SYMPOSIUM C
C: Ferroelectric Thin Films XII

November 30 - December 4, 2003

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*Invited paper
TUTORIAL

FT C: Ferroelectric Thin Films
Sunday, November 30, 2003
10:00 AM - 4:00 PM
Room 205 (Hynes)

The tutorial will cover important issues related to ferroelectric thin films: deposition techniques; integration aspects; electrical characterization; and application in new devices. It will start with a general overview and introduction of ferroelectric materials. Deposition methods will be discussed in view of relevant features and advantages for the major deposition methods MOCVD, CVD, sputtering and PLD. The key issues of integration which will be presented cover choice of electrode materials, nucleation and seeding, barrier and capping layers for stacked capacitors, etching processes, and resistance to forming gas anneals. The tutorial will give an introductory overview on measurement and interpretation of dielectric and ferroelectric properties. Domains in ferroelectric thin films, as well as effects introduced by thickness and size reduction, will be treated in some detail. The section on devices will cover most recent application, e.g., ferroelectric nonvolatile memories, integrated capacitor for tunable high frequency devices, piezoelectric infrared detectors, and piezoelastic MEMS.

Instructor:
Paul Murali, Swiss Federal Institute of Technology EPFL
Alexander Togante, Swiss Federal Institute of Technology EPFL
Susanne Hoffmann-Effert, Forschungszentrum Juelich
Stephen K. Streiffer, Argonne National Laboratory

SESSION C1: Fundamentals of Ferroelectric Materials: Emphasis on Strain
Chair: Angus Kirton and Alexander Togante
Monday, December 1, 2003
Room 203 (Hynes)

8:30 AM *C1.1
Theoretical Consideration of Ferroelectric Domains, Thin Films and Interfaces, Yoshisuke Ishibashi, Communication Studies, Aichi Shukukogaku University, Aichi Prefecture, Japan.

The structures of ferroelectric domains, thin films and interfaces are studied within the framework of the Landau-Ginzburg theory on the basis of models. Inhomogeneity of the polarization, which is a common feature in such structures, is supposed to increase the total free energy. To find the polarization profile the Euler-Lagrange equations have to be solved under boundary conditions appropriate to each case. In my system of this sort there is one order parameter, with which the system can be satisfactorily specified. In domains and domain walls it is the order parameter in respective domains and the Tilley-Zeeks model of thin films it is convenient to use the maximum or the minimum value of the polarization as the order parameter, which may be in the film or even outside the film. In models of the layered ferroelectrics the polarization at the interface may be more suitable for the order parameter. When there is a longitudinal component in the modulation of polarization, consideration of the depolarization field effect is indispensable in finding the polarization profiles. The depolarization field effect in the 90-degree domain walls, which must play an important role in forming the stable polarization profile, will be discussed.

9:00 AM C1.2
Stress evolution in integrated SrBi2Ta2O9 ferroelectric layers, Judith C. Liscen, J. A. Johnson, L. Goux and D. J. Wouters, SDPTIMEC, Leuven, Belgium.

The integration of ferroelectric materials with Si technology requires complex barrier layer schemes, whose combined stresses determine the mechanical stability of the system during subsequent processing steps. In this paper, we investigate the evolution of the stress of SrBi2Ta2O9 ( SrBi2Ta2O9: SBT) deposited by both metal organic vapor deposition (MOCVD) and solution spin-on techniques as evaluated by Raman spectroscopy. As deposited, the SBT layer is highly tensile and is highly dependent on the deposition technique used. The stress of the SBT layer itself is highly dependent on the orientation and microstructure of the film. Theoretical modeling reveals a change from tensile to compressive around 350 °C. Further investigations will reveal whether this is correlated to the ferroelectric transition temperature of SBT or the internal stress state of the substrate. The thermal cycling curve will qualitatively explained based on the thermal expansion behavior as reported for other ferroelectric thin films. When a Pt top electrode is deposited on the electrode/SBT stack, the stress is low compared to the Pt layer in the bottom electrode (±0.1 and ±1.2 GPa respectively), reflecting the fact that the SBT ceramic distorts the mechanical behavior of the system. These results help to understand the mechanical properties of the ferroelectric thin film for successful integration.

9:15 AM C1.3
The Contribution of Asymmetric Strain Fields in Epitaxial Pb(Ta0.5, Nb0.5)O3 Nanolayers to Ferroelectric Size Effects, Ming-Wen Chen, Isabella Szkirmanda, Roland Schölder, Dietrich Hess, Marin Alves and Ulrich Giesen, Experimental II, MPI of Microstructure Physics, Halle (Saale), Germany.

Planar-electrode-ferroelectric phase transition of Pb(Zr0.5, Ti0.5)O3 (PZT) films with a grain size close to the critical value is below 200nm. The phase transition is also accompanied by formation of 180° and ferroelectric 90° domains in order to minimize the electrostatic energy and residual internal stresses, respectively. In order to obtain a structural insight into the origin of size effects, it is therefore crucial to investigate single-domain nano-ferroelectrics. Using chemical solution deposition, PZT nanolayers were prepared at 800°C on Nd-doped SrTiO3 (001) substrates. High-resolution transmission electron microscopy (HRTEM) investigations on a large number of samples indicated that these nanolayers appear as truncated pyramids with an average height of ~3nm and lateral size of ~200nm. HRTEM studies also suggested that the PZT nanolayers are single-crystalline and single-domain with an epitaxial relationship of (100)PZT/(100)SrTiO3. The internal stress resulting from the phase transition and the lattice mismatch with the substrate is released by edge-type misfit dislocations observed at the interface, with Burgers vectors \( b = \langle 011 \rangle \). Performing quantitative HRTEM measurements on the displacements of the atomic columns using the geometric phase method [1], it has been revealed that the strain field imposed on misfit dislocations is strongly localized and of trivally symmetric character, extending only into the PZT side, affecting a PZT region with an estimated height of ~4 nm and width of ~8 nm. The PZT lattice is strongly distorted within this region, deviating from the regular tetragonal structure, and should thus not possess ferroelectricity. It is therefore sensible to suggest that symmetric strain fields in nanolayers have a potential influence on size effects of ferroelectric thin films.

10:15 AM C1.4
Substrate-Suppressed Phase Transition in Nano-Crystalline Freestanding BaTiO3 Thin Films, Igor Lubomirsky1, Jaya P. Nayak1, Ilan Zen2 and Alexander Raybould2,1 Materials Interfaces, Weizmann Institute, Rehovot, Israel, 1Materials and Nuclear Engineering, University of Maryland, College Park, Maryland.

Phase transitions accompanied by symmetry lowering are usually facilitated by an external mechanical stress. As a result, the cubic to tetragonal phase transition in BaTiO3 shifts up if the material is subjected to uniaxial or biaxial stress. We have investigated the para-ferroelectric phase transition in ferroelectric thin films. Randomly-oriented nano-crystalline BaTiO3 thin films were prepared with moderate residual tensile stress by sol-gel processing or RF sputtering. Low dielectric constant (110±50) and X-ray diffraction spectrum identified the films as being cubic at room temperature. Despite the tensile stress in the substrate-supported films, the freestanding films become corrugated, indicating 0.3-0.5% internal expansion. The fact that the cubic to tetragonal phase transition was responsible for the internal expansion has been confirmed by a five-fold increase of the dielectric constant (620±100) and a detectable piezoelectric effect. Thus in nano-crystalline freestanding films biaxial mechanical strain may suppress rather than facilitate phase transition accompanied by symmetry lowering. This seeming contradiction can be explained if intergranular stress and texture formation are taken into account for the calculation of free energy.

