as phase separation in manganites and high T_c superconducting cuprate. Scanning probe microscopy lithography, as a highly promising method for nano-lithography and fabricating nano-devices, has been used to create nano-patterns on metals, semiconductor. In this study, we have applied this technique to ultra thin films of Fe₃O₄ with high spin polarization and (La,Ba)MnO₃ with colossal magnetoresistance, fabricated by Laser-MBE technique. The Fe₃O₄ thin films (thickness: 25nm-10nm) exhibit ferrimagnetism at room temperature checked by SQUID and Kerr effect measurements. By applying bias voltage to AFM tip from -4V to -10V, insulating lines could be constructed in their width from 48nm to 150nm. Resistance of patterned area is higher than that of bare Fe₃O₄ surface by five order of magnitude. Moreover magnetic force microscope measurement also revealed that magnetic domain structure in the patterned region almost disappear whereas ferromagnetic domain structure with 150nm size was clearly imaged in the bare Fe₃O₄ surface. AFM lithography could be also performed in La_{0.8}Ba_{0.2}MnO₃ film with minimum line width of 50nm. We will discuss the electrical properties on nano-scale channel in these transition metal oxides with room temperature ferromagnetism.

H8.56

Microstructure and Transport Properties of SrRuO₃ thin

films. Gertjan Koster¹, Arturas Vailionis¹, James Reiner², Theodore Geballe¹ and Malcolm Beasley¹; ¹GLAM, Stanford University, Stanford, California; ²Yale University, New Haven, Connecticut.

Thin films of the itinerant ferromagnetic SrRuO₃ have been successfully grown by means of various deposition techniques by numerous groups. The films mostly are epitaxial and exhibit nearly single crystal micro-structural quality. Yet, apart from having a lower Curie temperature which has been shown to be caused by strain effects, the transport properties of thin films vary considerably. Most strikingly, the residual resistance at 4.2 K divided by the room temperature resistance (RRR value) can differ from being equal to the best single crystals to being almost two orders of magnitude lower. Although there are some apparent variations in morphologies, e.g., granular structure, from film to film these do not seem to be the most plausible microscopic origin of the observed range in RRRs. Different growth mechanisms, small variations in stoichiometry and strain effects have been suggested as possible causes. Here, we present a detailed micro-structural study of epitaxial SrRuO₃ thin films using high-resolution X-ray reciprocal space mapping and identify correlations with their RRRs. In addition we study the temperature dependence of the structural phase transitions known to SrRuO₃ as they appear to occur at much lower temperatures in thin films.

H8.57

Quasi single-crystalline SrRuO₃ epitaxial thin films: role of substrate vicinality and growth modes on functional

properties. Gervasi Herranz¹, Florencio Sanchez¹, Niko Dix¹, Josep Fontcuberta¹, Maria Victoria Garcia-Cuenca², Cesar Ferrater²,

Manuel Varela², Todora Angelova³, Ana Cross³ and Andres Cantarero³; ¹Institut de Ciència de Materials - CSIC, Bellaterra, Spain; ²Física Aplicada i Òptica, Universitat de Barcelona, Barcelona, Spain; ³Física Aplicada y Electromagnetismo, Instituto de Ciencia de Materiales, Universitat de Valencia, Barcelona, Spain.

SrRuO₃ is a quite unique metallic and ferromagnetic oxide that has been widely used as metallic electrode in various applications. SrRuO₃, together with the superconducting oxides, has also constituted the playground for much progress on understanding the epitaxial growth of complex oxides. Bulk form of SrRuO₃ is orthorhombic and, in principle in epitaxial films, multiple orientations of the unit cell could appear, which may have severe impact on some functional properties. However, epitaxial stress in thin films may largely modify the structure and thus distinction between microstructure effects and strain related is not a trivial task. Moreover, at least two other factors are of prime importance in thin film growth: the miscut angle (θ_v) and the growth mode of the epitaxy. In this paper we shall present some recent advances on the understanding of epitaxial growth of SrRuO₃ on SrTiO₃(001) by pulsed laser deposition. We have found that at early stages of growth, when the film thickness is of about few nanometers, there is a pattern of quasi-1D fingers formed by SrRuO₃ islands that nucleated and coalesced along the substrate steps. As growth progresses, the lateral coalescence of fingers results in a remarkable planarization of the film surface: well defined steps of one unit cell are observed for films thicker than 20nm. It is thus follows that the width of the substrate terraces shall have a major role on the surface morphology. We have subsequently grown films on substrates of various vicinalities θ_v . It turns out that the film morphology can be tuned from finger-like to multilayered islands or giant bunched steps by appropriate selection of substrate vicinality and/or film thickness. Remarkably enough it is found that substrate vicinality as small as $\theta_v \approx 0.04^\circ$ has a profound impact on the surface morphology and some physical properties. We have used the minima appearing at low temperature in the temperature dependent resistivity as a sensitive tool of substrate induced disorder. In contrast, the substrate vicinality does not appear to be critical on the selection of a single domain structure of the growing SrRuO₃ film. Indeed, exhaustive reciprocal space mapping by X-ray diffraction allows us to demonstrate that quasi-single crystalline films can be obtained on almost singular SrTiO₃(001) substrates ($\theta_v < 0.05^\circ$) thus relaxing the need of larger θ_v . Interestingly enough, the substrate induced stress imposes fully strained in-plane unit cell of SrRuO₃ which thus appear to be quasi-tetragonal. However, the orthorhombic symmetry is confirmed by accurate X-ray diffraction measurements and by angular dependence studies of Raman spectra. Magnetic measurements by Kerr magnetometry on these films indeed confirm the uniaxial in-plane anisotropy.

H8.58

Intrinsic versus Extrinsic Ferromagnetism in Cobalt Doped TiO₂ Thin Films. Sanjay Shinde, S. B. Ogale, T. Zhao, J. Higgins, S. Dhar, R. Ramesh, R. L. Greene and T. Venkatesan; University of Maryland, College Park, Maryland.

We have performed detailed structural, magnetic, and electrical characterization of the cobalt doped TiO₂ thin films in anatase and rutile forms grown by pulsed laser deposition on LaAlO₃ and R-Al₂O₃ substrates, respectively. Our results show that the cobalt distribution and hence the ferromagnetism in these films depends strongly on substrate temperature and oxygen pressure during growth. At lower growth temperatures, cobalt has limited solubility (< 2 %) in TiO₂ matrix, above which clusters of metallic cobalt are formed. On the other hand, at very high growth temperatures (875 °C), the solubility of cobalt increases, thereby yielding uniform distribution of cobalt in the film. Dependence of the oxygen partial pressure during growth was also examined. While cobalt is soluble for the films grown at 1e-4 Torr, anatase structure is unstable and Magneli phases stabilize in rutile structure for those grown in vacuum (1e-8 Torr). In the later case, superparamagnetic cobalt clusters are formed at the film-substrate interface. An important feature of this system is that the films in which cobalt is found to be uniformly distributed are highly insulating. Thus, the observation of ferromagnetism in these films indicate that itinerant carriers are not necessary for the ferromagnetic exchange in cobalt doped TiO₂. In such electrically insulating films, we also observed an electrical field induced reversible modulations of magnetization and coercivity at room temperature, thereby pointing out the intrinsic nature of the material. On the other hand, highly conducting films exhibited an anomalous Hall effect. Our magnetic and structural characterization data clearly shows that the anomalous Hall effect in these films arises from superparamagnetic/ferromagnetic cobalt clusters. These results will be discussed in details. Work supported under DARPA (# N000140210962) and NSF-MRSEC (# DMR-00-80008)

H8.59

The Dependence of Ferromagnetism on Sn Concentration in

ZnMnO:Sn Epitaxial Films. Mathew Ivill¹, Young-Woo Heo¹, Stephen Pearton¹, David Norton¹, Josh Kelly² and Arthur Hebard²; ¹Materials Science and Engineering, University of Florida, Gainesville, Florida; ²Physics Dept., University of Florida, Gainesville, Florida.

Diluted Magnetic Semiconductors (DMSs) are an essential part to the development of spintronic technology. By utilizing the spin of electrons and holes in these materials to carry information, a new generation of multifunctional devices may emerge that include low power spin-based FETs, spin-polarized LEDs, and systems for quantum computation. Both theory and experiment have shown Mn-doped ZnO to be a promising DMS for spintronic applications. In this report, we examine the magnetic properties of Mn-doped ZnO that has been codoped with Sn. The films were deposited by pulsed laser deposition with concentrations of 3 at% Mn and varying atomic percents of Sn (0.1, 0.01, and 0.001 at%). SQUID magnetometry measurements show the films retain ferromagnetic hysteresis up to 300K. The films also display an inverse relationship between the magnetization and Sn concentration, with the same relationship with the films' resistivity. This magnetic behavior appears similar to the bound magnetic polaron (BMP) model for magnetic semiconductors with low carrier concentrations. This work is supported by the Air Force Office of Scientific Research under award no. F49620-03-1-0370

H8.60

Structural and magnetic behavior of Zn_{1-x}Co_xFe₂O₄ material for spintronics. Maharaj S. Tomar¹, R. P. Guzman¹ and R. E.

Melgarejo¹; ¹Department of Physics, University of Puerto Rico, Mayaguez, Mayaguez, Puerto Rico; ²Department of Physics, University of Puerto Rico, Mayaguez, Mayaguez, Puerto Rico; ³Department of Physics, University of Puerto Rico, Mayaguez, Mayaguez, Puerto Rico.

Zinc oxide is a wide gap semiconductor with direct transition and can be used in spin injection optoelectronic if it could be coupled with a suitable ferromagnetic material. Therefore, magnetic ion substituted ZnO could be useful. We synthesized Co and Fe substituted ZnO powder using a solution route and thin films were deposited by spin coating. Zn_{1-x}Co_xFe₂O₄ powder and thin films were studied by x-ray diffraction, Raman spectroscopy for structural properties, and closed cycle SQUID was used for magnetic characterization. These studies indicate that Zn partially replaces Co site for particular composition and Zn_{1-x}Co_xFe₂O₄ showed ferromagnetic behavior for the Zn to Co ratio up to 1. Detailed structural and magnetic properties will be addressed. * We acknowledge the support for this work in part by NSF through the PREM proposal at University of Puerto Rico, Mayaguez, and AFOSR grant 49620-01-1-0454.

H8.61

Surface Stabilization and in-situ Analysis of Epitaxial SrRuO₃ Films. Junsoo Shin^{1,2}, Sergei V. Kalinin¹, E. Ward Plummer^{1,2} and Arthur P. Baddorf¹; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee.

Strontium ruthenium oxide, SrRuO₃, plays an important role in oxide electronic devices because of its metallic nature and lattice constant compatible with many transition metal perovskites. Use in device fabrication requires excellent surface and interface stability without reduction or loss of volatile oxides. Our previous studies have shown that exposure to atmosphere leads to decomposition of the surface at 300 °C, despite good crystalline order in electron diffraction before annealing. This decomposition was associated with hydrocarbons observed on the surface. We now provide additional evidence that hydrocarbons lead to instability, report success in stabilizing the surface after contamination by annealing in high pressures of oxygen, and explore the stability of epitaxial SrRuO₃ films that have not been exposed to atmosphere. Distinct differences in reflection high-energy electron diffraction patterns are observed if films exposed to air are preannealed to 600 °C in oxygen (10⁻² Torr) before annealing in vacuum. Preannealed films show no evidence of decomposition below 600 °C. Epitaxial SrRuO₃ thin films were also grown by pulsed-laser deposition using a stoichiometric target on (001) SrTiO₃ substrates and transferred in-situ to a surface characterization chamber. We report in-situ studies of intrinsic surface structure, chemistry and transport properties of SrRuO₃ using low energy electron diffraction, x-ray photoelectron spectroscopy, scanning tunneling microscopy and thermal desorption spectroscopy and compare results to ex-situ observations. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC and by the National Science Foundation grant DMR-0072998. Research performed as a Eugene P. Wigner Fellow (SVK).

H8.62

Thermal and Step-Flow Instabilities of Epitaxial SrRuO₃ Thin Films Grown by Pulsed Laser Deposition. Ho Nyung Lee, Matthew F. Chisholm, Matthew B. McKeon, Hans M. Christen,

Christopher M. Rouleau, Junsoo Shin, Sergei V. Kalinin, Arthur P. Baddorf and Douglas H. Lowndes; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The thermal stability of electrically conducting SrRuO₃ thin films grown by pulsed laser deposition on (001) SrTiO₃ substrates has been investigated by atomic force microscopy, reflection high-energy electron diffraction (RHEED), and x-ray photoelectron spectroscopy (XPS), under reducing conditions (25–800 °C in 10⁻⁷–10⁻² Torr O₂). The as-grown SrRuO₃ epitaxial films exhibit atomically flat surfaces with single unit-cell steps, even after exposure to air at room temperature. However, the combined *ex-situ* analyses upon annealing under the reducing conditions show different features on the film surface, such as islands and pits that could destroy or deteriorate the quality of epitaxial films grown subsequently, and reveal a dramatic change of the structure and composition. This study allowed us to determine a stability diagram for SrRuO₃ films, which indicates the temperature and oxygen pressure under which they can serve as bottom electrodes that transfer the high crystalline quality of single-crystal SrTiO₃ substrates to subsequent oxide films. In addition, the step-flow instability of single-stepped SrRuO₃ films also has been investigated as functions of the film thickness and the substrate miscut angle. Terrace-step bunching and the formation of multiple-stepped islands are observed typically when the film thickness exceeds a critical value, which depends mostly on the substrate miscut. In this presentation, therefore, we report our results of a systematic study showing the essential conditions for synthesizing nearly-perfect functional oxide films on SrRuO₃-electroded SrTiO₃. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, as part of a BES NSET initiative on Nanoscale Cooperative Phenomena and of the LDRD project.

H8.63

3d- and 4f- Element Doping in SnO₂ DMS Thin Films. K. Mohan Kant^{1,2}, K. Chandrasekaran², K. Sethupathi¹ and M.S.R. Rao^{1,2,3}; ¹Department of Physics, Indian Institute of Technology (IIT) Madras, Chennai, India; ²Materials Science Research Centre, Indian Institute of Technology (IIT) Madras, Chennai, India; ³Department of Physics, University of Maryland, College Park, Maryland.

Dilute Magnetic Semiconductors (DMS) belonging to the family of wide band gap oxides are potential materials for electro-magneto-optical devices. The Physics of the underlying exchange mechanism between the dopant magnetic spins is an interesting aspect to explore. From a combinatorial screening approach looking at the solid solubility of 3d-transition and 4f-lanthanide elements in SnO₂ and their magnetic properties, we report the observation of transparent ferromagnetism in Co doped SnO₂ PLD grown thin films on STO (001) substrates with the concentration of Co between 4 and 8 mol%. The magnetic and structural properties critically depend upon Co substitution in SnO₂ lattice. The appearance of the films at room temperature ranged from glassy to transparent behaviour depending upon the growth condition. In order to study the effect of doping of 4f-elements (which exhibit predominantly different magnetic behaviour from that of 3d-elements) into SnO₂, we have prepared Gd, Dy, Eb, Ho doped (4 to 8 mol%) compositions. Optical band gap is found to vary (from 3.5 eV to 3.4 eV) with increase in Ho-dopant concentration in SnO₂. Results of magnetic, transport and optical measurements will be discussed in detail. * also, at the Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, MD 20740, USA

H8.64

Strain-induced phase separation of CaxSr1-xRuO3 epitaxial thin films. Kyoung-Jin Choi and Chang-Beom Eom; Materials Science and Engineering, Univ. of Wisconsin at Madison, Madison, Wisconsin.

SrRuO₃ is a metallic oxide which has been used as an electrode for ferroelectric devices and magnetic tunnel junctions due to its low isotropic resistivity, excellent chemical and thermal stability, good surface smoothness, and high crystalline quality. Furthermore, the lattice parameter can be varied by simply substituting Sr with Ca i.e., making solid solution CaxSr1-xRuO₃ (0 ≤ X ≤ 1). The lattice parameters of CaxSr1-xRuO₃ (0 ≤ X ≤ 1) in pseudo-cubic structure range from 3.93 Å (SrRuO₃) to 3.85 Å (CaRuO₃), which offers suitable strain-engineered bottom electrodes with a wide range of lattice parameters to grow high-quality epitaxial heterostructures. We have deposited a series of epitaxial thin films of CaxSr1-xRuO₃ (x = 0, 0.25, 0.5, 0.75, 1) on various substrates including SrTiO₃, DyScO₃, and GdScO₃ using pulsed laser deposition (PLD). We have also determined the 3-dimensional strain state of the films using a high-resolution four-circle x-ray diffraction (XRD). Pure SrRuO₃ and CaRuO₃ thin films showed a single 110 peak in θ -2 θ scans. In

contrast, CaxSr1-xRuO₃ (x = 0.25, 0.5, 0.75) thin films showed double peaks; one is sharp peak and the other is very broad peak. The in-plane lattice parameter determined from the sharp peak is coherent with the lattice parameter of the substrate. Therefore, the broad peak is of partially relaxed. This suggests that the epitaxial thin films of CaxSr1-xRuO₃ (x = 0.25, 0.5, 0.75) are inhomogeneous and the phases separation was induced by epitaxial strain. In this talk, we will discuss the origin of the phase separation and the phase distribution in the films studies by using high resolution transmission electron microscopy (TEM) and micro x-ray diffraction techniques.

H8.65

Resistance switching at perovskite-oxide heterojunctions. Akihito Sawa¹, Takeshi Fujii^{1,2}, Masashi Kawasaki^{1,2} and Yoshinori Tokura^{1,3}; ¹CERC, AIST, Tsukuba, Japan; ²Institute for Materials Research, Tohoku University, Sendai, Japan; ³Department of Applied Physics, University of Tokyo, Tokyo, Japan.

Recently, considerable interest has been attracted by a reversible resistance switching behavior triggered by the application of short voltage pulses to metal/perovskite-oxide/metal sandwich structures, due to its possible device application as a nonvolatile resistance random access memory (R-RAM). The diversity of materials system expands to Pr_{0.7}Ca_{0.3}MnO₃ (PCMO), Cr-doped SrZrO₃, and SrTiO₃ (STO), indicating rich ingredient of underlying physics. However, the mechanism of the resistance switching behavior has not been understood, yet. In the present study, such resistance switching has been investigated for p-type and n-type semiconducting perovskite oxides such as PCMO and Nb-doped STO, respectively. The junction devices show rectifying *I* – *V* characteristics similar to those of Schottky barrier. The characteristics of the resistance switching and the rectification depend on the work function and electronegativity of metal electrodes. On the basis of the experimental results, we propose that the resistance switching is originated by a charging effect in the trapping states at the Schottky-like metal/perovskite-oxide interface.

H8.66

Characteristics of the HfO₂ film deposited using TDEAH and Hf(mp)₄ by Remote Plasma Enhanced Atomic Layer Deposition Method. Seokhoon Kim, Sangwook Park, Jinwoo Kim, Jihoon Choi and Hyeontag Jeon; Materials Science & Engineering, Hanyang University, Seoul, South Korea.

HfO₂ have been extensively investigated as alternatives to SiO₂ in the downscaling of metal-oxide semiconductor devices due to its high dielectric constant (25–30), high density (9.68 g/cm³), large bandgap (5.68 eV) and good thermal stability in contact with silicon. For these reasons, we investigated the HfO₂ gate dielectric material deposited by remote plasma enhanced atomic layer deposition (RPEALD) method. RPEALD method is expected to minimize the impurities of film and damage of substrate, increase the reactivity, widen the process window and improve the film qualities such as density. HfO₂ films were deposited using TDEAH containing no oxygen atoms and newly synthesized Hf(mp)₄ containing oxygen atoms as Hf precursor and oxygen plasma as reactant gas. In this study, plasma diagnostics was carried out by using Langmuir probe method to confirm the remote plasma and plasma density was decreased out of discharge region. We deposited HfO₂ films with RPEALD system and thickness of HfO₂ was controlled by the number of deposition cycle. After growing HfO₂ films, the electrical properties of HfO₂ of MOS capacitor were measured. The physical and chemical characteristics of HfO₂ film were analyzed by cross-sectional transmission electron microscope, Auger electron spectroscopy, X-ray photoemission spectroscopy. The electrical properties including EOT, hysteresis, leakage current and capacitance were evaluated by I-V and C-V measurements. This paper presents comparison of the characteristics of the HfO₂ deposited by RPEALD method using the two different metal organic precursor, TDEAH and Hf(mp)₄.

SESSION H9: Correlated Electrons
Chairs: Dave H. A. Blank and Jochen Mannhart
Thursday Morning, December 2, 2004
Grand Ballroom (Sheraton)

8:15 AM *H9.1

Complexity in Transition Metal Oxides. Elbio Dagotto,

¹University of Tennessee and Oak Ridge National Laboratory, Knoxville, Tennessee; ²Department of Physics, Florida State University, Tallahassee, Florida.

Recent developments in the context of theory and experiments for manganites and cuprates will be discussed. It will be argued that the presence of nanoscale phase separation is at the heart of the CMR phenomenon [1]. Simulation results support this view, as well as experimental data. These effects are not limited to manganites, but

they may appear in other compounds as well, such as the high-T_c cuprates. New results will be presented in this area, on the phenomenological competition between antiferromagnetism and d-wave superconductivity, suggesting the possibility of "colossal" effects in this context [2]. Clustered or mixed-phase states could form a new paradigm for the understanding of several compounds in condensed matter physics, where many degrees of freedom are simultaneously important. [1] A. Moreo et al., *Science* **{283}**, 2034 (1999); E.D., T. Hotta and A. Moreo, *Physics Reports* **{344}**,1 (2001); E.D., *{Nanoscale Phase Separation and Colossal Magnetoresistance}*, Springer-Verlag, 2002. [2] G. Alvarez et al., *cond-mat/0401474*.

8:45 AM *H9.2

Polarity Discontinuities at Oxide Heterointerfaces and in Confined Systems. David A. Muller¹, N. Nakagaw², Harold Y. Hwang² and Akira Ohtomo³; ¹Applied Physics, Cornell University, Ithaca, New York; ²Department of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba, Japan; ³Institute for Materials Research, Tohoku University, Sendai, Japan.

