SYMPOSIUM H
Functional and Multifunctional Oxide Films
November 29 - December 3, 2004

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Materials with Novel Electronic Properties - MaNEP

* Invited paper
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 (Tₑ ≈ 1100K) and antiferromagnetic (T_N ≈ 640K) orders at room temperature. Properties of BiFeO₃ have been puzzling. (1) Reported polarization value (< 10μC/cm²) 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 polarization were observed for all three orientations (55 μC/cm² for (001) films, 80 μC/cm² for (110) films, and 100 μC/cm² 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 N00014011767, N000140210340, N000140210126) and the National Science Foundation (grant #s MRSEC DMR-00-8008).

10:15 AM H1.5

Giants Ferroelectric Poling in Multiferroic BiFeO₃ Thin Films, Kuo-Young Yum¹, Dan Rabinovich¹, Minoula Noda², Saburo Nasu³ 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 substrate. The oxygen pressure was 0.05 Torr and the deposition temperature was fixed at 850°C. Pt top electrodes with 240 nm 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 μC/cm², which is considerably higher than previously reported for BFO. Moreover, the coercive field at 90 K allowed us to obtain GFP such as 146 μC/cm² and a saturation polarization (P_s) of 185 μC/cm² with a coercive field of 120 kV/cm at 20 V maximum applied voltage. These values are the highest for inorganic 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 weak ferromagnetic hysteresis characteristic with saturation magnetization 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.
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 - BiSrCuO (BSO) composition spreads in order to investigate their properties as a function of continuously changing composition. The compostoions spread 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 capacitors. In contrast, thin film growth 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 X-ray diffraction. Dielectric constant at the BSTO composition of 40-60% characteristic of a structural phase transition. The lattice constant was found to increase as one approaches the pure BTO end of the spread. We observed a sudden change in the lattice constant at the BSTO composition of 40-60% characteristic of a structural phase transition. Dielectric constant and loss tangent 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 BSTO, for both the S and P polarizations, suggesting that the ferroic properties degrade with BSTO, in agreement with the dielectric measurements.

11:00 AM *H1.8 Multiphase 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 electronic behavior, superconductivity, etc. The functional responses can typically be described in terms of thermodynamics or through the description of internal degrees of freedom like strain. Understanding the interactions between them has been the focus of much recent development. 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 discovery involves 3-dimensional coupling between the two materials and the matrix 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 and by the ONR under a MURI program.

11:30 AM H1.9 Multiferroic Perovskite-Spinel Oxide Nanostructures. Haimei Zheng 1, Junling Wang 1, F. Zavaliaris 2, Li Mohammadi-Ashtiani 1, D. G. Schlom 2 and R. Ramesh 1.

Department 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; 1Department of Materials Science and Engineering, University of California, Berkeley, California.

Ferroelectric/ferromagnetic perovskite-spinel oxide nanostructures have been synthesized by solid-state reaction. Spinel phase, i.e. CoFe₂O₄, or NiFe₂O₄ and perovskite phase i.e. BaTiO₃. BaTiO₃ spontaneously separated during heteroepitaxial growth on single crystal SrTiO₃ (001) substrates with or without bottom SrRuO₃ electrode phase microstructure. A ferroelectric nano-domain array is 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-00-80908.
situ synchrotron x-ray scattering at the Advanced Photon Source to characterize the strain state of SrTiO$_3$ epitaxial films grown on DyScO$_3$ at 1100°C by MBE, and their evolution 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, providing both thickness and lattice constant. 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 SrTiO$_3$. We will discuss the implications of these results for the growth of epitaxial films on novel substrates including (110) SrTiO$_3$ and (111) BaTiO$_3$.

2:15 PM H2.3

**Giants of Ferroelectricity in Strained BaTiO$_3$ Thin Films**

K. J. Choi, C. B. Eom, M. Biegalski, Y. L. Li, A. Sharan, Long-qing Chen, V. Gopalan, and D. G. Schlom

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 offers opportunity to modify the various ferroelectric properties. We deposited fully commensurate BaTiO$_3$ (a = 3.992 Å) on SrTiO$_3$ thin films on novel substrates including (110) DyScO$_3$ (a = 3.944 Å) and (110) GdScO$_3$ (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°C) four-circle x-ray diffraction and second harmonic generation measurements. Biaxial compressive strain dramatically enhanced the ferroelectric properties—both the ferroelectric transition temperature (Tc) and remanent polarization (Pr)—of BaTiO$_3$ on SrTiO$_3$ thin films on novel substrates including (110) DyScO$_3$ and (110) GdScO$_3$. This strain, imparted by commensurate epitaxy, can result in a Tc nearly 500 K higher and a Pr at least 250% higher than BaTiO$_3$ single crystals. This is the largest increase of Tc 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 Tc and high Pr needed for ferroelectric memories, and also a general method for achieving extraordinarily physical properties in thin films through strain engineering.

2:30 PM H2.4


Alok Sharan, Arvind Vasudeva Rao, Mike Beglais, Yulan L. Li, Long Qing Chen, Darrell G. Schlom, Venkataraman Gopalan, Kyoung Jin Choi, and Chang Beom Eom

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Second Harmonic Generation is used for in-situ probing of ferroelectric domain reversal and phase transitions in strained SrTiO$_3$ and BaTiO$_3$ thin films on unique substrate materials. Recently we have grown commensurately strained structures of epitaxial SrTiO$_3$ and BaTiO$_3$ thin films using unique substrate materials, such as DyScO$_3$ and Dy$_2$ScO$_5$. Enormous compressive strains (up to 1.5%) have been imparted on these materials. This strain, imparted by commensurate epitaxy, can result in a Tc of nearly 500 K higher and a Pr at least 250% higher than SrTiO$_3$ and BaTiO$_3$ single crystals. This is the largest increase of Tc 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 Tc and high Pr needed for ferroelectric memories, and also a general method for achieving extraordinarily physical properties in thin films through strain engineering.

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 regime to produce atomically-flat SrRuO$_3$ bottom electrodes on single-stepped (001) SrTiO$_3$ single crystals, onto which nearly perfect heterostructures can be grown.

Perovskite-type oxide heterostructures with atomically-flat interfaces, and single unit-cell step heights, have been grown on such substrates by PLD at 700°C in 10 mTorr O$_2$. The heterostructures were atomic-scale asymmetric three-component superlattices (TCSs) of BaTiO$_3$:SrTiO$_3$, and CaTiO$_3$ 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 (2600 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 BaTiO$_3$ layer fraction as little as 5%, had $P_r$ of $25 \mu C/cm^2$, an increase of almost 50% as compared to a BaTiO$_3$ 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 BaTiO$_3$.

This was seen to occur only when the BaTiO$_3$ thickness did not exceed the combined value for the SrTiO$_3$ and CaTiO$_3$ 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 also discuss potential enhancements to the ferroelectric polarization due to the local asymmetric Research sponsored by the U.S. Department of Energy under contract DE-AC05-000227275 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**

Gustavo Catalán, Mary Gregg, and Lesley Sinnamon

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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 that of bulk). Strain gradients may couple to ferroelectric polarization 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 PT/TiLSMO Heterostructure at the Parmagnet-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 magneto-electric (ME) effect has been observed in both single-phase materials such as YMnO$_3$ and composites of bonded thick piezoelectric/ferromagnetic layers. Attempts to harness this effect in epitaxial heterostructures grown on substrates such as SrTiO$_3$ show little effect because of the absence of the desired coupling on such 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 La$_{0.9}$Sr$_{0.1}$MnO$_3$ (LSMO) and a strong strain 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 manganese crystal has been shown to neutron diffraction to exist in an in-plane anisotropic lattice anomaly at $T_c$, with an expansion of the in-plane axis $\Delta a/a \approx 0.10$. 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 plan to carry out a series of experiments on this novel magnetic field dependent coupling between 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 La$_{0.9}$Sr$_{0.1}$MnO$_3$ epitaxial thin films. Ingrid C. Infante, Florencio Sanchez and Josep Fontcuberta; Instituto de Ciencia de Materiales - 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 La$_{2-x}$Ca$_x$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 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 varying from 20 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, in effect, a higher Curie temperature and larger saturation magnetization than (001) films. X-ray reciprocal space mapping was done to accurately tune 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 epitaxial 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 [110] direction, whereas the main strain direction (001) remains the easy magnetization axis. We will discuss the origin of structural anisotropic relaxation in this system and its impact on the properties of the films. The models that relate anisotropic magnetic properties controlled by the anisotropic film strain, which itself can be modified by the film thickness, clearly indicate the magnetoelastic origin of the anisotropy in (110) films. This contrasts with the magnetocrystalline dominated anisotropy in (001) films. Perspectives for exploiting the tunable in-plane anisotropy and extension of these findings to other functional oxide materials will also be addressed.

4:15 PM H2.9
Investigation on Room Temperature Operation of Resistive Bolometer with Strain Induced Thin Film of La$_{0.8}$Bi$_{0.2}$MnO$_3$. Hideaki Tachibana, Hideaki Tanaka and Tomoji Kawai; The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan.

The strain induced perovskite-type manganese oxide of La$_{0.8}$Bi$_{0.2}$MnO$_3$ (LBMO) thin film deposited on SrTiO$_3$(001) substrate is studied from the viewpoint of application for uncooled bolometer. 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 1800 msec, respectively. At room temperature, it was turned out that a very sensitive bolometer 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 La$_{0.8}$MnO$_{3+y}$ Films. Michael A. DeLeon', Trevor Tyson', Catherine Dubourdieu', Joseph Drvok' and Dario Arena'; 1Applied Physics, New Jersey Institute of Technology, Newark, New Jersey; 2Physics, CNRS, Grenoble, France; 3NSLS, Brookhaven National Labs, Upton, New York; 4Physics, Rutgers University, New Brunswick, New Jersey.

The magnetic and transport studies have been conducted on La$_{0.8}$MnO$_{3+y}$ films of thickness varying from 60 to 180nm. 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 1000, 300 and 60 A have magnetization ratios of 1.0:75:8.5:7. Measurement of the top 60 A of the films measured by XMCLE 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. Hsiang-Chung Wang and Chang-Beom Eom; Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Multiferroic oxides have drawn considerable 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 multiferroic material is crucial and need to be understood. BiFeO$_3$ has been reported to have both ferroelectric, with saturated polarization of 6 μC/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 (40 μC/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 dependent 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 dependent 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/Pieoelectrics
Chairs: Simon Philippot 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 produces single phase BFO. In this work, a series of calcinations 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, 0.7BiFeO$_3$– 0.3SrTiO$_3$ (BFO-BT) solid solutions
were synthesized. The calculation temperatures were varied from $800^\circ$C to $920^\circ$C in steps of $20^\circ$C for 8 to 20 minutes. XRD analysis confirmed that the pure material has synthesized at the calcinations temperature of $900^\circ$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 $O_2$ pressures and substrate temperatures. The corresponding 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, the ferroelectric hysteresis loops were obtained in thin films due to the high dielectric constant. 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$_{1-x}$Ti$_x$)O$_3$ (GaxFe$_{1-x}$Zr$_x$O$_3$) 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, Gafonel, magneto-electric, magnetic sensor

H3.3 Electromechanical Probing of BiFeO$_3$ Films. Catalin Harnagea, Cristian Victor Cojocaru and Alin Pignolet; University of Quebec, INRS-EMT, Varennes, Quebec, Canada.

Bismuth ferrite BiFeO$_3$ (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 hundred nm thick (therefore strained by the substrate) exhibit a spontaneous polarization of the order of $100 \mu C/cm^2$, more than one order of magnitude higher than that of BFO bulk single crystal. This enhanced ferroelectricity, together with the multiferroic effect in 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 piezoelectric 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 600 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 BaTiO$_3$). This is caused by the fact that, the crystal symmetry of BFO 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 PbTiO$_3$-CoFe$_2$O$_4$ Nanostructure in Constrained Films on SrTiO$_3$ Substrate. Jianhua Li, Alexander R. Ramsay,伊利金, Peter Schenck, and Martin Green; 1Materials 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.

Ferroelectric PbTiO$_3$-CoFe$_2$O$_4$ thin film nanostructures on SrTiO$_3$ substrate have been developed by pulsed laser deposition. The different composition and orientation of substrate are studied with films thickness close to 350nm. X-ray and TEM studies show that the films consist of CoFe$_2$O$_4$ nanopillars embedded in the PbTiO$_3$ 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 1/3CoFe$_2$O$_4$-2/3PbTiO$_3$ till 50nm at the composition 2/3CoFe$_2$O$_4$-1/3PbTiO$_3$. For (110), (100), and (111) film orientations, the pillars are normal to the substrates. The nanostructures demonstrate rectangular shape of ferromagnetic and ferroelectric hysteresis loops. The magnetization and polarization are decreased due to constraints between the two phases. The 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-02-80080 and NSF-MBSEU under contract No. DMR-02-10512.

H3.5 Theory and Modeling of Multiferroic Heterostructures. Julia Sluskin, Alexander R. Ramsay, and Andrei Artemyev; 1Materials Science and Engineering, University of Maryland, College Park, College Park, Maryland; 2Mechanical and Aerospace, Carleton University, Ottawa, Ontario, Canada.

We present thermodynamic theory and phase field modeling of the formation and performance properties of ferroelectric-ferromagnetic heterostructures. The elastic interactions between the phases dictate the domain architecture of the heterostructures and control their response to electrical field. For ferroelectric-ferromagnetic multilayer it is possible to observe 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.


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 mismatch, 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 assessed. 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 Fe$_2$O$_3$ nanowires embedded in a ferroelectric BiFeO$_3$ by a selfassembly 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, like clusters of the insulating ferrimagnetic spinel CoCr$_2$O$_4$ (CCO) on MgAl$_2$O$_4$ (001).

The structures of the surfaces are {111} facets, which form an angle greater than 60 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 (de)similarities of the growth of the spinel CCO structures with that of the widely studied 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, 63 (2004); [3] Luders et al., Phys. Rev. B 69 (24), in press; [4] Luders et al., submitted.
both ferroelectricity and ferromagnetism. We will also present in situ nonlinear optical studies of domain dynamics in ferroelectrics under external fields.


Multiferroic ceramics have been attracting considerable attention in the recent times owing to their interesting ferroelectric and magnetic properties in the same material platform. There have been significant achievements in the synthesis and understanding of multifunctional behavior in phase pure ferroelectromagnets with potential applications in tunable sensors and spintronic devices. Among several candidates possessed quasiperiodic 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 a considerable amount of work 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 in the fabrication kinetics which 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 these systems 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 EMF (electromagnetic 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.


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 magnetoelectric processes 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 MnO6 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. Order-Monopoles (o-M) 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, spin flop and induced by pulsed depolarization method. The relationship between the magnetic structure and the dielectric properties are discussed in terms of temperature dependences of magnetization and dielectric permittivity. Eventually, the control of ferroelectric domain switching by applying external magnetic field is presented.

### H3.10 Study of Highly Oriented 2T and 2TS Multifunctional Oxides for Satellite Communications. Marco Vittone, Giuseppina Fadeletti, Silais Kaculis, Gabriel Ingo, Luca Pandolfi and Carlos Zaldo.

Instituto per lo Studio dei Materiali Nanostruutturati-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 their potential use in important technologies and the fundamentally interesting relationship among their crystal chemistry, magnetic structure and physical properties. Especially, titanate based ceramics have attracted large attention because they have been used in a wide range of applications (Catalysis, Humidity Sensors, Industrial Chemical, 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 (εr), low dielectric loss (tanδ) and low temperature dependence of permittivity (Tcc) of great interest. The basic compound, ZrO2, has long been known to have a relatively low temperature coefficient of the dielectric constant, but the compound Zr0.8Sn0.2TiO4, has been found to have optimal properties at microwave frequencies (εr ~ 38, Tcc = 0 ppm °C-1 and tanδ < 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 to achieve the most suitable dielectric properties. Substrate temperature of 500-600 °C and deposition pressure of 5x10^-4 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 PbZr0.4Ti0.6O3 Film Spin-Coated on Pt Bottom Electrode Buffered with Thin La0.6Sr0.4O3 Layer. Jai-Hyun Kim and Woong Kil Choo.

Material Science and Engineering, KAIST, Taejon, 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 400 500 nm capacitor thickness of top electrode ferroelectric layer and 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 measured by leakage properties. We have studied ferroelectric properties of Pb(Zr0.6Ti0.4)O3 (PZT 40/60) film grown on Pt(111)/TiO2/SiO2/Si(100) bottom electrode buffered La0.6Sr0.4O3 (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 hysteres. 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 the temperature increasing to 375K. We measured the E-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 375K. However, above 375K, 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.


Materials and Process Simulation Center, Beckman Institute (135-74), California Institute of Technology, Pasadena, California; 2Max Planck Institut fur Festkörperforschung, Stuttgart, D-70199, 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 SrTiO$_3$ 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 wave basis sets are 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 surfaces in general are much more perturbed as shown also that the covalent component in the B-O chemical bonding decreases, the substrate clamping effect is significantly reduced and islands lithographically with different lateral sizes. As the pattern size thickness of the 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 (10$^2$ Hz to 10$^5$ Hz). Our results indicate three major features:

- A decrease of dielectric strength, reduced extrinsic domain wall contribution and insufficient 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.

H3.13 Meta-Stability of Barium Strontium Titanate in Thin Film Capacitor Structures. Akelin Lookman$^1$, Jonny McAneny$^1$, Robert M. Bowman$^1$, Marty J. Gregg$^2$, John Kut$^2$, Susanna Rios$^2$, Andreas Rueediger$^4$, Matt Dawber$^3$ and James F. Scott$^2$; $^1$Department of Pure & Applied Physics, Queen's University Belfast, Belfast, United Kingdom; $^2$Department of Earth Sciences, University of Cambridge, Cambridge, United Kingdom; $^3$DPMC, University of Geneva, Geneva 4, Switzerland; $^4$Centre 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 (10$^2$ Hz to 10$^5$ Hz). Our results indicate three major features that have not been observed in the literature to date: (i) $T_D$ (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 $T_D$, 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 the crystallinity 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 Sunghi Baik; MSEE, 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 critical thickness. 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. For instance, 25% of the 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 PdTiO$_3$ patterns on MgO(001), some of the a-domains turned into c-domains due to the relaxed tensile strain. In the PdTiO$_3$ 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 8635 (2000) [2] Y. K. Kim, K. Lee, and S. Baik, J. Appl. Phys., 92 256 (2004)

H3.15 High Quality Screen Printed PZT Thick Films Using Modified Chemical Solution for Piezo-MEMS Devices. Seunghyun 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 constants. Among ferroelectrics, PZT films are considered one of the most promising candidates for these applications since they can produce high mechanical strain under applied electric field. However, stress induced in PZT thick films due to clamping of the films by the substrate and other deposits such as electrodes, typically reduces 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 shown 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 of PZT MEMS devices in detail. This work was supported by National Research Laboratory Program (NRL)


Conducting RuO$_x$ thin films are promising for applications such as electrodes for ferroelectric devices and electrochemical reactions. In this study, RuO$_x$ thin films were deposited at room temperature by reactive rf magnetron-sputtering using Ar/O$_2$ discharge of varying ratios of O$_2$/Ar+O$_2$ over the range from 10% to 50%. With increasing oxygen content in the chamber, the film microstructure undergoes a transition from metal-rich nanocrystalline to 10% O$_2$ to nanocrystalline (amorphous) oxide at 20% O$_2$ and then to polycrystalline oxide films at oxygen contents higher than 20%. Texture changes continuously from (110) at 25% O$_2$ to (101) at 50% O$_2$. 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 measurement has shown that in contrast to the CSD 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 Halder$^1$, Theodor Schneller$^1$ and Rainer Waser$^{1,2}$; $^1$Institut für Werkstoffe der Elektrotechnik, RWTH -Aachen, Aachen, NRW, Germany; $^2$Institut für Festkörperforschung, Forschungszentrum Jülich, Jülich, Germany.

It is noted that post annealing at temperatures lower than 300°C did not produce any noticeable change in the leakage. In addition, microstructural studies involving XRD and SEM were also performed.
Development of TiO2 Thick Film Capacitors for use as Strain Gauge Sensors: Khalid Ibrahim Arshad, Arazan Arshad, Deirdre Mary Morris, Olga Korostynska, Fasa Jafer, John Harris and Seamus Clifford; Computer 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 nonlinearity 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 was fired at 1250 °C for five hours. After cooling the pellet was crushed to a fine powder, which was combined with PVBl 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, and hence piezoelectric 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 40 have been recorded. In addition, these 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 on their microstructure and piezoelectric properties has been investigated. As a result of this 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. 41-42. Brunette, D.M., Titanium in Medicine, Springer, 2001.