11:45 AM C1.5
In-Situ Studies of the Ferroelectric Phase Transition in Pt/TiO2/Thin Films, D. D. Fong1, G. B. Stephenson1, Stephen Streiffer1, J. A. Eastman2, Carol Thompson2, O. Auciello3, P. H. Foss4, D. S. Kim5 and C. B. Eom6, 1Materials Science Division, Argonne National Laboratory, Argonne, Illinois, 2Department of Physics, Northern Illinois University, DeKalb, Illinois, 3Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Investigations of size-dependent behavior in ferroelectrics have been
greatly complicated by the materials processing variations used to achieve different system length scales, and by the common and uncontrolled influence of space charge effects and their different character, are expected to induce large lattice distortion of Bi2O3 layer, leading to a quite distinct type of ionic displacement along a axis. In the present case, the space charge effects are mainly due to the presence of oxygen vacancies. In the present experiment, the space charge effects are mainly due to the presence of oxygen vacancies.
transition temperature in PZT and Bi$_2$TiO$_3$ and both the ferroelectric and structural transition temperatures in SrTiO$_3$ films. Comparison with SMOM and SACD and Bi$_2$TiO$_3$ thin film polarization microscopy measurements make it possible to locate, distinguish and characterize ferroelectric domains whose size and separation is smaller than the wavelength of light used and are otherwise invisible in conventional optical microscopy techniques. Ferroelectric thin films consisting of epitaxial Bi$_2$TiO$_3$ were deposited onto MgO (001) substrates using MOCVD. NSOM in reflection mode was used to directly observe the poly-domain structure. An Ar ion laser (λ = 514 nm) was used as a light source. The laser beam was directed through a silver coated optical fiber and 1/2-plane to produce the desired linear polarization direction. The images exhibited inhomogeneities in reflected intensity which was attributed to charge in the ferroelectric polarization layer micrometer length scales and were largely uncorrelated with topographic features. Further, the films were patterned with interdigitated gold electrodes for in-situ biasing experiments. Application of an in-plane static electric field resulted in domain reorientation. These results demonstrate the capabilities of reflection mode NSOM for imaging domain structure in ferroelectric materials. Currently we are utilizing transmission electron holography to directly image ferroelectric nano-domains in Bi$_2$TiO$_3$ thin films. Electron holography, a coherent interferometry technique based on interference of a reference wave with a scattered wave, is directly sensitive to the polarization change in solids. The presentation will highlight the correlation between domain structure obtained by NSOM and electron holography.

SESSION C2: Fundamentals of Ferroelectric Films

Emphasis on Characterization and Domains

Chair: Hiroshi Odagawa and Stephen Streiffer

Monday, December 1, 2003

Room 203 (Hynes)

1:30 PM C2.1

Development of Ultra-high Vacuum Scanning Nonlinear Dielectric Microscope and Observation of Ferroelectric Polarization Distribution in Ferroelectric Thin Films and Single Crystals, Hiroshi Odagawa and Yano Cho; Research Institute of Electrical Communication, Tohoku University, Sendai, Japan.

Recently, several researchers have studied and reported various techniques for determining ferroelectric polarization direction and observing domain structure with high spatial resolution. This study is important to clarify the relation between the material properties and the behavior of small ferroelectric domains, especially in polarization switching and domain wall movement. This is interesting not only from an academic standpoint but also has the potential of improving the device characteristics. We have proposed and developed a purely electrical technique for imaging the state of ferroelectric polarization and local crystal anisotropy of dielectric materials called “scanning nonlinear dielectric microscopy” (SNDM) [1]. To date, the spatial resolution of SNDM has been improved down to 0.5 nm, exceeding piezo-scanning force microscopy resolution. [2] In this paper, we will describe a newly developed ultra-high vacuum type scanning nonlinear dielectric microscope and measurement results of ferroelectric domain structures in various ferroelectric thin films and single crystals with nanometer resolution. In this experiment, ultra-high vacuum chambers are used to remove an undesirable influence of molecular layer on the sample surface, and the samples are prepared by ion beam cleaning or cleaving in the ultra-high vacuum atmosphere. Experimental results include a nano-scale observation of polarization distribution in PZT thin film and other ferroelectric thin films and single crystals, a domain movement in TGS single crystal after cleavage, and so on. [1] Y. Cho, A. Kirihara, and T. Sueki; Rev. Sci. Instrum. Vol. 66 [1995] 2397. [2] H. Odagawa and Y. Cho; Surface Science, Vol. 463, [2000] L621.

2:00 PM C2.2


The characterization of local ferroelectric properties has been greatly facilitated by Piezoresponsive Force Microscopy (PFM). The principle of PFM is the detection of the electromechanical response to an ac voltage applied at a tip/surface contact. It has proven useful in determining domain orientation, observing domain wall motion, and under some circumstances quantifying D33. There is a potential to examine fundamental processes involved in domain switching and ferroelectric relaxation if higher order response functions can be probed. To address this, we have measured the second harmonic of the electromechanical response to the ac imaging voltage on various ferroelectric thin films as a function of both frequency and amplitude of the voltage. A theoretical model has been established that relates ferroelectric second harmonic response to the polarization, allowing the second harmonic response to be calculated. This ferroelectric relaxation of several classes of materials will be compared, including BST, PZT, and Bi$_2$TiO$_3$. Differences in dipole interaction in these compounds will be discussed. The approach is extended to imaging, Second Harmonic Piezoresponsive Microscopy, that maps the distribution of relaxation times on surfaces by acquiring the spatial distribution of the second harmonic response.

2:15 PM C2.3

Probing Ferroelectric Domain Dynamics using Near-field Scanning Optical Microscopy and Transmission Electron Holography, Prashnya Prabhakaran, David Towner, Bruce Wessell and Vinnay Gunalan; Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

Ferroelectrics have scientifically interesting and technologically useful properties related to their spontaneous electric polarization.

Ferroelectric Bi$_2$TiO$_3$ thin films are being studied using Near-field Scanning Optical Microscopy (NSOM) and Electron Holography to facilitate understanding of the poling domain dynamics. Holographic techniques make it possible to locate, distinguish and characterize ferroelectric domains whose size and separation is smaller than the wavelength of light used and are otherwise invisible in conventional optical microscopy techniques. Ferroelectric thin films consisting of epitaxial Bi$_2$TiO$_3$ were deposited onto MgO (001) substrates using MOCVD. NSOM in reflection mode was used to directly observe the poly-domain structure. An Ar ion laser (λ = 514 nm) was used as a light source. The laser beam was directed through a silver coated optical fiber and 1/2-plane to produce the desired linear polarization direction. The images exhibited inhomogeneities in reflected intensity which was attributed to charge in the ferroelectric polarization layer micrometer length scales and were largely uncorrelated with topographic features. Further, the films were patterned with interdigitated gold electrodes for in-situ biasing experiments. Application of an in-plane static electric field resulted in domain reorientation. These results demonstrate the capabilities of reflection mode NSOM for imaging domain structure in ferroelectric materials. Currently we are utilizing transmission electron holography to directly image ferroelectric nano-domains in Bi$_2$TiO$_3$ thin films. Electron holography, a coherent interferometry technique based on interference of a reference wave with a scattered wave, is directly sensitive to the polarization change in solids. The presentation will highlight the correlation between domain structure obtained by NSOM and electron holography.

2:30 PM C2.4

Observation of Ferroelectric Domain Behavior in BiSm$_2$ Layer Structured Ferroelectrics with Raman Spectroscopy, Minoru Onaka$^{1,2}$, Mitsuaki Kikihana$^3$, Yuki Naguchi$^{2,3}$ and Masaru Miyazawa$^4$; "Materials Structures Lab., Tokyo Institute of Technology, Yokohama, Japan, "PRESTO, JST, Kanagawa, Saitama, Japan; "Institute of Industrial Science, University of Tokyo, Tokyo, Japan.