Perovskite oxides exhibit a wide range of physical properties, from insulators to superconductors, incorporating magnetism, and coupling to phonon instabilities. The close lattice match between many perovskites raises the possibility of growing epitaxial thin film heterostructures with different ground states may compete or interact. Among the many issues that arise, here we focus on the polarity mismatches that can lead to interfacial electronic structure quite distinct from the bulk. Growth kinetics and defect chemistry are important to understand such an experimentally realized interface, in which local rearrangements, defects, and vacancies can partially compensate the anticipated electronic structure. For highly kinetic growth, atomically abrupt perovskite interfaces and superlattices can be produced allowing control of the termination layer during growth, as well as the composition of the interface. The composition, valence, and excited states were measured on the atomic scale using spatially resolved electron energy loss spectroscopy, revealing natural charge decay lengths [1]. We contrast these lengths for materials with and without access to mixed valence states. In some cases, these extended interfacial states can be stabilized, leading to metallic behavior down to low temperature [2]. [1] A. Ohtomo, D. A. Muller, J. L. Grazul, H. Y. Hwang, *Artificial Charge-Modulation in Atomic-scale Perovskite Titanate Superlattices*, *Nature*, 419 378-380 (2002). [2] A. Ohtomo, H. Y. Hwang, *A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface*, *Nature*, 427, 423-425 (2004).

9:15 AM H9.3

Electric-Field Control of Ferromagnetism at Room Temperature on the Pb(Zr,Ti)O₃/(La,Ba)MnO₃ Heterostructure. Teruo Kanki¹, Masatoshi Ohnishi¹, Hidekazu Tanaka^{1,2} and Tomoji Kawai¹; ¹Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Japan; ²PRESTO, Japan Science and Technology Agency, Kawaguchi, Japan.

In recent year, the area of spintronics, namely electric devices which have novel magneto-transport properties based on the control and manipulation of the flow of spin polarized electron, has attracted considerable attention. Spintronics is a key technique in the area of future information and data storage technologies. Electric field control of ferromagnetism is one of important topics, but, control and switching of ferromagnetism at room temperature has been strongly required for practical applications of this type device. As one of the best candidate of room temperature spintronic material, La_{1-x}Ba_xMnO₃ (LBMO) perovskite manganite is useful because of showing room temperature ferromagnetism even in the ultra thin film [1]. Here we have constructed a field effect transistor structure using this LBMO channel by pulsed laser deposition (PLD) method leading to the ferromagnetic FET device working at room temperature. This FET is composed of a SrRuO₃ (SRO) bottom gate electrode, a ferroelectric PbZr_{0.2}Ti_{0.8}O₃ (PZT) gate insulator to utilize the ferroelectric remnant polarity and a ferromagnetic top LBMO channel (16nm), on the SrTiO₃(001) substrate. The resistivity and metal-insulator transition temperature (TP) of the channel layer could be modulated by 2.5K by switching ferroelectric remnant polarity at 283K [2]. As direct evidence of modulation of ferromagnetism, the change of magnetization was evaluated by magneto-circular dichroism (MCD) measurement. It was confirmed that the MCD value was reversibly modulated by switching the ferroelectric remnant polarity at 293K. We will discuss details on magnetism and electrical transport properties of the FET. [1] T.Kanki *etal*, *Appl.Phys.Lett.* **83**(2003)1184, [2] T.Kanki *etal*, *Appl.Phys.Lett.* **83**(2003)4860

9:30 AM H9.4

Magnetism in Pulsed Laser Deposited Zn-Doped Manganese Oxide Films. S. B. Ogale¹, Darshan C. Kundaliya¹, S. R. Shinde¹, S. Dhar¹, T. Venkatesan¹, S. E. Lofland², B. Varughese³, S. J. Welz⁴

and Nigel D. Browning⁴; ¹Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland; ²Department of Chemistry and Physics, Rowan University, Glassboro, New Jersey; ³Department of Chemistry, University of Maryland, College Park, Maryland; ⁴Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, California.

Thin films of manganese oxide without and with Zn doping were grown on sapphire and other crystalline substrates by pulsed laser ablation. The depositions were performed under different oxygen pressures and temperatures. Some diffusion/reaction studies were also performed on bilayers of ZnO and Manganese oxide phases. Phase stabilization, composition, and purity were studied by XRD and RBS techniques. Other techniques such as transmission electron microscopy, x-ray photoelectron spectroscopy, magnetic force microscopy were also used. Magnetization studies were carried out with squid magnetometry and vibrating sample magnetometry. In low temperature (<50 C) grown films and in low temperature diffused bilayers robust ferromagnetism was observed. The magnetism was found to weaken with increased Zn concentration. These results will be presented with the analysis of phase identification. Work supported under DARPA (# N000140210962) and NSF-MRSEC (# DMR-00-80008)

10:15 AM *H9.5

Electric Field Effect in Functional Oxides. Jochen Mannhart¹, Gennadij Yu. Logvenov¹, Christof W. Schneider¹, Akihito Sawa² and Thilo Kopp¹; ¹University of Augsburg, Center for Electronic Correlations and Magnetism, Augsburg, Germany; ²Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Field effect devices and quasiparticle injection devices provide the possibility to modulate the properties of compounds with correlated electron systems without altering their structure or chemistry. In contrast to the conventional semiconducting FETs, in correlated systems phase transitions may be induced by the gate charges, providing new opportunities for basic science and for innovative devices. In particular, phase-transition transistors have been proposed to break the scaling limits conventional, semiconducting FETs are facing. Since the carrier density of functional oxides exceeds the densities of standard semiconductors by orders of magnitude, the key parameter for oxide field effect devices is the maximum polarization that can be applied to the drain-source channels. To reproducibly achieve the required polarizations of several ten $\mu\text{C}/\text{cm}^2$ we have developed a novel, versatile device architecture. These devices allow exceptionally large polarizations, with local values reaching 50 $\mu\text{C}/\text{cm}^2$, to be routinely induced in functional oxides. The performance of the devices will be presented and discussed. This work is supported by the BMBF (project 13N6918) via the VDI and by the DFG via the Sonderforschungsbereich 484.

10:45 AM H9.6

Ferroelectric Field Effect Modulation of the Electronic Properties of Nb-doped SrTiO₃ Superconducting Films. K. S. Takahashi¹, D. Matthey¹, D. Jaccard¹, K. Shibuya², T. Ohnishi², M. Lippmaa² and J.-M. Triscone¹; ¹DPMC, University of Geneva, Geneva, Switzerland; ²ISSP, University of Tokyo, Tokyo, Japan.

We have performed ferroelectric field effect experiments using epitaxial heterostructures composed of ferroelectric Pb(Zr_{0.2}Ti_{0.8})O₃ (PZT) and superconducting Nb-doped SrTiO₃ (Nb-STO). The films were prepared on (001) SrTiO₃ substrates by off-axis radio-frequency magnetron sputtering and pulsed-laser deposition. Upon polarization reversal of the ferroelectric PZT layer, large differences in the resistivities and a clear shift of the critical temperature T_c were observed in the Nb-STO layer. Even if there are slight deviations from the bulk crystal data, the average electrostatic doping can be rather well mapped onto the chemical doping phase diagram.

11:00 AM H9.7

Quasiparticles injection from a half-metallic oxide into a conventional superconductor. Luana Fratila¹, Catherine Dubourdieu¹, Jean-Claude Villegier², Marta Rossell³, Oleg Lebedev³ and Gustaaf Van Tendeloo³; ¹Laboratoire des Matériaux et du Génie Physique, CNRS/INPG, St Martin d' Heres, France; ²DRFMC/LCP, CEA, Grenoble, France; ³RUCA EMAT, Antwerpen, Belgium.

Quasiparticles injection phenomena from a half metallic oxide into a conventional superconductor were investigated. Devices were patterned from La_{0.7}Sr_{0.3}MnO₃/SrTiO₃/Nb heterostructures. Epitaxial La_{0.7}Sr_{0.3}MnO₃/SrTiO₃ bilayers were grown on (001) SrTiO₃ substrates by pulsed-injection MOCVD and then the niobium film was grown on top by DC magnetron sputtering. The microstructure of the heterostructures was studied by atomic force

microscopy, transmission electron microscopy (TEM) and X-ray diffraction. Particularly, interfaces, which play a key role in the carrier transport, were studied by high-resolution TEM. A 6-T in-line device geometry was designed, with transversal injection from the ferromagnetic $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ electrode through the SrTiO_3 tunnel barrier into the superconductor. The tunnel barrier oxide thickness was varied in the range 2-8 nm. We find that the superconducting critical current I_c can be tuned (and even turned to zero) by quasiparticles injection with injection current I_{inj} of the order of hundreds of μA . Effect of the barrier thickness on the device gain $G = -dI_c/dI_{inj}$ will be discussed. A maximum dynamical gain of about 280 is measured at 1.7 K. Joule heating does not contribute significantly to the I_c suppression, in opposition with most of the previous studies. However, devices electrical characteristics are found to evolve with time. This aging effect will be discussed.

11:15 AM **H9.8**

Electrostatic Carrier Doping to Perovskite Transition-Metal Oxides. Isao H. Inoue¹, Hiroyuki Nakamura¹, Kazunori Ueno^{1,2,3}, Nao Takeshita¹, Chieko Terakura¹, Hidenori Takagi¹, Yasuhide Tomioka¹, Hiroyuki Yamada¹, Masashi Kawasaki^{1,3}, Hiroshi Akoh¹ and Yoshinori Tokura^{1,4}, ¹Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; ²Dept. Adv. Mater. Sci., Univ. Tokyo, Kashiwa, Japan; ³Inst. Mater. Res., Tohoku Univ., Sendai, Japan; ⁴Dept. Appl. Phys., Univ. Tokyo, Tokyo, Japan.

The most fascinating phenomenon of the strongly correlated electron systems is that an assemblage of as many as 10^{23}cm^{-3} electrons in a material do a complete turnaround simultaneously and coherently. The larger the number of the electrons involved in the phase transition, the more interesting and challenging the phenomenon becomes. This concept of correlated electron systems is bringing to life a noble electronic device, such as a Mott transistor; the correlated electron device is a sharp counterpart of the single-electron device generated by the present rapid progress of nanotechnology, which aims at manipulating the electron one by one. However, the attention given to the correlated electron device so far was not sufficient. The largest impediment is likely to be the lack of a method of the critical control of carrier density in those correlated materials especially near phase boundaries, where minute changes in carrier density can give rise to huge changes in materials properties. Another reason might be the fact that the fields of microelectronic technology and strongly correlated systems have historically followed rather disconnected paths with few interdisciplinary points of contact. Thus, we have been trying to span a bridge between the fields by attempting electrostatic fine-tuning of carrier number of, in particular, the perovskite-type transition-metal oxides. In this presentation, we describe two of our approaches to electrostatic carrier doping. One is to deposit a thin film of amorphous alumina directly on the top of the sample to be doped, and apply large electric field through the amorphous alumina. By this method, we have already succeeded to dope appreciable amount of carriers into undoped SrTiO_3 and KTaO_3 [1,2]. This method is being applied now to strongly correlated Mn oxides. The results are given in the presentation. Our alternative method is to fabricate thin films of transition-metal oxide on the top of the single-crystalline SrTiO_3 , and apply the gate electric field through SrTiO_3 . The interface between SrTiO_3 and SrZrO_3 has become metallic even at 2K by applying very large gate bias. The results of further investigations at much lower temperature (100mK) will be shown in the presentation. These two methods are quite versatile and should be applicable for a large class of systems under current heavy experimental investigation. [1] K. Ueno et al., Appl. Phys. Lett. **83**, 1755 (2003). [2] K. Ueno et al., Appl. Phys. Lett. **84**, 3726 (2004).

11:30 AM **H9.9**

Giant Planar Hall Effect in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ Thin Films. Jeng-Bang Yau¹, Yosi Bason², Xia Hong¹, Lior Klein² and Charles H. Ahn¹, ¹Applied Physics, Yale University, New Haven, Connecticut; ²Physics, Bar Ilan University, Ramat Gan, Israel.

We have observed sharp field-symmetric jumps in transverse resistivity measurements of colossal magnetoresistive (CMR) $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) thin films, which we attribute to a giant planar Hall effect (GPHE)¹ in combination with biaxial magnetic anisotropy². The planar Hall effect³ occurs in magnetic conductors and arises in systems with anisotropic magnetoresistance. Using epitaxial LSMO thin films grown on SrTiO_3 substrates, we have carried out magnetotransport measurements in a swept magnetic field in the plane of the films, observing jumps in the transverse (Hall) resistivity that persist up to temperatures above 175 K. These jumps yield a PHE that is 4 orders of magnitude larger than what is observed in 3d ferromagnetic metals, and similar to the PHE in (Ga,Mn)As observed by Tang *et al.*¹. ¹Tang *et al.*, Phys. Rev. Lett. **90**, 107201 (2003). ²McGuire *et al.*, IEEE Trans. Magn. **11**, 1018 (1975). ³Goldberg *et al.*, Phys. Rev. **94**, 1121 (1954).

SESSION H10: HTS and Artificial Multilayers
Chairs: Ivan Bozovic and Ron Feenstra
Thursday Afternoon, December 2, 2004
Grand Ballroom (Sheraton)

1:30 PM ***H10.1**

Scientific Challenges of Coated Superconductors of YBCO*. David Larbalestier, University of Wisconsin-Madison, Madison, Wisconsin.

Coated superconductors of YBCO, normally called coated conductors (CC), are metal-supported complex multilayer oxides which require exceptional structural and electrical qualities over lengths of kilometers. Two main types of architecture compete, one based on a deformation-textured metal template (RABiTS), the other based on an ion-beam oxide texturing. I will concentrate on recent work that addresses the microstructural and superconducting properties of YBCO conductors made on RABiTS. Because even low angle misorientations of $>4^\circ$ obstruct supercurrent, there is intense interest in the fabrication of quasi-perfect templates of Ni alloys that have FWHM of 5° or less. But Ni poisons YBCO, thus requiring that a diffusion barrier, normally YSZ, must be interposed between the template and the YBCO. A seed between the Ni and the YSZ and a cap layer, normally CeO₂, between the YSZ and YBCO must be interposed too. Finally it is desirable to grow the YBCO to a thickness of 2 mm or more. Remarkably these requirements are all within sight. Recent studies that we have been conducting with our collaborators of the growth and properties of such conductors will be presented. In particular we will show the results of correlated through thickness measurements of microstructure, grain misorientation, grain boundary meandering and their effects on current density will be presented. *Work carried out within the collaborations of the Wire Development Group with members at American Superconductor Corporation, ANL, LANL, ORNL and U. of Wisconsin and within the MURI on fundamental Science of Coated Conductors (Davis-Kansas-Stanford-Wisconsin).

2:00 PM ***H10.2**

Hybrid High-Tc / Low-Tc Superconducting Structures. Hans Hilgenkamp, Faculty of Science and Technology, University of Twente, Enschede, Netherlands.

Oxide high-temperature superconductors differ in many basic aspects from their metallic, low-Tc counterparts. One of the most striking differences is in the symmetry-properties of the superconducting condensate, an aspect directly related to the pairing mechanism underlying the superconductivity. Whereas conventional superconductors are described with an s-wave symmetry, for the cuprates this is predominantly a d-wave symmetry. Combining these two classes of superconductors in the form of hybrid thin film Josephson structures enables to utilize the intrinsic pi-phase shifts associated with the d-wave symmetry of the oxide superconductors. The fabrication of such hybrid structures will be described, along with various examples of basic studies, such as on the symmetry of p- and n-type high-Tc superconductors, novel effects like the spontaneous formation of ordered arrays of half-integer magnetic flux-quanta and new devices, as e.g. the switchable bistable superconducting quantum interference device.

2:30 PM **H10.3**

Oxides Films for Second Generation High Temperature Superconducting Tapes. Xuming Xiong and Venkat Selvamanickam; SuperPower, Inc, Schenectady, New York.

Xuming Xiong, Venkat Selvamanickam, Ping Hou, Jay Xie, Yiji Li, Yimen Chen, Jodi Reeves SuperPower, Inc. Schenectady, NY 12304 Second generation High Temperature Superconducting (HTS) tapes are being developed to commercialize HTS for electric power applications. Second generation HTS tapes or the so called coated conductors are based on films of HTS deposited on practical metal substrates. In order to prevent diffusion of metal elements into the HTS film, and to provide biaxial-textured templates for epitaxial growth of biaxially-textured HTS film, various functional oxide films are being developed as buffer structures. In order for coated conductors to be cost competitive, high-throughput processes have to be employed. High throughput in oxide buffer deposition can be achieved by using thinner films, fewer buffer layers, and high-rate deposition processes. At SuperPower, we use an ion beam assisted deposition (IBAD) method to achieve biaxial texture in the oxide buffer layer. Several IBAD processes with different oxides have been investigated. One or more oxide cap layers are deposited between the IBAD oxide film and the HTS film to improve the lattice match and to achieve a broader deposition window. In choosing and optimization of these cap layers, another consideration is surface smoothness which may affect multilayer growth and thick HTS film growth. With certain

IBAD layers, additional oxide films that serve as diffusion-barriers are used. In some approaches, the IBAD film and/or the oxide cap layer are multifunctional films serving the purpose of a diffusion barrier too. In order to achieve an optimal performance, buffer structures that provide a compromise among the various requirements are being developed.

2:45 PM H10.4

Non-Doped High-Tc Superconductivity in MBE-Grown T-(La, RE)₂CuO₄ (RE = Sm, Eu, Gd, Tb, Lu, Y) without Mott-Insulating Ground State. Hideki Yamamoto¹, Akio Tsukada¹, Masumi Noda^{2,1} and Michio Naito³; ¹NTT Basic Research Labs., NTT Corporation, Atsugi-shi, Kanagawa, Japan; ²Tokyo University of Science, Shinjuku-ku, Tokyo, Japan; ³Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo, Japan.

It is commonly believed that the high-Tc superconductivity develops in a Mott-insulator end-member with doped charge carriers. However, our recent observation of fairly high-Tc superconductivity (>20 K) in the isovalently-substituted T-(La³⁺, RE³⁺)₂CuO₄ (RE = rare earth elements) thin films prepared by MBE appears to be against this general belief. The purpose of the isovalent substitution is to stabilize the T phase of La₂CuO₄, and then the superconductors have no effective dopant, at least nominally. In this presentation, we describe our present understanding for the origin of the superconducting carriers in this new class of cuprate superconductors. There seems to be three possible scenarios: (i) oxygen deficiencies at the O(2) site [(La, RE)₂O₂ plane], and/or (ii) O(1) site [CuO₂ plane] serve as a source of effective carriers, and (iii) T-(La, RE)₂CuO₄ is not a Mott insulator, and has intrinsic carriers, as predicted by the band calculation for Nd₂CuO₄. Although the most straightforward approach is to investigate site-specific occupancy of oxygen very precisely, at present, there is no established technique available for thin films. Instead, we systematically investigated the in-plane lattice constant (a₀) with changing RE concentration x in La_{2-2x}RE_xCuO₄. It is known that the Cu-O bonds in the σ(x²-y²) bands in the CuO₂ plane have antibonding character, and hence, electron-doping lengthen and hole-doping shorten the Cu-O bond. This trend holds even when the electron-doping is achieved, as exemplified by (Nd, Ce)₂CuO₄, by the substitution of larger lanthanide ion (Nd³⁺) by smaller ion (Ce⁴⁺), and *viceversa*. For RE³⁺=Tb³⁺, the a₀ of the T-(La, RE)₂CuO₄ films monotonically decreased with increasing x for 0 < x < 0.75, whose extrapolation to x=2 agrees well to the reported value for bulk Tb₂CuO₄ (0.388 nm). The a₀ showed a similar systematic change also for RE³⁺=Y³⁺. These a₀ variation can simply be understood based on the ionic radius of the substituent RE³⁺ versus La³⁺, suggesting that our nominally non-doped T-(La³⁺, RE³⁺)₂CuO₄ samples are non-doped or almost non-doped and the third scenario is the most plausible. For electron-doped cuprates, the electronic phase diagram depends on details of crystal structure, especially on apical oxygen remnant, which is detrimental to superconductivity, but always exists in the as-grown samples. We believe the larger a₀ in the La-based T/ compounds enabled a more thorough removal of the apical oxygen and led to the new class of cuprate superconductors without Mott-insulating ground state.

3:30 PM *H10.5

The Growth of Thin Crystalline Oxide Films from the Vapor through Intermediate Liquid and Glass Phases. Gertjan Koster, GLAM, Stanford University, Stanford, California.

We report on our latest findings using real-time Fourier Transform Infrared (FTIR) radiance and reflectance measurements during ultra fast electron beam deposited [100 angstroms/sec] YBa₂Cu₃O₇ (YBCO) films [i]. The data can best be explained by assuming the presence of a liquid phase from which the YBCO crystal lattice grows [ii]. We have found the first real-time evidence for the liquid phase. It is inferred from the strong thin film interference fringes which appear in the reflectance spectrum. The fringes subsequently change amplitude when YBCO precipitates from the liquid; the rate of precipitation can be controlled by oxygen pressure and substrate temperature. We believe that crystal growth via liquid or glass precursors has potential for growing many oxide films where the phase diagram does not permit equilibrium between the vapor and the crystal phases. We demonstrate using an intermediate glass phase in the growth of YBa₂Cu₄O₈ (248) films where thermodynamic constraints prevent film growth directly from the vapor [iii]. The glass is formed by PLD at elevated temperatures to ensure high density, and possibly short-range cation order, from monolayer blocks using targets of BaCuO, YCuO and CuO in the sequence dictated by the 248 unit cell. *Ersitu* rate calibration has been adequate to keep the composition close to stoichiometric. The films are subsequently grown at high pressure and temperature. We have followed the growth kinetics either deductively or in real time by XRD at the Stanford Synchrotron Radiation Laboratory as a function of stoichiometry, of deposition sequence and of layer thickness. [i] G. Koster, J.H. Hu,

H.Y. Zhai, R.H. Hammond and M.R. Beasley, in preparation. [ii] T. Ohnishi, J.-U. Huh, R.H. Hammond and W. Jo, 2004 *J. Mater. Res.* **19** 977; A. Kursumovic *et al.*, preprint [iii] G. Koster, J.H. Lee, S. Brennan and T.H. Geballe, in preparation.