Electrical and Structural Characterization of Laser Ablated Ca Doped Barium Titanate Thin Films on Different Substrates. Victor Pushpara, S.B. Krupanidhi; University of Geneva, Geneva, Switzerland; 2Dept of Physics, University of Liege, Liege, Belgium.

We have fabricated 20 bi-layer Pt/TiO2/SrTiO3 superlattices with extremely fine periodicity (layers as thin as a 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 Pt/TiO2 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 TiO2 layer is thinned. However, in the thinnest PtO2 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.

Non-linear Dielectric Response in (111) and (100) Oriented 0.5Pb(Yb/3Nb/2)O3-0.5PbTiO3 Thin Films. Naznin Basseet Olabi 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, \( \varepsilon = \varepsilon_0 + \alpha E^2 \) and \( P = \varepsilon_0 E^2 / 2 \), where \( \varepsilon_0 \) is the static dielectric constant of the material, \( \varepsilon \) and \( P \) are the irreversible and reversible Rayleigh coefficients. This modified model predicts the dielectric properties of the Pb30%Y30%Bi70%Nb70%O120.5 films in the intermediate AC field and frequency regions relatively well. Furthermore, it shows a higher irreversible Rayleigh coefficients than (111) oriented films. However, the ratio of the irreversible to reversible coefficients is also higher in the (100) oriented films, showing a larger contribution to the dielectric constant due to the irreversible component (movement of the domain walls). This work on the piezoelectric nonlinearity for these films will also be described.
a Dead Layer in Ferroelectric Films due to Interfacial Misfit Dislocations. Ibrahim Burc Misirlioglu1, S. Parim Alpay1, A. L. Vasilev1, Mark Andow2, Valsinha Nagarajan2 and R. Ramesh3, 1Materiels Engineering Division, University of California, Berkeley, California; 2Department of Materials Science and Engineering of University of California, Berkeley, California; 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 the 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 strains 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 piezoelectric properties 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. This polarization gives rise to strong depolarizing 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 layers 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 in Active Lead Barium Titanate Films for MEMS Applications. Jennifer Lynn Ruglovsky1, Matthew Dicken2, Youngbe Park3, Stacey Boland1, Mohammed El-Nagar1, David Boyd1, Alexandros Papavassiliou2, Sossina M. Haile2, David Goodwin2, Kaushik Bhattacharya2 and Harry A. Atwater2, 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 tantum-totally-randomly-oriented films at similar grain size. We have produced high quality, textured Pb0.5Ba0.5TiO3 films via epitaxy on IBAD MgO template on amorphous Si3N4. Thin films of Pb0.5Ba0.5TiO3 were fabricated by two growth methods: metallorganic chemical vapor deposition (x=0) and sol-gel (x≠0) film synthesis. For both methods, the Pb0.5Ba0.5TiO3 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. Pro-stading 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 metal electrodes and several micro- and nano-electrodes for force measurements, allowing differentiation between 90° and 180° domains in Pb0.5Ba0.5TiO3 thin films. The edges of the microelectrodes 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 reorientation and switching mechanism. The effective piezoelectric coefficient (d33) and strain behavior are obtained in the nanoscale-subgran 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 Nanowires: Nanoscale Studies of Dielectric Phenomena in Porous Single Crystal Materials. We offer low-cost alternatives to the traditional porous single crystal substrates for dielectric studies. For example, silicon carbide, a single polycrystalline material, is an ideal dielectric substrate. The porosity of silicon carbide can be controlled by simple thermal etching, a technique that can be readily applied to optical or electronic devices. This work has been supported by the NSF-MRSEC under contract No. DMR-00-80008 and by NSF DMR-0132918.


B十字xSrTiO3 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 350-950°C for 30 min, while other substrates were deposited at substrate temperatures from 10 to 900°C. 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 on the substrate 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 measurements, allowing determination of 90° and 180°-domain configurations and the reconstruction of the three-dimensional polarization orientation arrangement. Using this approach, we have obtained clear evidence of 90° domain switching in the Pb十字xSr0.5Ti0.5O3 thin films with randomly oriented texture. Beltel synthesis was used to prepare sols with Pb十字xSr0.5Ti0.5O3 thin films grown on Pt substrates using atomic force microscopy (AFM) and piezoelectric force microscopy (PFM). Piezoelectric images, in combination with in-plane (IPP) and out-of-plane (OPP) polarization measurements, allow differentiation between 90° and 180°-domain configurations. Piezoelectric images were 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.
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 capacitor structures 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 with temperature. Strongly confined structures of 25,000 Å are obtained, and Curie-Weiss analysis demonstrates a 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 results were recovered in our experiments with the absence of substantial substrate clamping in our experiments, 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, i.e. 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. Levanyuk, Phys. Rev. Lett. 83, 4010 (1999) - 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, 1150 (2004)

**H3.30**

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

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The orientation dependence of the converse piezoelectric constants in epitaxial single domain piezoelectric films constrained by substrate is calculated. The calculations were supported by the experimental measurements of the longitudinal piezoelectric constants in Pb(Zr₀.₅₂Ti₀.₄₈)O₃ and (Mg'/3Nb₂/3)O₃-(1-x)PbTiO₃ films. Based on available experimental data, 3-D orientation dependences of d33 are predicted for epitaxial films of Pb(Zr₀.₅₂Ti₀.₄₈)O₃ and x Pb(Mg'/3Nb₂/3)O₃-(1-x)PbTiO₃. The calculations are compared with experimental results. This work is supported by the NSF under contract No. DMR-02-10512 and NSF-MRSEC under contract No. DMR-06-88008.

**H3.31**

**Capacitance Temperature Sensors using Oxygen Isotope Exchanged Strontium Titanate Single Crystals.**

Hiroshi Tabashima1, Ruiping Wang1, Naoki Shikakawa1, Bambang Prijamboedi1, Akira Shoji1 and Mitsuhiro Itoh1,1 National 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, SrTiO₃, shows dielectric constant (ε) of more than 20,000 at ~2K. Unfortunately, the temperature gradient of ε, dε/dT, decreases sharply at T < 10 K due to the quantum effect and the practical application of the pure SrTiO₃ as capacitance temperature sensor material is greatly limited. Recently, it was found that for partially oxygen isotope exchanged strontium titanate, SrTiO₁₋ₓOₓ-δ₋₀₋₂, where the exchange rate x is less than 0.30 and the quantum paraelectric phase is preserved, dε/dT at cryogenic temperature increases, a trend that is favorable for the capacitance thermometer. In this report, characteristics of (110)- and (100)-oriented SrTiO₁₋ₓOₓ-δ₋₀₋₂ 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 SrTiO₁₋ₓOₓ-δ₋₀₋₂ are 176 pF/K and 0.012 at 2.2 K, respectively. These values are the same order as those of commercially available bulk doped-SrTiO₃ capacitance temperature sensors. In comparison, the temperature sensitivity and dimensionless temperature sensitivity of SrTiO₃ 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 Joules heat of I²R, where R and I are resistance and current of thermometer, respectively. A thermometer element with smaller Joules 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.**

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Compositionally graded (1-x)PMN-(x)PT thin films were prepared with a compositional variation of PT (PbTiO₃) across the film. The films possess an enhanced nonlinear dielectric response and a high tunability near 65%, which is nearly, double the tunability of these films found to be 32 μC/cm² and 250μC/cm², respectively at 300°C. The hysteresis of these films showed a narrow 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. McPhillips,1 N. J. Donnelly, 2 J. M. Gregg, 1 R.M. Bowman, 1 G. McRobbie, 2, and S. Cochran, 2

1Department of Pure and Applied Physics, Queen’s University Belfast, Belfast, United Kingdom; 2Microsensor Science, School of Electrical and Electronic Engineering, ICT (EEP), University of Paisley, Paisley, United Kingdom.

We describe the characterisation of electromechanical and acoustic behaviour of thin film structures of Au/(1-x)Pt(Mg/3, Nb2/3)O3-xPbTiO3 (PMN-PT)/La1/3Sr2/3CoO3 grown by pulsed laser deposition onto LaMnO3 single crystal substrates. Using conventional慢慢, we have characterised the relaxor ferroelectric PMN-PT film system and determined a dielectric constant of up to 2000, ε33 of 100 pC/nm and Q33 of 1-9 x10⁻² C⁻⁴ cm⁻² [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 electrical properties and other phenomena related to ferroelectric materials. 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 very good agreement between the model and the experiment. The current interest in ferroelectric thin films is due to their potential applications in non-volatile memory. The theory was presented without any reference to the corresponding unconstrained phase-field simulations, a domain stability diagram was constructed, and the predicted domain structures were compared to those obtained experimentally. Domain structures and ferroelectric properties of epitaxial thin films are typically determined using complex and time-consuming techniques, such as XRD and TEM. In this work, BaTiO3 thin films were grown on (001) SrRuO3 substrates using Pulsed Laser Deposition (PLD). Optimised films, prepared at 725°C and 0.4 mbar, were characterised to confirm single phase SBT. The in-plane polarisation is probed using opposed inter-digital electrodes, and other novel electrode configurations. A series of polarisation measurements were taken on films fabricated with various TiO2 layer thicknesses. For a-ZTT deposited at 200°C, this parameter is ε_ε = Q(vol/m^3), the maximum areal charge induced on the electrodes. For a-ZTT deposited at 200°C, this parameter is ε_ε = Q(vol/m^3), and the optimal material and processing temperatures for ZrO.2SnO.2TiO.6O.2. 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 deposition 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.

**H3.36 Correlation of Structure and Electronic Properties to ZrO_2-SnO_2-TiO_2, a High Performance Dielectric.**

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1Department of Applied Physics, Cornell University, Ithaca, New York; 2Department of Physics, Cornell University, Ithaca, New York.

The amorphous dielectric ZrO_2-SnO_2-TiO_2 (a-ZTT) has been found to have a dielectric constant ε = 62 and breakdown field E_b = 4 MV/cm. For injecting charge into today’s smaller electronics, a critical parameter is ε_c = Q(vol/m^3). The maximum areal charge induced on the electrodes for a-ZTT deposited at 200°C this parameter is ε_c = 72 MV/cm, compared to 32 MV/cm for SiO_2 and 8 MV/cm for optimized Al_2O_3. We have examined the correlation between ferroelectric properties and atomic structure by varying the processing temperature for ZrO_2-SnO_2-TiO_2 samples. 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 deposition 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.


Yulan Li, Long-qing Chen, M. Biegalski, D. G. Schlom, A. Sharan, V. Gopalan, K. J. Choi, and C. B. Eom

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Domain structures and ferroelectric properties of epitaxial thin films cannot be determined dramatically different under the corresponding conditions in bulk single crystals. In this work, BaTiO3 ferroelectric thin films are used to study thermodynamic principles based on the phonon-mediated Landau theories and phase-field simulations. Since existing phonon-mediated theories 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 for 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 BaTiO3 films under compressive strain, and the phonon-mediated theories developed for BaTiO3 systems, a domain stability diagram was constructed, which describes 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 Banj Majumder, Anu Dixit, and Ranam S. Katyal

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

In order to study the aging effect of the precursor sol, we have prepared Pb1.10Zr0.2Ti0.7O2.47 (PTZ) thin films on platinumized silicon substrates using sols aged for 560, 500, 400, 275, and 200 days. All these films crystallized into rhombohedral perovskite structure and the surface roughness and grain size of PTZ 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
tan decreases monotonically with annealing 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 Bayliss law was investigated for both freshly prepared and aged films. The estimated irreversible domain wall displacement contribution to the ferroelectric permittivity was found to be systematically increased with aging time. Depolarization reversal electric fields respectively were found to control the observed dielectric and ferroelectric properties of aged PZT films.

H3.30 Steady State Leakage Currents in Ferroelectric Thin Films.
Herbert Schroeder, EEM, IFF, FZ Juelsch Gmb, Juelsch, 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 cases
of ferroelectric thin films. In this model the carrier injection /ejection
at the electrode interfaces is described by thermionic emission and is
combined with thermionic field emission breakdown properties of the thin ferroelectric
film, which is assumed as p-n homojunction 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 asymmetrically capacitors. The trend of the simulation data 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
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Materials Science, University of Connecticut, Storrs, Connecticut;
2Delphi Research Laboratories, Delphi Research Latoratories, 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 a non-symmetric loop behaviour, the 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 along with the effect of sample thickness and the film thickness. This work is supported by the National Science
Foundation under Grant No.DMR-0129218.

H3.41 Low Temperature Transport and Grain Boundary Induced
Phase Transition in SrTiO3. Rui Zhao1, Dawn A. Bonnell1 and
Gerould Duscher1. 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.
Atomicly abrupt SrTiO3 grain boundaries, which is often used as a
deposit, 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 0.99wt% Nb-doped SrTiO3, bicrystals with misorientation angles of 30.8° 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 analytical method 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 polarization 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 Curo-Woes law below the temperatures for the maximum resistance. This is a direct evidence of the presence 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^{-18} 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-FG02-05ER45815-A001.

H3.42 Polycrystal 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. The effect of grain boundaries has 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 Catalano2,
Michael Gorman3, Igor Lyubinetsky4 and Suchanampilai
Thevuthasan5, 1Materials Science and Engineering, University of
Virginia, Charlottesville, Virginia; 2Science, Technology, and Society,
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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
surfaces. By studying the interaction of cells with these nanoscale
adhesion site arrays, they hope to generate insight into multiple
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 pretreating 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 to 5x10^-6 Torr). The results show a
broad process space in which multiphase niobium oxides were created
by only select conditions generating single niobium oxide films.
Characterization results from atomic force microscopy, x-ray
photoluminescence 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.
Epitaxial Mixed Ruthenium Oxide Films: Tunable Lattice-Matched Bottom Electrodes for Complex Perovskite Oxides. Olivier Gautreau1, Catalin Harnagea1, Alexandre Dube1, Alain Pignolet1 and Teodor Veres2; 1INRS-Energie et Matériaux, 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 29/80, BTL, SBT), for which it promotes the epitaxial growth. In order to obtain a better lattice match to a variety of materials, we propose the use of a 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 has a lower relative lattice mismatch depending on the concentration of CRO. It enables therefore to grow epitaxial ferroelectric films with lower strain, 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.

Strained SrTiO₃ Films on DyScO₃ Substrates. Nora P. Ortega, Pijush Bhattacharya, Rasmi R. Das and 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 remanent polarization up to 10 μC/cm² at 250 K that exceeds 15,000 at low measurement frequencies. The dielectric dispersion will be discussed in terms of soft x-ray absorption near-edge structure (XANES) and x-ray emission (XES) spectroscopies, while Hand D depth profiles are 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 (15) than that of single layer SBN films. The switching polarization of SBT films was in the range of 10-7 A/cm². The leakage current density of the single layer and 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.

Microstructural and Electrical Characterization of PZT Thick Films on Metal Foils. Aiyung Wu1, Paula Maria Vilarinho1, Sudarsana 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.

Among the multilayer thin films of PZT/SBT, the latter is widely employed for the thick films, as a result of its good dielectric properties. The dielectric constant of the films was found to be lower (150) than that of single layer SBN 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 were deposited on Cu, Pt and Au foils by reactive MBE. The deposited films were sintered at different temperatures from 900 to 1030°C. The effect of adding a PtO₂ coating on the film surface was studied using transmission electron microscopy (TEM) and Rutherford backscattering (RBS). The electrical properties were improved in the films with PtO₂ coatings. The electrical properties of the films were correlated with the reaction region and the density of the films.

Electronic Structure of KDP and DKDP Hydrogen-Bonded Ferroelectric Oxides. Sergei O. Kucheyev1, C. Buntinx2,3,4; 1AFCRL MRL, 2Institute of Physics, Bulgarian Academy of Sciences, 3NIST, 4University of Maryland.

Among the thinlayer perovskites, SrBi₂Ta₂O₉ (SBT) and SrBi₂Nb₂O₉ (SBN) have been extensively studied for non-volatile random access memory applications. In the latter thin films, 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 assess the influence of the leakage current of SBN capacitors, in this work, we have fabricated multilayer thin films (SBT/SBN) on Pt/TiO₂/SiO₂/Si substrate. The thickness of all theses films are 400 nm with a stacking periodicity of SBT(50 nm)/SBN(50 nm) = 100 nm. X-ray diffraction studies showed that the 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.

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 16-18 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 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 294 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 Tc called KDP (x = 0) and DKDP (x = 0.44). The electronic structure of KDP and DKDP is affected by radiation damage and complex fundamental 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 (15) than that of single layer SBN films. The switching polarization of SBT films was in the range of 10-7 A/cm². The leakage current density of the single layer and 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.

Electronic Structure of KDP and DKDP Hydrogen-Bonded Ferroelectric Oxides. Sergio O. Kucheyev1, C. Buntinx2,3,4; 1AFCRL MRL, 2Institute of Physics, Bulgarian Academy of Sciences, 3NIST, 4University of Maryland.

Single crystals of normal and deuterated KD₃H₂(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 optoelectronic 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 60-100 cm, as required for high-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 material 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 deuteron–hydrogen exchange in crystals stored at ambient conditions. The electronic structure is studied by non-linear optical measurements and 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
films deposited using both sputtering and PLD will be compared. The tunability and low dielectric loss are desired for tunable 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. BST was etched selectively using buffered HF and 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 electrical properties of thin films deposited using both sputtering and PLD will be compared.

H3.50
Formation of Patterned Crystalline Oxide Structures using Photosensitive Metal-Organoins and Hydrothermal Processing. Clifford L. Henderson, Paul J. Román, 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 precursors 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 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 films that have been deposited thus far. The resulting physical and electrical properties in many applications are promising.

H3.51
Abstract Withdrawn

SESSION H4: Ferroelectrics/Piezoelectrics I

8:15 AM *H4.1
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 PbTiO3, 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 Tc suppression in thin films. Changes in the depolarization domain phase diagram for the PbTiO3/insulator cases also indicate an evolution in the interfacial 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
1Institut de Physique, Universite de Neuchatel, Neuchatel, Switzerland; 2DPMC, University of Geneva, Geneva, Switzerland; 3Dept. de Physique, Universite de Liege, Sart-Tilman, Belgium.

Ferroelectricity in ultra-thin films has been investigated in epitaxial c-axis PbTiO3 films prepared by off-axis magnetron sputtering onto (011) 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 PbTiO3 perovskite films with thicknesses ranging from 500 Å to 20 Å. Angle-scanned XPD, based on photoelectron spectroscopy, measures the angular distribution of photoelectrons emitted from a selected atomic species 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
1DPMC, University of Geneva, Geneva, Switzerland; 2Dept. de Physique, Universite de Liege, Sart-Tilman, Belgium.
Using a first-principles model Hamiltonian approach, the PbTiO$_3$ films, all Pb4f, Ti2p and O1s core-level peaks shift by up to 0.9 eV from that of ultimate potential for ferroelectricity. Recently, structural control of PbTiO$_3$ nanostructures were fabricated by self-assembly on Pt/SrTiO$_3$ and Pt/MgO by MOCVD. Using epitaxial relation and microstructures of self-assembled PtTiO$_3$ nanostructures were studied. Piezoelectric properties were also well understood in this paper. Structural control such as shape, size and arrangement was performed. Pyramidal-shaped, triangular-prism-shaped and square-shaped PtTiO$_3$ nanostructures were successfully prepared on Pt/SrTiO$_3$(111), (110) and (100) substrates, respectively. TEM observation and SEAD (selected area electron diffraction) showed that nanostructures have a tetragonal structure and a 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 (piezoresponsive force microscopy) measurement revealed that PtTiO$_3$ nanostructures on various substrates have piezo- and ferroelectricity. Raman spectroscopy results will also be discussed.