Recent studies of ferroelectric thin films have revived interest in properties of the ferroelectric domain structures. It becomes clear that some basic aspects of these properties remain unexplored, whereas they are of key importance for applications. In this study, we address some unique aspects of micro-Raman spectroscopy for characterization of bismuth layer structured ferroelectrics (BLSF), emphasizing use of soft mode as a probe to elucidate domain behaviors of these materials. Bi$_4$Ti$_3$O$_{12}$ (BIT) and SrBi$_2$Ti$_2$O$_7$ (SBT) single crystals were grown by a self-flux method, whereas La-doped BIT thin films were prepared by a sol-gel method. Polarization microscopy revealed clear 90° domain structures (with typical width ~20 μm) in the a - b plane for BIT and SBT. In BIT single crystal, the kwest frequency mode (soft mode) at ~30 cm$^{-1}$ appears exclusively for the a a polarization configuration (a // polar axis). We observe spike-like a and b domains well inside extended a and b-polarized areas, which were not conclusive with polarization microscopy. These domain characteristics are shared with other BLSF’s such as BIT and doped BIT, which demonstrates the usefulness of the soft-mode spectroscopy for the study of domain structures in BLSF’s. With Raman imaging of the soft-mode intensity, we also show the unambiguous identification of domain distribution in the thin film on the micron scale. In addition, we will discuss some results on in-situ observation of changes in the domain structure as a function of polarization field and temperature for La-doped BIT thin films.

3:30 PM C2.5

Dynamics of 90 Degree Domain Movement of Epitaxial Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ Thin Film Grown on Sr(100) Substrate Using Se(Te)3 Template Layer, Z. Ma$^5$, V. Nagurnjen$^5$, J. Melgans$^5$, R. Ramesh$^6$ and D. Schomberg$^6$; "Department of Materials Science and Engineering, University of Maryland at College Park, College Park, Maryland; "Department of Electrical and Computer Engineering, University of Maryland at College Park, College Park, Maryland; "Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

Dynamics of domain interfaces in a broad range of functional thin film materials is an area of great current interest in ferroelectric thin films. A significantly enhanced piezoelectric response should be observed if non-180° degree domain walls were to switch under electric field excitation. However, in continuous films, they are confined by the substrate, and therefore their contribution to the piezoelectric response is limited. In a recent paper we demonstrated 90° degree domain wall movement in discrete capacitors of epitaxial Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ films grown on STO substrate. The features of a 90° domain layer in these islands was imaged free via focused ion beam milling, then by eliminating the clamping imposed by the substrate. Consequently the out-of-plane D33 for these islands was found to be ~250 μεV/s. ~3 times the intrinsic value of 87 μεV/s. The authors fully exploit the large piezoelectric coefficients shown by these discrete
islands we created these heterostructures on perovskite terminated Si substrate. The domain structure of the PZT layer grown on buffered Si was found to be different from the one observed on the STO substrate. By cross section TEM and piezoresponse microscopy we find that the density of 90 degree domains is larger and the domains are finer than the film grown on STO. Therefore the motivation of this presentation is to examine the 90 degree domain structure using a variety of heterostructural tools and compare and contrast the dynamic behavior of the ferroelectric 90 degree domains as a function of the resulting microstructure. We also studied the polarization response of the nanostructured island formed with the multiwalled 90 degree ferroelectric domain in the absence of substrate charging, compared to that of the continuous film, although the critical DC bias to cause the onset of ferroelectric domain wall motion are significantly different. This work is supported by the NSF-MRSEC under contract No. DMR-0820988.

3:45 PM C2.6
Piezoresponse Force Microscopy: Fields below the Surface. Sergey V. Kalinin1, Junsuo Shin2, Mark Kuchinsky3, Edge
Kang81 and Arthur P. Baddorf1
1Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee; 3Department of Mechanical Engineering, Tufts University, Medford, Massachusetts.

In recent years, Piezoresponse Force Microscopy (PFM) has become the primary tool for the characterization of ferroelectric materials at nanoscale dimensions. In addition to its capability of controlling the local polarization state, PFM provides the capability for local spectroscopic measurements and polarization patterning. Quantitative interpretation of PFM hysteresis loops and polarization switching data requires knowledge of the tip-ferroelectric field distributions inside the ferroelectric material that can then be used to estimate the electrostatic and mechanical contribution to the domain energy. Here, we report the first analytical solution composed of elementary functions of the coupled electromechanical problem for piezoelastic indentation by a realistic SPE probe. These solutions are used to derive the electric field and strain distribution inside the ferroelectric material, providing a complete continuum mechanical description of the PFM imaging mechanism. Field distribution results provide a rigorous basis for the quantitative analysis of PFM spectroscopy and switching data. It is shown that the dielectric gap formation at the tip-surface junction due to surface contamination significantly affects the PFM imaging mechanism. Preliminary results of PFM imaging under controlled atmosphere conditions are discussed. In the second part, the frequency-dependent electrical (strain capacitance) and mechanical (buckling) non-local contributions of a typical cantilever to the PFM signal are analyzed and the guidelines for the optimal choice of the PFM probe are delineated.

4:00 PM C2.7
TEM Analysis of Dislocation Structures in Epitaxial Barium Strontium Titanate Thin Films. Bishnu Baric Minilkovich1, Alexandre Vasilev1, Neal Magde1, Mark Aindow1, Rammoorh Chitto1 and Pamir Alyag1
1Metallurgy and Materials Engineering, University of Connecticut, Storrs, Connecticut; 2Department of Materials and Nuclear Engineering, University of Maryland, College Park, Maryland.

Barium strontium titanate thin films are of considerable interest due to their desirable ferroelectric and dielectric properties. The characterization of these materials differ significantly from their bulk forms especially due to the presence of internal stresses and dislocation type defects that are higher in density to accommodate the mismatch between the substrate and the film. Considering that internal stresses are much higher in the vicinity of the dislocation core, one can expect a significant variation in the local electrical and mechanical properties of ferroelectric thin films. Indeed, it has been shown experimentally that the relative dielectric constant of epitaxial BST films is strongly dependent on the defect structure as well as the epitaxial stresses [2,3]. In our current program, we are studying the effects of lattice mismatch and deposition variables on the defect microstructure and electronic properties of epitaxial barium strontium titanate thin films. These data will be used to validate, and guide the further development of microstructure-property models for such systems. In addition, we will present preliminary results obtained from 001 LaA03 substrates with pulsed laser deposition. The defect structure of the films has been characterized via transmission electron microscopy and XPS, and the effects on the properties of the defects throughout the films. Plan view and cross-sectional observations showed that the thickness and morphology of the thinning and the misfit dislocations in the films varied with both film thickness and substrate type. Moreover, electron diffraction revealed that there are small deviations from the nominal orientation relationship. The significance of these observations for both the mechanisms of misfit relaxation in this system and the viability of strategies for defect reduction will discussed.

4:15 PM C2.8
Surface Properties and Thermodynamic Behavior of Epitaxial SrRuO3 Thin Films. Junsuo Shin1, Sergey V. Kalinin1, Hoon Yung Lee1, Hans M. Christen1 and Arthur P. Baddorf1
1Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Department of Materials Science and Astronomy, The University of Tennessee, Knoxville, Tennessee.