4:00 PM H10.6

Magnetic Interaction between Vortices and Magnetic Domains in Superconductor/ferromagnetic Multilayers. Qiang Li¹, Yufeng Hu¹, Zuxin Ye¹ and Weidong Si²; ¹Materials Science Department, Brookhaven National Lab, Upton, New York; ²Physics Department, Brookhaven National Lab, Upton, New York.

We report our studies of magnetic interaction between vortices in superconducting YBa₂Cu₃O_{7-δ} (YBCO) thin film and magnetic domains in ferromagnetic (FM) thin film with out-of-plane magnetization in multilayers. Several YBCO/La_{0.67}Sr_{0.33}MnO₃ and YBCO/Pr_{0.67}Sr_{0.33}MnO₃ multilayer structures were fabricated on LaAlO₃(100) substrates by using Pulsed Laser Deposition (PLD) technique. Due to the compressive strain between the substrate and the FM thin films, Pr_{0.67}Sr_{0.33}MnO₃ and La_{0.67}Sr_{0.33}MnO₃ thin films exhibit uniaxial perpendicular magnetic anisotropy and stripe domain structures. We performed detailed transport and bulk magnetization measurements, as well as high resolution magneto-optical imaging, of these multilayers. The results and implication to the practical application will be discussed. This work was supported by the U. S. Dept. of Energy, Office of Basic Energy Science, under contract No. DE-AC-02-98CH10886.

4:15 PM H10.7

Epitaxial Growth and Characterization of the First Five Members of the Sr_{n+1}Ru_nO_{3n+1} Ruddlesden-Popper Homologous Series. Wei Tian¹, Jeff H. Haeni¹, E. Hutchinson², Ben-li Sheu², M. M. Rosario², Peter Schiffer², Ying Liu² and Darrell G. Schlom¹; ¹Dept. of Materials Science and Engineering, Penn State University, University Park, Pennsylvania; ²Dept. of Physics, Penn State University, University Park, Pennsylvania.

Sr_{n+1}Ru_nO_{3n+1} Ruddlesden-Popper homologous series has attracted growing interest due to their interesting electronic and magnetic properties. One of the prominent examples is the discovery of spin-triplet superconductivity in the n = 1 member, i.e., Sr₂RuO₄. The synthesis of single-phase samples of the intermediate members (1 < n < ∞) is, however, a substantial challenge due to the lack of significant thermodynamic driving force. To overcome this problem, we use monolayer-by-monolayer deposition, with a correct absolute dose of cations, provided by MBE to synthesize Sr_{n+1}Ru_nO_{3n+1} phases with intermediate n. The first five members (n = 1 - 5) of the Sr_{n+1}Ru_nO_{3n+1} phases were grown on (001) SrTiO₃ and (001) (LaAlO₃)_{0.39}(SrAl_{1/2}Ta_{1/2}O₃)_{0.71} (LSAT) substrates by reactive oxide MBE. Transmission electron microscopy and four-circle x-ray diffractions indicate the formation of single-phase, c-axis oriented high-quality samples with the desired n = 1 - 5 Ruddlesden-Popper structures. Magnetic measurements reveal that the n = 3, 4, 5, and ∞ thin films are ferromagnetic, while no sign of ferromagnetism is observed for the n = 1 and 2 samples. Transport measurements corroborate the results obtained by the magnetic measurements. The results suggest that three perovskite layers are necessary to support ferromagnetism with a transition temperature slightly lower than that of the infinite-layer compound in such layered ruthenates.

4:30 PM H10.8

Exploring New Aurivillius Phases. Mark A. Zurbuchen¹, J. Schubert^{3,2}, Yunfa Jia², D. J. Comstock², Wei Tian², Vladimir Cherman³, Mike D. Biegalski², Marilyn E. Hawley⁴, Alexander K. Tagantsev³, Stephen K. Streiffer¹ and Darrell G. Schlom²; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania; ³Lab. de ceramique, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland; ⁴Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico; ⁵Institut für Schichten und Grenzflächen and Center of Nanoelectronic Systems for Information Technology, Forschungszentrum Jülich, Germany.

The physical constraint of epitaxy enables the synthesis of materials that are difficult to obtain by other means. A prime example is the growth of high-n Aurivillius phases such as (Sr₄Bi₄)Ti₇O₂₄ (n = 7) and Bi₉(Ti₃Mn₅)O₂₇ (n = 8), which consist of bismuth oxide double layers interleaved with slabs of n perovskite layers. These materials offer the opportunity to study the effects of the diminishing interaction between structural layers as the perovskite slab thickness increases with n. Pulsed laser deposition has recently been used to synthesize several new materials, including the highest-n Aurivillius phase ever made. Confirmation of the phase via x-ray diffraction and transmission electron microscopy will be presented. Anisotropy of the remanent ferroelectric polarization will be discussed in the context of the symmetry of the Aurivillius-series phases, and of the dimension of

the perovskite slabs. Characterization of these materials by several methods will be presented, and their use as a platform for investigation of behavioral trends as controlled by interface density will also be discussed.

4:45 PM H10.9

Quantitative measurements of piezoelectric response in PZT thin film capacitors using time-resolved synchrotron x-ray microdiffraction. Dal-Hyun Do¹, Dong Min Kim¹, Chang-Beom Eom¹, Eric M. Dufresne², Eric D. Isaacs³ and Paul G. Evans¹;
¹Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; ²Physics, University of Michigan, Ann Arbor, Michigan; ³Center for nanoscale materials at Argonne National Laboratory, Argonne, Illinois.

The piezoelectric response of lead zirconate titanate (PZT) has many applications in devices such as sensors and actuators. The polarization switching and piezoelectric response to external electric fields are closely linked and can be inhomogeneous on micron and smaller scales. We have investigated the fundamental local piezoelectric properties of epitaxial PZT thin film capacitors, employing time-resolved synchrotron x-ray microdiffraction with a submicron x-ray beam. Synchrotron microdiffraction as a structural probe has allowed us to observe the local piezoresponse and polarization switching in PZT capacitors directly through the change in the lattice constant in an applied electric field. Our 400 nm-thick PZT (001) thin films were grown epitaxially on (001) SrTiO₃ substrates with SrRuO₃ electrodes. Using 10 keV x-rays, we measured the lattice spacing change induced in PZT capacitor by a 1 ms voltage pulse to the bottom electrode. The top electrode and PZT layer were patterned using a focused ion beam (FIB) to vary the mechanical boundary conditions on different areas of a device with the expectation that piezoelectric coefficient, d_{33} , would be changed. We have found that PZT thin films had d_{33} values of 45-60 pmV⁻¹ at the center of the top electrode. The piezoelectric displacement can be strongly constrained by the substrate or PZT film surrounding the capacitor. At edges where the top electrode and film were removed with the FIB, the piezoelectric coefficient values were 25 % larger than near the edge of a shadow-masked electrode.

SESSION H11: Poster Session: HTS, Correlated
Electrons Optical and Semiconductor Oxides
Chairs: David Larbalesstier and Jochen Mannhart
Thursday Evening, December 2, 2004
8:00 PM
Exhibition Hall D (Hynes)

H11.1

Nano-Tubes Patterned Thin Films of Barium Strontium Titanate (BST). Xuezheng Wei and Nitin P. Padture; Department of Metallurgy and Materials Engineering, University of Connecticut, Storrs, Connecticut.

A novel, low-temperature synthesis method for producing Ba_xSr_{1-x}TiO₃ (BST) thin films patterned in the form of nano-tubes on Ti substrate is reported. In this two-step method, the Ti substrate is first anodized to produce a surface layer (300 nm thickness) of amorphous titanium oxide nano-tube (100 nm diameter) arrays. In the second step, the anodized substrate is subjected to hydrothermal treatment in aqueous Ba(OH)₂, Sr(OH)₂ solutions at 200 °C, where the nano-tube arrays serve as templates for their topotactic hydrothermal conversion to polycrystalline BST nano-tubes. A simple geometrical model is proposed to elucidate the mechanism of the hydrothermal growth of BST nano-tubes. This opens the possibility of tailoring the titanium oxide nano-tube arrays, and of using various precursor solutions and their combinations in hydrothermal bath, to produce ordered, patterned thin film structures of various Ti-containing ceramics. These could find use not only in a variety of electronic-device applications but also biomedical applications, where patterned thin films are desirable.

H11.2

Spin Cluster State in Polycrystalline La_{1-x}Sr_xCoO₃. Kwonkuk Yu¹, Hyoungkyoung Lee¹, Hyeryun Bae¹, Jeongsoo Park¹, Yeonseung Lee², V. G. Prokhorov³ and YoungPak Lee¹; ¹q-Psi and Dept. of Physics, Hanyang University, Seoul, South Korea; ²Division of Information Communication and Computer Engineering, Hanbat Nat'l University, Daejeon, South Korea; ³Institute of Metal Physics, Kiev, Ukraine.

Interest in strontium-doped lanthanum-cobalt oxides, La_{1-x}Sr_xCoO₃ (LSCO), has been motivated by the high ionic conductivity which makes them a promising electrode material for fuel cells and ferroelectric memory devices, where they improve reliability problems such as fatigue and imprint. LSCO belongs to a family of mixed-valency compounds. The parent compound LaCoO₃ is a unique

diamagnetic semiconductor with a spin gap of 20 - 30 meV and a charge gap of 0.1 eV. The substitution of La with Sr²⁺ leads to a mixed-valent state of the Co ion, giving rise to ferromagnetism for $x > 0.2$. The complicated magnetic and electronic phase diagram introduces a baffling complexity in interpreting the physical properties of LSCO compounds. In this study, the magnetic properties and the spin cluster state of polycrystalline LSCO were investigated. The polycrystalline bulk La_{1-x}Sr_xCoO₃ ($x = 0.15, 0.25$ and 0.30) samples were synthesized by the standard solid-state reaction. A stoichiometric mixture of high-purity (99.99% or better) La₂O₃, SrCO₃ and CoO₃ powders was fired in an Al₂O₃ crucible at 900°C in air with several intermediate grindings for the homogenization, followed by the final grinding before the powders were pressed into pellets. The pellets were annealed at 1500°C for 12 h in air, and cooled down to room temperature in the furnace. The x-ray diffraction analysis revealed that all the samples are in the typical perovskite structure of LSCO. The temperature dependence of magnetization in a field up to 100 Oe was obtained with a SQUID magnetometer in a temperature range of 10 - 300 K. The resistance measurements were carried out by using the conventional four-point-probe method in a temperature range of 10 - 300 K. The relative atomic concentration of LSCO samples was estimated by x-ray photoelectron spectroscopy. From the resistance analysis, it was found that the conductivity of samples increased gradually along with the Sr concentration. The mixed magnetic state of LSCO was investigated by high-resolution neutron diffraction, which elucidates that the coexistence of antiferromagnetic and ferromagnetic states leads to a spin cluster state below the Curie point T_C . This anomalous magnetic behavior in LSCO is explained by the existence of ferromagnetic grains in the nonferromagnetic background.

H11.3

Rapid growth of SmBa₂Cu₃O_y thin film grown by vapor-liquid-solid growth mode. Yusuke Ichino^{1,6}, Hisayoshi Matsuo¹, Yutaka Yoshida^{1,6}, Yoshiaki Takai¹, Kaname Matsumoto^{2,6}, Masashi Mukaida^{3,6}, Ataru Ichinose^{4,6} and Shigeru Horii^{5,6}; ¹Dept. of Energy Engineering and Science, Nagoya University, Nagoya, Japan; ²Dept. of Materials Science and Engineering, Kyoto University, Kyoto, Japan; ³Faculty of Engineering, Yamagata University, Yonezawa, Japan; ⁴CRIEPI, Yokosuka, Japan; ⁵Dep. of Applied Chemistry, The University of Tokyo, Tokyo, Japan; ⁶CREST-JST, Tokyo, Japan.

Vapor-liquid-solid (VLS) growth mode is expected to obtain the high quality REBa₂Cu₃O_y thin film with rapid growth rate, since the VLS growth mode is substantially same to the liquid phase epitaxy (LPE). We studied a growth rate dependence on superconductivity in a SmBa₂Cu₃O_y (Sm123) thin film grown by the VLS growth mode. In the case of a deposition under a low oxygen pressure, the Sm123 thin film obtained by the conventional pulsed laser deposition (PLD) method showed the a , c -axes mixed orientation and poor crystallinity, while the Sm123 thin film grown by the VLS mode was the completely c -axis oriented film and kept the high crystallinity as well as the film deposited by PLD at optimal conditions. Critical temperatures in Sm123 thin films grown by VLS growth mode were around 90 K independent of the deposition rate. However critical current densities (J_c 's) increased with the deposition rate increasing. When the deposition rate was higher than 60 nm/min, the J_c reached over 1 MA/cm² at 77 K in the self field. The maximum deposition rate, which corresponded to the maximum value on our apparatus, was 320 nm/min and this value was thirty times as high as that of the PLD. Even though the deposition rate was the maximum value, the J_c in Sm123 thin film grown by VLS mode was maintained at least 1 MA/cm². We argue that the VLS growth mode can achieve the high deposition rate as well as the LPE.

H11.4

Preparation of ZnO-Ga₂O₃ thin films by MOCVD using some β -diketonates as precursors. Yuzo Tasaki¹, Masanori Kabeya², Toshiaki Kanoko² and Shuji Yoshizawa²; ¹Toshima MFG Co., Ltd., Higashimatsuyama, Saitama, Japan; ²Meisei University, Hino, Tokyo, Japan.

ZnO-Ga₂O₃ which is less expensive than In₂O₃-SnO₂ (ITO) have been studied as transparent conductive films of displays, organic light-emitting devices and solar cells. In most of previous reports on preparation of ZnO-Ga₂O₃ by MOCVD, alkyl metals such as diethylzinc and trimethylgallium have been used as MOCVD precursors. Generally, metal β -diketonates are used for preparing oxide thin films rather than alkyl metals because of their stability to oxygen. Therefore, preparation of ZnO-Ga₂O₃ thin films using some β -diketonates as precursors was investigated. The evaluated zinc β -diketonates were bis[dipivaloylmethanato]zinc (Zn(DPM)₂), bis[isobutyrylpivaloylmethanato]zinc (Zn(IBM)₂), bis[diisobutyrylmethanato]zinc (Zn(DIBM)₂) and bis[2,2,6,6-tetramethyl-3,5-octanedionato]zinc (Zn(TMDD)₂). The evaluated gallium β -diketonates were the complexes which have the same ligands as the zinc β -diketonates, Ga(DPM)₃, Ga(IBM)₃, Ga(DIBM)₃ and Ga(TMDD)₃. ZnO or Ga₂O₃ thin films were

prepared using each precursor then Zn(TM0D)2-Ga(TM0D)3 and Zn(IBM)2-Ga(IBM)3 were selected as the appropriate combinations of precursors to prepare ZnO-Ga2O3 films. Zinc and gallium precursors were mixed with the various molar ratio and dissolved in anhydrous toluene. ZnO-Ga2O3 thin films were deposited using the precursor solutions on 3" Corning 1737 glass substrates at 400-600 deg C. The reactor pressure, the oxygen concentration and the deposition time were 1330Pa, 32% and 20min, respectively. Gallium contents in the obtained films were higher than that in the precursor solution when Zn(IBM)2-Ga(IBM)3 solution were used. On the other hand, gallium contents in the obtained films were lower than that in precursor solution when Zn(TM0D)2-Ga(TM0D)3 solution was used. The crystallinity and conductivity were affected by the gallium content in a film rather than the kind of precursor. The crystallinity of the films was lowered by increasing gallium content. The conductivity of the films without annealing in inert atmosphere was 5-100mohmcm. Neither the gallium content nor the kind of precursor affected transparency. The transparency of the films was more than 85% in the range of 400-1000nm.

H11.5

Effects of H₂O Partial Pressure on the Crystallinity of ZnO Thin Film and Electrical Characteristics of Film Bulk Acoustic Wave Resonators. Hajime Yamada, Yoshimitsu Ushimi, Hideki Kawamura, Masaki Takeuchi, Yukio Yoshino and Takahiro Makino; Murata Manufacturing Co., Ltd., Yasu-gun, Shiga, Japan.

We have improved electrical characteristics of film bulk acoustic wave (BAW) resonator. The BAW resonator, adopting secondary harmonics mode at about 1.8GHz, was fabricated with thickness of Al/ZnO/Al/SiO₂=0.18/1.45/0.18/1.45 microns, respectively. Both ZnO and SiO₂ were formed by rf sputtering while Al electrodes by electron beam evaporation. In this article we have studied effects of H₂O partial pressure on the crystallinity of ZnO thin film and electrical characteristics of BAW resonators. ZnO thin films were prepared at 250 centigrade substrate temperature, 5.66W/cm² rf power, 6/4 Ar/O₂ gas ratio and 0.6Pa gas pressure. H₂O gas was injected into the sputtering chamber, where the gas pressure, measured by a quadrupole mass spectrometer, was varied from 2.7*10⁻⁵ to 2.0*10⁻³ Pa. As the experimental result, effective electromechanical coupling coefficient of the BAW resonator remarkably improves from 1.8% to 4.7% for which the H₂O partial pressures correspond to 2.7*10⁻⁵Pa and 1.5*10⁻⁴Pa, respectively. In the ZnO film deposited at a high H₂O partial pressure of 1.5*10⁻⁴Pa, we have clearly observed columnar structure in cross-sectional TEM(Transmission Electron Microscope), and spotty pattern in TED(Transmission Electron Diffraction). In ZnO thin film deposited at a low H₂O partial pressure of 2.7*10⁻⁵Pa, mosaic structure in TEM, and both ring and spotty pattern in TED were observed. These results indicate that the crystallinity of ZnO thin film has been improved by H₂O in the sputtering chamber. In thermal desorption spectroscopy, we observed that the presence of hydroxyl group tends to increase with increasing H₂O partial pressure. The injection of H₂O during sputtering deposition gives good effects to the crystallinity of ZnO thin film and the electrical characteristics of BAW resonator.

H11.6

Highly Conducting Aluminum-doped Zinc Oxide Films for Polymeric Electroluminescent Devices. Zhu Furong, Hao Xiaotao, Ong Soo Kian, Li Yanqing and Tan Liwei; MNSC, Institute of Material Research and Engineering, Singapore, Singapore.

Transparent conducting oxide film has been widely used in flat panel displays including liquid crystal displays, plasma displays and OLEDs. The growth in production of flat screen TVs has led to a doubling in demand for indium tin oxide (ITO) materials. The shortage in indium resources worries the fast growing display industry and creates a need for the development of an efficient solution for low cost ITO alternatives. Aluminium-doped zinc oxide (AZO) is a possible alternative due to its unique optical and electrical characteristics. AZO thin films are also much cheaper compared to ITO. An optically transparent and electrically conductive AZO films that are suitable for organic electronics including photovoltaic cells and flexible displays is developed. A 200 nm thick AZO film with a root mean square roughness of 2 nm, an average transmittance of 83% in the visible wavelength region, and a sheet resistance of 30 Ohm/sq can be obtained at a low process temperature of about 800C. The performance of polymeric electroluminescent devices using AZO films with desired properties are discussed.

H11.7

Comparison of Metal Gate and MOS Gate ZnO Field Effect Transistors. C. J. Kao², Y. W. Heo¹, Rohit Khanna¹, F. Ren³, D. P. Norton¹, G. C. Chi² and Stephen Pearton¹; ¹MSE, University of Florida, Gainesville, Florida; ²Electrical Engineering, National Central University, Chung-Li, Taiwan; ³Chemical Engineering, University of Florida, Gainesville, Florida.

ZnO FETs with gate length of around 1 micron were fabricated on PLD grown layers on sapphire substrates. A strong dependence of device performance on the thickness and quality of the buffer between the substrate and active layers was observed. Devices fabricated on structures without a thick buffer did not show channel modulation. The effective barrier height of most metals on ZnO is found to be 0.8 eV or lower, leading to high gate leakage in metal gate transistors. Much lower leakage currents were observed on devices in which ozone cleaning was performed prior to gate metal deposition. AES analysis showed the effect of the ozone cleaning was removal of carbon-related surface contamination. The rectifying contacts are found to be extremely stable against high energy proton irradiation, showing little degradation even after doses equivalent to more than 10 years in low earth orbit. The use of MOS gates increases the voltage swing and hence the reverse breakdown voltage. We will present the temperature dependence of FET dc performance and compare these to the results of MEDICI simulations of the expected performance.

H11.8

Electrophoretic Deposition of Stabilized Metal Oxide Nanocrystal Films. Shengguo Jia, Jing Tang, Joan Raitano, Christopher Cheng, Michael L. Steigerwald, Louis E. Brus, Siu-Wai Chan and Irving P. Herman; MRSEC, Columbia University, New York, New York.

Metal oxide nanocrystal films are of wide interest because of their intriguing magnetic, optical, mechanical, thermal and electrical properties. The tunability of the properties of nanocrystals with changing size makes it important to develop techniques for deposition of high quality films for potential applications. We use electrophoretic deposition to make smooth and robust metal oxide nanoparticle films, including those composed of ZrO₂, HfO₂, and CeO₂ nanocrystals that are synthesized using nonhydrolytic sol-gel and homogeneous precipitation methods. The mechanism for depositing these films is described, along with their morphology, and optical and mechanical properties. The deposition of multifunctional films composed of these metal oxide nanocrystals and other nanocrystals is also reported. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award No. DMR-0213574 and by the New York State Office of Science, Technology and Academic Research (NYSTAR).

H11.9

Nanostructured Oxide Films From Chemical Vapor Deposition. Sanjay Mathur, Shen Hao and Sven Barth; CVD Division, Leibniz Institute of New Materials, Saarbruecken, Germany.