10:30 AM H4.6
Artificially Induced Cation Disorder by CompositionModulation in Multilayer PZT, Arjen Janssen1, Guus Rijnders1, Dave H. A. Blank1 and Beatrijs 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 applications. The maximum piezoelectric effect is found close to the morphotrophic phase boundary (MPB) due to the presence of a lower symmetry (monoclinic) phase providing an extra degree of freedom for the polarization. Through using layer-by-layer growth it is possible to investigate the influence of cation ordering on the piezoelectric properties of this phase with lower symmetry. Pulsed laser interlayer deposition, controlled by reflection high-energy electron diffraction (RHEED), is used for the monolayer growth with different compositions of PZT($\sqrt{2}$T)x(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

Single-crystal thin films of many ferroelectric materials can now be fabricated from bulk crystals by 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 MeV H$^+$ ions to form a 0.25µm wide implanted region beneath the surface of the crystal. Our TEM studies show the ion 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 solubility of He in the lattice and result in local strain 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 5nm and scale in size with the local concentration of the He implant dose. A comparison with the recent microcrystallographic 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 Li and NbO$_3$. X-ray studies of shallow implanted crystals have enabled us to determine the degree of strain in the implanted region as a function of implantation dose and heat treatment. J. M. Levy, R.M. Osgood, Jr., R. Liu, E. Cross, G.S. Cargill III, A. Kumar and H. Bakhruch, 1Fabrication of Single-Crystal

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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 at the interface between the ferroelectric material 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 coherent with different lattice parameters [1,2]. As a result of the c-axis epitaxial growth of PbTiO$_3$ on SrTiO$_3(001)$ orientation, PbTiO$_3$ substrates by X-ray diffraction reciprocal space mapping. The full width at half maximum of diffracted peak for the PtTiO$_3$ (002) plane is 0.06° as observed in X-ray diffraction rocking curve measurements, comparable to that of the single-crystal substrate. Pt/PbTiO$_3$ thin film is clearly shown in the reciprocal space map. 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 using XPS interface behavior and band structure between Pt and PbTiO$_3$. ARXPS indicated that 10 Å thick surface mixed layer of lead carbonate and lead oxide exists on the surface of the PbTiO$_3$ film. However, it is found that the surface band structure can be completely removed by HNO$_3$ treatment. During in situ XPS measurement as a function of Pt deposition on HNO$_3$, treated films, all Pb4f, Ti2p and O1s core-level peaks shift by up to 0.9 eV toward higher binding energy as a result of metallization-induced electron energy effect. Further, we extracted an energy offset of 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 of electron energy effect as well as chemical shift derived from the reported work function of Pt (5.3 eV), the electron affinity and the forbidden gap of PbTiO$_3$. To examine the Fermi level position, we have experimentally determined the Fermi level position of PbTiO$_3$ and PbTiO$_3$ doped with Pt metal as determined by photoelectron spectroscopy, the measured leakage conduction properties of Pt/PbTiO$_3/SrTiO_3$ thin film capacitors will be discussed.

10:15 AM H4.5

In the past several years, interest in ferroelectric nanostructures has increased greatly not only from the point of view of applications but also from that of fundamental research for ferroelectricity. Recently, structural control of PbTiO$_3$ nanostructures was successfully reported on the preparation and ferroelectricity of self-assembled Pt/SrTiO$_3$ 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 PtTiO$_3$ nanostructures were studied. Piezo- and ferroelectric properties were also discussed. In our experiments, Pt/srTiO$_3$ nanostructures were fabricated by self-assembly 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 PtTiO$_3$ nanostructures were successfully prepared on Pt/SrTiO$_3(111), (110)$ and (100) substrates, respectively. TEM observation and SEAD (selected area electron diffraction) showed that nanostructures have a tetragonal structure and a 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 (piezoresponsive force microscopy) measurement revealed that PtTiO$_3$ nanostructures on various substrates have piezo- and ferroelectricity. Raman spectroscopy results will also be discussed.

11:00 AM H4.8
MOCVD Growth and Ferroelectric Properties of PZT Ultrathin Films with Thicknesses below 10nm.

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 the films can sustain a stable ferroelectric polarization has been experimentally observed is likely to be several unit cells. One of the reasons for this is due to the increase in the surface area, which leads to a decrease in the perovskite 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 PbZT showed the Strasnov-Krutov dome growth mode. Island formation from 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 ±2V. Switching of 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 polarization. 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 Gregg 1, Mohammed Snaid 2, Paul Baxter 3, Robert M. Bowman 1, Finlay Morrison 1 and Jim Scott 2; 1 Pure and Applied Physics, Queens University Belfast, Belfast, United Kingdom; 2Department of Earth Sciences, University of Cambridge, 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 capacitors, 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 due to profile defects 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 induced by the substrate in the system, nor to the influence of an intrinsic universal interfacial capacitance associated with the metal-ferroelectric interface.

11:30 AM H4.10
Dielectric and Mechanical Properties of Self-Supported Ferroelectric Films. Vwa Lyakhoviskiy 1, Mark Greenberg 2, Ilya Zon 2, Ellen Wachtel 1 and Igor Lubomirsky 1; 1Materials & Interfaces, Weizmann Institute of Science, Rehovot, Israel; 2Chemical Support Unit, Weizmann Institute of Science, Rehovot, Israel.

Noncrystalline 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 μm lateral dimensions). The shape of the ferroelectric films undergoes an abrupt reversible change from a dome-like shape between 120 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 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 $130 \text{°C}$, no maximum in the temperature dependence of the pyroelectric signal was observed. Instead, the first derivative of the pyroelectric constant versus temperature shows a break 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 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, November 30, 2004
Grand Ballroom (Sheraton)

1:30 PM H5.1

We show how traditional atomistic-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, KNO3 and BaTiO3 are studied. The simulated 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 phase transitions in solid solutions and semiconductor materials.

2:00 PM H5.2
Interlayer Coupling and Stability of Single Domain State in a Ferroelectric Bilayer. S. Pamir Alpay 1, Zhigang Ban 1, Joseph Mantese 2 and Alexander Roytburd 3; 1Department of Materials & Nuclear Engineering, University of Maryland, College Park, Maryland.

Ferroelectric multilayers and superlattices have gained considerable interest due to their drastically different behavior from their constituent thin films. In this presentation, we analyze the interlayer coupling between 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

Nanoscopic Studies of Disorder-controlled Domain Wall Creep in Epitaxial Pb(Zro.2Tio.8)03 Thin Films. Patrycja Paruch1, Thomas Tybell2, Thierry Gianach1 and Jean-Marc Triscone3.

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 crystallite film with random defects (composition and density) of an elastic object in a disorder potential is governed by the competition between elasticity and pinning. A static field in equilibrium exhibits a roughness characterized by the exponent \( \xi \). In the presence of a weak driving force, \( F \), the manifold moves with a velocity \( v \propto \exp[-(F/\xi)^\beta] \), a motion known as creep. The dynamical exponent \( \beta = (d+2z)/2z \) is a function of both the dimensionality, \( d \), of the system and the nature of the disorder potential, via \( \xi \). Using atomic force microscopy (AFM) and epitaxial ferroelectric thin films we have investigated individually written nanoscopic switching domains, we have demonstrated this motion to be a creep process with the characteristic electric field dependence of the velocity \( v \propto \exp[-(E/E_c)^\beta] \), where \( E \) is an energy, \( E_c \) the temperature and \( \xi \) a critical field. The dynamical exponent \( \beta \) 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 it is related to 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 \( z \) by measuring the equilibrium roughness of the domain wall. For such experiments we treat the system as an elastic object in a disorder potential, via \( \xi \). We will also present results of studies on films on pure PbTiO3 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 x-axis inclinations) and observe a noticeable decrease in the dynamical exponent \( \beta \) in the presence of these defects. We will also present results of studies of nanoscopic switching domains 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, 057601 (2002). (3) R. C. Miller et al., Phys. Rev. 117, 1460 (1960).

2:30 PM H5.4


In the last several years, Piezoresponsive 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 PFM, and it is shown that the PFM signal is an electric field below the tip results in the domain nucleation irrespective of the presence of defects sites. The hysteresis loop is determined by the formation of the transient domain below the tip, the formation of which differs in the thin film is a small but important aspect of the current understanding of ferroelectric materials. A recent analysis of the PFM signal is 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. DMR02-35629).

2:45 PM H5.5

Bit Error Evaluation of Tbit/inch² Ferroelectric Data Storage. Yoshihiro Hirana 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 current technologies (magnetic, semiconductor). We have proposed a new technique based on scanning nonlinear dielectric microscopy (SNDM) for the detection of ferroelectric domains using a 2D polarization detector (LiTaO3) single crystal has been studied in detail. In a series of the studies, 1.5 Tbit/inch² data writing were demonstrated. Additionally, data transfer rate was also examined employing the prototype of data storage system. 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 patterns in high density. However, when a pulse voltage is applied to a sample using the sharp-pointed tip, the electric field is highly concentrated near the tip. Additionally, high homogeneity in thickness over a larger recording area is required. The reliability of SNDM medium is determined by the time-dependent nucleation of ferroelectric domains. 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 crystallite film with random defects (composition and density) of an elastic object in a disorder potential is governed by the competition between elasticity and pinning. The static field in equilibrium exhibits a roughness characterized by the exponent \( \xi \). In the presence of a weak driving field, \( F \), the manifold moves with a velocity \( v \propto \exp[-(F/\xi)^\beta] \), a motion known as creep. The dynamical exponent \( \beta \) is a function of both the dimensionality, \( d \), of the system and the nature of the disorder potential, via \( \xi \). Using atomic force microscopy (AFM) and epitaxial ferroelectric Pb(Zro.2Tio.8)03 thin films we have investigated individually written nanoscopic switching domains. We will also present results of studies on films on pure PbTiO3 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 x-axis inclinations) and observe a noticeable decrease in the dynamical exponent \( \beta \) in the presence of these defects. We will also present results of studies of nanoscopic switching domains 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, 057601 (2002). (3) R. C. Miller et al., Phys. Rev. 117, 1460 (1960).

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 topographic image or 2-D image on many applications as civil and criminal crime profiling to the real time three dimensional scanners (4-D) using matrix array transducers which will use the standard of medical practice. Clinical usage includes echocardiography 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 and technological advancements as beam forming technology and their clinical impact. Our own recent work has been concentrated in the field of real time 3D ultrasound scanning where we have developed matrix phased array transducers which are available for laser scanning operating at 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 up to 20 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 x 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 imaging 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 *H5.9
Functional Oxides in MEMS, Paul Muralt, Ceramics Laboratory, EPFL, Lausanne, Switzerland.

The earliest functional oxides investigated in MEMS were probably ZnO films in Lambwave devices during the mid 80's. Polart thin films have always been considered as potentially interesting to build micromachined devices, notably in actuators for MEMS. In addition, the use of high performance piezoelectric MEMS devices have been demonstrated such as linear actuators, strain, motion and pressure sensors, microphones, ultrasound actuators, micromotors and imaging devices. Pyroelectric thin films have been introduced 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 downsizing. 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 weaknesses in view of physical principles 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 downsizing bulk applications is treated by means of a piezoelectric thin film perspective. In this context, the thickness of the film is reduced from 1000µm to a thin film, which means that different resonating structure needs to be applied in µmTAS as compared to bulk transducers in order to be compatible with the thick device thickness range. Instead of a bulk wave one uses a deflection wave signal. Currently, thin film Pb(Zr,Ti)O3 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 compatible with tip fabrication. Gas detection is an interesting sensor application. Piezoelectric 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 detected by means of 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(Mg1/3Nb2/3)O3-PbTiO3 on Silicon for High-Performance Electromechanical Systems, Dong Min Kim1, Chang Beom Eom1, June Ouyang2, V. Nagarajan3, R. Ramesh3, V. Vaitheyanathan3, D. G. Schlom3,4,5. 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 more complex 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 synthesizing optimally-oriented, epitaxial thin films of Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT) on micropatterned (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, to reduce the constraint imposed by the underlying silicon substrate. When subdivided into 1µm2 capacitors by focused ion beam processing, a 4µm thick film shows a low-field d33 of 220 pm/V (85 kV/cm). Piezoelectric performance C) by MOCVD was also developed to produce highly (001) oriented Pt/Ti/AIO1-x films grown on annealed Pt/Ti/AIO1-x/UNCD substrates. Extensive chemical and structural analyses revealed that the sharp interfaces in the layered structure of Pt/PZT/Pr/Ti/AIO1-x/UNCD without interdiffusion or delamination through the oxide growth and post-deposition annealing, due to the formation of a thin amorphous TiAIO1-x layer. A result, promising ferroelectric piezoelectric micromachined ultrasonic transducers (pMUTs) is 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.

SESSION H6: Magnetic Oxide

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% in the tunnel barrier and high remnant polarization. Successful integration of MR of CrO2-based and high remnant polarization. Successful integration of CrO2-based half-metallic multilayer structures with Abbe-02, 020, 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, Atesigbe Mamasu, Takahito Terasima, Yuichi Shimakawa and Milio Takano, Institute for Chemical Research, Kyoto University, Kyoto, Japan.
We examined electroresistive effects of epitaxial La_{0.67}Sr_{0.33}MnO_{3} (LCMO) thin films on Lao.35CaO.65MnO_{3} (LSMO) trilayer junctions in order to produce high-quality interfaces through the use of an in situ structural epitaxial barrier. The insulating LSMO (a 3.98 Å) and low-strained ferromagnetic metal (FMM) at low temperatures. The transport properties of these inhomogeneous samples showed non-ohmic current–voltage characteristics that below FM transition temperature the mixed phase 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 of cation vacancies due to over-oxidization are essential. 

9:00 AM H6.3

Structural, transport and magnetic properties of R1-xAxMnO3 (R=La, Nd, A=Ca) thin films fabricated by laser MBE method. Takeshi Yanagida1, Teruo Kanki1, Bertrand Vilquin1, Hidekazu Tanaka2,3 and Tomoji Kawaz1; 1ISIR, Osaka University, Osaka, Japan; 2PRESTO, Kawaguchi, Japan.

The perovskite type manganese oxides (R1-xAxMnO3) 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 for applications (e.g. La, 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 insulating frustration and type, 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 1.16 Å and 0.99 Å of the ionic radius, respectively. R1-xAxMnO3 (R=La, Nd, A=Ca) thin films were fabricated via a PLD method. Note that single phase of these bulk materials were found to be not feasible by solid state reaction method due to CeO2 segregation phases. XRD measurements of these films showed the single phase of these films and did not show the impurity peaks of CeO2 segregation phases within the films. For La0.67Ca0.33MnO3 (LCMO) film system, the thin films grew in stoichiometric composition. As the oxygen partial pressure during film deposition increased from 10^-5 Torr to 1 Torr, the oxygen stoichiometry and the Mn occupation of the Mn sites increased. The resistivity of these films was found to increase linearly with the oxygen partial pressure and the Mn occupation of the Mn sites. The transport and magnetic properties. As the oxygen partial pressure increased from 10^-5 Torr to 1 Torr, the electrical resistivity was found to decrease linearly with the oxygen partial pressure. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interfusion, the JMR is not completely suppressed. We have previously demonstrated successful junctions using a paramagnetic barrier, CeO2. We observed JMRs of about 4% at 6K, 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. Junction magnetization measurements suggest interfusion 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 interfusion, the JMR is not completely suppressed. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interfusion, the JMR is not completely suppressed. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interfusion, the JMR is not completely suppressed. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interfusion, the JMR is not completely suppressed. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interfusion, the JMR is not completely suppressed. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interfusion, the JMR is not completely suppressed. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interfusion, the JMR is not completely suppressed. Despite the exchange biasing and magnetic frustration of the ferromagnetic layers next to the antiferromagnetic barrier and interfusion, the JMR is not completely suppressed.
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 synthesized the spinel 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 occurs at dopant concentrations 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 (are) operative.

10:45 AM H6.7

Ferroelectric Field Effect on Ferromagnetism in Diluted Magnetic Insulator Anatase CoTiO2. Z. Zhang1, S. R. Shinde2, S. B. Ogale1,2, H. Zheng3, T. Venkatesan2, R. Ramesh3, S. Das Sarma4, and J. Misewich4. 1 Materials Research Science and Engineering Center, Department of Materials Science and Engineering, The University of Maryland, College Park, Maryland; 2Materials Science & Technology Research, Department of Physics, The University of Maryland, College Park, Maryland; 3Department of Physics and Department of Materials Science and Engineering, University of California, Berkeley, California; 4Condensed Matter Theory Center, Department of Physics, University of Maryland, College Park, Maryland. 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 PbZr0.2Ti0.8O3 (PZT) layer were epitaxially grown on a conducting SrRuO3 buffered LaAlO3 substrate. The high density of states at the Fermi level 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 loop of the Co:TiO2 was measured by superconducting quantum interference device after positive or negative poling on PZT. A 15% decrease 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 field effect 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 Tetsuro1,2, Kawaguchi Kenji2, Kirihara Kazuhiko1, Kawasaki Koji1, Kimura Misewich3,4, Kawaguchi Kenji 1,2, Tani Takeo1, Yamaguchi Katsuhiko2 and Yamada Koji1, Saitama University, Saitama, Japan; 2Nanoarchitectonics Research Institute, 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 density data storage owing to its magnetic random access memory (MRAM). Most of MTJ’s consist of ferromagnetic metallic electrodes and insulative barrier layer. On the other hand, some research groups pay attention to ferromagnetic barrier MTJ (FM-MTJ) as spin filter device of FM-devices. 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 oxidation states of Eu. In this study, we consider EuO a good barrier material for the trial study of FM-MTJ. 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 layer. So, it is good for conducting studies. 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 a molecular beam epitaxy system are 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 (P02) is ranged from 2.0 x 10−6 to 1.0 x 10−5 Pa. In XPS spectra, both Eu2+ and Eu3+ 3d/2 peaks were observed around 1126 and 1135 eV for P02 > 6.0 x 10−6 Pa samples. It means that EuO layer is over oxidized. For P02 is 2.0 and 4.0 x 10−6 Pa samples, Eu2+ peaks disappeared. It is considered that P02 of 6.0 x 10−6 Pa is over oxidation condition to prepare nano-layer EuO. The optimum P02 decreases as the EuO layer thickness is decreased. Thus, we have to change P02 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 EuO 2.5 nm is a thin continuous layered structure rather than an island structure. The thickest EuO (10 nm) layer shows a little smaller MS (5.32 mb/atom) than ideal value (7.9 mb/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. Benner. 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 conductivity is more than 100 times larger than the perpendicular to the layers. We present a new insight on this issue using scanning tunneling microscopy (STM) on La1.4Sr1.6Mn2O7 single crystals cleaved in ultra high vacuum. STM spectroscopy reveals a gap Eg associated with the room temperature conductivity, 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 in-plane transport is much larger than the perpendicular. We have calculated the band structure of the La1.4Sr1.6Mn2O7(2.5) system at all temperatures, with a characteristic activation energy Eg. Furthermore, Eg 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. Ronnow and G. Aeppli.

SESSION H7: Oxide on Si/Gate Oxide

1:30 PM H7.1

MBE-Grown HfO2 Gate Dielectrics for Si Nano CMOS and III-V Semiconductor MOSFETs. J. Jay1, M. Hong2, J. P. Mannens3, W. J. Lee2, H. P. Chang2, Y. J. Lee2, C. H. Chu2, K. L. Jaw2, Y. L. Hsu2, K. Y. Lee2, C. H. Pan2, C. C. Huang2, 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 k 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 the world. The whole wide research thrust also represents an exciting opportunity for advancing new frontiers in the nanoscience and nanotechnology. However, the progress toward obtaining high performance high k MOSFET has been hampered due to the lack of good thermodynamic stability of the high k dielectrics in contact with Si. The high k dielectric interfaces in MOS gate stacks. The preferred materials choice like HfO2 for 45 nm 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 k rare earth oxides using advanced molecular beam epitaxy, we have recently undertaken studies of the high k 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 HfO2/Si interface. This heterostructure allows an alternate configuration yielding over 10% saving of the equivalent oxide thickness (EOT) to be less than 1.0 nm.

The stability of this HfO2/Si interface at high temperature is also examined by in-situ annealing tests during MEIS, and rapid thermal anneals under various atmospheres. The results of the annealing tests are compared to those obtained at room temperature. The results indicate that the high-field mobility of 312 cm2/Vs (77.5% of SiO2) is achieved. The high-field mobilities are increased through the incorporation of thicker gate dielectrics.

Furthermore, a key challenge in developing compound semiconductor MOSFETs is to identify suitable new high-k dielectrics having a low density of interfacial states (Dit) and low electrical leakage.Following our previous discovery of novel Ga2O3(Ga2O3) oxides for effective gate dielectrics, we have more recently evaluated several high-k dielectrics including HfO2 (ε = 20) and Sc2O3 (ε = 12) to passivate the compound semiconductor surface. Low electrical leakage films have been obtained for both HfO2 and Sc2O3 films deposited on GaAs (100) at room temperature by UHV deposition. 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 HfO2 High-k Gate Stacks, J.M. Peterson1, J. Barnett1, Claudio D. Young2, Rachel A. Brown2, Jim Guti1, Sundar Gopalan3, Paul D. Kirch1, John Robertson1, Ka Xiong1 and Stewart J. Clark2. 1Engineering, Cambridge University, Cambridge, United Kingdom; 2Physics, Durham University, Durham, United Kingdom.