Metallic strontium ruthenium oxide SrRuO3 has recently attracted significant attention as a prominent material for oxide electronics. To elucidate the properties of this material, we have studied the surface properties of SrRuO3 using a combination of electron spectroscopies, low energy electron diffraction (LEED) and scanning probe microscopy. SrRuO3 thin films were grown by pulsed laser deposition using a stoichiometric target on [001] SrTiO3 substrates. Atomic force microscopy (AFM) images taken in air confirm the high quality of grown films, showing uniformly spaced terraces with single steps on the film surface, which closely imitate those of the SrTiO3 substrate. After reinsertion into vacuum, a (1x1) Low Energy Electron Diffraction (LEED) pattern has been observed from the as-inserted sample at room temperature without thermal treatments, revealing an excellent chemical stability in air. Corresponding vacuum scanning tunneling microscopy (STM) imaging and spectroscopy show evidence of an inhomogeneous surface with insulating regions. The LEED pattern disappeared at 200 °C, indicating surface disordering. To quantitatively investigate this behavior, SrRuO3 thin films have been annealed in high vacuum in steps of 100 °C up to 800 °C and studied by LEED, x-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) and STM. The evolution of the surface topography, atomic and electronic structure, and valence state of ruthenium was characterized and compared with results of thermodynamic calculations. The implications of these results for prospective oxide electronic devices are discussed.

4:30 PM C2.9
Effect of Thermal strain on the ferroelectric phase transition in polycrystalline Ba0.5Sr0.5TiO3 thin films studied by Raman spectroscopy. Dmitri A. Tenev1, A. Teneva1, A. Sokolichina2, X X Xu2, T R Taylor2, P J Hansen1, J S Speck2 and R A York1
1Dept. of Physics, The Pennsylvania State University, University Park, Pennsylvania; 2Dept. of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; 3Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania.

We have applied Raman spectroscopy to study the influence of thermal strain on the vibrational properties of polycrystalline Ba0.5Sr0.5TiO3 thin films. The films were grown by magnetron sputtering on Pt/SiO2/Si substrate using different biasing on the target. The XRD analysis showed that the films are polycrystalline with the (001) orientation. The results show that the phase transition temperature, Tc, increases with decreasing thermal expansion coefficient of the substrate, i.e. increasing tensile stress in the films. This dependence is different from the theoretical predictions for epitaxial ferroelectric films, demonstrating that the theory of strain effects in epitaxial ferroelectric films cannot be simply applied to polycrystalline films. The complex structural nature of the polycrystalline films has to be taken into account when studying the strain dependence of the ferroelectric phase transition in these films.

4:45 PM C2.10
A Nephostes Study in Pb(Zr,Ti)O3 Thin Films. Ruey-Wen Wang1 and Paul C. McIntyre1
1Materials Science and Engineering, Stanford University, Stanford, California.

Ferroelectric thin films, such as Pb(Zr,Ti)O3 (PZT), are currently used in low density nonvolatile memories and are being considered for higher-density semiconductor memory applications. However, fundamental mechanisms controlling the reliable switching of PZT films remain unclear. In particular, the role played by potentially mobile point defects, such as oxygen vacancies, in processes such as imprint and fatigue has not been clearly elucidated. Up to now, no quantitative measurements on the activation energy and mobility of oxygen vacancies in PZT thin films have been reported. As first step toward such quantitative understanding, we have recently conducted a
series of $^{18}O$ tracer-diffusion experiments into state-of-the-art MOCVD grown PZT films to monitor vacancy diffusion at different temperatures (500°C) for various durations. Then, "q" incorporation, samples were pre-equilibrated in $^{18}O_2(g)$ at the same temperature and total pressure used for the following $^{18}O_2(g)$ annealing. The final $^{18}O$ profiles were obtained using secondary ion mass spectroscopy (SIMS), which provides a high depth resolution of 3.5 Å. The $^{18}O$ tracer results for annealing at relatively low temperatures and for shorter times show that the $^{18}O$ diffusion profiles in PZT thin films cannot simply be fitted by the solution of Fick's 2nd Law with constant (position-independent) diffusivity. Based on a previously developed model for point defect equilibrium in metal titanate thin films, an analysis of $^{18}O$ tracer-diffusion into 100 nm PZT thin films will be presented.

C3.1 Size effects in ultra-thin epitaxial ferroelectric heterostructures, Nagurny Vahanov1,4, Tong Zhao1, Jun Ouyang1, Haiwei Zheng1, Ramamoorthy Ramesh1, Wei Tran2, Xiaoping Pan2, Dong-Min Kim3, Chang-Bom Eom3, Herman Kubis4 and Rainer Waser4.

1Dept of Materials Science and Engineering, UW-Madison, Madison, Wisconsin; 2Dept of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; 3Dept of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; 4Institute of Electroceramic Materials, Research Center-Juelich, Juelich, Germany.

Recent ab initio calculations for a realistic BiTiO$_3$/SrRuO$_3$ ferroelectric electrode interface have shown that the critical thickness for ferroelectricity is of the order of 6 unit cells as a consequence of an electrostatic depolarizing field. While a theoretical understanding has been widely reported, there is a lack of direct experimental data for model ultra-thin (<10 nm) films, where external factors from the materials processing overly dominate the true size effect. Although ferroelectricity was detected in a 4 nm thick epitaxial PZT film, no quantitative measurements of the ferroelectric order parameters were shown. In this work we show a direct and systematic experimental study of the polarization, dielectric susceptibility and domain structure of PZT films grown heteroepitaxially with SrTiO$_3$ electrodes in the thickness range of from 4 to 160 nm. Our results suggest that for such a model system, the scaling law obeys the depinning mechanism, with the critical exponent -1. This work was supported by NSF MRSEC Grant #0808088. The work at University of Wisconsin is supported by NSF under contract No. DMR-0747380.

C3.2 Residual Stress Effects in Ferroelectric Thin Films, Thomas A. Berkel1, N. R. Sottos1, R. Ong2 and D. A. Payne2.

1Theoretical and Applied Mechanics, University of Illinois Urbana/Champaign, Urbana, Illinois; 2Material Science and Engineering, University of Illinois Urbana/Champaign, Urbana, Illinois.

Recent developments in soft lithographic patterning and microcontact printing techniques enable the integration of ferroelectric thin films on a chip, rather than add as a discrete component in the system. As integrated device applications push the characteristic length scale of these materials smaller and smaller, surface and interface effects dominate response, producing significant structural changes and characterization of mechanical properties, performance and reliability. In this paper, we investigate the complex roles of microstructure, interface effects and residual stresses on ferroelectric thin film performance. PZT films ranging in thickness from 200 nm to 1.0 mm are deposited by the sol-gel method onto a platinum Si substrate. The average residual stress in the films is calculated from laser reflectance measurements of wafer curvature during processing. Field induced displacements are then measured interferometrically with well-characterized residual stress sensors. Results indicate significant increases in film performance with a decrease in residual stress.

C3.3 Anisotropic In-plane Strain in Pb(Sr,Ti)O$_3$ Thin Film on NdGaO$_3$ Substrate, Yuan Lin1, Quoc Nguyen1, Xin Chen2 and A Bhalla2.

1Material Science & Technology Division, Los Alamos National Lab, Los Alamos, New Mexico; 2Texas Center for Superconductivity and Advanced Materials, and Department of Physics, University of Houston, Houston, Texas; 4Materials Research Lab., Penn State University, University Park, Pennsylvania.