Chemical synthesis of (nano)materials is based on the growth of solid-state structures from molecular scaffolds. Transformation of precursor compounds with bonding features that are also present in the solid-state material facilitates the construction of materials from well-defined building blocks. Although it is difficult to envisage a straightforward recipe, the molecule-derived-materials represent a viable strategy for the targeted synthesis of nanomaterials with different compositions and (micro)structures. If the intimate mixing of different elements present in the precursor persists until the desired ceramic or composite crystallizes, the typical problems of materials synthesis such as selective crystallization or segregation of constituents can be avoided. These issues are especially crucial for the gas phase synthesis of multi-component oxide films. To this end, we have developed various new metal-organic sources and examined their gas phase decomposition to deposit thin films with different compositions and morphologies. The nucleation and growth mechanism on different substrates were investigated in a broad temperature window to determine parameters for the phase selective deposition. The interplay between the rate of precursor delivery and substrate temperature was used to control the mean particle size in the films. The substrate temperature markedly influenced the morphology and Metal:Oxygen stoichiometry in the deposited films. In summary, the results illustrate that a predefined reaction chemistry of the precursors enforces a remarkable control over morphology, composition and particle size. A brief account on the synthesis, characterization and functional properties of different nanocrystalline oxide films will be presented. References 1. S. Mathur, V. Sivakov, H. Shen, and U. Werner Chem. Mater. 16(12), 2449, 2004. 2. S. Mathur, M. Veith, R. Rapalaviciute, H. Shen, G. F. Goya, W. L. Martins Filho and T. S. Berquo Chem. Mater. 16(10), 2004. 3. S. Mathur, M. Veith, T. Ruegamer, E. Hemmer and H. Shen Chem. Mater. 16(7), 1304, 2004. 4. S. Mathur and H. Shen in Encyclopedia of Nanoscience and Nanotechnology, Ed. H. S. Nalwa, American Scientific Publishers, 2004, Vol. 4, 131-191. 5. S. Mathur, H. Shen, N. Lecerf, A. Kjekshus, H. Fjellvag and G. F. Goya Adv. Mater. 14(19), 1405, 2002. 6. S. Mathur, M. Veith, H. Shen, S. Huefner and M. H. Jilavi Chem. Mater. 14(2), 568, 2002. 7. S. Mathur, M. Veith, V. Sivakov, H. Shen, V. Huch, and H. B. Gao Chem. Vap. Dep. 8(6), 277, 2002.

H11.10

First-Principles Calculations of F Centers in SrTiO₃ Perovskites.

Eugene Kotomin¹, Francesc Illas², Nuria Lopez², Javier Carrasco², Yuri Zhukovskij³, Yuri Mastrov¹ and Joachim Maier¹; ¹Phys.Chem., Max-Planck-Institut FKF, Stuttgart, Germany; ²Universitat de Barcelona, Barcelona, Spain; ³Institute for Solid State Physics, Riga, Latvia.

We studied the relaxed atomic and electronic structure as well as the formation and migration energy of the oxygen vacancy (F center) in the bulk and on the surface of SrTiO₃ perovskite crystals using several ab initio quantum chemical methods, supercells and slabs modeling different concentrations of defects. The calculations are performed using massive parallel version of the Crystal-2003 and VASP codes and supercells containing up to 240 atoms. We compare results of Density Functional Theory, Hartree-Fock, and DFT-HF hybrid methods. Optimisation of the lattice geometry around the F center shows the (100) expansion in the first coordination sphere (two nearest Ti atoms are displaced outwards the vacancy by 1.5-2 per cent of the lattice constant). The electronic density map indicates the redistribution of two electrons of the missing O atom between the vacancy and 3d AOs of the two nearest Ti atoms, in contrast to the usual F centers in ionic solids, where the two electrons are well localized in the vacancy.

H11.11

Growth of High-Quality Electron-Doped Infinite-Layer Superconducting Thin Films on Termination-Controlled DyScO₃ Substrates.

Shin-ichi Karimoto¹ and Michio Naito²; ¹Materials Science Division, NTT Basic Research Labs., Atsugi, Japan; ²Applied Physics, Tokyo Univ. of Agriculture and Technology, Koganei, Japan.

Infinite-layer (IL) cuprates are suitable for studying the physics of high- T_C superconductivity because of its simplest structure among the high- T_C cuprates. However, it is difficult to synthesize bulk single crystals of this compound because the IL structure can be stabilized only under high pressure. Another way to stabilize the IL phase is to utilize epitaxy. It is desirable to obtain high-quality epitaxial IL thin films, however, the efforts to grow high-quality IL thin films has been hampered by the lack of lattice-matched substrates. In this study, we adopted lattice-matched DyScO₃ substrates for the growth of electron-doped infinite-layer superconducting thin films (Sr_{1-x}La_xCuO₂) by molecular-beam epitaxy. The optimally-doped film seems to be free from strain, thus yielding a room-temperature resistivity as low as 75 $\mu\Omega\text{cm}$ and a low residual resistivity of 15 $\mu\Omega\text{cm}$ just above T_C . Also IL films showed a high T_C (42 K) comparable to that of the bulk value (43 K). We also found that an appropriate surface treatment of the DyScO₃ substrates is essential to grow high-quality IL thin films. The DyScO₃ substrates were annealed at 1100°C for 12 hours in flowing oxygen, and then etched using 0.1% HNO₃ with methanol. Without this surface treatment, the IL films often exhibited a two-step superconducting transition. We speculate that this is caused by the difference of the surface-termination of DyScO₃ substrates, which might affect to the initial growth of thin films.

H11.12

Electrical, Structural and Optical Properties of VO₂, V₂O₃ and Cr-Doped V₂O₃ Thin Films. Patricia A. Metcalf¹, Leonel P. Gonzalez⁴, Jacob O. Barnes⁴, Elliott Slamovich¹, Shekhar Guha³ and Jurgen M. Honig²; ¹Materials Engineering, Purdue University, West Lafayette, Indiana; ²Chemistry, Purdue University, West Lafayette, Indiana; ³Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson AFB, Ohio; ⁴Materials and Manufacturing Directorate, Anteon Corp., Dayton, Ohio.

VO₂, V₂O₃ and Cr-doped V₂O₃ thin films were prepared by the reduction of sol-gel derived vanadium oxide films. The films were grown on oriented quartz and sapphire substrates. Examination by x-ray diffraction, SEM, TEM, and atomic force microscopy showed the films to be comprised of highly oriented grains. Optical transmission measurements in the infrared region and electrical conductivity measurements revealed phase transitions characteristic of the bulk vanadium oxide materials. The phase transition in the V₂O₃ films occurs at a critical temperature of about 150 K and in the VO₂ films at a critical temperature of about 340 K, with the electrical conductivity changing by about 6 and 3 orders of magnitude, respectively. Vanadium oxide films are currently used in temperature sensing devices and are proposed for use in optical switching devices and sensors.

H11.13

Magnetic and Structural Characterization of Magneto-electric Epitaxial Oxide Multilayers.

Rajesh Vilas Chopdekar^{1,2} and Yuri Suzuki²; ¹School of Applied Physics, Cornell University, Ithaca, New

York; ²Department of Materials Science and Engineering, UC Berkeley, Berkeley, California.

In an effort to engineer a material that couples magnetic and electrical responses, we are studying bilayers and multilayers composed of magnetostrictive cobalt ferrite (CoFe₂O₄) and piezoelectric barium titanate (BaTiO₃) epitaxial thin films. The strain-mediated coupling of the magnetomechanical response of the cobalt ferrite layer with the electromechanical response of the barium titanate layer is of interest for sensor and transducer applications. Pulsed laser deposition allows for growth of the spinel and perovskite structure materials while maintaining stoichiometry of each layer as well as low surface roughness of the stack as a whole. As a first step, we have optimized growth of cobalt ferrite, barium titanate, and the highly conductive oxide strontium ruthenate (SrRuO₃) as individual films grown on strontium titanate (SrTiO₃) single crystalline substrates. Layers of strontium ruthenate will be deposited at the top and bottom of the multilayer to facilitate electrical contact to the magneto-electric stack. Rutherford Backscattering Spectrometry analysis of indicates that these films match the stoichiometry of the corresponding target materials. X-ray diffraction shows that the films are epitaxial both on strontium titanate and barium titanate single crystalline substrates. In addition, atomic force microscopy confirms a low (<2nm) rms surface roughness of the thin films. As a model system, a single layer of cobalt ferrite grown on a single crystalline barium titanate substrate was examined in detail to probe the strength of the magneto-electric coupling. Through substrate-film coupling, the magnetic response of the cobalt ferrite is sensitive to changes in epitaxial misfit strain imposed by the substrate. This strain can be tuned by both temperature and an applied electric field across the piezoelectric substrate. Barium titanate undergoes numerous phase transitions as a function of temperature: cubic structure above 410K, tetragonal above 290K, orthorhombic above 190K (monoclinic in a pseudo-cubic setting) and rhombohedral at lower temperatures. Therefore the surface lattice can be dynamically changed in an attempt to significantly alter the ground state of the epitaxial film. A change in magnetization of -30% was observed in the cobalt ferrite between 300K and 100K due to the large strain changes from the phase transitions of barium titanate.

H11.14

Photoinduced Resistivity Changes in Bi_{0.4}Ca_{0.6}MnO₃ Thin Films.

Vera N. Smolyaninova¹, M. Rajeswari¹, Robert Kennedy¹, M. Overby¹, L. Aldaco¹, S. E. Lofland², Z. Li³ and R. L. Greene³; ¹Dept. of Physics, Astronomy and Geosciences, Towson University, Towson, Maryland; ²Department of Chemistry and Physics, Rowan University, Glassboro, New Jersey; ³Department of Physics, University of Maryland, College Park, Maryland.

Doped rare-earth manganites R_{1-x}A_xMnO₃ (R being a trivalent rare earth and A being a divalent alkaline-earth ion) exhibit a large diversity in electronic, magnetic, and orbital states due to the complex interplay of the corresponding degrees of freedom. Charge-ordered (CO) state of manganites can be drastically modified by application of magnetic field, electric field, or electromagnetic wave irradiation leading to insulator to metal transition. A photoinduced insulator to metal transition in manganese oxides is especially interesting from the point of view of creating photonic band-gap materials, which allow control of dispersion and propagation of light. Recently reported permanent photoinduced changes in single crystal Bi_{0.3}Ca_{0.7}MnO₃ [1] support the feasibility of optical recording in manganites. Since visible light penetrates into Bi_{1-x}Ca_xMnO₃ over a rather short length, thin films of this material are necessary for photonic device applications. We report a study of photoinduced resistivity changes in thin films of charge-ordered Bi_{0.4}Ca_{0.6}MnO₃ manganites with CO temperature around room temperature. Effects of film thickness and choice of substrate on the photoinduced effects will be presented. Dynamics of photoinduced changes will be discussed. This work is supported by NSF, Grant No. DMR-0348939, and DMR-0116619. [1] I. I. Smolyaninov, V. N. Smolyaninova, C. C. Davis, S-W. Cheong, and R. L. Greene, Phys. Rev. Lett. 87,127204 (2001).

H11.15

Preparation and Characterization of Metallorganic Chemical Vapor Deposited Nickel Oxide and Lithium Nickel Oxide Thin Films Using Single Solid Precursors.

Ezekiel Oladele Ajayi¹, Marcus A. Eleruja², G. O. Egharevba³ and C. Jeynes⁴; ¹Physics, Obafemi Awolowo University, Ile-Ife, Nigeria; ²Physics, Obafemi Awolowo University, Ile-Ife; ³Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria; ⁴Department of Electronic and Electrical Engineering, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom.

ABSTRACT. Thin films of undoped Nickel Oxide and Lithium Nickel Oxide thin films were deposited through the pyrolysis of Nickel Acetylacetonate and Lithium Nickel Acetylacetonate respectively at temperature range 350 degree celcius to 420 degree celcius . The

single solid source precursors, Nickel Acetylacetonate and Lithium Nickel Acetylacetonate was prepared and characterized using Energy Dispersive X-Ray Fluorescence (EDXRF) and Infrared Spectrophotometry. The composition, optical and electrical properties of the prepared thin films were analysed using a variety of techniques, such as Rutherford Backscattering Spectroscopy (RBS), Energy Dispersive X-Ray Fluorescence (EDXRF), UV-Visible Spectrophotometry and van der Pauw conductivity method. The abundance of the metals in the prepared thin films did not reflect the ratio of the metals in the precursor but was found to depend on the deposition temperature. The energy gaps of the undoped nickel oxide and lithium nickel oxide thin films are 3.5 eV and 2.05 eV respectively. The electrical conductivity showed that lithium nickel oxide thin film has an activation energy of 0.11 eV. The conduction was explained by hopping mechanism.

H11.16

Preparation and Characterization of Metallorganic Chemical Vapour Deposition Chromium Oxide and Lithium Chromium Oxide Thin Films Using Single Solid Precursors.

Ezekiel Oladele Ajayi¹, Marcus A. Eleruja¹, O. Osasona², Olumide Oluwole Akinwunmi¹, G. O. Egharevba³ and C. Jeynes⁴; ¹Physics, Obafemi Awolowo University, Ile-Ife, Nigeria; ²Electronic and Electrical Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria; ³Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria; ⁴Electronic and Electrical Engineering, University of Surrey, Guildford, Surrey GU2 7XH.

Thin Films of Chromium oxide and Lithium Chromium Oxide were deposited on to sodalime glass substrates at a temperature of 420 degree Celsius by the pyrolysis of Chromium Acetylacetonate and a mixture of Lithium hydroxide/Chromium Acetylacetonate (1:2) respectively, using Metallorganic Chemical Vapour Deposition (MOCVD) technique. The Chromium oxide thin films were also prepared through a similar method by the pyrolysis of The prepared thin films were characterized by using Rutherford Backscattering Spectroscopy (RBS) and Ultraviolet-Visible Spectrophotometry. The stoichiometry of the prepared films was found to be Li:Cr:O = 36:18:46. A direct allowed band gap of 3.42 eV was obtained for Lithium Chromium Oxide thin films from the UV-Visible spectrum taken with a blank sodalime substrate in the path of the reference beam. The band gap value obtained, showed a narrowing of the band gap obtained for the Chromium oxide thin films.

H11.17

Visible electroluminescence of doped YAlO₃ single crystals.

Masanori Ando¹, Toru Sakaguchi¹, Akio Yamanaka², Yutaka Kawabe² and Eiichi Hanamura²; ¹Photonics Res Inst, Ntl Inst of Adv Ind Sci & Tech (AIST) and CREST, JST, Ikeda, Osaka prefecture, Japan; ²Faculty of Photonics Sci & Tech, Chitose Inst of Sci & Tech and CREST, JST, Chitose, Hokkaido prefecture, Japan.

Perovskite-type transition-metal oxides (RAlO₃ (R=Y, La, Nd, Sm, etc.)) attract much interest due to their unique property and potential applicability in opto-electronics. The unique property comes from the large oscillator strength of the charge-transfer excitation reflecting the large overlap-integral between the transition-metal 3d-orbital and the oxygen 2p sigma-orbital. The charge-transfer excitation, photo-excited electrons and holes can propagate in the perovskite-type oxide crystals. We have already reported that oxygen-deficient YAlO₃ and LaAlO₃ single crystals show strong photoluminescence (PL) in blue and green region. The PL originates from the excited state formed at oxygen defect site. The PL can be controlled by doping ions with different valence number at R³⁺ sites. The oxygen vacancies are stabilized by the doping. The large mobilities of photo-excited electrons and holes in these perovskite crystals make us expect to observe electroluminescence (EL) which will lead to the light emitting diode (LED). In this paper we report the visible EL of doped YAlO₃ crystals for the first time. Two types of perovskite single crystals with low electrical conductivity, 0.1%Ti-YAlO₃ and 1%Ti-YAlO₃ were prepared by floating-zone method from the mixture of Y₂O₃, Al₂O₃ and TiO₂ powders. Each perovskite single crystal rod was cut into a disc. Thin films (thickness=0.1-0.2 mm) of the crystals were prepared by polishing the surface of the discs. The Au and Al electrodes were formed on the surface and backside of the thin oxide crystal film by DC sputtering deposition and by vacuum evaporation, respectively. The electrodes were connected to a high voltage AC power supply equipped with a function generator. Both the 0.1% Ti-YAlO₃ and 1% Ti-YAlO₃ films showed green EL by applying AC electric field stronger than about $\pm 3 \times 10^6$ V/m in the frequency range from 0.2 Hz to several hundred Hz. The EL was observed when applying rectangular AC waveform, on the other hand, no EL was observed by using sine and triangular AC waveforms. This suggests that the fast change of electric field is needed for the EL emission of these oxide crystal films. The EL spectrum of each film was narrower than the PL spectrum. The mechanism of the EL is still not clear, but a possibility is that the electrons in the oxide crystals are accelerated by the high

electric field and excite the oxygen vacancy luminescent centers by impact, followed by the radiative transitions of the excited electrons to the ground state.

H11.18

Study of Low Temperature Process for Transparent Conductive CdxSnyOz Films by Combinatorial Material Library Method. Tien-Heng Huang, Ren-Jye Wu, Wen-Hsuan Chao, Lih-Ping Wang, S.-H. Wang and Hung-Chiao Cheng; Polymer Physics and Analytical Department, Union Chemical Laboratories, ITRI, Hsinchu, Taiwan.

Transparent conductive oxides (TCOs) attract a lot of fundamental and technological interest recently. Their high conductivity and optical transmittance in the visible range of wavelength are very useful in various industries. Most TCOs need to be synthesized and/or annealed at high temperature to improve the electrical and optical properties. However, producing high quality TCO films at low temperature becomes more important for using flexible substrates. The ternary TCO of CdxSnyOz, were studied with a combinatorial continuous-compositional-spread method in this research. A custom-built radio-frequency (RF) sputtering system was used to synthesize CdxSnyOz material libraries at room temperature. Different sputtering conditions were studied. The CdxSnyOz films were investigated by various characterization techniques. The electrical resistance phase diagram of CdxSnyOz compounds was obtained. The electrical resistance of CdxSnyOz film was lower than $1.5 \times 10^{-4} \Omega\text{-cm}$ and the optical transmittance greater than 80% even at low sputtering temperature. The structure of CdxSnyOz compounds was studied by X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). XRD patterns indicate that the structural characteristics of CdxSnyOz compounds varied from amorphous to crystalline state, depending on the position of material libraries. Both amorphous and crystalline CdxSnyOz films could exhibit low electrical resistivity and high optical transmittance. The carrier concentrations and mobility depended on the amount of doped Sn. The possible explanations for the electrical conductivity of various compositional and structural states were discussed. In addition, UV/visible transmittance spectra show that the UV transmittance of CdxSnyOz films could be improved by changing the amount of doped Sn. The reasons caused the change of optical transmittance are also discussed.

H11.19

Thermodynamically Stable SrTiO₃ (100) Substrate with Perfect TiO₂ Termination. Tsuyoshi Ohnishi¹, Hiroshi

Kumigashira², Keisuke Shibuya¹, Masaharu Oshima², Hideomi Koinuma³ and Mikk Lippmaa¹; ¹The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba, Japan; ²Department of Applied Physics, The University of Tokyo, Tokyo, Japan; ³Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Nowadays, BHF treated SrTiO₃ (100) substrates are commercially available and widely used for various thin film growth toward heterointerface synthesis, superlattice fabrication and so on. The chemical etching makes the atomically flat surface with TiO₂ termination. It is probable that this chemically cleaved surface, possibly having an atomic arrangement of bulk crystal, is unstable thermodynamically. As the proof, the surface step-and-terrace structure reorganizes when the substrate is heated up to the film growth temperature. By taking advantage of this thermal atomic relaxation, well-defined surface with step edges evenly distributed can be obtained by high temperature annealing at, say 1000 °C, in 10⁻⁶ Torr of oxygen. This atomic relaxation process is, however, always accompanied with SrO uprising to the surface, confirmed by ion scattering spectroscopy. The SrO starts emerging and saturates at such a low temperature as 300-400 °C, resulting in a mixed termination of TiO₂ and SrO, although the segregated SrO is still minority (less than 30 % of surface coverage). Ion scattering and photoemission spectroscopy revealed that this SrO was not in the perovskite crystal lattice but floating on the surface as a certain form, affecting the properties of the film deposited on the surface, e.g. incorporated in the film and disturbing accurate doping control in La_{1-x}Sr_xMnO₃, for example. This time, we could successfully synthesize the thermodynamically stable, ideal SrTiO₃ (100) substrate with 100 % TiO₂ termination. This surface is thermally very stable, and the well-defined step-and-terrace structure and the perfect TiO₂ termination sustain under high temperature heating.

H11.20

Abstract Withdrawn

H11.21

Electrochromic Films Deposited by Laser Assisted Molecular Beam Deposition. Robert L. DeLeon¹, Nehal S. Chokshi¹, Gary S. Tompa¹ and P. V. Ashrit²; ¹AMBP Tech Corp., Amherst, New York;

The benefits of realizing an electrochromic module deposited onto transparent plastics such as poly (ethylene terephthalate) PET would reduce costs and weight while enabling the realization of flexible electrochromic modules. The main challenge in realizing a flexible module is the limited process temperatures of the PET substrate while depositing the WO₃, V₂O₅ and ITO films. Utilizing a unique technique dubbed LAMBD (Laser Assisted Molecular Beam Deposition), WOX films have been successfully deposited at room temperature. The LAMBD process is an improvement over Pulsed Laser Deposition. The unique feature of LAMBD is the concurrent pulsing of a reactive gas with the laser ablation of Tungsten to create Tungsten Oxide clusters. Furthermore, the clusters are cooled through the adiabatic expansion process enabling deposition onto plastic substrates. WOX room temperature grown films have been deposited under various conditions. The intercalation of lithium has been carried out on selected films utilizing a dry (in vacuo) technique or the standard electrochemical process. SEM, XPS and optical characterization have been used to characterize the morphology, chemistry and electrochromic properties of the deposited and Lithium intercalated films. The growth parameters of oxygen pulse pressure and laser pulse energy, the post deposition treatments of laser annealing and furnace annealing are correlated to morphology, chemistry and electrochromic properties of the resultant films.