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 interface screening oxide between the high-k gate dielectric and the compound semiconductor. In reduction of 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 SOI 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 HfO2 high-k gate stacks. We have fabricated HfO2 high-k gate stacks with thicknesses and capacitor structures 200 nm Si < 100> wafers using a conventional CMOS process with a 1000°C/10s final anneal. In order to evaluate the oxide thickness and its screening effect on transistor mobility, several bottom interface oxides are compared: a 1 nm oxanized oxide, a 1.2 nm thermal oxide, and a standard 1.6 nm rapid thermal nitrided oxide. After completion of CMOS processing, standard CV and LV analysis was done to evaluate EOT, CEE, Vth, 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 oxanized oxide achieves a peak mobility of 216 cm2/Vs (63.9% of the SiO2 universal mobility), the 1.2 nm thermal oxide achieves an additional 20% of the SiO2 universal mobility, while the 1.6 nm rapid thermal nitrided oxide achieves 312 cm2/Vs (77.5% of SiO2).

2:00 PM *H7.3 Calculation of Band Gap and Defect Levels in Functional Oxides, John J. M. Liu1, Ka Xiong2, and Stuart J. Clark1. 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 GW approximation. However only recently it was found that the GW approximation gets the experimental band gap, but this loses any predictive power. It can be corrected by methods such as the GW approximation, but this is computationally expensive. It can be corrected by lower cost methods such as using the screened charge approximation (sX) methods and others [1] have found to be quite accurate and reliable. However, for oxides, sX has the disadvantage of requiring the use of non-conserving pseudopotentials. These require a cutoff energy of up to 1000 eV for oxygen, whereas the technologically ultra-slow 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 one to use large supercell calculations of surfaces, interfaces and defects. As examples, we calculate the minimum band gaps as SiO2 9.2 eV, Al2O3 9.3 eV, Mg2O3 9.5 eV, LaAlO3 6.9 eV, HfO2 6.1 eV, ZrSiO4 7.6 eV, SrCaO2 4.1 eV. Calculations of vacancy energy levels are also given. [1] C. G. Ray, J. E. Ryan, and D. M. Kolafa, Phys. Rev. B 64, 121201 (2001) [2] P. P. Rushton, D. J. Toker, 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, Mary Christine Huang1, Bernard Angus2, Olivier Voldoire3, Israel Baumwell2, Karen Paz Bastos2, Leonardo Miotti2, Camille Cohen3 and Christophe Cardinard1. 1Université Paris Sud, Orsay, France; 2Instituto de Fisica, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil; 3Université Paris 6 et 7, Paris, France; 4IMN, Nantes, France.

There is currently an extensive research effort to find an alternative dielectric gate material to replace SiO2 in metal oxide semiconductor field effect transistors (MOSFETs). LaAlO3 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 eV for electrons and 3.2 eV for holes). R02 is proposed as a gate electrode. LaAlO3 films were deposited directly onto silicon substrates by rf magnetron sputtering of a LaAlO3 target in argon atmosphere. Thin film properties are studied as a function of deposition parameters (rf power, process pressure) and thermal processings (in 02 or Ar atmosphere, pressures 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 ± 0.5 g/cm3 close to the bulk material one (6.5g/cm3). The thermal stability of LaAlO3 has been investigated under typical conditions of MOSFET processing. After high temperature annealing are investigated with sub-nanometric depth resolution via the narrow resonances of 16O(p)15N at 151 keV (fwhm=100eV) and 27Al(p,2)Si at 409.4keV (fwhm=40eV) respectively. After a thermal treatment at 1000°C for 20s under 10 Pa and 0.5 Pa of oxygen, Al diffusion has been only observed for a oxygen pressure of 0.5 Pa. The interfacial characteristics of LaAlO3/Si were measured by spectroscopic ellipsometry, X-ray reflectometry, XPS and RBS in channeling 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 LV characteristics on RuO2/LaAlO3/Si MIS structure. After a thermal treatment at 600°C, the C-V curves exhibit well defined inversion and depletion regimes which indicate a low interfacial state density. With the device biased in accumulation regime, a permittivity of 15 was deduced. Low leakage current is detected for films deposited at 0.5 Pa or at 0.5 Pa and annealed at 600°C under 1 atm of oxygen.

2:45 PM H7.5 Physical properties and crystallization temperature of rare earth metal doped YAG Films, Iaco Cappelletti1,2,3*, Hans Christian Jellison1, Christopher Rouleau1, Mark Reeves3, Shuogang Huang3, Junhui Jia2 and Darrell Schklom1. 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, State College, Pennsylvania.

The physical and crystallization temperature of rare earth metal doped YAG (Y3Al5O12) films were measured by x-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. X-ray diffraction measurements were made on films deposited on Si(111) substrates in various rare earth metal concentrations and at different deposition temperatures. The films were deposited by an RF magnetron sputtering configuration. The substrates were kept at room temperature during deposition. The crystallization temperature was determined by XRD measurements at different heating rates. A peak shift in the XRD peak positions was observed as the concentration of rare earth metal was increased. The peak shift was found to be linearly correlated with the rare earth metal concentration. The crystallization temperature was found to decrease as the rare earth metal concentration was increased. The films deposited at higher temperatures were found to have a higher crystallization temperature compared to those deposited at lower temperatures. The films deposited at higher rare earth metal concentrations were found to have a lower crystallization temperature compared to those deposited at lower rare earth metal concentrations.
The crystalization temperature of materials is a critical parameter to be considered when selecting high-dielectric constant materials. A low crystalization 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 (ReScO₃, where Re = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) has motivated us to investigate crystalization temperatures systematically by employing a temperature-gradient deposition method. In this approach, pulsed laser deposition is used to grow ReScO₃ films simultaneously on 15 LaAlO₃ substrates held at different temperatures in the range of 290 - 800 °C. Subsequent annealing by X-ray diffraction allows us to compare the crystalization 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 λ = 331 - 800 nm), and the optical bandgap, and dielectric permittivity (at ± 1.6 GHz). The resulting phase map of dielectric constant, lattice parameter, and crystalization 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 Y₂O₃ Thin Film. Jin-Seong Park, Philippe De Rouffinac and Roy G. Gordon; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Y₂O₃ thin films were deposited by yttrium tri(N,N-diisopropylaminocladimate) and water by atomic layer deposition (ALD) at 295°C. The self-limiting surface reaction yielded a growth rate of 0.1 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 Y₂O₃, with the (222) and (400) peaks reflected by X-ray diffraction (XRD). The composition of yttrium oxide was O/Y = 1.9 by Rutherford backscattering spectroscopy (RBS) after air exposure. Oxygen rich phase might come from adsorbed hydroxyl groups during air exposure because the internal photoelectron spectroscopy (XPS) of the peak intensity of OH bonding was decreased after annealing. The electrical properties and cross section TEM studies on the hetero-structure of Sc₂O₃/Y₂O₃ will also be presented.

3:45 PM H7.7
The atomic structure of epitaxial Sc₂O₃/Si interfaces. Dmitri O. Klenov, Lisa F. Edge*, V. Vaitheyanathan, Darrell Schlom* and Susanne Stommer1; 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 SiO₂ is determined by the atomic structure of the interface between the oxide and Si. Scandium oxide (Sc₂O₃) is a promising gate dielectric because it has a high dielectric constant (13) and large bandgap of 6.3 eV. Sc₂O₃ (222) peak, suggesting that, this film thickness exceeds the critical thickness, and the film is partially relaxed. However, upon slow cooling to room temperature, the SrTiO₃ 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 SrTiO₃ epilayer after annealing. The combined effects of the Si(100) substrate and activities at the SiO₂/Si interface on the strain state of the SrTiO₃ films will be discussed. In addition, we show that epitaxial (Ba,Sr)TiO₃-based capacitors with 66% tunability and 1.0% dielectric loss were successfully fabricated on SOI substrates using this approach.

4:00 PM H7.8
MBE Growth and Characterization of High-Quality Single Crystal Sc₂O₃ Films on Si(111). Ming-Jong, H. Y. Lee, A. R. Kortan1, J. Kwo1, C. P. Chen1, Y. F. Hsieh1, H. M. Cheng1, Y. L. Hwang2 and J. P. Mannan1; 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., Hsinchu, Taiwan.

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 for the growth of GaN directly on Si. Here we report the MBE growth and single-crystal synchrotron x-ray characterization of very high quality Sc₂O₃ films grown on Si (111). The Sc₂O₃ films of 4 and 18 nm thickness were deposited by e-beam evaporation on Si in a quartz bubble MBE/UV bakeout chamber. Surface structure was confirmed 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 cup. Steady RHEED patterns along the in-plane orientation relationship, as confirmed by both x-ray and in-situ x-ray diffraction. The composition of yttrium oxide was O/Y = 1.9 by Rutherford backscattering spectroscopy (RBS) after air exposure. Oxygen rich phase might come from adsorbed hydroxyl groups during air exposure because the internal photoelectron spectroscopy (XPS) of the peak intensity of OH bonding was decreased after annealing. The electrical properties and cross section TEM studies on the hetero-structure of Sc₂O₃/Si will also be presented.
Colossal magnetoresistive (CMR) La0.67Ca0.33MnO3 (LCMO) and La0.67Sr0.33MnO3 (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 at 223K and 2.0%/K at 292K and differential magnetoresistance dlnR/dH, -7.3% at 4K and -1.4%/K have been achieved for LCMO/MgO/GaAs and LSMO/MgO/GaAs heterostructural systems, respectively. Comparison of the measured LCMO and LSMO films grown directly onto the bulk MgO(001) single crystal demonstrates the identity of LCMO/MgO/GaAs and LSMO/MgO/GaAs heterostructural systems. The diffracted c-axis orientation and LCMO films grown on MgO buffered GaAs substrates have been synthesized at 750°C. The Bi2Sr2CaCu2Ox dielectric property has been achieved from the strain manipulation of the ferroelectric phase.[1] HfO2 is found in the temperature range 650-750°C to the fact that HfO2 is typically crystalline as-deposited whereas HfSiOx remains amorphous (and free of grain boundaries) up to 800-850°C crystallization temperature.

H8.1 High-Performance Gate Dielectric Compositions in the Ternary Y2O3-HfO2-Al2O3 System.

Dmitry Anotolyevich Kukuruznyak, Ken Hasegawa, Puthut Ahmet, Takahiro Nagata and Toyohiro Chikyow; Nano-materials Assembly, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; Materials 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 superior uniformity, compositional and structural phase diagram was established with combinatorial XRD (Rigaku, Bruker). In the range between Hf0.65Y1.35O2 and Hf2.0Y0.5O2.5 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 formation of oxygen vacancies. Addition of Al2O3 to Y2O3-HfO2 alloys 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 Y2.2Hf1.8O7 and Al2O3Hf1.4Ox 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. Atoms mixing in arbitrary proportions yields local spatial fluctuations of the number of nearest neighbors, dangling bonds, and electronic defects. Discovered composition-dependent atomic arrangements metastable properties of binary Y2O3-HfO2 means to form a single fluoride phase. Among the layered compounds, 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 electrical and thermoelectric properties of Ca3Co4O9 thin films. We have successfully grown the c-axis oriented Ca3Co4O9 thin film 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 thin films and show similar behaviors as in the single crystal samples.

H8.2 Diffusion Barrier Properties of High-k Based Gate Dielectrics Between Si and Silicide-forming Gate Metals.

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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 PtSi formation in Si(substrate)/Hf-based gate dielectric/Pt samples as a function of gate dielectric type, thickness, and metallicity. We attribute the better diffusion barrier properties of HfSiOx (vs. HfO2) in the temperature range 650-750°C to the fact that HfO2 is typically crystalline as-deposited whereas HfSiOx remains amorphous (and free of grain boundaries) up to 800-850°C crystallization temperature.

H8.3 Growth and Characterization of Pulsed Laser Deposited Rare Earth-Based Manganites onto Si(100) Semiconductor using SrTiO3 Template Layer.

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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 progress on the direct integration of SrTiO3 (STO) onto Si has opened a possibility to integrate both STO and R1-xBxMnO3 into this technologically important semiconductor. In order to explore this possibility, we have successfully fabricated R1-xBxMnO3/STO/Si heterostructures using multitarget pulsed laser deposition system. We demonstrate the growth of La1-xBaxMnO3 (LBMO) and La1-xSrMnO3 (LSMO) epitaxial films on Si (100) substrates buffered by heteroepitaxial 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. These films produce many generic approaches to the integration of multicomponent high-k films on semiconducting surfaces, which can impact a variety of technologies. Apart from IR imaging, epitaxial perovskite heterostructures can be fabricated for photovoltaic and field effect transistors (FET), and other room temperature spintronic devices, controlling ferromagnetism both by light and electric fields.

H8.4 Fabrication of Epitaxial PZT/Pt/Al2O3/Si Structure and its Ferroelectric Characteristics.

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and transmission electron microscopy confirmed the formation of superlattice structure with designed composition modulation. The dielectric properties were enhanced from the strain manipulation of the superlattice with decreasing the stacking periodicity. The ferroelectricity also increases and a linear ferroelectric is found in 327K and 2.0%/K. This will produce many generic approaches to the integration of multicomponent high-k films on semiconducting surfaces, which can impact a variety of technologies. Apart from IR imaging, epitaxial perovskite heterostructures can be fabricated for photovoltaic and field effect transistors (FET), and other room temperature spintronic devices, controlling ferromagnetism both by light and electric fields.
In this paper, we proposed epitaxial $\gamma$-Al$_2$O$_3$ 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 PZT films on a single crystal $\gamma$-Al$_2$O$_3$/Si substrates. Pb(Zr$_{0.55}$Ti$_{0.45}$)$_2$O$_3$ (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 SrTiO$_3$ single crystal substrates were reported. Epitaxial Pt/Pt/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. Therefore, we have been searching for an alternative substrate on Si substrates using chemical vapor deposition (CVD). The $\gamma$-Al$_2$O$_3$ films have been applied for an insulator for SOI substrates [1] and buffer layers for heteroepitaxial growth [2]. The fabrication of the epitaxial $\gamma$-Al$_2$O$_3$ films on Si substrates was carried out using a CVD method. 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 PZT films on (001) and (111) $\gamma$-Al$_2$O$_3$/Si substrates sputtered above 600 °C. Furthermore, Ar room temperature, polycrystalline Pt films were obtained on substrates. Epitaxial PZT(001) films with various compositions were obtained on the (001) and (011) substrates. These PZT(111) films were also fabricated on the (111)/$\gamma$-Al$_2$O$_3$/Si(111) substrates. Epitaxial PZT films showed better ferroelectric properties and pyroelectric properties than polycrystalline PZT films. The P-E hysteresis loops of epitaxial PZT films were observed with remanent polarization of 14.3 $\mu$C/cm$^2$ and coercive field of 50 kV/cm. Especially, maximum pyroelectric coefficients of epitaxial films appeared and values were 1.8 $\mu$C/cm$^2$K and 1.4 $\mu$C/cm$^2$K on Zr/Ti ratio of 40/60 for the PZT(001) film and the ratio of 82/18 for the PZT(111) film, respectively. These pyroelectric coefficients are the same as the PZT ceramics. We expect that this epitaxial Pt/Pt/$\gamma$-Al$_2$O$_3$/Si structure can be applied to Si integrated ferroelectric sensor devices. Refs. [1] B. H. Park, J. Appl. Phys. 99, 07B708 (2006); [2] D. Aki et al., J. Cryst. Growth 259, 90 (2003).

**H8.6**

**Etching of Heteroepitaxial**

La$_{0.67}$(Sr,Ca)$_{0.33}$MnO$_3$/Bi$_2$Ti$_3$O$_7$/CeO$_2$/YSZ/Si Film Structures for IR Bolometer Applications. Joo-Hyung Kim, Sergey I. Khartsev and Alexander M. Grushin; Condensed Matter Physics, Royal Institute of Technology, Stockholm-Kista, Sweden.

La$_{0.67}$(Sr,Ca)$_{0.33}$MnO$_3$ (LSMCO) films have been grown by a pulsed laser deposition on Si(001) substrates buffered with Bi$_2$Ti$_3$O$_7$/CeO$_2$/YSZ layers. X-ray diffraction showed cube-on-cube growth of an epitaxial Bi$_2$Ti$_3$O$_7$/CeO$_2$/YSZ heterostructure on Si whereas the LSMCO layer grows in the "diagonal-on-side" manner on top of the Bi$_2$Ti$_3$O$_7$/CeO$_2$/YSZ template. LSMCO composition has been optimized to get the maximum of pyroelectric coefficients of epitaxial films. The experimental data allows us to estimate, the extrinsic contribution of $\gamma$-Al$_2$O$_3$ thin film on Si substrates and the nature of this contribution. The as-deposited films were partially crystallized and became fully crystallized after post-deposition annealing (PDA) at 800°C. Interfacial layer (IL) thickness between HfO$_2$ and Si substrate was increased by 50% by post-deposition annealing (PDA) at 800°C. Interfacial layer thickness increases 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.

**H8.7**

**Elaboration and Characterization of Y-Doped HfO$_2$ Thin Films Grown by MOCVD.** Ermal Ramet, Catharina Dubois, Christophe Dulou, Marc Duguépoint, Pierre Rocha, Bernd Holländer and Cyril Millon; Laboratoire des Matériaux et du Genie Physique, CNRS / INPG, St Martin d'Heres, France; Laboratoire de Physique de la Matiere, CNRS / INSA Lyon, Villeurbanne, France; FORTH/IKT/DPT/DESY/GRC, CEA Grenoble, Grenoble, France; Forschungszentrum, Juelich, Germany.

The deposition of HfO$_2$ films on Si substrates by metal organic chemical vapor deposition (MOCVD) is an emerging technology for the fabrication of high-k dielectrics for nanoscale devices. In this work, we report the fabrication and characterization of Y-doped HfO$_2$ thin films deposited on Si by MOCVD. The films were characterized in terms of their microstructural properties, dielectric constant, and leakage current density. The results show that the incorporation of Y into the HfO$_2$ lattice decreases the leakage current density. The leakage current largely increases with the temperature. However, it was found that the inhibition of crystallization and obtaining of smooth 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. For Hf$_{0.9}$Si$_{0.1}$O$_2$ film deposition, various Si precursor vapor was introduced simultaneously with the TEAH.
Zirconia, ZrO2, and Hafnia, HfO2, thin films have been deposited on single-crystal MgO (100), Si (100), and amorphous SiO2 by both eV. The temperature dependence of the optical properties has also occur at temperatures as low as optical properties of the interface layers have been determined and oxidation as well as reactive-sputtering. The optical properties of the thin films grown on Si and amorphous SiO2 by RF reactive sputtering and metal oxidation. Ciro Manuel Lopez', N. A. Hafiyaz Al Quraishi, 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.

Optical, Electronic, and Interface studies on ZrO2 and HfO2 thin films grown on Si and amorphous SiO2 by RF reactive sputtering and metal oxidation. Cirno Manuel Lopez'. N. A. Hafiyaz Al Quraishi, 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.

In this paper, we propose a novel growth method of ultrathin single-crystalline γ-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 substrate with the thickness of 10-15 nm. The substrates were inserted into a vacuum system that provides a mixed source molecular beam epitaxy (MBE) for the crystalline γ-Al2O3 growth using solid Al as aluminium source and N2O gas as oxygen source. During the epitaxial growth, the substrates temperature and the AL-Knudsen cell temperature and N2O gas pressure were maintained at 750 °C, 1120 °C and 3.2 x 10-2 Pa, respectively. 3. Results and discussions As a result, the epitaxial γ-Al2O3 films and a c-axis oriented γ-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 microscopy (AFM) images that show the typical root mean square (RMS) values of 0.25-0.30 nm for the 2.5 nm 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 higher binding energy) and chemical oxide layer disappeared (i.e. Only Si2p peaks 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 single-crystalline γ-Al2O3 films and a c-axis oriented γ-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. Shahjahban et al. Jpn. J. Appl. Phys. 40 (2002) 2602 [3] M. Shahjahban et al. Jpn. J. Appl. Phys. 41(2002) 1474

Comparative Study of Post-Deposition Plasma Treatments on
HF02 Layers in Cylindrical DRAM Capacitors.
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HF02 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 HF02 is increased due to both residual carbons in HF02 film, originated from its own deposition process and crystallization. In order to lower 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 HF02 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, 250°C. 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 HF02 was used as dielectric layer in this application. It was demonstrated that leakage current of TIT capacitors with plasma-treated HF02 thin layer decreased about 1 order at ±2.5V compared to that of TIT capacitor without plasma treatment. In summary, post plasma treatment of HF02 for cylindrical capacitor is effectively reduced by the post plasma treatment with high step coverage. It is concluded that TIT capacitor with HF02 thin film can be applied to DRAM device with 70nm Design Rule and beyond.