Anisotropic in-plane strain can be induced in Pb(Sr,Ti)O$_3$ (PST) thin film by using an orthorhombic NdGaO$_3$ [110] as a substrate which has in-plane lattice parameters of 7.7245 Å along [110] and 7.7016 Å along [001]. The PST film was deposited by laser ablation and was characterized using high-resolution X-ray diffraction. Rocking curves with a full width at half maximum of less than 0.04 degree illustrated that the film had a nearly perfect crystallization quality. Reciprocal space maps around the [110], [110] and [004] reflections of PST films revealed an in-plane strain modulation along [110] and [010] orientation. Cogitate capacitance measurements also showed the systematic changes in dielectric constant and tunability due to the strain, which was another indicator of in-plane strain anisotropy.

C3.4 Spontaneous Buckling of Nanocrystalline Self-Supported Ferroelectric Films, Isha Feldman1, Ilyna Zen1, Vera Lykovskaya1, Elen Wachtel2, Alexander Rogovskiy2 and Igor Lakhomovskiy1.

1Materials & Interfaces, Weizmann Institute, Rehovot, Israel; 2Materials and Nuclear Engineering, University of Maryland, College Park, Maryland; 3Research Support, Weizmann Institute, Rehovot.

Thin ferroelectric films are very promising for a number of applications ranging from actuators to ferroelectric memories. In most of these applications the films are clamped. However, a number of applications, such as surface acoustic wave filters, piezoelectric transducers, gyroscopic sensors etc., employ the films that have some freedom to bend. We have investigated stability of nanocrystalline tethered ferroelectric membranes with respect to spontaneous buckling. It has been found that depending on the geometrical constraints the membranes may assume a single dome shape or buckle with a curvature radius, which is constant or varying within the membrane. Upon certain conditions one can observe coexistence of totally flat areas with regions that have a curvature radius as small as 0.05 mm. A theoretical description based on formation of a dynamic self-adjustable crystallographic texture was developed. This theory correctly relates the curvature radius with crystallographic parameters and film thickness. However, the symmetry and temperature dependence of the buckling patterns above the para-ferroelectric transition temperature require further investigation.

Buckling instability is observed only in nanocrystalline self-supported ferroelectric films and by its nature the buckling is similar to the buckling of lipid membranes. Since, the enthalpy associated with buckling can be comparable with that of the para-ferroelectric transition, this phenomenon has to be taken into account during design and construction of the devices employing nanocrystalline ferroelectric films.

C3.5 Strain Effect in multiferroic BiFeO$_3$ Thin Films, Junling Wang1, Haiwei Zheng2, Dwight Viehland2, Vahnam Nagurny1, Venugopal Vaithyanathan3, Darrell G. Schom3, Manfred Wuttig1 and Ramamoorthy Ramesh1.

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In recent years the ferroelectric material BiFeO$_3$ (BFO), which has both ferroelectric (T=110K) and G-type antiferromagnetic (T_N=64K) orders, has attracted immense research interest. This unique system is responsive to a variety of stimuli (i.e. electric field, magnetic field, stress etc.) thereby creating pathways for novel and exciting applications. In this study, BFO films with different orientation were deposited using pulsed laser deposition (PLD). [001], [111] and [111] cut SrTiO$_3$ (STO) single crystal substrates were chosen to systematically move the biaxial epitaxial strain from [110] plane to [111] plane. X-ray diffraction (XRD) and transmission electron microscopy (TEM) study show that the film structure changes from monoclinic to rhombohedral, corresponding to the strain direction. Effect of this change on the physical properties was studied by ferroelectric polarization (dielecric constant and piezoelectric coefficient) measurements. All the films show dramatically enhanced ferroelectric property compared with bulk. Origin of this enhancement will be discussed. We find that the spontaneous polarization system is partially increased from 0.7(011 oriented film) to 85µC/cm$^2$ (110 oriented film) with a commensurate decrease in the piezoelectric coefficient and dielectric susceptibility respectively. Thickness and crystalline quality of these films demonstrate the importance of strain and
substrate induced changes to the crystal phase. This work is supported by the Office of Naval Research MURI N0001400110761 and the National Science Foundation MRISEC DMR-0808018

C3.6 Suppression of low-temperature phases by strain in epitaxial BaTiO3 thin films. Dmitri A. Tenne3, A. Sudarsanam4, M H Zhu1, A R James1, X X Xi1,2,7, Y L Li7, L Q Chen7, J Lettieri2, D G Schom3,5, W Tian1 and X Q Pan1. ¹Dept. of Physics, The Pennsylvania State University, University Park, Pennsylvania, ²Dept. of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, ³Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania, ⁴Dept. of Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan.

Lattice dynamics and phase transitions in BaTiO3 thin films grown by pulsed laser deposition on SrTiO3 and LaAlO3 substrates with SrRuO3 buffer layers have been studied by Raman scattering. Comparison of the Raman spectra over the temperature range 5-320 K for the films and single BaTiO3 crystals shows that the phase transitions between different ferroelectric phases (tetragonal-orthorhombic-chalcopyhedral) characteristic for bulk barium titanate, are suppressed in the films. This behavior is explained by the presence of strain in BaTiO3 films, caused by thermal mismatch with underlying SrRuO3 layers. X-ray diffraction analysis shows that the films are under tensional strain, and the room temperature value for the strain with respect to the bulk BaTiO3 is 0.54%. Our calculations of domain structures based on the thermodynamic phase-field approach predict an orthorhombic phase with in-plane polarization to be the stable phase for such values of biaxial strain. Theory predicts this phase to be stable for tensile-strained films over the entire temperature phase diagram. Experimental Raman results provided a direct proof of the theoretical thermodynamic calculations. Observations of strain effects on phase diagram in ferroelectric thin films.


Thin films of BaxSr1-xTiO3 (BST) are being actively investigated for applications in dynamic random access memories (DRAM) because of their properties such as high dielectric constant, low leakage current, and low fatigue. Several approaches have been used to improve the properties of thin films such as doping with nickel oxide dopants, graded compositions, and layered structures. We have found that interposing layers of an electronic insulator such as ZrO2 in between BST layers results in a significant reduction in leakage current. In this paper the phase transition behavior and low temperature electrical properties of these multilayered films are presented. The structures consist of alternate layers of Ba0.8Sr0.2TiO3 and ZrO2 deposited by a sol-gel process on platinum substrates. The thickness and the number of layers are varied while keeping the total thickness of the film constant. The single layer BST film has a Curie temperature of 280 K which is the transition from a cubic phase to the ferroelectric tetragonal phase occurs. A further transition at about 160 K occurs which may correspond to the cubic to rhombohedral transition. In the multilayered films these transitions become very broad and are spread over a large temperature range. A structure with several thin layers of ZrO2 interposed between the BST layers produces a low broad transition than a single layer of ZrO2 of the same total thickness. This is attributed to more uniform distribution, as determined by XPS, of ZrO2 in the multilayer structure due to smaller diffusion distances. In the sample with single thick ZrO2 layer a very wide distribution of the Curie temperature was obtained. This results in a considerable region with nearly a constant dielectric constant over a wide temperature range indicating that this approach may also be useful in applications requiring a low temperature coefficient of capacitance.

C3.8 Dipole Screening of Pyroelectric and Ferroelectric Grains in Semiconductor Matrix. Alexandre Dmitriev1, Vladimir Shvets1, Seung-Hyun Kim2, ¹Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal, ²Insect Inc., Ansan Technopark 707, 1271-11, Se-1 Dong, Songgro, Ansan, Kyunggi 425-791, South Korea.