H11.22
Electro-Optic Properties of Epitaxial BaTiO₃ Thin Films and Their Dependence on Domain Structure. Anthony L. Meier, Pingsheng Tang, David J. Towner and B. W. Wessels; Materials Science and Engineering, Northwestern University, Evanston, Illinois.

The multi-functional ferroelectric oxide BaTiO₃ is an excellent candidate for broadband electro-optic modulators due to its large electro-optic coefficient. This large electro-optic coefficient opens the way for integration of electro-optic modulators with device lengths of a few millimeters with low driving voltages. The electro-optic properties at 1.55 μm wavelength were measured in epitaxial BaTiO₃ thin films prepared by MOCVD and related to the ferroelectric domain structure. The electro-optic response of BaTiO₃ is given by the third-rank linear electro-optic tensor r_{ijk} which due to symmetry of the permittivity tensor is usually written in Voigt notation as r_{ij} . Measurements of r_{eff} were made for propagation in both the $\langle 100 \rangle$ and the $\langle 110 \rangle$ directions using a waveguide structure. In both cases the electric field was in the plane of the film perpendicular to the propagation direction. Electro-optic coefficients as large as 160 pm/V were measured in thin films for light propagation along the BaTiO₃ $\langle 100 \rangle$ direction while the measured r_{eff} values for propagation along the $\langle 110 \rangle$ direction are as high as 360 pm/V. These coefficients are as much as an order of magnitude larger than that of LiNbO₃ and to the best of our knowledge are the largest reported values for any material system measured in the waveguide geometry. Films were polydomain as determined by x-ray diffraction. Both the BaTiO₃(002) and (200) peaks were observed indicating the presence of both *a* and *c*-domains. In analyzing the electro-optic properties of a polydomain structure, contributions from the different domain variants must be taken into consideration. The larger r_{eff} values observed for propagation along the BaTiO₃ $\langle 110 \rangle$ direction are attributed to an r_{42} contribution from all four *a*-domain variants as opposed to a contribution from the r_{42} component from just two of the *a*-domain variants for propagation along the BaTiO₃ $\langle 100 \rangle$ direction. Furthermore, the geometry of the $\langle 110 \rangle$ oriented waveguides allows for in-plane poling of all of the *a*-domain variants with improved stability of the poled domain structure relative to that of the $\langle 100 \rangle$ waveguide. In the $\langle 100 \rangle$ oriented waveguides, application of a bias does not result in poling of the *a*-domain variants that contribute an r_{42} component to the measured r_{eff} . Only those *a*-domains that contribute an r_{13} and an r_{33} component are poled by an applied bias. The bias dependence of r_{eff} was investigated for both $\langle 100 \rangle$ and $\langle 110 \rangle$ oriented waveguides. The measured coefficient, r_{eff} , was typically bias dependent. The bias dependence of r_{eff} was attributed to its effect on the domain structure. The relationship between the r_{eff} and the relative areal domain fractions and r_{eff} and the tetragonality were investigated. Temperature dependent x-ray diffraction was used to relate the temperature dependence of r_{eff} to the domain structure. Using the temperature dependent x-ray data, a preliminary domain stability map is presented.

H11.23
Optical Properties of Hafnium Oxide Films Grown by Laser Assisted Molecular Beam Deposition. Lianchao Sun¹, Robert L. Deleon², Nehal S. Chokshi², Gary S. Tompa² and James F. Garvey²; ¹Sun International (USA), Acton, Massachusetts; ²AMBP Tech Corporation, Amherst, New York.

Hafnium oxide thin films have successfully been deposited on silicon substrates by Laser Assisted Molecular Beam Deposition (LAMBD).

The films were grown at the substrate temperature of 300 °C and 27 °C at process pressure 1 Torr. The LAMBD process uses a pulsed laser to create hot plasma to ablate material from a rotating hafnium target rod. Oxygen was used as the carrier gas to entrain the ablated material in a cooling expansion process. The choice of carrier gas exerts considerable control over the process; it can control both the chemical composition and the temperature of the ablation plasma.. Depositions yielded controlled thickness of 5 nm to 100 nm of stoichiometric HfO₂ films. In this work the film microstructure will be compared to the microstructure of films deposited by LAMBD at room temperature. Optical characterization of high dielectric constant (k) hafnium oxide (HfO₂) was performed by means of spectroscopic ellipsometry (SE). The relationship between microstructure and their optical properties will be discussed in this paper.

H11.24
Hydrogen and Ozone Gas Sensing Using Multiple ZnO Nanorods. Byoung Sam Kang¹, Fan Ren¹, Young Woo Heo², Brent Gila², David Norton² and Stephen Pearton²; ¹Chemical Engineering, University of Florida, Gainesville, Florida; ²Materials Science and Engineering, University of Florida, Gainesville, Florida.

ZnO nanorods grown by site selective Molecular Beam Epitaxy show current-voltage characteristics that are sensitive to the presence of hydrogen or ozone in the measurement ambient for temperatures as low as 112 degC for hydrogen or room temperature for ozone. The sensitivity to hydrogen increases sharply with temperature and multiple nanorods contacted at both ends by Ohmic electrodes show currents of 10-8A at 200 degC and a differential current change of 18% when changing from a pure nitrogen ambient to 10% hydrogen in nitrogen. The nanorods are able to detect small concentrations (3% by flow) of ozone in nitrogen, with changes in current of 10-7 A at 25 degC. The sensitivity was 18% for ozone at room temperature. The nanorods also show a strong response to above bandgap illumination with ultraviolet light.

H11.25
Observation of electrical transition time of the metal-insulator transition for VO₂ thin films. Byung Gyu Chae, Doo Hyeon Youn, Hyun Tak Kim and Kwang Yong Kang; Basic research laboratory, ETRI, Daejeon, South Korea.

VO₂ thin films undergo a metal-insulator transition (MIT) near 67 °C with abrupt changes in the electrical resistivity and the infrared-transmittance. These properties make VO₂ films useful for applications to electrical and optical switching devices. In this research, we observe electrical transition time of the MIT for VO₂ films with switching pulse. VO₂ films were successfully deposited on Al₂O₃ substrate by pulsed-laser deposition with KrF excimer laser. Pure VO₂ films were obtained in the range of 55 – 60 mTorr in an Ar + 10% O₂ ambient. Two Au/Cr electrodes with 5 μm interval were patterned on the film by lift-off method. The resistivity of (100)-oriented VO₂ films abruptly changes with the order of 10⁴ at 65 °C. An abrupt increase of current appears at an MIT electric field (or voltage) when an electric field (or voltage) is applied to the film. When pulses with few μs widths and a voltage over the MIT voltage are applied to the films, the current waveforms due to MIT are observed with the applied pulses. And the transition time of MIT is found to be about few ns.

H11.26
Abstract Withdrawn

H11.27
Electrical Conduction Control of ZnO Films Prepared by Pulsed Laser Deposition in Ozone Ambient. Kenji Ebihara, ¹Electrical and Computer Engineering, Kumamoto University, Kumamoto, Japan; ²Electrical Engineering, Sasebo National College of Technology, Sasebo, Japan.

Kenji Ebihara, San-Moo Park, Koudai Tokumasu, Tomoaki Ikegami, Tamiko Ohshima* Graduate School of Science and Technology, Department of Electrical and Computer Engineering, Kumamoto Univ., 2-39-1 Kurokami, Kumamoto 860-8555, JAPAN (*) Department of Electrical Engineering, Sasebo National College of Technology, Okishin 1-1, Sasebo, Nagasaki 857-1193, JAPAN ZnO has attracted much attention because of the good optical, electrical and piezoelectrical properties. For development of optical devices based on ZnO, it is necessary to prepare both p- and n-type ZnO films. However, ZnO has suffered from major disadvantage of lack of reproducible p-type materials. Electrical conduction of ZnO films has been controlled by several techniques such as doping by acceptor impurities (N, P and As) and co-doping with Ga (donor) in NH₃, N₂, N₂O, NO₂. We have developed the ozone and nitric monoxide (NO) radical assisted pulsed laser deposition for preparation of intrinsic p-type ZnO films. Radical oxygen incorporation into the deposited ZnO is shown to be effective to prepare the p-type

conduction which was confirmed using the Seebeck coefficient measurement. It is shown that ozone concentration between 3000ppm and 5000ppm in 200mTorr O₂ is appropriate condition for p-type ZnO film preparation. The ZnO films using present KrF PLD process were deposited at a laser fluence of 2 J/cm² on the quartz substrate heated to 400°C. The electrical properties for the p-type ZnO films obtained here were electrical resistivity of 1.9-7.3 ohm-cm and Seebeck coefficient from 7.9 to 62 μV/K. New type pulsed laser ablation process (separated pulsed laser deposition :SPLD) will be proposed for oxide thin film preparation using ozone and NO. In the SPLD consisting of the ablation chamber and the deposition chamber with the orifice, the oxide films can be deposited independently on the ablation chamber conditions such as pressure and ambient gas. LiMn₂O₄, organic light emitting films (Alq₃, TPD) as well as ZnO were deposited.

H11.28

Imaging Local Surface Potential during Photocatalytic Reaction on TiO₂ Single Crystal Surfaces. Yuhei Miki¹,

Toshihisa Horiuchi¹, Kenji Ishida¹, Kei Kobayashi², Hirofumi Yamada^{1,3} and Kazumi Matsushige^{1,2}; ¹Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan; ²International Innovation Center, Kyoto University, Kyoto, Japan; ³Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Kyoto, Japan.

Titanium dioxide (TiO₂) is attracting many researchers' attentions for its photocatalytic properties such as photo-induced oxidation power and high hydrophilicity since 1972 when photo-induced water splitting on TiO₂ electrode was discovered. Its photocatalytic properties have been extensively studied in a wide variety of research fields for industrial applications such as water splitting, antifogging, and environmental purification of air and water. Although these features have been investigated from various standpoints, fundamental mechanisms of photocatalytic reactions have not been fully understood yet. In this study, in order to understand the photo-induced reactions between adsorbed molecules and induced holes and electrons on TiO₂, we employed Kelvin-probe force microscopy (KFM) which is a variation of atomic force microscopy capable of imaging local surface potential distribution. We performed surface potential imaging on rutile-type TiO₂(110), (100), and (001) single crystal surfaces. A half of each sample surface was coated with 40-nm-thick metal (Au or Pt). In general, the photocatalytic activity of TiO₂ is increased by depositing metals such as Pd and Pt on its surface, because the deposited metals expedite the transport of photo-generated electrons to reducible molecules and thus improve the charge separation efficiency. KFM observation was conducted both in a vacuum condition and in ambient. We repeatedly scanned a 5μm×5μm area including TiO₂ and metal regions at a scan rate of 45 minutes/image. During scanning, UV light from a high-pressure Hg lamp was irradiated on the sample through a heat absorption filter to avoid any heating of the sample. We observed an increase of the surface potential by several hundred mV on TiO₂ region immediately after the irradiation, which might be understood by the formation of space charge layer due to charge separation caused by transfer of photo-excited holes and electrons toward the surface and the bulk, respectively. Furthermore, we observed an increase the surface potential on the Au electrode by nearly 200 mV for Au/TiO₂(110) and Au/TiO₂(100) samples in ambient, which was not seen for Au/TiO₂(001). This increase can be explained by the assumption that the protons (H⁺) were separated from neutral hydroxyl radicals (·OH) by photo-induced electrical potential on TiO₂. This result might indirectly confirm that H⁺ and ·OH pairs were created at the first stage in the photocatalytic process. Such a potential increase was not seen on Pt surface in ambient, which might further confirm the reduction of protons to molecular hydrogens. On the other hand, we also observed a large potential increase by about 3 V on Pt electrode in vacuum. This result might be applied to a high-speed fuel conversion of methanol or ethanol to hydrogen in a fuel cell.

H11.29

Bi₂MoO₆-Based Natural-Superlattice of Bismuth-Layer-Structured Ferroelectric Thin films. Akira Shibuya¹, Minoru Noda¹, Masanori Okuyama¹ and Keisuke Saito²; ¹Department of Systems Innovation, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan; ²BRUKER AXS K.K., Yokohama, Kanagawa, Japan.

Recently, natural-superlattice of bismuth-layer-structured ferroelectric (BLSF) materials has attracted much interest as polarization enhancement is expected by structural modification of pseudo-perovskite layers through Bi₂O₂ layer. The crystal structures of BLSF are generally formulated as (Bi₂O₂)²⁺(A_{m-1}B_mO_{3m+1})²⁻ and m is the number of BO₆ octahedra in the pseudo-perovskite blocks. Basically, crystal structures of natural-superlattice BLSF are intergrowths consisting of one-half of unit cells of sequential m number BLSF materials such as m=1-2, 2-3, 3-4. Two kinds of

perovskite blocks are, in turn, sandwiched between Bi₂O₂ layers. In this paper, we report on Bi₂MoO₆ (BM) (m=1)-based natural-superlattice-structured BLSF thin films, which are Bi₂MoO₆-Bi₃TiNbO₉ (BM-BTN)(m=1-2) and Bi₂MoO₆-Bi₄Ti₃O₁₂ (BM-BIT) (m=1-3). BM-BTN(m=1-2) and BM-BIT(m=1-3) thin films have been prepared on SrTiO₃ (STO) (001) single crystal and Pt/TiO₂/SiO₂/Si substrates by pulsed laser deposition (PLD) method. The c-lattice constant (6.73 nm) of the epitaxial BM-BTN (m=1-2) film on STO is very close to the value (6.54 nm) of the superlattice structure of one BM unit cell and two BTN unit cells. Polycrystalline BM-BTN (m=1-2) thin film on Pt/TiO₂/SiO₂/Si substrate deposited at 450°C and post-annealed at 650°C shows long-range superlattice of 15.5 nm iterative layer which corresponds to 50 unit cells consisting of (113)-oriented BM (m=1) and (115)-oriented BTN (m=2). On the other hands, the c-lattice constant (2.47 nm) of BM-BIT (m=1-3) is very close to the value (2.45 nm) of the superlattice structure consisting of one-half BM (m=1) unit cell and one-half BIT (m=3) unit cell. This natural-superlattice structure consisting of non-sequential m number BLSF materials such as m=1-3 has never been reported before. Therefore, the BM-based natural-superlattice structures have unique crystal properties different from conventional natural-superlattice structures. BM(m=1) is widely recognized not only as a ferroelectric material but also as a catalyst for use in selective oxidation. From this viewpoint, unusual BM-based natural-superlattice structures may be attributed to catalytic property of BM(m=1). The remanent polarization of polycrystalline BM-BTN (m=1-2) is estimated to be 40 μC/cm². Polycrystalline BM-BIT (m=1-3) thin film on Pt/TiO₂/SiO₂/Si substrate deposited at 450°C and post-annealed at 650°C is found to include both BIT (m=3) and BM-BIT (m=1-3) phases from XRD pattern. The polycrystalline BM-BIT (m=1-3) film has much larger remanent polarization (2P_r = 54 μC/cm²) than polycrystalline BIT (m=3) thin film on Pt/TiO₂/SiO₂/Si substrate prepared by PLD under the same process condition. The P_r and coercive field (E_c) of the P-E hysteresis loops show good saturation behavior for the applied field. BM-based natural-superlattice-structured BLSF thin films have not only unique crystal properties but also good ferroelectric properties.

H11.30

Growth of Separated and Oriented ZnO Nanorods by Chemical Vapor Deposition Combined with Laser Ablation.

Takashi Kimpura, Shinya Sasaki, Tomomasa Satoh and Takashi Hirate; Electrical, Electronics and Information Engineering, Kanagawa University, Yokohama, Japan.

ZnO is an attractive II-VI compound semiconductor material for various optoelectronic devices due to its wide band gap of 3.37 eV at room temperature and its large excitonic binding energy of about 60 meV. Recently, growth of various nano-structures of ZnO such as nanorod, nanobelt, nanowall, etc. has been reported. In our previous works on growth of ZnO nanorods, we have obtained fabrication of ZnO nanorods with a flat tip oriented vertically to Si(111) substrate and have reported on possible application of the nanorods to electroluminescent devices. In this case, the ZnO nanorods have a continuous ZnO layer under separated ZnO nanorods. It was revealed through our later study that the ZnO layer which exists between substrate and ZnO nanorods is desirable to be eliminated to obtain excellent electroluminescent characteristics. In this paper we report on the fabrication method and experimental results to obtain ZnO nanorods without the ZnO layer. The obtained nanorods are vertically oriented to Si(111) substrate are separated to each other and grow directly from substrate. The fabrication method in this study is a low pressure thermal chemical vapor deposition (CVD) combined with laser ablation, which method is almost same method used in our previous study except that the laser-ablated material is different. In the previous study Er is used as material for laser ablation. The other several materials are investigated in this study and it is found that a sintered ZnO pellet is most promising to obtain the ZnO nanorods without a continuous ZnO layer. Metal Zn vapor and O₂ gas are used as precursors to synthesize ZnO and N₂ is used as carrier gas. A sintered ZnO pellet is placed near a Si(111) in a deposition chamber and ablated by a pulsed Nd:YAG laser beam (wavelength =1.064 μm, pulse width = 8 ns, frequency of laser = 10 shots/sec) during growth of ZnO. When the laser ablation is not used, randomly oriented ZnO nano whiskers only are grown and oriented ZnO nanorods are not grown. The growth conditions to obtain the ZnO nanorods described above are as follows. O₂ flow rate is 1.5 sccm. The growth temperature is 500 °C. The growth pressure is 40 Pa. The laser energy is 0.12 J/shot and the laser-irradiated area on the sintered ZnO pellet is 0.13 mm². The SEM analysis showed that the obtained ZnO nanorods are completely separated to each other without any continuous ZnO layer, and grown approximately normal to a Si(111) substrate. The tip of ZnO nanorods is flat. When a growth time is 15 min, the diameter of nanorod is about 180 nm and the height is about 750 nm. The average separation between adjacent ZnO nanorods is about 500 nm.

H11.31

Preliminary Infrared Analysis of Thin-Film Neodymium

Nickelate. David Canchal Arias, Robert M. Bowman and Paul Dawson; School of Maths & Physics, Queen's University of Belfast, Belfast, United Kingdom.

Neodymium nickelate is a rare earth perovskite that undergoes a metal-insulator transition with temperature. Here we report infrared measurements on thin film NdNiO₃ for the first time and relate these to the results of other characterisation methods. The films were grown on either NdGaO₃ (110) or LaAlO₃ (100) substrates by pulsed laser deposition from a sintered target formed from a mix of NiO and Nd₂O₃ powders. XRD analysis confirms good epitaxial film growth in the (001) orientation while EDX measurements show very good conformity to the ideal 1:1 Nd:Ni stoichiometry.

Resistance-temperature (R-T) measurements, taken using a 4-probe technique, show that the films on the gallate and aluminate substrates undergo a resistivity change factor of 25 and 120 respectively across the transition. However, these factors are somewhat less than for bulk specimens (up to 1000) and for high quality films grown previously in our laboratory (factors of 150 and 500 respectively). In addition, Arrhenius plots show rather low activation energies, e.g. 291 meV on cooling and 187 meV on heating for the films on the gallate substrates. Attenuated total reflection (ATR) curves taken at wavelength 3.392 μm using a lab-built in-vacuo prism coupler (prism/coupling gap/sample configuration with a remotely adjustable coupling gap) are theoretically modelled to yield a dielectric function of $8.1 + i 12.7$ at 300 K and $11.0 + i 9.1$ at 100 K. Fourier transform spectroscopy (FTS) in the range 100 to 500 cm⁻¹ shows absorption features centred at 190 cm⁻¹ and 325 cm⁻¹ at 100 K, in good agreement with FT spectra obtained by other workers on bulk specimens. Although these features are substantially reduced at 300 K, they do not disappear and the FT spectra retain a fair amount of detailed structure. The IR data thus confirm the message of the R-T measurements that for these samples the metal-insulator transition is not fully developed; they reflect the characteristics of a semiconducting state in which the charge transfer gap between the occupied O 2p valence state and the unoccupied Ni 3d conduction band is not filled at higher temperature. Thus, while the dielectric function determined by ATR moves in the direction of more metallic character at high temperature there is no sign reversal of the (positive) real part that would denote a good metallic state. Likewise the retention of structure in the FT spectra contrasts with bulk spectra at 300 K that vary monotonically with wavenumber, as expected for a well-developed metallic state. Indeed, the suppression of the metal-insulator transition is arguably more marked in the optical data than in the case of dc measurements, so although the R-T results are not as good as hoped for, the efficacy of infrared ATR and FTS characterisation is confirmed.

H11.32

Thick Films of In₂O₃/SiO₂ as Optical Gamma Radiation

Sensors. Khalil Ibrahim Arshak, Jonathan Molloy and Olga Korostynska; Computer and Electronic Engineering, University of Limerick, Limerick, Limerick, Ireland.

Ionising radiation arises from both natural and man-made sources and is used in numerous technological applications. High-energy gamma radiation changes the physical properties of the materials they penetrate, so an adequate dosimetry is highly essential. In this work, the effect of gamma radiation on the optical properties of In₂O₃ and SiO₂ thick films were explored because of their importance for the design of compact and cost-effective dosimeter devices. Reactivity of oxide materials is closely connected to the presence of oxygen vacancies, which are known as colour centres or F centres [2]. It is believed that ionising radiation causes structural defects leading to their density change on increase in exposure to gamma rays [3]. These changes affect both the optical and the electrical properties of the materials. Mixing oxides in various proportions can control the properties of semiconductor films [4, 5]. It was reported that films of SiO₂ have an open structure which contains a large number of dangling bond centres and the density of these centres decreases as the indium oxide content is increased in the complex SiO₂/In₂O₃ samples [4]. This gives rise to an increase in the porosity of the resulting film and consequently, the optical energy gap decreases. In this work, polymer pastes of In₂O₃/SiO₂ mixtures in various proportions were made. These are: 75 wt% of In₂O₃ and 25 wt% of SiO₂; 50 wt% of In₂O₃ and 50 wt% of SiO₂; and 25 wt% of In₂O₃ and 75 wt% of SiO₂. The pastes were screen-printed using DEK RS 1202 automatic screen printer on glass substrates. All devices were exposed to a disc-type ¹³⁷Cs source with an activity of 370 kBq. The absorption spectra were recorded using CARY 1E UV-Visible Spectrophotometer. Films with composition 25 wt.% of In₂O₃ and 75 wt.% of SiO₂ showed an increase in optical density value from 1.97 before irradiation to 2.06 after irradiation with a dose level of 0.55 mSv. Additional irradiation of these films led to a decline in the optical density values to 1.99 at a dose of 1.72 mSv. Films made with 50 wt.% of In₂O₃ and 50 wt.% of

SiO₂ showed a more pronounced increase in the value of their optical density from 3.05 to 3.24 after irradiation with a dose of 1.72 mSv. Films made with 75 wt.% of In₂O₃ and 25 wt.% of SiO₂ showed an increase in the value of their optical density from 2.05 before irradiation to 3.54 after irradiation with a dose of 1.72 mSv. The values of the optical band gap E_{opt} were obtained in the view of the Mott and Davis theory. It was found that E_{opt} decreased with the increase in radiation dose to a certain level, which was composition-dependant. 1. Committee on Biological Effects of Ionizing Radiation V, 1990. 2. Zhu, Nucl. Instrum. Meth. A, 413 (1998). 3. Pacchioni and Pescarmona, Surface Science, 412-413 (1998). 4. Arshak et al., J. Mat. Science Let., 3 (1984). 5. Tominaga et al., Vacuum, 59 (2000).