H8.16 Changes in the Chemical State of N-Incorporated HF02 Thin Films. Kwun Bum Chung,2, Mann-Ho Cho2, Chung Nam Whang1, Dae Won Moon2, Dong Won Lee3 and Dae-Hong Ko1. 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 HF02 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, H1/Mg 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 decreased as the annealing temperature increased. However, the lower binding energy shift at annealing temperature above 800°C, resulting from the incorporation of nitrogen into HF02 films. In addition, absorption spectra of N-K edge also showed the dramatic chemical state changes at the 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 HF02 films at the annealing temperature of 800°C and critically affected the electrical characteristics.


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 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-ion and also the KOH etches off the Si substrate seriously. Therefore, in this work we have newly prepared (Pb,Ba)(Zr,Ti)O3 (PBTZ) thin films by hydrothermal treatment using Ba(OH)2 related solution as alkali mineralizer other than KOH. After sol-gel solution of PBTZ 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 35 ml Ba(OH)2 and Pb(OH)2 mixed solution. The TiO2 layer was applied on Si wafer, the films were dried at 150°C for 10 min. and pre-baked at 300°C for 30 min. After 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 layer was applied on Si wafer, the films were dried at 150°C for 10 min. and pre-baked at 300°C for 30 min. The internal stress in PZT films were discussed. YSZ and CeO2 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(Zr0.52Ti0.48)O3 thin films was also deposited by MOCVD. The internal stress in ferroelectric PZT thin films was measured by thin film X-ray diffractometer using sin2θ method. The internal stresses of PZT thin films with and without 25nm Pt buffer layer on Si substrate were 0.47GPa and 0.87GPa, respectively. The internal stress in PZT/LSBCO (YSZ)/Si structure (without stress control-buffer layer) was 2.22GPa. As the results, 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, Rasoul Schreder 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 insulator works in principle, they often have low capacitance Cl, which leads to transistors that require high switching voltage. For much lower k materials, that might reasonably 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, plasma-based anodic 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 prominent oxide produced is aluminium oxide (Al2O3) and titanium oxide (TiO2). Sputtered Aluminium on plastic film is cheaplyavaliable commercially, and its oxide is characterized by high electric breakdown (7.7 MV/cm) and relatively high k, which should enable very low voltage operation. Here, we present our recent work on low-voltage, high-capacitance, flexible OFET 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 at 1 V. Materials. Sources. T. P. Kelly, D. W. Muyres, P. F. Bunde, T. P. Smith, T. D. Jones, Mat. Res. Soc. Symp. Proc., 771, L6.5-1 (2003) [2] G. Wang, J. Svensen, D. Mose, A. J. Heeger, J. Appl. Phys., 93, 6137 (2003) [3] L. A. Majewski, M. Grill, S. D. Ogier, V. V. Yacoby, J. Vac. Sci. Tech., A17, 7 (2003) [4] L. A. Majewski, R. Schroeder, M. Grill, J. Phys. D: Appl. Phys. 37, 21 (2004) [5] L. A. Majewski, R. Schroeder, M. Grill, Synth. Met. 144, 97 (2004) [6] L. A. Majewski, R. Schroeder, M. Grill, submitted to Adv. Mater. H8.20 Integration of Yttrium Oxide Films in MIM Capacitors, Christoph Durand1, Catherine Dubourdieu1, Christophe Vallee1, Serge Blonkowski1, Michael Derivaz1, Maurice Kahn1 and Marceline Collet1; 1Laboratoire des Technologies de la Microélectronique, CNRS, Grenoble, France; 2Laboratoire des Matériaux et du Genie Physique, CNRS/INPG, St Martin d’Heres, France; 3STMicroelectronics, Crelles, France. High-K materials are extensively studied for the replacement of SiO2 in future silicon-based microelectronic applications. Among these applications the non-metallic-metal insulator (MMI) 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 wafers. A low-temperature deposition of 100 °C was used to avoid stress and prevent the formation of different layers at higher temperatures. During the annealing, both the substrate and the film temperatures were controlled between 20 °C and 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 determine 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 100 μF/cm2 with electrical breakdown fields Ebd 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 10 μF/cm2 with a breakdown voltage of 5 V. The effect of films thickness on the device performance (capacitance, Ebd, 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 La1−xSrxMnO3 Films. Flavia Dana Stancu1, Neila Cuculescu1, Vasile Dima1, Cristian Cuculescu2, Catherine Dubourdieu2, and Jacques Richard2; 1IMEP ENSERG, 23 avenue des Martyrs, BP257 38016, Grenoble, France; 2LMGP ENSP, UMR CNRS 5628, ENSP BP 46 38402, St Martin d'Heres, France; 3CRTIT CNRS, 25 avenue des Martyrs, 38042, Grenoble, France. Until now the majority of magneto-transport studies performed on manganese oxides such as La1−xSrMnO3 (A = Ca, Sr; Ba) were realized in the low magnetic field regime (for frequencies varying from 0 to up to some GHz) is of interest both from theoretical and application point of view. Such a study could answer to questions such as: i) Does the colossal magnetoresistance 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 La0.9Sr1.8MnO3 films grown on silicon as a function of temperature (from 100 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 effect, 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, the magneto-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 down to 100 K. These results have already mentioned due to the polycrystalline nature of the films, it seems that there is no phenomenological difference in the variation of the magneto-transport 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. Meere1, John Peck2, Jin P. Natwora, Michael M. Litwin, Michael T. Moescrop, Demong Zhang and Cynthia A. Hoever, Electronics, Praxair, Tonawandas, New York. In recent years there has been increasing interest in the development and utilization of silicates for next-generation dielectrics and barriers. Some of the integration difficulties identified for single binary oxides (e.g, SiO2) have been addressed by incorporating silicon into deposited films (e.g, HISON). 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 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, HMDS, TEOS), their utility for dielectric applications 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 precursors 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 hafnium oxides. Further, the comparison with common hafnium precursors (e.g, HCl, hafnium amides) will be discussed. Additionally, we have developed a methodology for optimizing 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. Yon Liang1, Jimmy Yu1, Jay Coutts2, Karen Moore1, Clarence Tracy1, Dino Ferrusco3, Leo Fonseca4, Alex Demkov5 and Phil Tobin2; 1APRL, Freescale Inc, Tempe, Arizona; 2APRL, 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, HfO2, and SiO2, 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 HfO2, whereas in SiO2 and HfO2/Si/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 chemical degradation of the two interfaces occurs. Detailed analysis of XPS and UPS spectra indicates that the HfO2/Si interface is vulnerable to UHV annealing. In addition to photocurrent, electrical results on HfO2/SiO2/Si will also be presented to compare and contrast with the photocurrent data.

**H8.24** Lanthana-Based Oxides as High-k Gate Dielectrics: Processing Issues for MIS Devices with EOT < 1.0 nanometer, Daniel J. Lichtenstein 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-k gate dielectrics due to their promising bulk properties such as a large bandgap, high dielectric constant (8-28), and stability of their high degradation temperatures. Particular interest has been focused on lanthanum'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-k gate dielectrics can competitively replace conventional silicon or silicon oxynitride dielectrics, and meet future ITRS goals. Using UHV reactive deposition to deposit the lanthanum-based dielectrics, we have fabricated 50 x 50 x 10 μm² MIS device stacks having an EOT of 0.70 nm, corresponding leakage current J (Vb+1V) of 5 x 10⁻₁⁴ 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 x/y/t, suggesting it is more prone to post-processing. Gate metal (Ti) capping in situ is crucial for maintaining low EOT for all processing conditions examined. The effects of the substrate - dielectric interface, post-metalization annealing up to 1000°C, and forming gas anneals on MIS device having EOT of < 1.0 nm will be presented.

**H8.25** The characterization of HfSiO films by atomic layer deposition, Dongyeon Lee¹, Dongshub Sub¹, Yong Soek Kim¹, Dae-Hong Ko³ 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 0.1μm 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 by ALD (atomic layer deposition) using HfCl₄ and tris(dimethylamino)silane ([((CH₃)₂N)₃Si]H₂) 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 the observed electrical properties as well as electrical characteristics using TEM, XRD, and XPS as well as CV and I-V measurements. To grow the HfO₂ 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 analysis, 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 for MOSCAP structures, in order to investigate the C-V and L-V characterization of the HfSiO films as annealing temperature increase up to 1000°C. The C-F values of the HfSiO films slightly change in annealing temperature up to 900°C. Especially, Vt 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. Ukirde¹, C. Duk Lim¹, M. Quevedo-Lopez² and M. EI 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 500°C to 900°C. 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. A discussion 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 post-processing procedures 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 high-k 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 structures during annealing in hydrogen ambient in combination with pre-processing 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, Hsiao-Chen Wei¹, Michael Lysaght¹, Michael Campin¹, Brendan Foran¹ and Prashant Majhi²; ¹International SEMATECH, Austin, Texas; ²Phillips Assigned 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 Spectron (EDXS) and Electron Energy Loss Spectra (EELS) have been utilized to study elemental properties of oxygen, tungsten, 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 deposition hafnium silicate (HfO₂)(SiO₂)ₓ-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 analyses indicates distinctly different interfacial reactions corresponding to the Ru/SiO₂ and Ru/HfSiOx systems. The onset of interfacial reaction of Ru/SiO₂ has been identified by the detection of Si oxidation starting associated with RuO₂ at 500°C in the dielectric and in the Si substrate as observed in EELS chemical scan profiles. 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 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 La₄₋ₓSrₓAg₃MnO₉₊₄ Thin Epitaxial Films, Oleg Garbenko¹, Oleg Melnikov¹, Andrey Kaul¹, Alexander Taldenkov², Natalia Babushkina², Rita Szynack², Ljudmila Koroleva², Yuri Suhorukov² and Natalia Loshkareva²; ¹ Institute for Low Temperature and Structural Chemistry, Kharkiv, Ukraine; ² Institute of Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia.
We report here for the first time the preparation and properties of La$_{1-x}$Ag$_x$MnO$_{3+y}$ thin epitaxial films. The original two-step preparation procedure was developed. At the first step La$_{1-x}$MnO$_{3+y}$ were grown epitaxially by MOCVD on the single-crystal substrates (001) and (110) SrTiO$_3$ (STO) and (001) ZrO$_2$(Y$_2$O$_3$). Treatment in the vapor of the metallic silver in oxygen atmosphere (at 1 bar or 20 bar) at room temperature and the second step resulted in the selective absorption of silver by La$_{1-x}$MnO$_{3+y}$ 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 La$_{1-x}$MnO$_{3+y}$ films. The films prepared were characterized by XRD, SEM with EDX, high resolution TEM, XPS, magnetization, electrical resistivity and magnetic properties of the thin films. We have found that resistivity peak temperature ($T_p$) possessed a maximum of 380 K at $x = 0.15$ in the series with $x = y$ (La$_{1-x}$Ag$_x$MnO$_{3+y}$). 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 La$_{1-x}$Ag$_x$MnO$_{3+y}$ epitaxial films 22% at 310 K and 50% at 290 K. The room temperature K-optical magnetotransmission as high as 16% (IT) 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 Epitaxial Cobalt Oxide (A=Ca or Sr) Thin Films**, Satoshi Yotsushahi, Tatsuo Kanno and Hideaki Adachi; Advanced Technology Research Laboratories, Matsushita Electric Industrial Co., Ltd., Sorsaku-gun, Kyoto, Japan.

Epitaxial thin films of new layered cobalt oxides $A_x$CoO$_3$ ($A$=Sr or 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 $A_x$CoO$_3$ films is a monoclinic $\beta$-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 $\rho_{//}$ for $A_x$CoO$_3$ but also that perpendicular to the CoO$_2$ plane can be measured. The resistivity parallel to the CoO$_2$ plane $\rho_{//}$ for the Sr$_x$CoO$_3$ is as low as 2 m$\Omega$cm at room temperature and shows metallic behavior. The ratio of perpendicular resistivity and parallel one $\rho_{/\parallel}$ increases from 20 at room temperature to 90 at 300K. More isotropic nature was observed in the Seebeck coefficient. Parallel Seebeck coefficients $S_{//}$ of $A_x$CoO$_3$ are approximately 60 $\mu$V/K at room temperature and the perpendicular one $S_{\perp}$ is about a half of $S_{//}$.

**H8.31**

**Microstructure of Sm$_{2-x}$Ce$_x$CuO$_4$ thin films of n-type thermoelectric material**, Mika Ueno, Tomoki Yoshikawa, Yusuke Ichino, Ichiro Sato and Yoshiaki Takai; Faculty of Engineering, Kyushu University, Fukuoka, Japan.

The Co-based oxides such as NaCoO$_2$ and CaCoO$_2$ 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. Sm$_{2-x}$Ce$_x$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 (001) 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/mK$^2$ at 323 K as an n-type thermoelectric material. The value of the power factor in SCCO thin films is as high as that in Bi$_2$Te$_3$ material. In this study, we discuss the microstructure of SCCO thin films. The microstructure was 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 cm$^2$/Vs and 6.22 cm$^2$/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 a-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 Energy Technology Foundation and the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (B), 15360479, 2004.

**H8.52**

**Thermoelectric Properties of RE$_{2-\delta}$M$_2$CuO$_4$ Thin Films Deposited by the PLD Method**, Tomoki Yoshikawa, Mika Ueno, Tomoki Nayaoyama, Yusuke Ichino, Yutaka Yoshida and Yoshiaki Takai; Faculty of Engineering, Kyushu University, Fukuoka, 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 range 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 - 800K). Therefore we studied the RE$_{2}$CuO$_4$ (RECO) as the high-performance oxide thermoelectric materials in the middle temperature range. It is well known that carrier doped RE$_{2-\delta}$M$_2$CuO$_4$ (REMCO) becomes a superconductor. The crystal structure of RECO is almost similar to that of K$_n$NiF$_3$ and RECO has strong electric anisotropy. In this study, we prepared Sm$_{2-\delta}$Ce$_x$CuO$_4$ (SCCO) as the n-type film and La$_2-\delta$M$_2$CuO$_4$ (LMCO:M = Ca, Sr, 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 and the 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 an 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/mK$^2$ at 323 K was achieved by the SCCO thin film with $x = 0.02$. This value is about ten times higher than that in Nd$_{0.95}$Ce$_{0.05}$CuO$_4$ bulk at 320 K. Also, as a result of repeated measurements of the thermoelectric properties in the high temperature range more than 800 K, the high stability of the SCCO thin film 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), 15360479, 2004 and the Thermal & Electric Energy Technology Foundation.

**H8.53**

**Interplay between A-site and B-site Driven Instabilities in Perovskite Alloys**, Marco Formari$^1$, Monica Ghota$^2$, Samed H. Haliloglu$^3$ and David J. Singh$^1$; Dept. of Physics, Central Michigan University, Mt. Pleasant, Michigan; Center for Computational Materials Science, Naval Research Laboratory, Washington, District of Columbia; Dept. 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 substitution 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 perovskite compounds and classified them according to different classes: (1) stable cubic, e.g. Bi$_2$Zr$_2$O$_6$, (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 to the role of the A-site substitution, the role of zone boundary instabilities will be discussed. 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 cantor-cation interaction. In addition we will propose qualitative strategies to predict novel ferroelectric and piezoelectric compounds.

**H8.54**

**Electronic Structure and Large Faraday Effect for Ferrimagnetic Zinc Ferrite Thin Film Prepared By a Sputtering Method**, Seiko Nakashima$^1$, Koji Fujita$^1$, Katsuhisa Tanaka$^1$, Kazuyuki Hirao$^2$, Tomyoji Yamamoto$^2$ and Isao Tomioka$^2$; $^1$Material Chemistry Laboratory, Kyushu University, Fukuoka, Japan; $^2$Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, Japan; $^3$Materials Science and Engineering, Kyoto University, Kyoto, Japan.

As is well known, the stable phase of zinc ferrite (ZnFe$_2$O$_4$) 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$_2$O$_4$ is an antiferromagnet with Néel temperature as low as 10 K and is paramagnetic at room temperature. Recently, we fabricated ZnFe$_2$O$_4$ thin films by using a sputtering method, and showed that the thin film exhibits ferromagnetic behavior even at room temperature. X-ray diffraction analysis and energy dispersive X-ray spectroscopy indicated that the thin film is composed of nonmagnetic Zn$^{2+}$ ions, whose concentration 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 magnetic 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$_2$O$_4$ thin film is caused by highly disordered arrangement of Fe$^{3+}$ ions 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ thin film. A maximum of absolute value of Faraday rotation 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 (Gd,Er) quantum dots: the absolute value of Faraday rotation angle is 2.85x10$^6$ degree/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$_2$O$_4$ 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. Bitoki and A. Pradhan; NSU, Norfolk, Virginia.

Ferromagnetic resonances (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$_x$MnO$_3$ and La$_{1-x}$Ba$_x$MnO$_3$. The FMR line width increased with decrease in temperature in La$_{1-x}$Sr$_x$MnO$_3$ films and was practically independent on temperature in La$_{1-x}$Ba$_x$MnO$_3$. This can be attributed to the different degree of magnetic homogeneity of the films. Novel layered structures La$_{1-x}$Ba$_x$MnO$_3$ in silicon with intermediate layer of SrTiO$_3$ were characterized by FMR as highly homogeneous, with the same magnetic anisotropy of 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 photoduced transition.

**H8.36**

Effects of Cu-Doping on the Artificial Grain Boundary in Epitaxial YBa$_2$Cu$_2$O$_{7-\delta}$ 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$_2$Cu$_2$O$_{7-\delta}$ (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 Cu$^{2+}$ 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$_2$Cu$_2$O$_{7-\delta}$ 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 interface. 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 a thin film 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 100 nm.

**H8.37**

Anomalous Hall Effect and Hall Angle Measurements on Sr$_{1-x}$Ru$_x$O$_3$ Thin Films. Peter Krokoff$^1$, Iwao Oikubi$^1$, Hans Christen$^1$, John Cerny$^2$, David Mandrus$^3$ and Brian Sales$^4$.

Condensed Matter Sciences Division, Oak Ridge Natl Laboratory, Oak Ridge, Tennessee; $^1$Dept. of Physics, University at Buffalo, Buffalo, New York.

Early measurements of the Hall effect in both SrRuO$_3$ and Sr$_{1-x}$Ru$_x$O$_3$ revealed an unexpected sign change. We have prepared and measured samples across the entire span in between the spin transition boundaries members to obtain insights into the origin of this sign change. The anomalous part (x M) and ordinary part (x 1/nC) 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 $R_H$ 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)$^n$ with α = 2 for samples near the ferromagnetic quantum phase transition at 7% Ca. This $T^n$ scaling of cot(θH) holds over the entire temperature range measured (5-350K).

**H8.38**


School of Applied Physics & Engineering Physics, Cornell University, New York; $^2$Department of Materials Science & Engineering, Cornell University, Ithaca, New York; $^3$Department of Materials Science & Engineering, UC Berkeley, Berkeley, California.

Researchers have achieved excellent practical efficiency in the growth of high quality oxide thin films by Pulsed Laser Deposition (PLD). These materials exhibit a range of functional properties that may be incorporated into films for use in a variety of 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 disturb 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), $\Delta T$ is independent of the state of the surface during homopy and, in contrast, our experimental measurements of $\Delta T$ during a single pulse homopy depend on the surface morphology. The correlation between $\Delta T$ and the 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 $\Delta T$ 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 Inada, Mikito Sugiyama, and Masakazu Matsu; Crystallographic Materials Science, Nagoya University, Nagoya, Japan.

Thin films of ordered double perovskite Sr$_2$FeMoO$_6$ and Sr$_2$CrReO$_6$ 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$_2$FeMoO$_6$ thin films on Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-buffered SrTiO$_3$ and Sr$_2$CrReO$_6$ 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 structures.

**H8.40**

Interface Properties and Spin Polarization of La0.7Sr0.3MnO3 in TMR Junctions. Hidefumi Asano, Mikito Sugiyama, Hirohito Inanbure, Kanemasa Inada, and Masakazu Matsu; Crystallographic Materials Science, Nagoya University, Nagoya, Japan.
Tunneling magnetoresistance (TMR) junctions based on the doped manganites such as half-metallic La1-xSrxMnO3 (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 and Andreev reflection (AR) in junction using LSMO, LSMO/SrTiO3 (STO)/LSMO, and LSMO/SrTiO3 (STO)/LSMO (for LSL junction), Co/STO/LSMO (for CSL junction), and Nb/Sr/AlN/LSMO (for NAL junction) multi layers were fabricated by the magnetron sputtering method on 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 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 in all samples in 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 resistance changed according to 1/T to a power of 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 forming at the upper interface of LSMO 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 factors that rule the spin polarization of LSMO by the comparison of results acquired from TMR effect and Andreev reflection.