The physical phenomena at the interfaces of pyroelectric semiconductor layers or ferroelectric semiconductor systems depend on the screening of the pyroelectric or ferroelectric spontaneous polarization by free carriers in the semiconductor. In this paper, we consider the size dependent nonlinear screening effects in a composite system consisting of pyroelectric grains (or ferroelectric grains in a pyroelectric phase) inserted into a doped semiconductor matrix. We show that for realistic parameters, screening of the grain polarization charges corresponds to a new screening regime, which has not been discussed before. In this regime, the characteristics screening length (i.e. the radius of the depletion region at the grain boundary) is much larger than the Debye length and then the grain radius, but much smaller than the conventional depletion length (which is the width of the depletion region at a high electric field due to a plane interface for a very thick pyroelectric layer or for a very large grain). One of the main features of this new regime is the presence of the depolarization field in the pyroelectric (in contrast to the conventional screening regime with a zero depolarization field). The results were observed for only very large grains). In the new screening regime, the polarization charges are much smaller then the polarization charges but the separation between the screening charges is much larger than the grain size, which allows for screening of the polarization dipole. These results can have important applications, since the size of the depletion region is one of the key parameters that govern the transport phenomenon in a semiconductor matrix with pyroelectric (or ferroelectric) insertions. We discuss potential device applications of such systems. This work has been supported by ONR (Project Monitor Dr. Colin Wood), RFBR and INTAS.


Ferroelectric surfaces with polarity patterned domains of LnO3:0.3 (LNO:0.3) and Pb(Zr0.53Ti0.47)O3 (PZT) thin films were explored using in situ UV-photoelectron emission microscopy (PEEM). The photo-electrons were excited with UV-light from the tunable UV free electron laser (FEL) at the Stanford University DOE beamline. The PZT thin films, with photon energies from 4.0 to 6.5 eV, the surfaces were examined at room temperature and at elevated temperatures. The brightness contrast between different polar domains of the surfaces was observed through the difference of the photoelectric yield. The polarity of the domains was identified by piezoresponse force microscopy (PFM) and chemical etching. In both LNO and PZT, bright emission was detected from negative domain ends (negative domains), indicating that the photoemission threshold of the LNO is lower than that of the positive domain. For LNO, the photothreshold of the negative domains measured by PEEM was 4.6 eV, while for PZT, the threshold of the negative domains was less than 4.3 eV. A reduction in emission intensity was observed in the samples annealed and can be understood in terms of a reduction in bound polarization charges. Moreover, the image contrast of the PZT surface disappeared at near the Curie temperature of ~300°C. The PEEM polarity contrast of the ferroelectric domains is discussed in terms of the built-in internal field and the surface band bending induced by the polarization bound surface charges. * Research supported by the ONR and the AFSOR through the MFEL programs.

C3.10 Ferroelectric Domain Structure and Local Piezoelectric Properties of Sol-Gel Derived Pb(Zr-xTi-x)O3 Films. Ignacio Daza1, Vladimir Shvets1, Natalya Slavin2, Seung-Hyun Kim2, ¹Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal; ²Insect Inc., Ansan Technopark 707, 1271-11, Se-1 Dong, Songgro, Ansan, Kyunggi 425-791, South Korea.

In the past several years, ferroelectric films have received significant attention in view of their applications in nonvolatile ferroelectric memories, pyroelectric detectors, electromechanical actuators, and field effect transistors. Since the size of these devices is getting smaller and smaller, it is essential to approach sub-mum range, the local techniques to investigate dielectric, ferroelectric and piezoelectric properties of the films at such scale are becoming increasingly important. One of these techniques, Piezoresponse Force Microscopy (PFM), has been successfully used to investigate the physical properties of ferroelectrics at the scale limited by only the size of the PFM tip (~10 nm). However, the lack of the experimental data on films of different compositions and thicknesses (and their comparison with corresponding macroscopic results) limits the understanding of the contrast nature and its dependence on the microstructure and texture of the films. In this work, high-resolution PFM and I-V measurements have been performed on Pb(Zr-x)O3 thin films with Ti concentration x=0.30, 0.48 and 0.70. The chemical solution route has been used to prepare these polycrystalline films with the thickness 1-4.5 mm. The films were spin-coated onto Pt/Ti/SiO2/Si substrates and processed at 650°C. The orientation of the films was varied from purely (111) (related to the orientation of Pt bottom electrode) to a more random texture. Statistical processing of the obtained domain images has been used to analyze the relationship between the texture (or composition) of the films and their respective
piezoelectric properties. In general, the films with more random orientation demonstrated broader distribution of the piezoelectric signal, which can be used to evaluate the preferred orientation by pure electrical means. We also observed a correlation between the grain size and the nanoscale piezoelectric response. Self-polarization (i.e., the difference between the number of oppositely oriented domains in a nanocrystal) has not been investigated in detail. Self-polarization was found to depend on the composition, thickness and texture of the films being more pronounced for rhombohedral films. Finally, local piezoelectric hysteresis and macroscopic polarization hysteresis were compared and analyzed.

C3.11 Interface states of laser ablated BaTiO3 and Ba0.9Ca0.1TiO3 thin films in MFS structure determined by DLTS and CV technique, Victor Pushparaj1, S H Kuppanan2 and Santh R Saha3.

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The Metal Ferroelectric Semiconductor field effect transistor (MFSFET) structure has been widely investigated for their use in the ferroelectric memories due to their unique capability of shrinking the memory cell dimensions. This is because the charge is induced by remnant polarization of ferroelectric materials, eventually control the surface conductivity of the Si substrates. BaTiO3 and Ba0.9Ca0.1TiO3 thin films were deposited on the p-type Si substrate by pulsed excimer laser ablation technique. The C V measurement was performed at 1 MHz exhibited a clockwise rotating hysteresis loop with a wide memory window for the Metal Ferroelectric Semiconductor field effect transistor (MFSFET) structure. The low frequency C V measurements exhibited the response of the minority carriers in the inversion region while at 1 MHz the C V is of a high frequency type with minimum capacitance in the inversion region. The interface states of metal/ferroelectric were observed from the C V spectrum of the fabricated MFSFET. The C V spectrum and these peaks were attributed to the presence of the discrete interface states present in the semiconductor ferroelectric interface. The distribution of calculated interface states were mapped with the silicon energy band gap for both the undoped and Ca-doped BaTiO3 thin films using both the C V and DLTS method. The interface states of the Ca-doped BaTiO3 thin films were found to be higher than the pure BaTiO3 thin films. An extensive investigation on the structural correlation with the interface states has been carried out.

C3.12 First-principles Study on Electronic Structure of PZTN Systems, Hiroshi Miyama1, Takamitsu Higuchi1, Taku Aoyama1, Takashi Kijima2, Eiji Natou3, Tatsuya Shimodo1 and Tatsuro Oguchi4.

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Kijima et al. found that Pb(Zr, Ti)O3 (PZT) with 20% Nb or B site replaces high resistance in thin films. [1] In this study, from a viewpoint of the electronic structure we should investigate the compositions enable such high resistances in PZT. We adopt the density functional theory using the FLAPW method. We calculate the electronic structure of a super cell, Pb0.95Zr0.05Ti1-xNbxO3 which contains 2x2x2 ABO3 type structure. Here, Zr (Ti) ratio is 1 to 2. In the case of x=0.25 the density of states (DOS) suggests that electrons which numbers correspond to the excess electrons carried in by Nb are introduced at the conduction band minimum (CBM) which mainly consists of Ti3d orbitals. For this case, if Pb atoms of δ=x/2=0.125 are substituted without the oxygen vacancy, holes appear at valence band maximum (VBM) which consists of oxygen-2p orbital and they cancel out the doped electrons at the CBM. Hence the system recovers insulator state. The calculation of best of formations indicates that this insulator state is more stable than the conduction state of the case of no Pb deficit. The increase of equilibrium lattice constants are within +1.0% comparing with the case of δ=2x=0.125. The bandgap of PbTiO3 is about 1.8 eV. This work suggests that PZT in the Pb oxygen vacancy drastically reduces the bandgap. The additional oxygen-2p orbital energy of the nearest-neighbor Ti3d through the Mardelund potential. We suppose that in PZT the Nb added at the B site suppress the oxygen vacancy and PZTN could have higher resistance rather than PZT which loses Pb atom accompanying oxygen vacancies. [1] MRS fall meeting (2008)

C3.13 Pressure as a Probe of the Physics of 18O - Substituted SrTiO3, George A. Samara1, E.L. Venturini1 and M Ichisaka2, 3Sandia National Laboratories, Albuquerque, New Mexico; 1Tokyo Institute of Technology, Yokohama, Japan.