H11.33

Combinatorial Preparation and Characterization of Thin-film

Optical Amplifier Oxides. K. E. Downey¹, A. R. Bhagwat², R. B. van Dover¹ and A. L. Gaeta²; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Applied and Engineering Physics, Cornell University, Ithaca, New York.

Optical integration is an attractive approach to reducing the cost of optical functions in data networks, while also offering the promise of increasing performance and decreasing size. The integration of materials providing necessary functionality (i.e., on-chip amplification) presents a challenge, which our research addresses. We have used a combinatorial composition-spread approach to identify and evaluate possible amplifier materials rapidly. Using a combination of off-axis and on-axis reactive sputtering, we are able to explore five-component systems. This high-throughput synthesis technique is complemented by rapid optical characterization of the resulting thin films. Compositionally dependent properties such as the lifetime and amplitude of Er³⁺ fluorescence are investigated using a 980 nm pump beam and collection with a time-resolved detector. Promising materials are identified by a figure of merit produced by multiplying the fluorescence lifetime with its amplitude. The composition-spread technique allows us to determine precisely the maximum Er concentration that can be incorporated before Er-Er interactions quench the transition; we can simultaneously determine the optimum levels of substitutions in the SiO₂ matrix to increase the radiative transition probability and/or decrease Er-Er interactions. We have identified compositions in the Er-Bi-Al-Si-O system that perform significantly better than any composition in the benchmark Er-Ln-Al-Si-O system. We will report on the systematic dependence of fluorescence on composition in a range of inorganic oxide systems, with an eye toward identifying the most promising candidates for further development.

H11.34

Raman Scattering and Optical Studies of Transition Metal

(Fe, Co, V) Doped TiO₂ Films. Ratna Naik¹, P. Kharel¹, P. Talagala¹, Georgy M. Tsoi¹, V. M. Naik², R. Suryanarayanan³ and Gregory W. Auner⁴; ¹Department of Physics, Wayne State University, Detroit, Michigan; ²Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan; ³LPCEs, Université Paris-Sud, Orsay, France; ⁴Department of Electrical and Computer Engineering, Wayne State University, Detroit, Michigan.

Recently, there has been a great deal of interest in finding room temperature ferromagnetism in transparent transition metal (Fe, Co, V) doped TiO₂, ZnO and other materials, so called diluted magnetic semiconductors. In the present study anatase and rutile forms of TiO₂ and their transition metal (TM) doped (5 atomic %) films have been successfully made using a simple spin coating metalorganic decomposition method using different concentrations of organic metal precursor solutions. Final annealing of the films in air at 550 °C yields only the anatase phase, whereas 750 °C annealing shows only the rutile phase of TiO₂, as confirmed by Raman scattering. The films were further subjected to a vacuum (10⁻⁶ torr) annealing at 500 °C for 30 minutes. The Raman spectra of TM doped anatase and rutile TiO₂ films remain unaltered upon TM-substitution, without indication of any TM oxide formation. Similarly, the optical absorption spectra remain almost unaffected upon TM- substitution indicating that TM ions may have occupied the substitutional sites in the TiO₂ host lattice. The Magnetization versus magnetic field data measured using a SQUID magnetometer show that TM-doped films, without vacuum annealing, are only weakly ferromagnetic at 5 K. But the vacuum annealed samples show an enhanced ferromagnetic signal at 5 K. The effect of vacuum annealing on temperature dependent magnetization measurements will be presented.

H11.35

Optical Coatings for Gravitational Wave Detectors.

Gregory Harry¹, Helena Armandula², Eric Black², David R. M.

Crooks³, Gianpiero Cagnoli³, Martin Fejer⁴, Jim Hough³, Steven D. Penn⁵, Sheila Rowan³ and Peter Sneddon³; ¹LIGO Laboratory, MIT, Cambridge, Massachusetts; ²LIGO Laboratory, California Institute of

Technology, Pasadena, California; ³Physics and Astronomy, Glasgow University, Glasgow, United Kingdom; ⁴Edward Ginzton Laboratory, Stanford University, Stanford, California; ⁵Physics, Hobart and William Smith Colleges, Geneva, New York.

The detection of gravitational waves is one of the great outstanding problems of experimental physics, and success would confirm a prediction of Einstein's theory of general relativity. Current interferometric observatories are operating and taking astronomical data, however actual detection of these waves may not occur until the next generation detectors are built. Reducing position noise in the interferometer mirrors is the primary concern when designing these new interferometers. Thermal noise from the optical coatings of the interferometer mirrors limits the sensitivity in the most sensitive band and thus limits the ability to do astrophysics with these instruments. The mechanical properties of the coating, and especially the mechanical loss, must be carefully controlled while optical and thermal properties remain within the stringent specifications needed for a high power interferometer. I will discuss the results of experiments looking at mechanical loss in silica/tantala coatings, progress that has been made to develop lower thermal noise coatings, the challenges that must be overcome, and the plans that have been developed to meet these challenges.

H11.36

Transparent, conducting Nanocomposite thin films of the Magnéli phases of vanadium oxides— M.B Sahana and S.A. Shivashankar; Indian Institute of Science, Bangalore, Karnataka, India.

Different stoichiometric compositions of vanadium oxide exhibit a sharp semiconductor–metal (S–M) transition at temperatures ranging from 80 K to 435 K. Indeed, adjacent phases in the V–O phase diagram have different electrical and optical properties at a particular temperature. For example, V_2O_3 is metallic, whereas V_3O_5 is semiconducting and IR-transparent at room temperature. For this reason, it may be expected that composite thin films of two such vanadium oxides would have attractive electrical and optical properties. It is known that the crystallite size of metals and semiconductors has drastic effects on their physical properties. Below 10 nm, novel quantum phenomena are often found that would not appear in larger grains. However, the influence of the grain size on the properties of ordered–defect structures such as Magnéli phases of vanadium oxides are not known, especially in the nanometer regime. The remarkable properties of vanadium oxides and the quantum phenomena in nanoparticles can together lead to attractive properties if nanocomposite thin films of vanadium oxides can be prepared. Such thin film nanocomposites of vanadium oxides have been synthesized by metalorganic chemical vapor deposition simultaneously on $Al_2O_3(110)$ and fused quartz. The films comprising nanocrystallites of V_2O_3 and V_3O_5 deposited on $Al_2O_3(110)$ is metallic and transparent in the visible region at room temperature, and exhibits two S–M transitions. By contrast, the film deposited on fused quartz is semiconducting from 20 to 450 K, and transparent in the visible region. Detailed characterization of these films has been carried out in an attempt to understand the unusual characteristics of the film on $Al_2O_3(110)$. A large increase in the band gap (≥ 2 eV) of ordered defect vanadium oxides is observed in these films, presumably due to the nanometric crystallites.

H11.37

Gas-Phase Nanoparticle Dynamics During Laser Synthesis of Zinc Oxide Nanostructures. Lorenzo Smith, Masashi Matsumura and Renato Camata; University of Alabama - Birmingham, Birmingham, Alabama.

Zinc Oxide (ZnO) is a promising wide bandgap semiconductor for applications in UV light emitting devices and sensors. For several years ZnO research has focused intensely on optimization of bulk and epitaxial growth, p-type doping, and production of high quality metal contacts. More recently these efforts have expanded to include synthesis, properties, and device integration of ZnO nanostructures. A variety of such low-dimensional structures (e.g., nanocrystals, nanowires, nanohelices, nanotubes) have been demonstrated exhibiting greater purity and better crystal quality than bulk crystals and epilayers as low defect concentrations are statistically favored in these nanoscale systems. These nanostructures present potential for important applications particularly in biosensing devices and other nanoscale transducers. A challenging problem facing this area however involves the controlled assembly and integration of these nanoscale objects into anisotropic and highly functional systems of complex architecture. Aerosol processes provide a flexible platform for controlled generation and deposition of gas-borne ZnO nanocrystals and their integration into nanoparticle-based systems with complex architecture. In this work we have combined laser synthesis and on-line aerosol processing to improve control over the synthesis of ZnO nanostructures. This approach presents some unique advantages

over pure thermal evaporation methods as it may allow the creation of nanostructures in controlled arrangements in the micron scale and enable novel devices. We have used the aerosol technique known as differential mobility analysis to perform high-resolution particle spectrometry in the 1-25 nm size range and study the gas-phase dynamics of nanoparticles formed during KrF pulsed laser vaporization of ZnO targets. These targets are vaporized in inert gas atmosphere with background pressures in the 70-760 Torr range and laser fluences of 1-5 J/cm². In-situ measurements reveal that during ZnO vaporization at relatively low laser fluences (<1 J/cm²) the gas-suspended nanoparticle population that ensues exhibits lognormal size distributions with a concentration peak in the 5-10 nm size range. As the laser fluence increases above 2 J/cm² the peak of the distribution shifts to diameters well above 25 nm. By adjusting the inert background pressure, the laser energy density, and the aerosol dilution rate, we have been able to monitor and control the aggregation process of these gas-suspended ZnO nanoparticles for delivery to selected locations on a substrate and potential integration into functional systems. We acknowledge support from the National Science Foundation (NSF)- Research Experiences for Undergraduates (REU)-site award to the University of Alabama at Birmingham (UAB) under Grant No. DMR-0243640, and Major Research Instrumentation Grant, No. DMR-0116098.

H11.38

A First Principles/Kinetic Monte Carlo Study of Oxygen Diffusion in YSZ-based Oxides. Ramanathan Krishnamurthy^{2,1}, Young-Gui Yoon^{1,3}, Konstantin N. Kudin^{1,3}, Roberto Car^{3,1} and David J. Srolovitz^{2,1}; ¹Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey; ²Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; ³Department of Chemistry, Princeton University, Princeton, New Jersey.

Yttria stabilized zirconia films and other fluorite-based oxide films are used for a wide variety of oxygen ion conducting applications, all of which critically depend on the oxygen diffusivity. We present a multi-scale modeling approach to study oxygen diffusion in yttria stabilized zirconia. We employ density functional theory methods to calculate activation energies for oxygen migration in different local cation environments. These results serve as input to a kinetic Monte Carlo study of oxygen ion diffusivity as a function of temperature and yttria content. The simulations show that the oxygen diffusivity attains a maximum value around 10 mol% yttria. This variation in the oxygen diffusivity with yttria mole fraction and the calculated values for the diffusivity agree well with experiment. The competing effects of increased oxygen vacancy concentration and increasing activation energy and correlation effects for oxygen diffusion with increasing yttria mole fraction are responsible for the observed dopant content dependence of the oxygen diffusivity. We analyze the cation-dopant induced correlation effects and the results of the analysis support the above explanation. This methodology is extended to predict the effects of lanthanide additions on oxygen diffusion in YSZ. A simple picture emerges based on lanthanide cation size. The implications of these results for solid oxide fuel cell electrolytes, gas sensors and thermal barrier coatings will be discussed.

H11.39

Growth and Some Interesting Characteristics of $La_{0.7}Sr_{0.3}MnO_3/ZnO$ Heterostructures. Ashutosh Tiwari and J. Narayan; Materials Science & Engineering, north carolina state university, raleigh, North Carolina.

We will present some of our very exciting recent results about the growth and electrical characteristics of $La_{0.7}Sr_{0.3}MnO_3/ZnO$ heterostructures on sapphire (0001) substrates by using pulsed laser deposition technique. These junctions provide an effective way to control the electrical and magnetic characteristics of giant magnetoresistive $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films by using the built-in electric field at the LSMO/ZnO interface. In LSMO charge carriers are holes while in ZnO electrons are the dominant charge carriers. So when a junction of LSMO and ZnO is formed, a thin depletion layer appears at the junction. Thickness of this layer and, hence, the carrier concentration in the system can be modulated by applying the external bias across the junction. We chose ZnO as the counter electrode in this study because: (i) under the normal conditions of deposition it tends to be oxygen deficient and exhibits n-type behavior, and (ii) by changing the oxygen stoichiometry it is possible to have a control over carrier concentration. 1. Ashutosh Tiwari and J. Narayan Applied physics letters 83, 1773, 2003.

H11.40

Application of Chemical Lithography and Chemical Etching on Fabrication of ZnO Based Microstructures. Kenji Takahashi^{2,1}, Takeshi Ohgaki¹, Hiroshi Funakubo², Hajime Haneda¹ and Naoki Ohashi¹; ¹National Institute for Materials Science, Tsukuba, Japan; ²Tokyo Institute of Technology, Yokohama, Japan.

Zinc oxide is an attracting material for opto-electronic applications. In order to obtain highly functional structures of ZnO, microfabrication is dismissible technology. It is well-known that ZnO is able to be etched with acid solutions, e.g., HCl. However, there are few prior studies on micro-fabrication of ZnO using chemical etching method. In this study, we investigated chemical etching of ZnO in order to realize fine patterning on ZnO single crystal substrate. We used electron beam lithography technique to obtain resist patterns on (000-1), (11-20) and (10-20) surface of ZnO crystals. Chemical etching was carried out with aqueous solution of HNO₃, H₂SO₄ and CH₃COOH. The etched surface was characterized with SEM, optical microscope and AFM. It was revealed that relatively low pH gave high resolution of micro-patterns after etching. With relatively low concentration of acids we obtained hexagonally shaped pits, while randomly etched pattern was obtained by using acid solution with high concentration. Particularly, by using CH₃COOH solution of lower pH, the highest resolution of etched pattern was achieved. Subsequent observation revealed that the etched pits had crystallographic orientation of (10-11) and (11-23). Detailed etching behavior will be presented at the conference site. This study was partly supported by Grant in Aid for Scientific Research from MEXT, Japan and also by NEDO, Japan.

H11.41

The role of substrates on the growth and electroacoustic properties of ZnO thin films by chemical solution deposition and RF magnetron sputtering. Sang Hoon Yoon, Yuquan Li and Dong-Joo Kim; Materials Research and Education Center, Auburn University, Auburn, Alabama.

Acoustic wave devices such as surface acoustic wave (SAW) and flexural plate wave (FPW) devices are currently investigated for chemical and biological sensors. For these applications, ZnO is one of good candidates as a piezoelectric layer in acoustic wave devices due to its high piezoelectric and electromechanical coupling coefficient as well as good thermal stability. To obtain films of high piezoelectric activity capable of launching acoustic waves into a substrate, it is important to grow high degree of orientation and to elucidate growth mechanisms of piezoelectric film. In this study, ZnO thin films were prepared by chemical solution deposition and RF magnetron sputtering. Process parameters such as temperature, time and atmosphere were systematically investigated on various substrates. Different layers deposited on silicon wafers such as amorphous SiO₂ and SiN, crystalline Pt and Al with different orientations were investigated to determine the role of substrates in the preferred orientation or growth behavior of deposited ZnO. It was found that the degree of preferred orientation was strongly affected by the orientation of substrates, and comparing with the sputtering, the chemical solution deposition turned out to be more sensitive to the orientation of substrate. Physical properties, including microstructure and surface roughness of ZnO films were also investigated along with the preferred orientation. The electroacoustic properties of microfabricated devices will be discussed in context with preferred orientation, roughness, and microstructure.

H11.42

Properties of Low Temperature Oxides for Deposition on Plastic Substrates. Burag Yagliglu, Hyo-Young Yeom, Kristin Conaty and David Paine; Engineering, Brown University, Providence, Rhode Island.

The deposition of oxide materials on plastic substrates presents a new set of challenges to the thin film deposition and processing community. The use of polymeric substrates for new oxide semiconductors however opens huge opportunities for large area sensors, displays, and other large area electronics. Current polymeric substrate materials (PET, PEN, Polyimide, PMMA, Polycarbonate) are heat sensitive and lose integrity if heated to the temperatures needed for the deposition of crystalline oxides. In this work we have studied the properties of degenerate semiconducting amorphous oxides of 10wt% ZnO doped In₂O₃ (IZO) used for transparent conductor applications. These materials were deposited by DC magnetron sputter deposition at room temperature onto glass and PET substrates. The as-deposited films are amorphous and their crystallization temperature is 350°C which is much higher than the crystallization temperature of the most widely used transparent conducting oxide, 10 wt.% SnO₂ doped In₂O₃, 150°C. We have examined the change in electrical properties of IZO films by annealing at temperatures below crystallization in air. Hall measurements have confirmed that the oxygen vacancies are consumed during the annealing process. In the amorphous state these oxygen vacancies act as donors and dope the material to n-type. The oxidation of vacancies results in a measurable film volume change. We use this volume change combined with the change in carrier density to characterize oxygen vacancies in the amorphous state.

H11.43

Time-resolved spectroscopy of ZnO thin films grown by

Pulsed Laser Deposition. Maurice Cheung¹, Alexander N.

Cartwright¹, Timothy E. Murphy², Jamie D. Phillips² and Willie E. Bowen²; ¹Department of Electrical Engineering, University at Buffalo, Buffalo, New York; ²Department of Electrical Engineering and Computer Science, The University of Michigan, Ann Arbor, Michigan.

Temperature dependent time resolved photoluminescence (TRPL) measurements to determine the emission spectra and carrier lifetimes were conducted for ZnO thin film samples grown by pulsed laser deposition (PLD). Here, we report the results of these spectroscopic studies for temperatures from 15K to room temperature for three different ZnO samples: two grown on sapphire, and the other grown on glass. Each sample in this series has a unique photoluminescence (PL) characteristic. Specifically, at 15K, each of the samples showed two distinct emission PL peaks. Conductivity measurements showed that one of the samples that was grown on sapphire conducts poorly when compared with the other two samples, and a correlation between PL characteristics and conductivity was observed. Each of the samples with good conductivity showed a strong emission peak at the bandgap (3.4 eV) accompanied by a broad emission peak from deep level emission due to the intrinsic defects in the material. For the sample with poor conductivity, the spectra was dominated by the deep level emission that had a broad spectrum peaked at 2.4 eV with the high-energy peak slightly below that of the bandgap (3.2 eV). Moreover, at room temperature, the deep level emission completely dominated the PL of the poorly conducting sample, and the high-energy peak almost disappeared completely; while the bandgap emission remained dominant in the better quality samples. This observation suggests that, as expected, the defect density, as well as the density of the channels to these defect states, is higher in the poorly conducting sample. Moreover, all samples showed rapid temporal decay for the high-energy emission and slower decay for the deep level emission. The non-exponential PL decay from these samples is well fitted with a stretched exponential function. In general, the effective lifetime of the short lived band-edge decay was on the order of 10 ps, while the deep level emission was characterized by a gradual decay of a few hundreds picoseconds. These observations suggest that the optically excited carriers transfer rapidly from band-edge states to the deep level states and recombine (radiatively and non-radiatively) from these deep levels. These results, along with a rate equation model, will be presented. More importantly, we will discuss the ramifications of these data for the possibility of devices fabricated from these materials.

H11.44

Pulsed Electron Beam Deposition of Epitaxial Gallium Oxide on Sapphire. Christian Mion¹, Hugh Porter¹, John F. Muth¹, Ailing Cai¹, Amit Chugh² and Jagdish Narayan²; ¹ECE Dept Box 7911, NC State University, Raleigh, North Carolina; ²Materials Science and Engineering, NC State University, Raleigh, North Carolina.

Traditional conducting oxides such as Indium Tin Oxide and ZnO typically are attenuating in the UV portion of the optical spectrum. The wide band gap semiconductor β -Ga₂O₃ has a band gap of 4.9 eV and is transparent to 250 nm. Using pulsed electron beam deposition a series of β -Ga₂O₃ films were grown at between room temperature and 1050 C on c-axis double side polished substrates. At temperatures below 400 C amorphous films were produced. The optical absorption edge of the amorphous films was 320 nm. With increasing temperature the optical absorption edge moved to higher energies with increasing transparency. The optimum film growth temperature was found to be 850 C with a resulting absorption edge of 240nm. Transparency was greater than 80% throughout the UV and NIR portions of the spectrum. High resolution transmission electron microscopy showed these films were epitaxial with the sapphire substrate. The in-plane orientation was found to be (010) β -Ga₂O₃ // (01 $\bar{1}$ 0) α -Al₂O₃, and (201) β -Ga₂O₃ // (2 $\bar{1}$ $\bar{1}$ 0) α -Al₂O₃ with 4 lattice constants of β -Ga₂O₃ in the (010) direction matching very closely with 3 lattice constants of sapphire in the (01 $\bar{1}$ 0) direction, and 2 lattice constants of the β -Ga₂O₃ in the (201) direction matching very closely with 3 lattice constants of sapphire in the (2110) direction. The resulting lattice mismatches are -1.6% and +3.13% respectively.

H11.45

Transient Properties Of ZnO/Al₂O₃ Photoconductors. Kaveh Moazzami, Tim Murphy and Jamie Dean Phillips; Department of Electrical Engineering and Computer Science, The University Of Michigan, Ann Arbor, Michigan.