**H8.41 Growth and Magnetic Properties of R(Ba, Sr)MnO3/STO/Si Heterostructures. Jacob Dalziel, Kai Zhang, Somadatta Mohanty and A. K. Pradhan; Center for Materials Research, Norfolk State University, Norfolk, Virginia.**

We have demonstrated the successful fabrication and high performance of epitaxial R(Ba, Sr)MnO3/STO/Si heterostructures with a Tc 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 La0.75Sr0.25MnO3 and La0.5Sr0.5MnO3 epitaxial films on STO(100) buffered Si substrates exhibit high magnetization properties in the vicinity of room temperature. Our results suggest the scope of the integration of epitaxial manganite films-on-on substrates, such as Si, using STO buffered template/buffer layer. This will produce many generic approaches to the integration of monolithic oxide thin films on semiconductor 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, Ashinotech Tiwan and J. Naryan; Materials Science & Engineering, North Carolina State University, Raleigh, North Carolina.**

We have performed a systematic study of structural, optical, and magnetic properties of epitaxial ZnO:Co films grown by laser molecular beam epitaxy. The observed interface (ZnO:Co/Si) revealed Co segregation at the interfaces which a high-resolution transmission electron microscopy, coupled with electron energy loss spectroscopy and STEM-Z (scanning transmission electron microscopy-atom 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, Jung-Sik Lee, Liliana Stan, Leonardo Corboz, Raymond F. DeGraff, Paul N. Andreetta, and Quan Xu Jin; Materials Science & Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico.**

An itinerant ferromagnet SrRuO3 (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 information 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 SiO2/Si substrates using the technique of 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 stresses, 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 1.14 μB per Ba atom, which agrees with the known value for bulk crystal. The magnetization measured with field-cooling warming showed very good agreement with Bloch's 3/2 law in low temperatures, which is well known as the result of spin-wave excitation: M(T)/M(0) = 1 - 2JT. The film with most biaxial lattice parameters showed A value of 2.0 x 10^-4 K^3/2 which is close to the theoretically estimated value (1.6 x 10^-4 K^3/2) while strained films showed larger A values, reflecting large 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 interatomic distance.

**H8.44 High Throughput Characterization of Conductivity by the Low-Temperature Scanning Microwave Microscope. Sabeh Okazaki1, Noriaki Okazaki2, Seiichiro Yaginuma3, Ryuta Tsuchihashi1, Yuji Matsumoto1,4, Hideomi Koinuma3 and Tetsuya Hasegawa2,5; Department 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 (SMM) has been attracting much attention as a high-throughput electric-property screening tool in the context of nanomaterials and technology. We have developed SMM 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 measurement of the combinatorial samples in films, while the latter is more advantageous in that one can evaluate dielectric loss/conductance from the measurement of Q-value shift. In this research, we report on the high-throughput characterization of Nb2O5 films on Nb/Ti/Au electrodes using thin film by using a newly developed low-temperature SMM. We used a high-Q 4/2 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 Nb2O5 is formed on Ba12Ca10B2Co2S6 (N-CBCO) which was manufactured on a STO substrate by the tri-axial epitaxy method. First, we measured the temperature dependence of the (1/Q), which is considered as a measure of sample resistivity. With increasing temperature from 300K to 80K, (1/Q) decreases 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 between 490 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 (1/Q) measured at temperatures lower than 60K showed a stepwise change, where low (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 SMM as a sharp jump in (1/Q).

**H8.45 Magnetic and Transport Properties of Transition Metal-Doped TiO2 Thin Films Grown by Laser Molecular Beam Epitaxy. Go Kinoz1, Go Kimoto2, Yuki Hirono2, Yuki Yamamoto2, Hidetsuka Sugaya3, Kazuhisa Inaba3, Yuji Matsumoto4, Hideomi Koinuma4, and Manashi Kawasak5; Materials Science & Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico.**
Epitaxial TiO2 films were fabricated on r- and c-axis substrates by laser molecular beam epitaxy. Ablation with Co-doped and Fe-doped TiO2 target produced single phase rutile films. Fe-doped TiO2 r-films were prepared in vacuum at a substrate temperature of 950 °C. The oxygen pressure during deposition was 103 Torr. The pulsed KrF excimer laser (248 nm) with a laser beam intensity of 1-3 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 r-films by magneto-optical studies carried out at room temperature. The magnetic hysteresis loops could also be observed even at room temperature. Scanning tunneling microscopy 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. Rutherford, Xianglin Ke, Dong Min Kim, Mark Rzchowski and Chang-Beom Eom.

The inherent nanoscale structure of organic molecules permits assembly with atomic-scale precision, a feature that is being taken advantage of to create 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 the SAM 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 50 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 a well-defined tunnel barrier. 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, L-V characteristics and spin dependent tunneling behavior will also be discussed.

**H8.47**

**Metal-Insulator Transition of Sr2/3Bi1/3FeO3 Eptaxial Film.** Naoki Hayashi, Shigeto Muranaka, Takahito Terashima and Mikio Takano.

Sr2/3Bi1/3FeO3 (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 films grown in this study show global CMR properties will change. The present work is concerned with the interfacial microstructure of LSMO thin films. Epitaxial thin films of (001)SrRuO3/SrO.67SrO.33MnO3 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 [001] and [010] directions. The origin of the cross pattern will be discussed. The microstructure will be correlated to magnetic and electric properties.

**H8.48**

**Field Effect Experiments in NdBa2Cu3O7-δ Ultrathin Films using SrTiO3 Single Crystal Gate Insulator.** Daniel Matthew, Stefano Gariglio and Jean-Marc Triscone; DPMC, University of Geneva, Geneva, Switzerland.

We report on the electrostatic modulation of superconductivity in ultrathin NdBa2Cu3O7-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. TiO2 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 applied polarization 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 ∆U/U is almost constant as a function of the applied magnetic field and correlated to the relative change in the critical temperature (ΔTc/Tc) through a relation derived from a vortex liquid resistivity based on thermally activated behaviour.

**H8.49**

**Active Defects in La0.67Sr0.33MnO3 Thin Films.** Tomas Liljefors, Robert Gunnarsson and Eva Olsson.

Active Defects in La0.67Sr0.33MnO3 (LSMO) thin films. The films were grown 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 [001] and [010] directions. The origin of the cross pattern will be discussed. The microstructure will be correlated to magnetic and electric properties.
We report superconducting properties of PLD - ErBa2Cu3Oy/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 range below 760°C, in which \( J_c \)'s before and after annealing are almost same and showed to be approximately 90K, \( J_c \) were obviously enlarged to the order of \( 10^6 \) A/cm² by an oxygen post-annealing in comparison with those of the as-deposited films (\( 0.5 \times 10^3 \) A/cm²). 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 measurements and normal state resistivities. In the as-grown films fabricated through a non-equilibrium process such as the PLD method, even though the as-deposited film showed \( T_c \) of 90K, a homogenization process of oxygen contents in whole part of the grown 123 films 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-REBa2Cu3Oy (RE: rare earth elements) coated conductors and superconducting devices.

Abstract Withdrawn
**H8.58**


We have performed detailed structural, magnetic, and electrical characterization of the cobalt doped TiO2 thin films in anatase and rutile forms grown on laser deposited LaAlO3 and R-Al2O3 substrates, respectively. Our results show that the cobalt distribution and hence the ferromagnetism in these films depend strongly on substrate temperature and oxygen pressure during growth.

At low oxygen partial pressure, the films have significant solubility for cobalt and thus relax the need of larger unit cells 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 ($\theta < 0.05^\circ$) thus relaxing the need of larger unit cells of the growing SrRuO3 film. Interestingly enough, the substrate induced stress is completely suppressed in anatase unit-cell of SrRuO3, which thus appear to be quasi-tetragonal. However, the orthorhombic symmetry is not confirmed by X-ray diffraction measurements and angular dependence studies of Raman spectra. Magnetic measurements by Kerr magnetometry on these films indeed confirm the uniaxial in-plane anisotropy.

**H8.60**

**Structural and magnetic behavior of Zn1-xCo2Fe2O4 powder for spintronic applications.** Manuel Varela 2, Todora Angelova 3, Ana Cross 3 and Andres Cantarero 2; 1Institut de Ciencia de Materiales - CSIC, Bellaterra, Spain; 2Fisica Aplicada y Electromagnetismo, Instituto de Ciencia de Materiales, Universitat de Valencia, Barcelona, Barcelona, Spain; 3Fisica Aplicada y Electromagnetismo, Instituto de Ciencia de Materiales, Universitat de Valencia, Barcelona, Spain.

SrRuO3 is a 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 epitaxiality of these oxides and the orthorhombic and, in principle, in epitaxial films, multiple orientations of 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 this distinction between small 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 ($\theta_v$) 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 thin 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 29nm. It is thus followed that the width of the substrate terraces shall have a major role on the surface morphology. We have subsequently grown films of SrRuO3 oxides of various thicknesses, $\theta_v$. It turns out that the film morphology can be tuned from fingers to multilayered fingers or grain bunched steps by appropriate selection of substrate vicinality and/or film thickness. Remarkably enough it is found that substrate vicinality as small as $\theta_v < 0.04^\circ$ has a profound impact on the two-dimensionality of the 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 unit cells of the growing SrRuO3 film. Interestingly enough, the substrate induced stress is completely suppressed in anatase unit-cell of SrRuO3, which thus appear to be quasi-tetragonal. However, the orthorhombic symmetry is not confirmed by X-ray diffraction measurements and angular dependence studies of Raman spectra. Magnetic measurements by Kerr magnetometry on these films indeed confirm the uniaxial in-plane anisotropy.

**H8.61**

**Surface Stabilization and in-situ Analysis of Epitaxial SrRuO3 Films.** Junsoo Shin 1,2, Sergei V. Kalinin 1,2, E. Ward Plummer 1,2 and Arthur P. Badding 1; 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 for loss of volatile oxides. Our previous work on Eu-doped SrTiO3 showed 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 oxygen atmosphere. Distinct differences in electron diffraction patterns observed are if films exposed to air were annealed 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.

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**H8.62**


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 computing. In this paper, we report on the epitaxial growth of SrRuO3 on SrTiO3(001) substrates, respectively. Our results show that the cobalt doped SrRuO3 can 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 codoping of Mn and Sn concentrations with the same atomic percent of (0.1, 0.1, and 0.001 at%). SQUID magnetometry measurements show the films retain ferromagnetic hysteresis up to 300 K. The films also display an inverse relationship between the magnetization and Sn concentration, with the same atomic percent of Mn and Sn concentrations 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. FA9550-08-1-0370.
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 using atomic force microscopy, reflection high-energy electron diffraction (RHEED), and x-ray photoelectron spectroscopy (XPS), under reducing conditions (25–800 °C in 10⁻⁶–10⁻⁷ Torr O₂). The as-grown SrRuO₃ epitaxial films exhibit atomically flat surfaces with nanometer-scale steps, even after exposure to elevated room-temperature temperatures. 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 allows us to determine a stability diagram for SrRuO₃ films, which indicates the temperature and oxygen pressure under which they can serve as bottom electrodes to 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 formation 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. A part of this work was done on Nanoscale Cooperative Phenomena and of the LDRD project.

H8.03


Dilute Magnetic Semiconductors (DMS) belonging to the family of wide band gap materials 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 2d 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 form that of 3d-elements) into SnO₂, we have prepared Gd, Dy, Er, Ho doped (4 to 8 mol%) compositions. The composition is found to vary (from 3.6 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.

H8.04

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 SrRuO₃ (a = 3.65 Å) to 3.85 Å as x increases from 0 to 1. 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) on SrTiO₃ (SrRuO₃) thin films grown on STO(001) substrates 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 Ca₅RuO₃ thin films showed a single 110 peak in 2θ-2θ 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 is induced by epitaxial strain. In this talk, we will discuss the origin of the phase separation and the phase distribution in the films synthesized by using high resolution transmission electron microscopy (TEM) and x-ray diffraction techniques.
they may appear in other compounds as well, such as the high-Tc cuprates. New results will be presented in this area, on the phenomenon of the interaction between ferromagnetism 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 coexist simultaneously important. [1] A. Moreo et al., Science (283), 2034 (1999); E. 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/0411474.

8:45 AM H9.3 Polar Disorder at Oxide Heterointerfaces and in Confined Systems. David A. Muller1, N. Nakagawa2, Harold Y. Hung3 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 defects chemistry are important to understand such an experimentally realized interface, in which bulk magnetic phases, defects, and vacancies can 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. Hung, Artificial Charge-Mediated in Atomic-scale Perovskite-


9:15 AM H9.3 Electric-Field Control of Ferromagnetism at Room Temperature on the Pb(Zr,Ti)O3/(La,Ba)MnO3 Heterostructure. Tetsu Kanki1, Masatoshi Ohnishi2, Hidekazu Tanaka3, and Tomoji Kawai1, 1Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Japan; 2PRESTO, Japan Science and Technology Agency, Kawaguchi, Japan.

In recent years, the area of spintronics, namely devices that use spin as an additional degree of freedom for data storage, has attracted considerable attention. Recent works in the physics of bulk ferromagnets and new techniques to tune the magnetic state and control the magnetic properties of magnetic thin films and nanostructures have allowed for an increased understanding of the role of electric fields in magnetic systems. The 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 magnetic materials, La1-xBaxMnO3 (LBM) perovskite manganese 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 LBM 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 Pb(Zr0.25Ti0.75)O3 (PZT) and superconducting Nb-doped SrTiO3 (Nb-STO). The films were grown on sapphire and other crystalline substrates by pulsed laser deposition. Upon polarization switching, the magnetic properties of the channel were reversibly switched from ferromagnetic to paramagnetic state. By using this effect, the ferromagnetic susceptibility at 293K can be modulated by 2.5K by switching ferroelectric remnant polarity at 293K. We will discuss details on ferroelectric PbZr0.2Ti0.803 (PZT) gate insulator to utilize the showing room temperature ferromagnetism even in the ultra thin film 

Temperature on the Pb(Zr,Ti)O3/(La,Ba)MnO3 (LBMO) perovskite manganite is useful because of the possibility to modulate the electronic properties of the 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 Pb(Zr0.25Ti0.75)O3 (PZT) and superconducting Nb-doped SrTiO3 (Nb-STO). The films were grown on sapphire and other crystalline substrates by pulsed laser deposition. Upon polarization switching, the magnetic properties of the channel were reversibly switched from ferromagnetic to paramagnetic state. By using this effect, the ferromagnetic susceptibility at 293K can be modulated by 2.5K by switching ferroelectric remnant polarity at 293K. We will discuss details on ferroelectric PbZr0.2Ti0.803 (PZT) gate insulator to utilize the showing room temperature ferromagnetism even in the ultra thin film 

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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 for the fabrication of 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 $>5^\circ$ 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 CeO$_2$, between the YSZ and YBCO must be interposed too. Finally it is desirable to grow the YBCO to a thickness by 2 mm or more. Remarkably these requirements can all be achieved.

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 under 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).

**12:00 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 films 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 the effects of the d-wave symmetry of the oxide superconductors. The fabrication of hybrid structures was described along with the effects of the d-wave symmetry of the oxide superconductors.
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 utilized for preparing the film growth, but not as an actual part of the film itself.

4:00 PM H10.6 Magnetic Interaction between Vortices and Magnetic Domains in Superconductor/ferromagnetic Multilayers. Qiang Li¹, Yufeng Hu¹, Zixin 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 YBa₂Cu₃O₇₋ₓ (YBCO) thin film and magnetic domains in ferromagnetic (FM) films with magnetic anisotropy in multilayers. Several YBCO/La₂₋ₓSrₓMnO₃ and YBCO/Pr₀.₇Sr₀.₃MnO₃ 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 YBCO film, Pr₀.₇Sr₀.₃MnO₃ 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 implications to the practical application will be discussed. This work was supported by the U.S. Dept of Energy, Office of Basic Energy Sciences, under contract No. DE-AC02-98CH10886.

4:15 PM H10.7 Epitaxial Growth and Characterization of the First Five Members of the Sr₂RuO₄₋ₓ Ruddlesden-Popper Homologous Series. Wei Tian¹, Jeff H. Haesen², E. Hutchinson², Ben-Ni Shey², M. M. Rosari², Peter Schiffer², Ying Liu² and Darrell G. Schrom²; ¹Dept. of Materials Science and Engineering, Penn State University, University Park, Pennsylvania; ²Dept. of Physics, Penn State University, University Park, Pennsylvania.

Sr₂RuO₄₋ₓ thin films have potential for high superconductivity, but the stoichiometric films are insulating. To overcome this problem, we use monolayer-by-monolayer deposition, with a correct absolute dose of cations, provided by MBE to synthesize Sr₂RuO₄₋ₓ films with intermediate n = 1 - 5 Ruddlesden-Popper structures. Magnetic measurements reveal that these films are ferromagnetic, while no sign of ferromagnetism is observed in the Sr₂RuO₄₋₂ phases. We report on the synthesis and characterization of the Sr₂RuO₄₋ₓ thin film series.

5:30 PM *H10.5 The Growth of Thin Crystalline Oxide Films from the Vapor. Gertjan Koster, GLAM, Stanford University, Stanford, California.

We report on our latest findings using real-time Fourier Transform Infrared (FTIR) and reflectance measurements during ultrafast electron beam deposited [100] angstroms/sec YBa₂Cu₃O₇ (YBCO) films. The glass 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 to the electronic absorption spectrum as the YBCO film grows. From the reflectance spectrum, it can be inferred that there is a liquid phase.

4:30 PM H10.8 Exploring New Aurivillius Phases. Mark A. Zurbach¹, J. Schubert¹, Yufan Jin¹, D. J. Comstock¹, Wei Tian¹, Vladimir Chernenko², Mike D. Bezeglio², Martha L. Holwell², Alexander K. Tagantsev², Stephen K. Streiffer² and Darrell G. Schrom²; ¹Dept. of Materials Science and Engineering, Penn State University, University Park, Pennslyvania; ²Dept. of Electrical and Computer Engineering, Northwestern University, Evanston, Illinois.

Aurivillius phases have been a subject of much research due to the potential of these phases for the growth of high-quality films, especially by metal-organic chemical vapor deposition (MOCVD). Aurivillius phases are a family of perovskite-related materials that have the general formula AB₂O₄₋ₓ, where A and B are cations that form a superstructure. The growth of high-n Aurivillius phases such as Sr₅Ba₆Ti₄O₁₇ (n = 7) and Ba₄(Ti₇Mn₃)O₁₇ (n = 8), which consist of bismuth oxide double layers interleaved with slabs of niobate perovskites, has been reported. These materials offer the opportunity to study the effects of changes in the interaction between structural layers as the perovskite slab thickness increases with n. Pulse laser deposition has recently been used to synthesize several new materials, including the highest-n Aurivillius phases, by this method. The results 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 H10.0
Quantitative measurements of piezoelectric response in PZT thin film capacitors using time-resolved synchrotron x-ray microdiffraction. DaHyun Dg 1, Dong Min Kim 1, Chang-Beom Eom 1, Eric M. Dufresne 2, Eric D. Isaacs 3 and Paul G Evans 4.

1 Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin, University of Michigan, Ann Arbor, Michigan; 2Center 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 20 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 boundary conditions on different areas of a device with the expectation that piezoelectric coefficient, d33, would be changed. We have found that PZT thin films had d33 values of 45-60 pm/V at the center of the top electrode. The piezoelectric displacement can be spatially constrained by patterning the FIB 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.

H11.1

A novel, low-temperature synthesis method for producing Ba0.7Sr0.3TiO3 (BST) thin films patterned in the form of nanotubes 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 nanotube (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 nanotube arrays serve as templates for the topotactic hydrothermal conversion to polycrystalline BST nanotubes. A simple geometrical model is proposed to elucidate the mechanism of the hydrothermal growth of BST nanotubes. This opens the possibility of tailoring the titanium oxide nanotube arrays, and of using various precursor solutions for 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 La1-xSrxCoxO3. Kwankuk Yu 1, Hyoungkyoung Lee 1, Hyeryun Bae 1, Jongsoo Park 1, Yeonseoung Lee 2, Shin Seok Koh 1, and Sung Jin Park 1.

1 Dept. of Physics, Hanyang University, Seoul, South Korea; 2Division of Information Computing and Communication Engineering, Hanbat Nat'l University, Daejeon, South Korea; 3Institute of Metal Physics, Kiev, Ukraine.