Studies of the dielectric properties and phase behavior of an 18O-substituted SrTiO3 (> 97% 18O), or STO-18, crystal at 1 bar and as functions of hydrostatic pressure and applied dc biasing electric field, have shed much light on the mechanism of ferroelectric transition. 18O-induced ferroelectric transition in this material. Dielectric measurements reveal an equilibrium phase transition (Tc ~ 24 K at 1 bar) and an enhancement of the dielectric constant, δε, over that of normal (i.e., 16O) SrTiO3, or STO-16, by 10% to 15% over the temperature range above Tc. This enhancement is quantitatively shown to be attributed to additional softening of the ferroelectric soft mode frequency (ωc) of STO-16, in agreement with lattice dynamic calculations. Thus, in STO-18 two effects due to the heavier mass of 18O contribute to the transition: (i) this additional softening of ωc and (ii) damping of quantum fluctuations. Pressure lowers Tc at the large initial rate of 20 K/Kbar and completely suppresses the ferroelectric state leading to a quantum paraelectric state at ~ 0.7 kbar, confirming earlier results. Very large effects of a biasing dc electric fields on the peak temperature and δε are also observed in the quantum regime reflecting the small characteristic energies of the system. The results also reveal a dielectric relaxation process near 10 K with interesting properties. The implications of all the results on our understanding of the physics of STO-18 are discussed.


New mechanism of superfast domain kinetics has been discovered recently by the domain kinetics project at the Argonne National Laboratory using lithium tantalate. It was shown that the input of conventional growth of isolated domains is negligible. The wall motion is driven by domain merging and determined by concentration of nuclei/residual domains. The mechanism has been investigated in details by computer simulation. The experimental measurements were performed in commercial single crystalline CIT. Liquid electrolyte 1-mm-diameter electrodes allow us to TV record the domain evolution in the whole switching process using microscope with subsequent image processing. The unique possibility to establish the correspondence between switching current data and domain kinetics was realized. Analysis of the instantaneous patterns allows us to distinguish mechanisms of domain evolution in CIT. Switching from the single domain state starts with appearance of small domains with the density up to 100 per-mm-square and subsequent growth with velocity about one micron per second. The prevailing switching process is a fast anisotropic wall motion defined by step generation by merging of moving walls with isolated triangular domains and rapid growth of arisen steps along the wall. A supermobile domain walls with the highest step concentration form after large domains merging. Domain simulator of the discovered mechanism of domain growth with step generation due to domain merging only has been done. The crucial dependence of the switching parameters on the nuclear concentration has been found. It is proposed that this mechanism allow to explain the superfast domain growth in thin films. The research was made possible in part by RFBR (Grant 01-03-17483), by RFBR-DFG (Grant 02-02-04006), by Ministry of Education RF (Grant E103-4-A-205) and by program "Basic Research in Russian Universities" (Grant UR.06.01.61), and by Award No.REC.005 of CRDF.

C3.15 Electrical Behavior in Complex Oxide Thin Films, Mark A. Zurbuchen, Peter M Baldo, Sanjib Saha, Marquis A Kirk, Loren J Thompson, Jeffrey A Eastman and Stephan K Streefler; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

The properties of complex oxides are controlled by their defect structure, but a fundamental understanding of how the properties of these materials are determined by the underlying defects (vacancies, impurities, interfaces, etc.) has still not been achieved. Despite intensive investigation using microscopic measurements, many unknowns remain regarding their defect chemistry and structure, and the relationship of these defects to the aggregate electrical behavior. We have used a customized electrical probe station to study the electronic transport and polarization behavior of complex oxide films and microstructures, in order to ascertain a better understanding of the defect chemistry of complex oxide thin films. The system is designed to enable electrical transport measurements up to 1000 °C in controlled p2 atmosphere, from 1 to 1010 bar, at 1 to 109 bar to 106 bar. High sensitivity voltage and current measurements are possible through four fully triaxially shielded probes which are
repositionable in situ over an area of several mm$^2$. We present some of our initial results obtained using this system, including the establishment of a baseline using mixed LiO$\nu$ and epitaxial (Ba,Sr)TiO$_3$ and Pb(Zr,Ti)O$_3$ films, as well as some results for polycrystalline structures. These studies are aided by e-beam patterning to isolate individual structures, and TEM diffuse scattering studies of defect structures in the same films.

C3.16 Effect of Interface Capacitance on Dielectric Dispersion of PMN-PT Relaxor Thin Films. Apurba Laha$^1$ and Sahara Bala Kuprasadhi$^2$. $^1$Materials Research Center, Indian Institute of Science, Bangalore, Karnataka, India; $^2$Materials Research Center, Indian Institute of Science, Bangalore, Karnataka, India.

xPb(Mg$_{1/3}$Ni$_{2/3}$)$_2$O$_3$-xPbTiO$_3$ (x=0, 1.0, 0.8, 0.3) PMN-PT relaxor thin films were deposited on platinum coated silicon substrate using pulsed excimer laser ablation technique. The substrate temperature and partial preparation pressure during deposition were in the range of 600 to 750 $^\circ$C and 100 to 300 mTorr, respectively. The dielectric properties of as-deposited films were studied as a function of frequency over a wide range of temperature. The frequency dispersion of dielectric constant in the temperature zone higher than the temperature of dielectric maxima (Tm). This dispersion in higher temperatures was attributed to the effect passive layers to the overall dielectric response of the heterostructure. These passive layers could be formed at interfaces between the film and electrodes and at the grain boundaries. The response from the grain boundaries was minimized by controlling the grain structure of the films. The leakage currents and film resistivity, especially the top electrode which was deposited at room temperature, could be the main influential factor to promote the passive layer formation. This problem was rectified by single step and multi step post deposition annealing of top electrodes at different atmospheres. The microstructure at both the interfaces was also investigated by the scanning electron microscopy. The films deposited at higher temperatures ($>$ 675 $^\circ$C) showed diffused interface at bottom electrode. We have also analyzed the thickness dependent dielectric constant of the ferroelectric hysteresis phase e.g. coercive field, remnant polarization etc. to identify the passive layers.

C3.17 Raman Spectra of Sns-3Bi4Ti3O12 Thin Films. Jian Wang$^1$, Guangxu Cheng$^2$, Hongwei Cheng$^2$, Shantao Zheng$^2$ and Yanfeng Chen$^3$. $^1$Physics, Nanjing University, Nanjing, Jiangsu, China; $^2$National Laboratory of Solid State Microstructures, Center of Materials Analysis, Nanjing, Jiangsu, China; $^3$Science and Technology of Materials, Nanjing University, Nanjing, Jiangsu, China.