ZnO is a wide bandgap semiconductor material with properties desirable for optoelectronic devices operating in the ultraviolet spectral region. The formation of p-n junctions will be required for many optoelectronic devices utilizing ZnO, where the dynamic response of minority carriers will need to be understood. The transient response of majority carriers due to photoresponse is often used to infer minority carrier properties. In this work, photoconductors were fabricated from ZnO material deposited on

c-plane sapphire. ZnO materials deposited by pulsed laser deposition and molecular beam epitaxy were both examined. Pulsed laser deposition of ZnO resulted in polycrystalline thin films with a predominant c-axis orientation. Epitaxial growth along the c-axis was observed for deposition by molecular beam epitaxy. ZnO photoconductors were placed in a resistive circuit, where photoresponse was observed in the ultraviolet spectral region. The photoconductive decay was examined after excitation from a pulsed laser operating at a $\lambda=248\text{nm}$ with a pulse width of approximately 20ns. A slow and fast photoconductive response is observed, where decay times of the slow and fast response are dependent upon material quality. The slow response exhibits a decay on the order of seconds, and is likely due to traps or deep levels in the ZnO material. The fast decay time is believed to be representative of the minority carrier lifetime, and is on range of nanoseconds. The frequency dependence of the noise current for the photoconductors was also determined using a spectrum analyzer. The noise current shows a clear $1/f$ dependence for the frequency range measured, indicated that noise current is dominated by defects in the ZnO material. The photoresponse and noise characteristics of ZnO photoconductors will be presented and related to independent measurements of the electronic and structural properties of the ZnO/Al₂O₃ materials.

H11.46

Pulsed Electron Beam Deposition of Single Crystal ZnO on Sapphire. Hugh Porter, Christian Mion, Ailing Cai and John F. Muth; ECE Dept Box 7911, NC State University, Raleigh, North Carolina.

Thin films of ZnO on C-plane (0001) sapphire ($\alpha\text{-Al}_2\text{O}_3$) substrates were grown by Pulsed Electron Beam Deposition (PED). The electron pulses used to ablate the target were approximately 0.8 Joules and 100 ns in duration. The surface morphology of the target was found to influence deposition efficiency, indicating that a combination of ablative and thermal evaporation was occurring. Measurements by x-ray diffraction indicate single crystal c-axis oriented epitaxial films. Intense band edge photoluminescence and cathodoluminescence as well as strong excitonic features in optical transmission demonstrated the high optical quality of the films. The A and B excitons were clearly resolved at 77 K and prism coupling measurements indicated good waveguide properties. This suggests that pulsed electron beam deposition is a viable method of producing ZnO thin films.

H11.47

Systematic investigation of electrical and optical properties of Sr_{1-x}Ba_xNb₂O₆ films. Isao Ohkubo^{1,2}, Hans Christen¹, Gerald Jellison¹, Christopher Rouleau¹, Douglas Lowndes¹, Mark Reeves³ and Shuang Huang³; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Department of Applied Chemistry, School of Engineering, University of Tokyo, Tokyo; ³Department of Physics, George Washington University, Washington, District of Columbia.

Optical switching and modulation remains a major technological challenge in many photonic applications, with optical switching relying on electric field induced changes of the refractive index (Pockels effect). Bulk Sr_{1-x}Ba_xNb₂O₆ (SBN) shows a particularly large Pockels coefficient ($r_{33} \approx 1400 \text{ pm/V}$ for $x = 0.25$, i.e. 30 times larger than that of the most commonly used material, LiNbO₃). Here we present results on thin SBN films obtained via a pulsed-laser high-throughput deposition method, in which the composition of the deposited material varies laterally across a substrate plate. Physical properties obtained at different positions on the substrate can then be correlated to the chemical composition of the material. In particular, we use a 2-modulator generalized ellipsometer to determine the refractive index in the range $\lambda = 300 - 800 \text{ nm}$, and scanning microwave microscopy to determine the dielectric constant at $f = 1.6 \text{ GHz}$. A variable-temperature stage on the latter system allows us to observe changes related to the ferroelectric transition of SBN. Results provide insight as to which regions in the composition space may be appropriate for specific applications. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC.

H11.48

MOCVD Growth and Characterization of Epitaxial ZnO Films on GaN and other Substrates. Ian Ferguson¹, Kandoor Shalini¹, Ming Pan¹, Ian T. Ferguson¹, Shanti Ganesan², William B. Nemeth² and Jeff Nause²; ¹School of Electrical and Electrical Engineering, Georgia Institute of Technology, Atlanta, Georgia; ²Cermet Inc, Atlanta, Georgia.

ZnO is a candidate for many optoelectronics applications due to its high excitonic binding energy of 60 meV. Its main competitor, GaN, is also a direct bandgap material (3.5 eV) and has an exciton binding energy of 23 meV (about three times less than ZnO). Moreover, ZnO is more resistant to radiation compared to its peers such as SiC, GaAs

and GaN. ZnO films have been grown by many methods such as molecular beam epitaxy (MBE), sputtering, pulsed laser deposition (PLD) and chemical vapor deposition (CVD). However, Metal Organic Chemical Vapor Deposition (MOCVD) offers advantages such as uniform deposition over a large area, ability to integrate into device techniques, conformal coverage, and is the preferred method for the growth of high quality epitaxial films. High quality ZnO films were grown at substrate temperatures between 450 °C and 550 °C and pressures between 1 and 50 Torr using sapphire and Si (111) substrates for growth times of 1-2 hours. Initial characterization techniques of ZnO on Si(111) and sapphire included X-ray diffraction (XRD), ellipsometry and Hall measurements. XRD gave a full width at half maximum (FWHM) of 100 arc seconds and photoluminescence results gave a FWHM of 20 meV. Ellipsometry measurements gave a refractive index of 2.0 for the undoped samples and 1.8-2.2 for doped samples. An electron concentration of 10^{17} and mobility of $200 \text{ cm}^2/\text{V/s}$ were obtained from Hall measurements. This work will be used as the base for understanding the growth of ZnO on GaN and associated devices.

H11.49

Anisotropic Porosity of Hybrid Organic/Inorganic Polyisocyanate Sol-Gel Films. Douglas Anson Loy¹ and Jonathan Mark Stoddard¹; ¹Material Science and Technology-7, Los Alamos National Laboratory, Los Alamos, New Mexico; ²Materials Science and Technology-7, Los Alamos National Laboratory, Los Alamos, New Mexico.

The ability to form polymeric liquid crystalline assemblies coupled with a relatively low depolymerization temperature (<150 oC) make polyisocyanates excellent candidates for preparing thin films with functionalized, anisotropic porosity. In this study, we have prepared poly(3-triethoxysilylpropyl isocyanate) by a cyanide initiated anionic polymerization to provide a rigid-rod polymer that can be sol-gel polymerized into highly crosslinked matrices. Films of the polyisocyanate cast from chloroform were found to be liquid crystalline, but failed to form suitable films upon exposure of the pendant alkoxy silane groups to sol-gel polymerization conditions. Free-standing sol-gel films were formed from solution-casting a mixture of polyisocyanate, an inorganic silica precursor such as tetraethylorthosilicate or bis(triethoxysilyl)methane, and aqueous formic acid (88%) as catalyst. The polyisocyanate/sol-gel hybrid films were heated to 250 oC and 300 oC to depolymerize the isocyanate. The encapsulation of the polyisocyanate into the inorganic silica matrix raised the onset temperature of depolymerization by 100 oC. Alternatively, treatment with strong acid or base resulted in decomposition of the isocyanate backbone. The morphology, surface area, and chemical functionality of the ordered sol-gel films will be discussed as well as potential applications.

H11.50

Optical Property dependence on Stoichiometry of Vanadium Oxide. Dilan Seneviratne and Harry L. Tuller; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Vanadium (IV) oxide is an interesting material system exhibiting a metal-semiconductor transition. It has possible applications in optical switching, variable optical attenuation, and smart windows. We investigate this material system and present data related to the growth of the films and characterization of electrical and optical properties. The phase stability limits and nonstoichiometry of the different vanadium oxide phases will be examined by coulometric titration. The optical properties of vanadium dioxide will be examined and correlated with variations in stoichiometry.

H11.51

Chemical Solution Deposition for YBa₂Cu₃O_{7-x}/SrTiO₃/Ni-W Superconducting Composites. Jacob J. Richardson¹, Paul G. Clem¹, Michael P. Siegal¹, Donald L. Overmyer¹, James A. Voigt¹, Terry G. Holesinger², Dominic F. Lee³ and Fred A. List³; ¹Sandia National Laboratories, Albuquerque, New Mexico; ²Los Alamos National Laboratory, Los Alamos, New Mexico; ³Oak Ridge National Laboratory, Oak Ridge, Tennessee.

High quality epitaxial YBa₂Cu₃O_{7-x} (YBCO)/buffer/metal superconducting composites have important power generation/distribution and electronics applications, but to be commercially viable, fabrication time and costs must be drastically reduced. Of the current deposition methods, chemical solution deposition (CSD) perhaps has the most potential for rapid throughput, economical fabrication but, while attractive, an all CSD composite presents a unique set of engineering challenges. This talk will present some of these challenges and the techniques used at Sandia to better understand and overcome them. Primary focus will be given to the YBCO/SrTiO₃/Ni-W composite structure and to the tailoring of solution chemistry and process conditions in order to

control critical parameters such as film thickness, epitaxial growth, substrate oxidation, and processing speed. In particular, a non-vacuum method for growing epitaxial perovskite layers on base metal substrates such as Ni will be presented, as well as metrics for measuring thin film oxygen diffusivity. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the US Dept. of Energy NNSA under contract DE-AC04-94A185000.

H11.52

Effect of Additives to the MgO Protective Layer for AC-PDP. Deok Hai Park and Se-Young Choi; School of New Materials Science and Engineering, Yonsei University, Seoul, South Korea.

Recently, FPD (Flat Panel Display) plays a great role in a many fields. One of them is the AC-type plasma display panels (PDP). PDPs are competing against the liquid crystal display in wall-hung TV applications. Especially, PDP has advantages for a high dimension TV over 40 inches. However, there are some practical problems such as production cost and power consumption, etc. Therefore, we choose the proper component materials to overcome the problems. The components of AC-PDPs are glass substrate, two electrodes, transparent dielectric layer and a protective oxide film such as MgO having a high melting point. Particularly, the protective layer can influence discharge voltage and life time. The voltage for discharge has been known to depend mainly on SEE (Secondary Electron Emission coefficient) and then work function of a protective layer. Active research and development have been made on various material which has high SEE and low work function. We researched on the three candidate materials such as BaO, Gd₂O₃, and TiO₂. BaO has known as an electron emission sources because of its low work function. In the case of Gd₂O₃, it may prevent the absorption of blue emission of protective layer. We search for the promising additive material. TiO₂ is superior to other materials as additives to the MgO. UV-VIS spectrometric measurement shows that transmittance of T₂ which is 3.8at% TiO₂ added to MgO is 89.158 at 546nm. The surface morphology of T₂ is smoother than conventional MgO. Dielectric constant is 23.37772. Also, secondary electron emission coefficient represented higher than commercial MgO. The value is ranged from 0.109 to 0.2060. The microstructure of T₂ thin film is a fine-grained microstructure less than 20nm in grain size and cross-sectional view represented columnar structure. Finally, T₂ is feasible for the new protective layer.

H11.53

Low Temperature Atomic Layer Deposition of Al₂O₃/TiO₂ Multilayer Coatings on Polymeric Substrates. Gerry Triani, Peter J. Evans, Kim S. Finnie, Bruno A. Latella, Darren J. Attard, David R. G. Mitchell, Michael James, Christophe J. Barbe and John R. Bartlett; Materials and Engineering Science, ANSTO, Menai, New South Wales, Australia.

Atomic layer deposition is a versatile technique for depositing functional coatings on accessible surfaces with precise control of thickness and nanostructure. One such example is the deposition of multi-layer films as anti-reflection coatings on polymer substrates. This paper investigates the deposition and characterization of Al₂O₃/TiO₂ multilayer films on polycarbonate substrates at temperatures below 100 °C using TiCl₄, Al(CH₃)₃ and H₂O as precursors. In-situ quartz crystal microbalance measurements were used to map the process chemistry of films deposited at both 80 and 100 °C and to identify the process conditions required to achieve reproducible film growth for both layers. A suite of analytical techniques was used to explore the evolution of nanostructure and composition as a function of deposition parameters and to compare the results observed on the polymeric substrates at low deposition temperatures with those obtained at higher temperatures on Si <100> substrates. Cross-sectional transmission electron microscopy revealed sharp coating/substrate and TiO₂/Al₂O₃ interfaces on both the polymeric and Si substrates, with uniform, strongly adherent coatings in both cases. Secondary ion mass spectrometry (SIMS) depth profiling indicated that the amount of residual chlorine from the TiCl₄/H₂O reaction was influenced by the deposition conditions, with decreasing deposition temperature leading to a corresponding increase in the quantity of chloride species retained within the coatings. Similarly, the amount of carbon retained within the alumina layers, due to incomplete conversion of Al(CH₃)₃ into Al₂O₃·xH₂O, increased with decreasing deposition temperature. The refractive indices of the TiO₂ and Al₂O₃ layers deposited at 80 °C on the polymeric substrate (2.24 and 1.61, respectively) were lower than the corresponding values obtained at higher temperatures (200 °C on Si substrates, 2.39 and 1.66, respectively), reflecting higher porosities in the low-temperature coatings. The mechanical properties and adhesion of the individual layers and Al₂O₃/TiO₂ bi-layers to the underlying substrate were also investigated using instrumented nano indentation and tensile testing. The mechanical properties of the layers reflected good adhesion to the substrate, with adhesion energies of 9 and 71 J/m² for the TiO₂ and

Al₂O₃ layers, respectively, at 80 °C. Transverse cracking was observed in all cases above a critical strain of ca. 8 %, which was most evident for the TiO₂ layers. However, debonding occurred after cracking for all coatings, as expected for strongly adherent layers. The effect of processing conditions on mechanical properties will be discussed.

H11.54

Preparation of p-type transparent thin films with high electrical conductivity by sol-gel method. Dae-Sung Kim and Se-Young Choi; Yonsei University, Seoul, South Korea.

Transparent conductive oxides (TCO) are widely and practically used as transparent electrodes in flat panel displays, solar cells and touch panels. Utilization of these materials is essential for the development of the large area devices, which need high optical transparency and high conductivity, and further efforts to reduce the resistivity as well as to explore new materials are highly expected. Transparent optoelectronic devices such as transparent diodes, transistors and light-emitting diodes (LEDs) will require both transparent n-type and p-type materials. However, most of the known TCOs such as ZnO, ITO and SnO₂ etc. are all n-type materials. Transparent p-type conductors, on the other hand, have attracted much attention. The essential feature of the approach is to select a monovalent copper as the major constituents. However, the simplest oxide of Cu⁺, Cu₂O, has rather a small band gap (2.1 eV) and it is not transparent in visible region. The Cu⁺ delafossite CuMO₂, which is composed of alternate stacking of O-Cu-O dumbbells and MO₆ octahedral layers, was selected as one of the promising materials for p-type TCOs. Thin films of Cu⁺ delafossites were prepared and their optical transparency and p-type conductivity were experimentally evidenced. The Cu-based materials, in combination with n-type transparent semiconductors, will be enabling p-n junction based oxide devices. If transparent p-n junctions are available, TCOs will become significantly more useful, because many active functions of semiconductors are due to p-n junctions. In this work, the CuMO₂ thin films were deposited by sol-gel process. The x-ray diffraction was used to investigate crystal phase and structure. Optical constants were investigated by using spectroscopic ellipsometer and UV/VIS/NIR spectrometer. Electrical conductivity was also investigated by four-point-probe.

H11.55

Structure-property relationships in epitaxial ZnO thin films grown by femtosecond and nanosecond pulsed laser ablation. Arnold Allenic¹, Yong Che², Zhendong Hu², Wei Guo¹ and Xiaoqing Pan¹; ¹Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ²Materials Research Group, IMRA America Inc., Ann Arbor, Michigan.

The ZnO semiconductor continues to receive considerable attention for optoelectronic applications. In this work, we focus on the synthesis and characterization of single-crystalline ZnO thin films on the (0001) sapphire substrates by both femtosecond (fs) and nanosecond (ns) pulsed laser ablation. We present a systematic comparison of so-grown films in terms of crystallinity, surface morphology, microstructure, electrical and optical properties for a wide range of processing conditions. All films were grown epitaxially on the (0001) surface of the sapphire substrate. The out-of-plane mosaic spread was determined by rocking curve measurements and it was found that better crystallinity could be achieved with fs laser ablation, especially for low temperature growth. Surface roughening is more severe with fs laser ablation for high temperature growth. The in-plan microstructure of the film and the atomic structure of the film-substrate interface were studied by transmission electron microscopy. Hall measurements of undoped ZnO revealed n-type conduction with mobility one order of magnitude higher for films grown by fs laser ablation. Transparency of films grown by fs laser ablation depends strongly on the background pressure and was significantly enhanced at high O₂ pressure.

H11.56

Barium Metaplumbate (BaPbO₃) and Lanthanum Nickelate (LaNiO₃) Conductive Oxide Electrodes for Oriented Ferroelectric Thin Films. Stacey W. Boland, Melody Grubbs and Sossina M. Haile; Department of Materials Science, California Institute of Technology, Pasadena, California.

Recently, it has been suggested large strains can be obtained through domain switching of highly-oriented tetragonal ferroelectrics such as Pb_{1-x}Ba_xTiO₃ (PBT). To successfully integrate such films into usable large strain devices, orientation must be achieved on an electroded substrate. Films deposited on metallic electrodes such as Pt, however, are randomly oriented due to poor lattice matching between the cubic electrode layer and tetragonal perovskite film. It has also been widely shown in literature that Pt electrodes are associated with increased fatigue due to the migration of oxygen vacancies to the film-electrode interface. Conductive oxide electrodes provide an attractive alternative to Pt for use in ferroelectric devices.

Though their conductivity is somewhat less than Pt, conductive oxides with perovskite structures and good lattice matching have been shown to enhance ferroelectric properties and improve the fatigue characteristics of perovskite ferroelectrics. It is believed the improved properties result from the ability of the conductive oxide electrodes to serve as a sink for oxygen vacancies which migrate to the film-electrode interface. Sol-gel processes were examined for the preparation of two conductive oxides, barium metaplumbate (BaPbO_3 , BPO) and lanthanum nickelate (LaNiO_3 , LNO). LNO has been widely studied, and several simple sol-gel processes have already been reported in literature. BPO has been studied to a lesser extent, however it is particularly suited for use with $\text{Pb}_{1-x}\text{Ba}_x\text{TiO}_3$, as it provides good lattice matching without introducing additional cation species. Several procedures have been reported for producing BPO, but all involve multiple steps, high-vacuum processes, or high processing temperatures. Low temperature and ambient pressure processes are more desirable for facile integration of ferroelectrics into conventional Si-based processing. Here, an economical single-step, single ligand sol-gel process for producing oriented BPO thin films at low temperatures is presented. Thin film LNO and BPO electrodes were produced via spin-coating onto single crystal $\text{MgO}(100)$ substrates. Conducting oxide powders and thin films were examined by x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), micro-Raman spectroscopy, and simultaneous thermal analysis (STA). The orientation of thin film electrodes was determined via XRD. The effect of deposition parameters, including number of layers, pyrolysis temperature, calcination temperature, and heating rate on orientation and conductivity is discussed.

SESSION H12: Optical and Semiconductor Oxides
 Chairs: Scott Chambers and Masashi Kawasaki
 Friday Morning, December 3, 2004
 Grand Ballroom (Sheraton)

8:30 AM H12.1

Effect of Postgrowth Annealing Temperature on Structural, Optical, and Electrical Properties of ZnO Films Grown on Al_2O_3 by RF Magnetron Sputtering Technique.

Chul-Hwan Choi and Seon-Hyo Kim; Material Science and Engineering, Pohang University of Science and Technology, Pohang, Kyungbuk, South Korea.

ZnO thin films on (0001) sapphire substrates were deposited by RF magnetron sputtering. In order to investigate the effect of post-annealing temperature on structural, optical, and electrical properties, ZnO films were annealed in ambient Ar for an hour at various temperatures ranging from 400°C to 800°C after film deposition. High-resolution x-ray diffraction analysis (HRXRD), photoluminescence spectroscopy (PL), UV-VIS-IR spectroscopy, Hall measurements and field emission scanning electron microscopy (FE-SEM) were used to characterize as-grown and post-annealed ZnO films. XRD scan spectra of as-grown and post-annealed ZnO films show typical ZnO (0002) diffraction peaks around 34.4°. XRD θ -rocking curve FWHM values of annealed ZnO (0002) films deposited in the 400-600°C temperature indicate that c-axis alignment significantly improves with the post-annealing procedure. In contrast, that of annealed ZnO film deposited at 700°C is hardly changed by heat treatment. Phi scans of post-annealed ZnO (104) films clearly show typical six fold symmetry of hexagonal ZnO film. And FWHM values of annealed ZnO film phi scans gradually decrease as annealing temperature increases, indicating that crystal quality in the out of plan of ZnO film was also improved with post heat treatment. In room temperature photoluminescence spectra, as-grown ZnO films show broad deep level emission peaks centered at 2.1 and 2.9eV, respectively. However, post-annealed ZnO films clearly show near band edge emission peaks of 3.26eV with strong broad deep level emission peaks of 1.8-2.7eV, which is attributed to native defects of ZnO such as Oxygen vacancies or Zn interstitials. In addition, low temperature photoluminescence spectra (15K) of post-annealed ZnO film show strong near band edge emission peaks of 3.38eV with very weak deep level emission peaks. UV-VIS-IR spectroscopy shows that the transmittance of as-grown and post-annealed ZnO films in the visible (400-700 nm) range is over 80%, which indicates that post annealing procedure does not influence the transmittance of ZnO films. By plotting versus λ , estimated band gaps are similar to band gaps measured by PL. With Hall measurement, we observed that post-annealed ZnO films are all n-type and their hall resistivity decreased from tens of to the order of 10-1 with annealing temperature increases. Carrier concentration varies from 1.12×10^{16} to 1.37×10^{18} with annealing temperature. FE-SEM analysis shows that surface morphology gets smoother and grain size increases as annealing temperature increases. In addition, we investigated the effect of Mg doping on PL characteristics. Blue shift is observed as Mg concentration increases.