Interest in strontium-doped lanthanum-cobalt oxides, La1-xSrxCoxO3 (LSCO), has been motivated by the high ionic conductivity which makes them a candidate material for fuel cell 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 La1-xSrxCoxO3 (x = 0.15, 0.25 and 0.30) samples were synthesized by the standard solid-state reaction. A stoichiometric mixture of high-purity (99.999% or better) La2O3, SrCO3 and Co2O3 powders was fired in an Al2O3 crucible at 1250 °C 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 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 Tc. This anomalous magnetic behavior in LSCO is explained by the existence of ferromagnetic grains in the nonferromagnetic background.

H11.3
Rapid growth of SmBa2Cu3O7 thin film grown by vapor-liquid-solid growth mode. Yasuaki Ichinokawa 1,2, Hisayoshi Matsuo 3, Yutaka Yoshida 3,4, Yoshihiko Takagi 3,5, Kunane Matsumoto 2,6, Masahide Komatsubara 3,4, Atsushi Hayashi 2,5, and Shinya Ichihashi 2,5.

3 Dept. of Science and Engineering, Ryukoku University, Ory innovation Laboratory, Japan; 4 Dept. of Science, University of Tokyo, Japan; 6CREST-JST, Tokyo, Japan.

Vapor-liquid-solid (VLS) growth mode is expected to obtain high quality SmBa2Cu3O7 thin films with rapid growth rate. While the VLS growth mode is substantially same to the liquid phase epitaxy (LPE). We studied a growth rate dependence on superconductivity in a SmBa2Cu3O7 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 of Sm123 thin films grown by VLS growth mode were around 90 K independent of the deposition rate. However critical current densities (Jc) increased with the deposition rate increasing. When the deposition rate was higher than 60 \( \mu \)m/min, the Jc 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 micron/minute and this value was three times as high as the usual deposition rate. Even though the deposition rate was the maximum value, the Jc in Sm123 thin film grown by VLS mode was maintained at least 1 MA/cm². We argue that the VLS growth mode can achieve high critical current density as well as the LPE.

H11.4
Preparation of ZnO-Ga2O3 thin films by MOCVD using some Zn-diketonates as precursors. Yuzo Tasaki 1,2, Masanori Kabeya 1,2, Toshiaki Kanokoda 3 and Shuji Yoshizawa 3.

1 Japan; 2Toshiba MFG Co., Ltd., Higashihitachiyama, Saitama, Japan; 3Meisei University, Hino, Tokyo, Japan.

ZnO-Ga2O3 which is less expensive than In2O3-SnO2 (ITO) have been widely used as transparent conductive films of displays, organic light-emitting devices and solar cells. In most of previous reports on preparation of ZnO-Ga2O3 thin films by MOCVD, alkyl metals such as diethylzinc and trimethylgallium have been used as MOCVD precursors. Generally, metal Zn-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 Zn-diketonates as precursors was investigated. The evaluated zinc Zn-diketonates were bis[di-pivaloylmethanato]zinc (Zn(DPM)2), bis[diobutyrylmethanato]zinc (Zn(DBM)2), bis[di-isobutyrylmethanato]zinc (Zn(DBIM)2) and bis[2,2,6,6-tetramethyl-3,5-octanedionato]zinc (Zn(TMDO)2). The evaluated gallium Zn-diketonates were the complexes which have the same ligands as the zinc Zn-diketonates. Ga(DPM)3, Ga(DBIM)3, Ga(DBD)3 and Ga(TMDO)3. ZnO or Ga2O3 thin films were...
prepared using each precursor then Zn(TMOD)2-Ga(TMDO)3 and Zn(IBPM)2-Ga(IBPM)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\(^\circ\) Corning 1737 glass substrates at 400-600°C, and the gas pressure and the deposition time were 1350Pa, 32% and 20min, respectively. Gallium contents in the obtained films were higher than that in the precursor solution when Zn(IBPM)2-Ga(IBPM)3 solution was used. On the other hand, gallium contents in ZnO-Ga2O3 obtained films were lower than that in precursor solution when Zn(TMOD)2-Ga(TMDO)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 lower as the gallium contents were increased. The conductivity of the films without annealing in inert atmosphere was 5-1000 mohmcm. Neither the gallium content nor the kind of precursor affected transparency. The transparencies of the films were more than 85% in the range of 400-1000nm.

**H11.5**

Effects of H\(_2\)O Partial Pressure on the Crystallinity of ZnO Thin Film and Electrical Characteristics of Film Bulk Acoustic Wave Resonators, Hajime Yamada, Yoshitomi Usami, Hioki Kawamura, Masaki Takeuchi, Yukio Yoshino, and Takahiro Makino; Murata Manufacturing Co., Ltd., Yagi-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 450nm. The resonant frequency of the BAW resonator was tuned to 1.8GHz. Both ZnO and SiO\(_2\) were formed by rf sputtering while Al electrodes by electron beam evaporation. In this article we have studied effects of H\(_2\)O partial pressure on the crystallinity of ZnO thin film and electrical characteristics of BAW resonators. The ZnO and SiO\(_2\) thin films were prepared at 250 centigrade substrate temperature, 5.65/cm\(^2\) rf power, 0.1/Ar/O\(_2\) gas ratio and 0.69 pressure gas. H\(_2\)O gas was injected into the sputtering chamber, where the gas pressure, measured by a quadrupole mass spectrometer, was varied from 2.7\(\times\)10\(^{-5}\) to 2.0\(\times\)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 H\(_2\)O partial pressure corresponds to 2.7\(\times\)10\(^{-5}\) Pa and 1.5\(\times\)10\(^{-4}\) Pa, respectively. In the ZnO film deposited at a high H\(_2\)O partial pressure of 1.5\(\times\)10\(^{-4}\) Pa, 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 H\(_2\)O partial pressure of 2.7\(\times\)10\(^{-5}\) Pa, mosaics 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 H\(_2\)O in the sputtering chamber. In thermal desorption spectroscopy, we observed that the presence of hydroxyl group tends to increase with increasing H\(_2\)O partial pressure. The injection of H\(_2\)O 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 Electrochromic Devices, Zhu Fongh, Hao Xiaotao, Ong Soo Kian, Li Yangting, 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 resources worries the fast growing display industry and creates a need for low cost ITO alternatives. Aluminum-doped zinc oxide (AZO) is a possible alternative due to its unique optical and electrical characteristics. AZO thin films are 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 80% in the visible wavelength region, and a sheet resistance of 30 Ohm/sq can be obtained at a low process temperature of about 800°C. The performance of polymeric electrochromic devices using AZO films with desired properties are discussed.

**H11.7**

Comparison of Metal Gate and MOS Gate ZnO Field Effect Transistors, C. J. Ka0 2 , Y. W. Heo', Rohit Khanna', F. Ren 3 , D. P. Norton 1, G. C. Chi 2 and Stephen Peartson 1. 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 PIII-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 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 that the cleaning was removed on gate metal deposition. We will present the temperature dependence of FET dc performance and compare these to the results of MEDICI simulations of the expected performance.
Eugene Kotomin 1, Francese Illas 2, Nuria Lopez 2, Javier Carrasco 3 and R. L. Greene 1

ABSTRACT. Thin films of undoped Nickel Oxide and Lithium Nickel Oxide thin films were deposited on the pyrolysis of Nickel Acetaldehyde and Lithium Nickel Acetylacetonate respectively, at temperature range 300 degree Celsius to 420 degree Celsius. The films were deposited on the pyrolysis of Nickel Acetaldehyde and Lithium Nickel Acetylacetonate respectively, at temperature range 300 degree Celsius to 420 degree Celsius.

Ezekiel Oladele Ajayi1, Marcus A. Elejuwa1, O. Osaosu2, Omuide Oluwole Akinwumi1, G. O. Egbaevo2 and C. Jeynes3; 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 degrees Celsius by the Metalorganic Chemical Vapour Deposition (MOCVD) technique. The Chromium oxide thin films were also prepared through the photolithography method. The stoichiometry of the prepared thin films was found to be LiCr2O3. 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 band 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 YAIO3 single crystals.

Masanori Ando1, Tora Sakaguchi2, Akio Yamasak2, Yukawa Kunio2 and Eichi Hanamura2; 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.

Perovskite-type transition-metal oxides (RAIO3 (R=Y, La, Nd, Sm, etc.)) attract much interest due to their unique property and potential applications in optoelectronics. The perovskites form 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-exciton formation and the nature of the excited state of the oxide crystals. We have already reported that oxygen-deficient YAIO3 and LAIO3 single crystals show strong photoluminescence (PL) in blue and green region. The PL originates from the excited state formed at oxygen deficient site. The PL can be controlled by doping ions with different valence states at R+3 sites. The oxygen vacancies are doped by the sodium ions. 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 YAIO3 crystals for the first time. Two types of perovskite single crystals with low electrical conductivity, 1% Ti-YAIO3 and 1% Ti-YAIO3 were prepared by the photolithography method from the mixture of YAIO3, 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 disc. The Au and Al electrodes were formed on the top and bottom side of these perovskite single crystal thin films 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-YAIO3 and 1% Ti-YAIO3 films showed green EL by applying AC electric field stronger than about ±5x104 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.


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 synthetized 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 materials 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 x 10-4 G-ohm 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 pattern showed 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, the 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 Kurogi2, Keisuke Shibuya1, Masahiro Oshima3, Hideomi Komiyama1 and Mlikk Lipman1; 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. Perovskite-type transition-metal oxide thin films are very attractive for the heterointerface synthesis, superlattice fabrication and so on. The chemical etching makes the atomically flat surface suitable for TiO2 termination. It is probable that this chemically cleaved surface, possibly having an atomic terrrace-type structure, is thermodynamically stable. 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 relaxation, well-defined surface with step edges evenly distributed can be obtained by high temperature annealing at, say 1000 °C, in 10-4 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 La1-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 J. DeLeo1, Nehal S. Chokshi1, Gary S. Tompa1 and P. V. Ashir2; 1AMBP Tech Corp., Amherst, New York; 2Polymer Physics and Analytical Department, Union Chemical Laboratories, ITRI, Hsinchu, Taiwan.

Abstract Withdrawn
The benefits of realizing an electrochromic module deposited onto transparent plastics such as poly (ethylene teraphthalate) PET would reduce costs and weight while enabling the realization of flexible electrochromic modules. The main challenge in realizing a flexible module is the high processing temperature of the PET and easy-to-react nature of the PET during the adiabatic expansion process. To address the above, we have deposited the W03, V025 and ITO films. Utilizing a unique technique dubbed LAMBD (Laser Assisted Molecular Beam Deposition), W03 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. W03 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.

H1.22

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 micrometers with low driving voltages. The electro-optic properties at 1.55 μm wavelength were measured in epitaxial BaTiO3 thin films grown on Si 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 rijk which due to symmetry is usually written in Voigt notation as r_{ij}. Measurements of r_{ij} were made for propagation in both the <100> and the <110> 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<100> direction while the measured r_{13} values for propagation along the <110> direction are as high as 360 pm/V.

H1.25
Observation of electrical transition time of the metal-insulator transition for V02 thin films. Byung Gyu Chaò Doo, Hyeob Yoon, Hyunchang Chae, Doo Hyeob Yoon, Hyun Tak Kim and Kwang Yong Kang, Basic research laboratory, ETRI, Daejeon, South Korea.

V02 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 V02 films useful for applications to electrical and optical switching devices. In this research, we observe electrical transition time of the MIT for V02 films with switching pulse. V02 films were successfully deposited on Al2O3 substrate by pulsed-laser deposition with KrF excimer laser. Pure V02 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 V02 films abruptly changes with the order of 10^4 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 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.

H1.26
Abstract Withdrawn

H1.27
Electrical Conduction Control of ZnO Films Prepared by Pulsed Laser Deposition in Ozone Ambient. Kenji Ebihara, 1 Electrical and Computer Engineering, Kumamoto University, 2Kumamoto, Japan; 3Electrical Engineering, Sasebo National College of Technology. Sasebo Japan.

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 on the other hand, ozone sensitive nanorods are measured in thin films for light propagation along the BaTiO3<100> direction. The films were grown at the substrate temperature of 200 °C and 27 O°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 activation 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.

H1.24
Hydrogen and Ozone Gas Sensing Using Multiple ZnO Nanorods. Byung Sam Kang 1, 2, Fan Ren 1, Young Woo Heo 1, Brent Gila 1, David Norton 2 and Stephen Pearton 1, 2.

1Chemical Engineering, University of Florida, Gainesville, Florida; 2Materials Science and Engineering, University of Florida, Gainesville, Florida.

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conduction which was confirmed using the Seebeck coefficient measurement. It is shown that oxygen concentration between 3000 ppm and 5000 ppm in 296°C Er 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 evaluated with a density of 1.5 × 10¹⁷ cm⁻³ and a 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 oxygen and NO. In the SPLD process, consisting of a pulsed laser ablation chamber and substrate chamber, with or without the pulse, the oxide films can be deposited independently on the ablation chamber conditions such as pressure and ambient gas, LiMnSiO₄, organic light-emitting films (AISpTmPF) as well as ZnO were deposited.

H11.28
Imaging Local Surface Potential during Photocatalytic Reaction on TiO₂ Single Crystal Surfaces. Yuhei Mikita
Toshihisa Horiuchi, Kenji Ishida, Kei Kobayashi, Hirofumi Yamada, and Kazumi Matsushige
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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 various research fields for industrial applications such as water splitting, anti-fogging, and environmental purification of air and water. Although these features have been investigated from various standpoints, fundamental mechanisms of the photocatalytic reaction 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 45 nm-thick metal layers of Pt and Au, respectively. In general, the photocatalytic activity of TiO₂ is increased by depositing metal such as Pt and Au 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 in both a vacuum condition and ambient air. We repeatedly scanned a 5 μm x 5 μm area including TiO₂ and metal layers at a scan rate of 48 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 explained by excited state charge transfer between the metal and TiO₂. Furthermore, we observed an increase in the surface potential on the metal film after the irradiation for Au/TiO₂ (100) 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 HT 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 air, 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 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 Shibuya
Minoru Noda, Masaaki Okiyama, and Kazuaki Sato
1Graduate School of Engineering, Osaka University, Toyonaka, Osaka, Japan; 2BKR UNIVERSAL INC., Yokohama, Kanagawa, Japan.

Recently, natural-superlattices of bismuth-layer-structured ferroelectric (BSLF) materials have attracted much interest as polarization enhancement is expected by structural modification of pseudo-perovskite layers through Bi₂O₂ layer. The crystal structures of BSLFs are generally formulated as (Bi₂O₂)n(B₅O₆)ₙ₋₁(B₅O₆)n⁺₁(F) and m is the number of BO₂ octahedra in the pseudo-perovskite blocks. Basically, crystal structures of natural-superlattice BSLFs are intergrowths consisting of one-half of unit cells of sequential n number BSLF materials such as n=1-3. Two kinds of perovskite blocks are, in turn, sandwiched between Bi₂O₂ layers. In this paper, we report on Bi₂MoO₆ (BM) (n=1)-based natural-superlattice structures, thin films, which are Bi₂MoO₆-Bi₂TiO₅O₆ (BM-BTO) (m=1-2) and Bi₂MoO₆-Bi₄Ti₃O₁₂ (BM-BIT) (m=1-3). BM-BTO (m=1-2) and BM-BIT (m=1-3) thin films have been prepared on SrTiO₃ (STO) (100) single crystal and Pt/TiO₂/SiO₂/Si substrate by pulsed laser deposition method. The c-lattice constant (6.73 nm) of the epitaxial BM-BTO (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 BTO unit cells. Polycrystalline BM-BTO (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 (110)-oriented BM (m=1) and (111)-oriented BTO (m=2). Of the other films, 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 BTO (m=3) unit cell. This natural-superlattice structure consisting of non-scalar number in BSLF 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 properties of BM (m=1). The remanent polarization of polycrystalline BM-BTO (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 BM (m=1) and BM-BTO (m=1-3). BM-BTN (m=1-3) thin film has much larger remanent polarization (P_r=54 μC/cm²) than polycrystalline BM-BIT (m=3) thin film on Pt/TiO₂/SiO₂/Si substrate prepared by PLD under the same conditions. The P_r shows a large hysteresis loop shows good saturation behavior for the applied field. BM-based natural-superlattice-structured BSLF thin films do not have 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. Toshiaki Kimpara, Shinya Sasaki, Tomomasa Satoh and Takashi Hirata
Electrical, Electronics and Information Engineering, Kanagawa University, Yokohama, Japan.

ZnO is an attractive II-VI group 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 nanostructures of ZnO such as nanorods, nanowires, nanoribbons, 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 electronic/microelectronic devices. In this paper, the ZnO crystals having 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 the present study, 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. ZnO is used as a precursors to synthesize ZnO and N₂ is used as a 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 laser power is 40 PW. The laser pulse frequency is 1 J/hot 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 these are approximately normal to a Si(111) substrate. The diameter 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.
Preliminary Infrared Analysis of Thin-Film Neodymium Nickelate Films. 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 NdNiO$_3$ for the first time and relate these to the results of other characterisation methods. The films were grown on either LaAlO$_3$ or SrTiO$_3$. Fourier transform spectroscopy (FTS) in the range 100 to 500 cm$^{-1}$ shows absorption expected for a well-developed metallic state. Indeed, the suppression 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 isolate 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 Er$^{3+}$ fluorescence are investigated using a 980 nm pump beam and collection with a time-resolved detector. Promising materials are identified for more effective thin films by coupling the fluorescence lifetime with its amplitude. The composition-spread technique allows us to determine 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 SiO$_2$ 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 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.

Thick Films of In$_2$O$_3$/SiO as Optical Gamma Radiation Sensors. Khalil Ibrahim Arshak, Jonathan Molloy and Olga Korostynska, Department of Electronic Engineering, University of Limerick, Limerick, Limerick, Ireland.

Ionizing radiation arises from both natural and man-made sources and is used in numerous 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 In$_2$O$_3$ and SiO 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 ionizing 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 resulting films. It was reported that In$_2$O$_3$/SiO have an open structure which contains a number of dangling bond centres and the density of these centres decreases as the indium oxide content is increased in the complex SiO/In$_2$O$_3$ samples [4]. This gives rise to a decrease in the porosity of the resulting film and consequently, the optical energy gap decreases. In this work, polymer pastes of In$_2$O$_3$/SiO mixtures in various proportions were made. These are: 75 wt% of In$_2$O$_3$ and 25 wt% of SiO, 50 wt% of In$_2$O$_3$ and 50 wt% of SiO, 25 wt% of In$_2$O$_3$ and 75 wt% of SiO, and 50 wt% of SiO. Bulk pastes were screen-printed using DEK RS 1202 automatic screen printer on glass substrates. All devices were exposed to a disc-type 137Cs source giving rise to an increase in the value of their optical density from 1.97 before irradiation to 2.06 after irradiation with a dose of 1.72 mSv. Films made with 50 wt% of In$_2$O$_3$ and 50 wt% of SiO 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 In$_2$O$_3$ and 25 wt% of SiO 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 $E_{opt}$ are estimated 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.


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 isolate 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 Er$^{3+}$ fluorescence are investigated using a 980 nm pump beam and collection with a time-resolved detector. Promising materials are identified for more effective thin films by coupling the fluorescence lifetime with its amplitude. The composition-spread technique allows us to determine 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 SiO$_2$ 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 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.

Thick Films of In$_2$O$_3$/SiO as Optical Gamma Radiation Sensors. Khalil Ibrahim Arshak, Jonathan Molloy and Olga Korostynska, Department of Electronic Engineering, University of Limerick, Limerick, Limerick, Ireland.

Recent work has shown that there is a great deal of interest in finding room temperature ferromagnetism in transparent transition metal (Fe, Co, V) doped TiO$_2$, ZnO and other materials, so called diluted magnetic semiconductors. In the present study anatase and rutile forms of TiO$_2$ 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 850°C yields only the anatase phase, whereas 750°C annealing shows only the rutile phase of TiO$_2$, 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 TiO$_2$ films remain unchanged 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 TiO$_2$ host lattice. The 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.
The detection of gravitational waves is one of the great outstanding 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 Magneli phases of vanadium oxides**—M.B. Sahana and S.A. Shivasankar; 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 exhibit different electronic properties for a particular temperature. For example, $V_3O_5$ is metallic, whereas $V_4O_8$ 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 Magneli 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 $Al_2O_3$ and $V_2O_5$ deposited on $Al_2O_3$ (110) is metallic 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 films on $Al_2O_3$ (110). A large increase in the band gap ($\approx 2 eV$) of ordered 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, Massashi 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 epitaxially grown crystals, 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, nanohelixes, nanotubes) have been demonstrated exhibiting greater purity and better crystal quality than bulk crystals and epilayers as low defect concentrations are statistically favorable 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 actual devices and 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 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 an argon 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-phase nanoparticles that emerge from the plasma have a lognormal size distribution 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 devices.

**H11.39**

**Growth and Some Interesting Characteristics of La0.1Sr0.9MnO3/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 La0.1Sr0.9MnO3/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 La0.1Sr0.9MnO3 (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. These results show that gas-suspended ZnO nanoparticles for delivery to selected locations on a substrate and potential integration into functional devices. These targets are vaporized in an argon 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-phase nanoparticles that emerge from the plasma have a lognormal size distribution 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 devices.

**H11.40**

**Application of Chemical Lithography and Chemical Etching on Fabrication of ZnO Based Microstructured Components**, Kenji Takahashi, Takeshi Ohtagaki, Hiroshi Funakubo, Hajime Haneda, and Masataki Okabe; National Institute for Materials Science, Tsukuba, Japan; and Tokyo Institute of Technology, Yokohama, Japan.
Zinc oxide is an attracting material for opto-electronic applications. In order to obtain functional structures of ZnO, microfabrication is a necessary 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 methods. In this study, we investigated the chemical etching properties of ZnO for the purpose of fabricating micro-structured ZnO in order to create thin film pattern on ZnO single crystal substrate. We used electron beam lithography technique to obtain resist patterns on (00-1), (11-20) and (10-20) surface of ZnO crystals. Chemical etching was carried out with aqueous solution of HCl 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 hexagonal shaped pits. The randomly shaped 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 these etched pits had cubic crystallographic orientation (10-11-1) 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. Sung Heon Yoon, Yuqian 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 Scientific Research from MEXT, Japan and also by NEDO, Japan. Films are amorphous and their crystallization temperature is 350°C. The role of substrates on the growth and electroacoustic properties of ZnO thin films prepared by chemical solution deposition and RF magnetron sputtering will be discussed. Process parameters such as temperature, time and atmosphere were systematically investigated on various substrates. Different layers on silicon wafer, glass, IZO, Pt and Al with different orientations were investigated to determine the role of substrates in the preferred orientation. The electroacoustic properties of microfabricated devices will be discussed in context with preferred orientation, roughness, and microstructure.

**H11.42**


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 of technologic interest is possible for several reasons: the use of polymeric materials allows new processing techniques to be explored, new applications to be developed, and new device geometries to be fabricated. These materials are used in a variety of applications such as smart windows, sensors, and displays. The deposition of oxide materials on plastic substrates satisfies these needs. 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 substrates that have been investigated are polyethylene terephthalate, polypropylene, polyethylene, polystyrene, and poly(methyl methacrylate). These polymeric substrates have been investigated for the deposition of ZnO thin films. In this study ZnO thin films were deposited on polyethylene terephthalate using chemical solution deposition and RF magnetron sputtering. Process parameters such as temperature, time and atmosphere were systematically investigated on various substrates. Different layers on silicon wafer, glass, IZO, Pt and Al with different orientations were investigated to determine the role of substrates in the preferred orientation. The electroacoustic properties of microfabricated devices will be discussed in context with preferred orientation, roughness, and microstructure.

**H11.43**

Time-resolved spectroscopy of ZnO thin films grown by Pulsed Laser Deposition. Maurice Cheung, Tim Murphy, Jamie Dean Phillips, Kristin Cartwright, Timothy E. Murphy, Jamie D. Phillips and Willie E. Bowles; 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 role of non-radiative and radiative 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 on glass. Each sample in this series has a unique photoluminescence (PL) characteristic. Specifically, at 15K, each of the samples showed two distinct emission peaks. Conductivity measurements showed that one of the samples that was grown on sapphire conducted 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 (3.2 eV) accompanied by a broad emission peak from 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 higher quality samples. This observation suggests that, as expected, the defect density, as well as the density of the channels to these defects states, is higher in the poorly conducting sample. Moreover, all samples showed a 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 low energy emission was on the order of 10 ps, while the deep level emission was characterized by a gradual decay of a few hundreds picoseconds.

**H11.44**

Pulsed Electron Beam Deposition of Epitaxial Gallium Oxide on Sapphire. Christian Miao, Hugh Porter, John F. Mathis, Ailing Ca, Chul G. Kang, and Jagdish Narayan; 1ECE Dept Box 7911, NC State University, Raleigh, North Carolina; 2Materials Science and Engineering, NC State University, Raleigh, North Carolina.

Traditionally conducting oxides such as Indium Tin Oxide and Zinc Oxide 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 techniques, a series of β-Ga2O3 films were grown at room temperature on 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 250 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 240 nm. Transmittance 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 (011) β-Ga2O3 // (011)α-Al2O3, and (201) β-Ga2O3 // (201) α-Al2O3 with 4 lattice constants of β-Ga2O3 in the (011) direction matching very closely with 3 lattice constants of sapphire in the (011) direction, and 2 lattice constants of the β-Ga2O3 in the (2110) direction matching very closely with 3 lattice constants of sapphire in the (2110) direction. The resulting lattice mismatch are -1.4% and +3.3% 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 need to be understood. The dynamic response of minority carriers will need to be understood. The use of polymeric substrates for new oxide semiconductors hence opens huge opportunities for large area sensors, displays, and other large area electronics. Current polymeric substrates that have been investigated are polyethylene terephthalate, polypropylene, polyethylene, polystyrene, and poly(methyl methacrylate). These polymeric substrates have been investigated for the deposition of ZnO thin films. In this study ZnO thin films were deposited on polyethylene terephthalate using chemical solution deposition and RF magnetron sputtering. Process parameters such as temperature, time and atmosphere were systematically investigated on various substrates. Different layers on silicon wafer, glass, IZO, Pt and Al with different orientations were investigated to determine the role of substrates in the preferred orientation. The electroacoustic properties of microfabricated devices will be discussed in context with preferred orientation, roughness, and microstructure.

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 substrates that have been investigated are polyethylene terephthalate, polypropylene, polyethylene, polystyrene, and poly(methyl methacrylate). These polymeric substrates have been investigated for the deposition of ZnO thin films. In this study ZnO thin films were deposited on polyethylene terephthalate using chemical solution deposition and RF magnetron sputtering. Process parameters such as temperature, time and atmosphere were systematically investigated on various substrates. Different layers on silicon wafer, glass, IZO, Pt and Al with different orientations were investigated to determine the role of substrates in the preferred orientation. The electroacoustic properties of microfabricated devices will be discussed in context with preferred orientation, roughness, and microstructure.

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c-plane sapphire. ZnO materials deposited by pulsed laser deposition and molecular beam epitaxy were both examined. Pulsed laser deposition (PLD) and chemical vapor deposition (CVD) have been predominant methods for the deposition of molecular beam epitaxy. ZnO photocathodes were placed in a resistive circuit, where photocathode response was observed in the ultraviolet spectral region. The photoconductive decay was examined after excitation from a pulsed laser operating at a λ=248nm with a pulse width of approximately 20ns. A slow and fast photoconductive response was 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, indicating that noise current is generated by defects in the ZnO material. The photoresponse and noise characteristics of ZnO photocathodes will be presented and related to independent measurements of the electronic and structural properties of the ZnO:Al thin films.

H11.46
Pulsed Electron Beam Deposition of Single Crystal ZnO on Sapphire, Hugh Porter, Christian Mion, Ailing Cai and John F. Muth; ECE Dept 7811, NC State University, Raleigh, North Carolina.

Thin films of ZnO on C-plane (001) sapphire (α-Al2O3) substrates were grown by Pulsed Electron Beam Deposition (PEBD). The electron pulses used to ablate the target were approximately 0.8 Joulies and 100 ns in duration. The surface morphology of the target was found to influence deposition efficiency, indicating that a combination of ablative and thermally driven processes occurs. Measurements of the 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 27 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 Sr1-xBa2xNb2O6 Films, Isso Oikubo, Hua Christian, Gerald Jellison, Christopher Rouleau, Douglas Lowade, Mark Reaves, and Shuoguang Huang; 1Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; and 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 Sr1-xBa2xNb2O6 (SBN) shows a particularly large Pockels coefficient (r33 ~ 1500 pm/V for x = 0.25, i.e. 30 times higher than 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 composition of the material. In particular, we use a 2-modulator generalized ellipsometer to determine the refractive index in the range λ = 300 - 800 nm, and scanning microwave microscopy to determine the dielectric constant at f = 1.6 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 future applications. This work was accomplished 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 Ferguson, Kandoor Shalini, Ming Pan, I. T. Holesinger, Shanty Ganesan, William B. Nemeth; 1School of Electrical Engineering, and 2School of Materials Engineering, Georgia Institute of Technology, Atlanta, Georgia; 3Cermet 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 Si, 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). Here, Organic Chemical Vapor Deposition (OCVD) 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 ZnO 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 used on ZnO on Si(111) substrates 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 cm^{2}/V is/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 Polycyanurate Sol-Gel Films. Douglas Anson Loy; and Jonathan Mark Stoddard; 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 °C) makes polycyanurates excellent candidates for preparing thin-film optical devices that are formed through a polymerizable, 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 glassy matrices. Measurements of the polycyanurate cast from chloroform were found to be liquid crystalline, but failed to form suitable films upon exposure of the pendant alkoxysilane groups to sol-gel polymerization conditions. Free-standing sol-gel films were formed from solution-casting a mixture of polycyanurate, an inorganic silica precursor such as tetrachlorohydrosilicate or bis(triethoxysilyl)methane, and aqueous formic acid (88%) as a catalyst. The polycyanurate/sol-gel hybrid films were heated to 250 °C and 300 °C to depolymerize the polycyanurate. The encapsulation of the polycyanurate into the inorganic silica matrix raised the onset temperature of depolymerization by 100 °C. Alternatively, treatment with strong acid or base resulted in decomposition of the inorganic 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 and high optical quality of the films. The A and B excitons were clearly resolved at 27 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. The encapsulation of the polymeric liquid crystalline assemblies coupled with a relatively low depolymerization temperature (<150 °C) makes polycyanurates excellent candidates for preparing thin-film optical devices that are formed through a polymerizable, 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 glassy matrices. Measurements of the polycyanurate cast from chloroform were found to be liquid crystalline, but failed to form suitable films upon exposure of the pendant alkoxysilane groups to sol-gel polymerization conditions. Free-standing sol-gel films were formed from solution-casting a mixture of polycyanurate, an inorganic silica precursor such as tetrachlorohydrosilicate or bis(triethoxysilyl)methane, and aqueous formic acid (88%) as a catalyst. The polycyanurate/sol-gel hybrid films were heated to 250 °C and 300 °C to depolymerize the polycyanurate. The morphologies, surface area, and chemical functionality of the ordered sol-gel films will be discussed as well as potential applications.

H11.51
Chemical Solution Deposition for YBa2Cu3O7-x / SrTiO3/Ni-W Superconducting Composites. Donald I. Overmyer, James A. Voigt, Terry G. Holesinger, Dominic F. Lee; Los Alamos National Laboratory, Los Alamos, New Mexico; 2Los Alamos National Laboratory, Los Alamos, New Mexico; and 3Oak Ridge National Laboratory, Oak Ridge, Tennessee.

High quality epitaxial YBa2Cu3O7-x (YBCO)/buffer/metal superconducting composites have important power generation and 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-assisted growing process is employed on base metal substrates such as Ni will be presented, as well as metrics for measuring thin film oxygen diffusion. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the US Department of Energy NNSA under contract DE-AC04-94AL85000.

H11.53 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 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, FDP has advantages for a high dimension T.V. over PDP. Therefore, there are strongly adhesion 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. These materials are known as an electron emission source 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 23.3772. 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.

H11.54 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 high need high 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) require both 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 nonmonovalent copper as the major constituents. However, the simplest oxide of Cu+, Cu2+, 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 be become significantly more useful, because many active functions of semiconductors are due to p-n junctions. In this work, the Cu+ delafossite 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.


Atomic layer deposition is a versatile technique for depositing films that are otherwise inaccessible 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 layered films on polymeric 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 substrates and Si(100) substrates, with ultra-smooth surfaces strongly indicative of uniform multilayer coatings in both cases. Secondary ion mass spectrometry (SIMS) depth profiling indicated that the amount of residual chloride from the TiCl4/H2O reaction was influenced by the deposition conditions, with decreased 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, 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 (2.30 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 Al2O3 layers. However, exfoliation occurred at the film-substrate interface for all coatings, as expected for strongly adherent layers. The effect of processing conditions on mechanical properties will be discussed.

H11.56 Barium Metaphosphate (BaPb03) and Lanthanum Nickelate (LaNiO3) Conductive Oxide Electrodes for Oriented Ferroelectric Thin Films. Stacey W. Boland, Melody Grubbs and Sossama 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 Pb0.75Ba0.25TiO3 (PBT). To successfully integrate such films into large area devices, which need high 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) require both 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 nonmonovalent copper as the major constituents. However, the simplest oxide of Cu+, Cu2+, 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 be become significantly more useful, because many active functions of semiconductors are due to p-n junctions. In this work, the Cu+ delafossite 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.
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 are examined for the preparation of two conductive oxides, bario-manganese (Ba₅P₂O₆·BPO) and lanthanum nickelate (LaNiO₂, LNO). LNO has been widely studied, and several simple sol-gel processes have already been reported previously. BPO has been studied to a lesser extent, however it is particularly suited for use with Pb₁₋ₓBₐ₂O₄, as it provides good lattice matching without introducing additional cation species. Several procedures have been reported for producing BPO, but all involve high temperature, highly aggressive solutions and 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 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 deposition cycles, first characteristic as-grown and post-anneal, 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 Al₂O₃ by RF Magnetron Sputtering Technique

Chul-Ho Han, Choon-Ho Yoo, Kyung Seok Kwon, and Byung-Ho Kim, Materials 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 300°C to 900°C after film deposition. High-resolution x-ray diffraction analysis (HRXRD), photoluminescence spectroscopy (PL), U-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 #-rocking curve FWHM values of as-grown ZnO (0002) films deposited at 400°C and 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. Photoluminescence spectra of ZnO thin films clearly show typical sixfold symmetry of hexagonal ZnO film and FWHM values of annealed ZnO film drastically decrease as annealing temperature increases, indicating that crystal quality in the out of plane 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 1.1 and 2.6eV, respectively. However, post-annealed ZnO films clearly show near band edge emission peaks of 3.2eV with very weak deep level emission peaks of 1.8 and 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 films show strong near band edge emission peaks of 3.3eV with very weak deep level emission peaks. U-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 , estimated band gap is similar to band gaps measured by PL. With Hall measurements, we observed that post-annealed ZnO films are all n-type and their Hall resistivity decreases with increasing the post-annealing temperature increases. Carrier concentration varies from 1.1x10¹⁷ to 1.3x10¹⁸ 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 n-ZnO 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, ZnO/ZnO Thin Film Structures. Since the discovery of high mobility semiconducting, piezoelectric and pyroelectric properties of ZnO nanorod/ZnO thin film structures, ZnO nanorod/ZnO thin film structures were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction, 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 Chiu, Wan-Yu Wu, Growth of Single Crystal ZnO Nanorods on (0001) MgxZn1_xO substrates by Non-thermal Plasma Deposition, Diamond and Related Materials 12 (2003) 1841-1844.

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9:00 AM H12.3
High Quality MBE-grown ZnO/MgO Nanorod Structures for Spintronic and UV Applications

Jianwei Dong1, A. Oinasjı1, B. Hertog2, A.M. Dabiran3, P.P. Chow1, S.J. Pearton1, 2, 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 fractional binding energy of 1.0 meV [1], ZnO is an attractive material for use in UV light emitters. In addition, the bandgap of Mg₁₋ₓZnₓO compounds span the range of 3.4 to 7.5 eV, which opens up the opportunity for broad-bandgap emitters, leading to enhanced device performance. The high-quality single-crystal Mg₁₋ₓZnₓO epilayer, doped with MgZn₁₋ₓO also holds promise as a 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 Mg₁₋ₓZnₓO epilayers, doped with Fe, Mn, Co, and magnetic impurities such as Eu and Mn introduced by either in-situ doping or ion implantation. High efficiency RF-plasma oxygen source, designed and produced by SVT Associates was utilized to grow high quality thin films. 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 Mg₁₋ₓZnₓO films were deposited on c-plane sapphire substrates, p-AlGaN and SiC substrates. Both doped and undoped Mg₁₋ₓZnₓO films 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. Optical reflectometry measured from 377 nm to 228 nm (Eg from 3.3 to 5.4 eV) was observed at room temperature in Mg₁₋ₓZnₓO compounds with x varying from 0 to 0.98, respectively. Double heterostructures (DHs) utilizing a p-AlGaN/SiC collector/electrode and 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 Shemtob, P.O. Box 250, Wright-Patterson AFB, Dayton, Ohio 45433-7900, 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 Nanotubes, Fang-Yi Jen1, Tsung-Yi Tang1, Cheng-Ming Wu2, Chih-Chung Yang1, Bao-ping Zhang2 and Yusaburo Segawa2; 1Institute of Electro-Optical Eng., National Taiwan University, Taipei, Taiwan; 2Physical and Chemical Research (RIKEN), Sendai, Japan.

ZnO has been attractive for its 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 3.36, 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 (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 slowest 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, Torece M. Barnes, Jackie Leaf, Kyle Olson and Colin A. Welden; 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, electronic, and piezoelectric properties, and its wide 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 N2/O2 mixtures. Both the OES and QMS data show that at equal elemental N2/O2 ratios, Hema nitridation exhibits 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/O2 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.
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 photovoltaic effect 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 Yb2Ru3O7-x (YBCO) in a YBCO/STO:Nb heterostructure and observed an enhancement of the superconducting critical temperature Tc 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 Tc. In this work, we apply the PCI method to an n-type superconductor Sr1-xNdxCu02 (SNCO) in a SNCO/STO:Nb heterostructure and study the current-voltage and photoelectric properties under UV light illumination. A Sr1-xNdxCuO2 (x=0.1) thin film was prepared on a SrTiO3 (100) single crystal substrate doped with 0.5% Nb (STO:Nb). The film deposition was carried out by using the pulsed laser deposition technique with a KrF excimer laser (λ = 248 nm). A xe lamp was used. All the measurements were carried out in open air. The film thickness (d) was 248 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 in room temperature. The current density (J) or the 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 open-circuit voltage VOC of 0.5 V and a short-circuit current density JSC of 7.5 x 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 Tc of the SNCO film. Results will be presented.

11:15 AM H12.10
Synthesis of ZnO nanorods with controllable orientation and area-density, Ming-Ts 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 3.37 eV and 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 sputtering 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 afore-mentioned 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 electrole plating technique. ZnO nanorods were deposited under various conditions: growth parameters 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 substrate holder surface. The area density, on the other hand, is affected by not only the angle but also the characteristics of the electrodes copper interlayer, which is decisive for the formation of ZnO nanorods.

11:30 AM H12.11
Amorphous Oxide Semiconductor Exhibiting Large Hall Mobility (> 10 cm^2/Vs): Electronic Structure, Carrier Transport and Device Applications of a-InGaZnO4, Namura Kenji1, Toshio Kamiya1, Hiroshi Ohba2, Akira Takagi1, Hiroshi Yamauchi1, Masahiro Hirano2 and Hideo Hosono1,2; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan, 1Hosono Transparent Electro-Active Materials Project, JST, Kawasaki, Japan.

Transparent amorphous oxide semiconductors (AOS) 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]. AOS exhibit good carrier transport properties characterized by large Hall mobility and absence of Hall voltage sign double anomaly. AOS having chemical compositions of In2O3-Ga2O3-ZnO (m = 1-4), a-IGZO are n-type semiconductors and exhibit Hall mobilities > 10 cm^2/Vs at carrier concentrations larger than 10^19/cm^3 [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 In2O3-ZnO sintered target. Films were deposited on SiO2 glass substrates at room temperature. Carrier concentration of the films was varied from <10^15 to 10^19/cm^3. Hall effect measurements 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 (Ne) and was sharply increased from 3 to > 10^14 cm^2/Vs as carrier concentration increased. The temperature dependence of Ne changed from thermally-activated behavior to degenerated behavior at 1.0x10^17 /cm^3, while that of μ_Hall shows thermally activated behavior even when carrier concentrations 3.0x10^14/cm^3. These results suggested that Fermi levels exist in band-tail states originating from structural randomness when Ne < 3.0x10^14/cm^3. 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. Obta, M. Hirao, K. Shimizu, T. Kamiya and Hideo Hosono, Adv. Mater. 15, 1490 (2003). [2] M. Orita, H. Obta, M. Hirao, S. Narushima and H. Hosono, Phil. Mag. B 81, 501 (2000).