8:45 AM H12.2

Synthesis and Characterization of a Novel Integrated ZnO Nanorod/ZnO Thin Film Structure.

Tar-Lei Chou and Jyh-Ming Ting; Department of Materials Science and Engineering, National Cheng Kung University, Taiwan, Tainan, Taiwan.

Zinc oxide (ZnO) is an excellent material for use in optoelectronic applications due to its wide direct band gap of 3.33eV. Among its various forms, ZnO nanorod has become an important one as a result of the advance of nanotechnology. In previous papers [1, 2], we have reported a new route for ZnO nanorod synthesis using a sputter deposition technique. It was found that the formation of ZnO nanorods critically depends on a decisive layer of copper. The copper layer allows an initial formation of ZnO thin film and subsequent formation of ZnO nanorods without changing any conditions during the synthesis. Recently we have found ZnO nanorod/ZnO thin film structure a potential application in solar cells as an integrated current collector/electrode. For such an application, it is essential to understand the characteristics of ZnO nanorod/ZnO thin film structures. As a result, we report in this paper our investigation on the morphology, microstructure, electrical properties, and optical properties of ZnO nanorod/ZnO thin film structures. ZnO nanorod/ZnO thin film structures were deposited using a magnetron sputter deposition technique. Both Si and glass were used as the substrates. Prior to the deposition of ZnO nanorod/ZnO thin film structures, the substrates were pre-coated with Cu using an electroless plating technique. During the sputter deposition process, ZnO thin film was first obtained on Cu pre-coated substrate and followed by the formation of ZnO nanorods. ZnO nanorod/ZnO thin film structures were deposited under different deposition times, O₂/Ar ratios, and substrate temperatures. The resulting ZnO nanorod/ZnO thin film structures were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry, and micro-cathodoluminescence (CL). It was found that the ZnO nanorod/ZnO thin film structures obtained exhibit different physical dimensions, degree of crystallinity, oxygen contents, electrical resistance, optical band gaps, and optical transmittances. Correlation between the results of characterizations and the deposition parameters is discussed. 1. Y.S. Chang and Jyh-Ming Ting, Growth of ZnO Thin Films and Whiskers, Thin Solid Films, 398-399 (2001) 29-34. 2. Jyh-Ming Ting, Wen-Ting Chiou, Wan-Yu Wu, Growth of Single Crystal ZnO Nanowires Using Sputter Deposition, Diamond and Related Materials 12 (2003) 1841-1844. *Corresponding author. Tel.: +886-6-275-7575, ext. 62949; fax: +886-6-238-5613 E-mail address: jting@mail.ncku.edu.tw (J.-M. Ting)

9:00 AM H12.3

High Quality MBE-grown ZnO/MgZnO Structures for Spintronic and UV Applications.

Jianwei Dong¹, A. Osinsky¹, B. Hertog¹, A.M. Dabiran¹, P.P. Chow¹, S.J. Pearton², X.Y. Dong³ and C.J. Palmstrom³; ¹SVT Associates, Inc., Eden Prairie, Minnesota; ²Department of Materials Science and Engineering, University of Florida, Gainesville, Florida; ³Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Wurtzite ZnO is a multifunctional material demonstrating semiconducting, piezoelectric and pyroelectric properties. With a free-exciton binding energy of 60 meV [1], ZnO is an ideal candidate for UV light emitters. In addition, the bandgap of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ compounds span the range of 3.4 to 7.9 eV, which opens up the opportunity for bandgap engineering leading to optimized device performance. The wide-bandgap MgZnO also holds promise as a host material for magnetic impurities such as Mn and Co, forming the so-called dilute magnetic semiconductors, which could lead to high temperature spintronic applications. In this paper we present data on growth, characterization and properties of high quality single-crystal $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ epitaxial films, deposited by RF-plasma enhanced molecular beam epitaxy (MBE). Doping characteristics of Ga donors and magnetic impurities such as Eu and Mn introduced by either in-situ doping or ion implantation have been explored. High efficiency RF-plasma oxygen source, designed and produced by SVT Associates was utilized to grow high quality layers. In-situ monitoring techniques such as reflection high-energy electron diffraction (RHEED) and optical reflectometry were used to optimize the growth conditions. High quality hexagonal $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films were deposited on c- and r-plane sapphires, p-AlGaN and SiC substrates. Both doped and undoped ZnO/MgZnO single and double heterostructures were characterized using X-ray diffraction, cathodoluminescence (CL), AFM, SIMS, Hall measurements, SQUID magnetometry and AMR. Films implanted with 3% Mn ions demonstrated ferromagnetic properties at room temperature. Strong CL emission ranging from 377 nm to 228 nm (Eg from 3.3 to 5.4 eV) was observed at room temperature in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ compounds with x varying from 0 to 0.58, respectively. Double heterostructures (DHS) utilizing a p-AlGaN film as a hole emitter combined with a n-type ZnO active region and a n-MgZnO cap layer have been grown, processed and characterized for

potential application in UV devices. This research was supported by DoD contract #FA9550-04-C-0010, monitored by Lt. Colonel Todd Steiner. **Reference** : [1] D.P. Norton, Y.W. Heo, M.P. Ivill, K. Ip, S.J. Pearton, M.F. Chisholm, and T. Steiner, *Materials Today* **7**, 34 (2004).

9:15 AM H12.4

Ultrafast Carrier Dynamics in Highly Aligned ZnO Nano-tubes. Fang-Yi Jen¹, Tsung-Yi Tang¹, Cheng-Ming Wu¹,

Chih-Chung Yang¹, Bao-ping Zhang² and Yusaburo Segawa²,
¹Institute of Electro-Optical Eng., National Taiwan University, Taipei, Taiwan; ²Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN), Sendai, Japan.

ZnO has been attractive for highly efficient photon emission. It has certain advantages over the widely used GaN, such as the significantly larger exciton binding energy (60 meV) when compared with that of GaN (about 30 meV). Recently, nano-scale ZnO structures, like rods, tubes, and walls, have been widely grown and characterized. Optically pumped lasing was also reported. However, the ultrafast carrier dynamics in such nano-structures have not been well studied yet. In this paper, we explore the carrier dynamics in highly aligned ZnO nano-tubes with time-resolved photoluminescence technique (TRPL). The tube samples were grown with MOCVD at 350-450 °C. The TRPL measurement was excited with the second-harmonic of a fs Ti:sapphire laser. The photoluminescence (PL) signals were monitored with a streak camera of 20 ps in temporal resolution. The PL spectrum at 10 K shows four peaks at 3.364, 3.31, 3.24, and 3.217 eV, corresponding to the emissions of the donor-bound exciton (D0X), the first donor-acceptor pair (DAP1), the LO photon-assisted donor-acceptor pair, and the second donor-acceptor pair (DAP2), respectively. With the excitation photon energy at 3.483 eV, the PL decay profiles at the energies of D0X and DAP1 were recorded at various temperatures. The PL intensity at the D0X peak shows a single-component decay with the decay times ranging from 100 to 500 ps as temperature increases from 10 to 140 K. That at the DAP1 peak shows a three-component decay. The time constant of the first-stage decay (the fastest) ranges from 380 ps at 10 K to about 85 ps at 140 K. That of the second-stage decay ranges from 640 ps at 10 K to 300 ps at 110 K. Above 60 K, a secondary peak of PL intensity appears within the second decay stage. The third decay stage (the slowest) has a time constant from 2 ns to 1 ns in the low temperature range. It is speculated that the fast decay of the D0X peak is due to carrier relaxation down into lower states. The first-stage decay of the DAP1 peak is also attributed to the fast carrier relaxation down into lower energy states. However, because of the carrier supply from the higher-energy states (say, D0X), this decay becomes slower, forming the second-stage decay or even the secondary peak. The third decay stage describes carrier recombination for photon emission.

9:30 AM H12.5

Controlled Nitrogen Incorporation in ZnO Films Grown by Plasma Assisted Chemical Vapor Deposition. Teresa M. Barnes, Jackie Leaf, Kyle Olson and Colin A. Wolden; Dept. of Chemical Engineering, Colorado School of Mines, Golden, Colorado.

Zinc oxide (ZnO) is a versatile II-VI semiconductor that has generated tremendous interest due to its unique combination of optical, electrical, and mechanical properties. Its potential for p-type conductivity is unique among transparent conducting oxides, and its bandgap is ideal for applications such as UV lasers and short wavelength LEDs. Nitrogen is widely used in studies of p-type behavior in ZnO, but very little is known about the nitrogen incorporation mechanism in ZnO. Nitrogen incorporation was studied using high vacuum plasma-assisted chemical vapor deposition (HVP-CVD). An inductively coupled plasma (ICP) source was used for the generation of radicals and atomic species. Radicals from the ICP source and organometallic precursors diffuse into a high vacuum environment where they combine to form metal oxide thin films on a heated substrate. The process is differentiated from conventional CVD approaches in that the collisionless environment precludes gas-phase reactions with the metal precursor. Optical emission spectroscopy (OES) is used to monitor active species concentrations in the plasma, while the high vacuum deposition chamber is monitored with a quadrupole mass spectrometer (QMS). Here, we present a systematic study of nitrogen incorporation from plasma activated N₂/O₂ and N₂O/O₂ mixtures. Both the OES and QMS data show that at equal elemental N/O ratios, these plasma mixtures exhibit nearly identical compositions. The precursors form O₂, N₂, O, N, NO, and excited N₂^{*} in the plasma. Analysis of the film composition with X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) revealed nitrogen incorporation increased steadily as the fraction of N₂ or N₂O in the plasma feed increased. Detailed optical, electrical, and structural characterizations were also performed. The mechanism of nitrogen doping in ZnO and film properties will be discussed as a function of the chemistry in the deposition environment.

9:45 AM H12.6

Transport Properties of Phosphorus Doped (Zn,Mg)O Thin Films and Devices. Yuanjie Li, Youngwoo Heo, Yongwook Kwon and David Norton; Department of Materials Science and Engineering, University of Florida, Gainesville, Florida.

ZnO is an interesting semiconducting oxide, having a direct band gap of 3.37 eV and a large excitonic binding energy of 60meV. Achieving reliable p-type material remains a major challenge facing further development of ZnO based devices. Recent efforts have focused on ZnO p-type doping with N, P or As. We have previously reported on P-doped (Zn,Mg)O based device structure whose properties are consistent with phosphorus substitution introducing an acceptor level. However, the p-type behavior was highly dependent on the growth process and annealing conditions. In this paper, the systematic study of the relationship of doping concentrations, growth conditions, and post-annealing with the transport properties will be discussed. Another important issue related to P-doped (Zn,Mg)O thin films is the low carrier mobility due to defects resulting from lattice and thermal mismatch between the ZnO layer and the substrate. The possibility of depositing a semi-insulating ZnO buffer layer on the substrate before the growth of the P-doped (Zn,Mg)O layer will be discussed. Improved crystallinity thin films can be realized by the insertion of an undoped ZnO buffer layer. Field effect device structures with undoped ZnO/P-doped (Zn,Mg)O thin films as the channel materials on sapphire using pulsed laser deposition will be described.

10:30 AM H12.7

2-Deg at ZnO/ZnMgO Heterointerface. M. Yano^{1,2}, K. Koike^{1,2}, K. Hama¹, I. Nakashima¹, M. Ozaki¹, K. Ogata², S. Sasa^{1,2} and M. Inoue^{1,2}, ¹New Materials Research Center, Osaka Institute of Technology, Asahi-ku Ohmiya, Osaka 535-8585, Japan; ²Bio Venture Center, Osaka Institute of Technology, Asahi-ku Ohmiya, Osaka 535-8585, Japan.

The formation and characterization of 2-DEG at ZnO/ZnMgO heterointerface are reported. Samples were (0001)-oriented O-polarity single-crystalline films grown on *a*-plane sapphire substrates by plasma-assisted molecular beam epitaxy. Both unintentionally doped 50-nm-thick ZnO layers with and without Zn_{0.6}Mg_{0.4}O cap layer were grown on a thick (400 nm) Zn_{0.6}Mg_{0.4}O buffer layer, and were found to have a high electron mobility of about 170 cm²/Vs at 300 K which increased to more than 400 cm²/Vs at 100 K by keeping up the large value even at much lower temperatures. This mobility was associated with a temperature-independent electron density of about 2×10¹⁸ /cm³ (1×10¹³ /cm²). Such a high mobility with a high density was very different from that of a pseudo-bulk 500-nm-thick ZnO layer without Zn_{0.6}Mg_{0.4}O buffer layer; the electron mobility and density in pseudo-bulk ZnO were typically 100 cm²/Vs and 3×10¹⁷ /cm³ at 300 K, respectively, and the mobility decreased rapidly with temperature after reaching the peak value of about 200-300 cm²/Vs at around 150 K. We attribute the high electron mobility in ZnO/Zn_{0.6}Mg_{0.4}O to 2-DEG formation; the lattice mismatch between constituent materials can yield a positive sheet charge to accumulate the 2-DEG at bottom heterointerface by the piezoelectric polarization towards the substrate. Although the direction of polarization is inconvenient for the modulation of 2-DEG density using a gate electrode on O-polarity surface, we have succeeded in obtaining all ZnO-based HFETs with the gate electrode on insulating ZnMgO cap layer by controlling the internal electric field and carrier density in ZnO well.

10:45 AM H12.8

A Wet Chemical Route to One-dimensional, Single-Crystalline Transparent Conducting Oxide (TCO) Nanostructures. Bin Cheng¹, Joette M. Russell¹, Wensheng Shi¹, Lei Zhang¹ and Edward T. Samulski^{1,2}; ¹Chemistry, University of North Carolina, Chapel Hill, North Carolina; ²Curriculum in Applied Materials Sciences, University of North Carolina, Chapel Hill, North Carolina.

One-dimensional (1-D), transparent, conducting oxide (e.g. SnO₂, ZnO) nanostructures were prepared in solution under low-temperature conditions.^{1,2} The aspect ratios of the 1-D nanorods are tunable by delicately-selected experimental conditions, allowing for generation of materials ranging in size from nanorods to nanowires. The structures of the as-synthesized nanorods and nanowires were characterized by XRD, TEM, SAED and HRTEM, and the optical properties of these materials are reported. References 1. Bin Cheng, Edward T. Samulski, Chem. Commun. 2004, 986-987; 2. Bin Cheng, Joette M. Russell, Wensheng Shi, Lei Zhang, Edward T. Samulski, J. Am. Chem. Soc. 2004, 126, 5972-5973.

11:00 AM H12.9

Photogenerated carrier injection to transition metal oxides. Yuji Muraoka, Takaki Muramatsu and Zenji Hiroi; ISSP, Univ. of

Recently, we reported an efficient way for hole doping, which is a photocarrier injection (PCI) method in TMO heterostructures [1,2]. We prepared an insulating thin film of vanadium dioxide (VO₂) on an n-type TiO₂ substrate doped with Nb, and observed a remarkable decrease in resistance under ultraviolet (UV) light irradiation. We also observed a positive photovoltage of 0.5 V to the film. To explain these observations, we have proposed a simple band picture where only hole carriers created by absorbing a light in TiO₂:Nb are injected to the film through the interface, resulting in the reduced resistance of the VO₂ film. More recently, we have applied this PCI method to YBa₂Cu₃O_{7-x} (YBCO) in a YBCO/SrTiO₃:Nb heterostructure and observed an enhancement of the superconducting critical temperature T_c in underdoped YBCO films under UV light irradiation [3]. From our estimation of injected carrier density, the most of injected hole carriers is considered to exist near the interface, giving rise to a hole-rich thin layer with an enhanced T_c. In this work, we apply the PCI method to an n-type superconductor Sr_{1-x}NdxCuO₂ (SNCO) in a SNCO/SrTiO₃:Nb heterostructure and study the current-voltage and photovoltaic properties under UV light illumination. A Sr_{1-x}NdxCuO₂ (x=0.11) thin film was prepared on a SrTiO₃ (100) single crystal substrate doped with 0.05 wt% Nb (STO:Nb). The film deposition was carried out by using the pulsed laser deposition technique with a KrF excimer laser (λ = 248 nm). The film thickness was 300 nm. Resistivity measurements show that the films become superconducting at 10 K. As the source of a UV light (λ = 300 - 400 nm), a Xe lamp was used. All the measurements were carried out at room temperature. The current density (J)-voltage (V) curves of the YBCO/STO:Nb heterostructure were measured in the dark and under UV light irradiation. In the dark, the J-V curve exhibits marked rectifying behavior: the current increases steeply around a positive bias voltage of 0.5 V. Under UV light irradiation, the J-V curve shifts downward with an open-circuit voltage VOC of 0.5 V and a short-circuit current density JSC of 7.5 × 10⁻⁵ A/cm², as in a conventional semiconductor photodiode. The observed VOC is positive to the SNCO film as in the VO₂/TiO₂:Nb heterostructure, implying that hole carriers are injected certainly to the film. Observed VOC increases linearly with light irradiance in a wide range of 10⁻⁵ < L < 10⁻² mW/cm². At higher irradiance, it tends to saturate toward 0.5 V. We are now studying the effect of PCI on T_c of the SNCO film. Results will be presented. [1] Y. Muraoka, T. Yamauchi, Y. Ueda and Z. Hiroi, J. Phys.: Condens. Matter 14 (2002) L757. [2] Y. Muraoka and Z. Hiroi, J. Phys. Soc. Jpn. 72 (2003) 781. [3] Y. Muraoka, T. Yamauchi, T. Muramatsu, J. Yamaura and Z. Hiroi, J. Magn. Magn. Mater. 272-276 (2004) 448.

11:15 AM H12.10

Synthesis of ZnO nanorods with controllable orientation and area-density. Ming-Ta Chen and Jyh-Ming Ting; National Cheng Kung University, Tainan, Taiwan, Tainan, Taiwan.

Zinc oxide (ZnO) is an excellent material for use in optoelectronic applications due to its wide direct band gap of 3.33eV. Among its various forms, ZnO nanorod has become an important one as a result of the advance of nanotechnology. In previous papers[1,2], we have reported a new route for ZnO nanorod synthesis using a sputter deposition technique. It was also found that the orientation and the area density of ZnO nanorods seem to depend on the geometry of the target-substrate holder setup. Recently we have found ZnO nanorod/ZnO thin film structure a potential application in solar cells as an integrated current collector/electrode. For such an application, it is important to grow ZnO nanorods with desirable orientations and area densities. As a result, we have investigated the effect of the aforementioned geometry and other growth parameters on the orientation and area density of ZnO nanorods. ZnO nanorods were deposited using a magnetron sputter deposition technique. Silicon wafers were used as the substrates. Prior to the deposition of ZnO nanorods, the substrates were pre-coated with Cu using an electroless plating technique. ZnO nanorods were deposited under various geometries of the target-substrate holder setup, deposition times, O₂/Ar ratios, and substrate temperatures. It was found that the nanorod orientation is primarily determined by the angle between the target surface and the substrate holder surface. The area density, on the other hand, is affected by not only the angle but also the characteristics of the electroless copper interlayer, which is decisive for the formation of ZnO nanorods.

11:30 AM H12.11

Amorphous Oxide Semiconductor Exhibiting Large Hall Mobility (> 10 cm²/Vs): Electronic Structure, Carrier Transport and Device Applications of a-InGaZnO₄.

Nomura Kenji^{1,2}, Toshio Kamiya^{1,2}, Hiromichi Ohta², Akihiro Takagi¹, Hiroshi Ynagi¹, Masahiro Hirano² and Hideo Hosono^{1,2}; ¹Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; ²Hosono Transparent Electro-Active Materials Project, JST, Kawasaki, Japan.

Transparent amorphous oxide semiconductors (AOSs) are expected as a material for developing novel devices because of their unique properties such as highly optical transparency in visible region and wide controllability of carrier concentration from insulator to metallic states. Further, they could be deposited at low temperatures such as room temperature, which enables the formation of optoelectronic devices on inexpensive plastic substrates[1]. AOSs exhibit good carrier transport properties characterized by large Hall mobility and absence of Hall voltage sign double anomaly. AOSs having chemical compositions of In₂O₃-Ga₂O₃-(ZnO)_m (m = 1 - 4), a-IGZO, are n-type semiconductors and exhibit Hall mobilities > 10 cm²/Vs at carrier concentrations larger than 10²⁰ /cm³[2]. However, detailed carrier transport properties, especially at low carrier concentrations, has not been clarified yet. In this study, we have investigated carrier transport properties in a-IGZO in detail. Electronic structure and transport mechanisms are discussed based on temperature dependence of Hall effect measurements. We used a pulsed laser ablation technique using crystalline InGaZnO₄ sintered target. Films were deposited on SiO₂ glass substrates at room temperature. Carrier concentration of the films was varied from <10¹⁵ - 10²⁰ /cm³. Hall effect measurement was carried out using the van der Pauw configuration in the temperature range from room temperature to 30 K. The Hall mobility (μ_{Hall}) strongly depended on carrier concentration (N_e) and was sharply increased from 3 to > 13 cm²/Vs as carrier concentration increased. The temperature dependence of N_e changed from thermally-activated behavior to degenerated behavior at 1.0×10¹⁷ /cm³, while that of μ_{Hall} shows thermally activated behavior even when carrier concentrations 3.0×10¹⁸ /cm³. These results suggested that Fermi levels exist in band-tail states originating from structural randomness when N_e is < 3.0×10¹⁸ /cm³. As definite Hall voltages were observed, the tail states are not localized. This carrier transport mechanism is completely different from that in covalent amorphous semiconductors such as a-Si:H. Device applications including amorphous oxide p/n junctions utilizing recently found p-type AOS[1] will also be presented. [1] S. Narushima, K. Ueda, H. Mizoguchi, H. Ohta, M. Hirano, K. Shimizu, T. Kamiya and Hideo Hosono, *Adv. Mater.* **15**, 1409 (2003). [2] M. Orita, H. Ohta, M. Hirano, S. Narushima and H. Hosono, *Phil. Mag. B* **81**, 501 (2000).