A series of Ionic-Type Phosphoryl Crystal (ITPC), Sns-3Bi4Ti3O12 thin films were made by PLD (Laser pulse deposition). SBT/ITO/NOO/TAO. There is a sharp peak at 821-831 cm$^{-1}$ in these Raman spectra of samples (only m=3.4 and 5), however, the SBT/ITO is observed only in the other three samples. Raman spectra were studied within the temperature range of 80-823K. For reducing temperature process, the main peak at 821-831 cm$^{-1}$ was varied, including their FWHM and I. It is shown interest in split up the high frequency peak (142 cm$^{-1}$) into two peaks at 138 cm$^{-1}$ and 145 cm$^{-1}$, respectively, for m=5.6. But there is no splitting of low frequency peak and the main peak has not varied, for m=3.4. In the reverse process, the situation of main peak is similar to above statement, but there is no peak split in low frequency range. The results can be interpreted by fundamental principles and properties of these materials.


Microstructure studies of ultra-thin BaTiO$_3$ thin films (2-60 nm thick) show nano-domains having a width as small as one unit cell. Only 180° nano-domains and 90° domain boundaries are formed in multi-domain structures. The domain-boundaries are formed at (111) twin boundaries. Most of the domains are oriented in parallel to the film plane but out-of-plane domains are also observed. The films exhibit ferroelectric behavior characterized by a polarization hysteresis loop. A remnant polarization of 30 C/cm$^2$ and coercive field of 0.7 MV/cm were measured in vertical to the film plane. Temperature-dependent polarization measurements show two peaks of the dielectric constant at about 700C and 1100C. These peaks are attributed to two Curie temperatures associated with out-of-plane and in-plane domain’s orientation, respectively. The switching response of the nano-domains is relatively fast in the range of few nanoseconds. The switching time decreases with increasing the applied electric field according to a power law dependence of T=2.5. Fatigue tests show an initial degradation of the remnant polarization at about 100 cycles under a continuous bias field of 5 V/cm, after which the remnant polarization decreases with increasing the number of cycles, and the fatigue is not observed at 1 kHz. The leakage current of the films, which is of about 10-8 A/cm$^2$ under applied field of 0.1 MV/cm, increases with applied electric field according to a characteristic behavior of hopping mechanism. The thermodynamic criteria for the formation and stability of the BaTiO$_3$ nano-domains are presented and discussed.

C3.19 Orientation of BaTiO3 thin films deposited on different substrates. Changgu Li$^1$, Gustaf Van Tendeloo$^2$ and Eugen Schubert$^3$. $^1$Materials Science and Engineering, U. of Illinois at Urbana, Urbana, Illinois; $^2$EAMT-RUCA, University of Antwerp, Antwerp, Belgium; $^3$ Institute of Thin Films, Juelich Research Center, Juelich, Germany.

BaTiO$_3$ thin films were epitaxially grown on SrTiO$_3$, La$_2$O$_3$, MgO, and Mo substrates. The BaTiO$_3$ substrates by means of pulsed laser ablation. The film microstructure was investigated by means of transmission electron microscopy. Dislocations, antiphase boundaries and stacking faults are main defects found in the films. These defects are characterized by means of high-resolution electron microscopy. It was found the microstructure of these BaTiO$_3$ films is significantly different: the defects, defect densities and defect distributions are strongly substrate-dependent.

C3.20 Abstract Withdrawn


SrRuO$_3$ is a widely studied conducting oxide for applications of ferroelectric, ferromagnetic, and superconducting materials. Due to its relatively small lattice mismatch with most perovskite-type oxides, e.g., 0.0% with SrTiO$_3$, and to its relatively high resistivity, it is often used as a bottom electrode in epitaxial ferroelectric capacitors. It is well-known that due to the volatility of Ru$_2$O$_5$, SrRuO$_3$ is unstable at high temperatures in a low-oxygen pressure ambient, i.e., under the very conditions where most studies on the growth of nearly perfect oxide films and superlattices by molecular beam epitaxy (MBE) and laser-MBE are carried out. If not for the lack of systematic studies on the stability SrRuO$_3$ films in integrated device applications, the idea of having SrRuO$_3$ as a bottom electrode and synthesizing nearly-ideal ferroelectric films thereon may seem mutually exclusive. In this contribution, we explore this idea by growing epitaxial SrRuO$_3$ thin films with single-terrace steps by pulsed laser deposited (PLD) at 700 $^\circ$C in 100 mTorr O$_2$ on single-stoichiometric SrTiO$_3$(001), and characterized the stability of the films as a function of temperature (25 $-$ 800 $^\circ$C) and oxygen pressure (10$^{-7}$ $-$ 10$^{-2}$ Torr) by ex-situ reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), atomic force microscopy (AFM), scanning tunneling microscopy (STM), and photoelectron spectroscopy (XPS). The combined ex-situ analysis showed different features on the film surface, including islands and pits, that could destroy or deteriorate the quality of epitaxial films grown subsequently, and revealed a dramatic change of the structure and composition due mostly to high-temperature anneals under low oxygen background pressure. The present study allows us to determine a stability phase diagram (oxygen pressure and temperature) for SrRuO$_3$ films, which indicates conditions under which they can serve as bottom electrodes and transfer with high fidelity the crystallinity of single-crystal SrTiO$_3$ substrates to the subsequent oxide films. In addition, the preparation of single-stoichiometric SrTiO$_3$ substrates and epitaxial SrRuO$_3$ superlattices using such SrRuO$_3$ bottom electrodes will also be presented. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, as part of a BES NSET initiative on Nanoscale Cooperative Phenomena.

C3.22 In-plane orientation control of SrTiO$_3$(111) epitaxy on sapphire(0001). Igan Ohkubo, Hans M. Christen and Matthew F. Chisholm; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Perovskite titanate thin films are important in ferro- and dielectric materials both for device application and in basic research, but most previous efforts have focused on (001)-oriented layers. From the viewpoint of oxide heteroepitaxy and heterointerface issues, growth of
oriented STiO3 on substrate (0001) is very attractive with a lattice mismatch of less than 0.5%. The oxygen substrates in STiO3 have a face centered cubic structure (FCC) [111] direction, whereas in substrate, having a high closed packed structure ([ABABAB...]. Here we have grown STiO3 [111] thin films on substrate (0001) substrates by pulsed laser deposition (PLD) under various growth conditions. Using growth rates typical for PLD, STiO3 was found to crystallize with two in-plane orientations, STiO3[21-1]//substrate[100] and STiO3[21-1]//substrate[100]. This orientation change is discussed in terms of thermodynamic stability and growth kinetics. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22755 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, as part of the Laboratory Directed Research and Development Program.

C. 23
High Pressure Deposition of Epitaxial PZT Films on Sr(Nb,Ti)O3, Jesus L. Heirain,
O. Blumke1, J. M. Siqueiros2, E. Martinez2 and E. Andrade2.
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Thin ferroelectric films of Pb(Zr0.52Ti0.48)O3 (PZT) were successfully grown on Sr(Nb,Ti)O3 (SNTO) single crystal substrates by rf high pressure sputtering. Pure O2 was used as working gas at pressures above 1 Torr. Deposition temperature was varied from 550 °C to 600 °C. Under these conditions we were able to deposit films at a rate of 2.7 Å/s, the film crystallized by XRD and scribes, showed c-axis orientation. FWHM of 0.36 ± 0.02 was measured in the rocking curves. In plane and out of plane orientation was also determined by x-ray diffraction. Using radio-frequency magnetron sputtering, the [001]PZT[001]STO and [010]PZT[010]STO film composition and film-substrate interface characteristics were studied by RBS. A good fit to the experimental RBS spectra was obtained assuming anion displacement ratios of 0.97 ± 0.03 for Pb/Zr/Ti=1,32 ± 0.02 for Pb/O2 and 1.2 ± 0.1 for Sr/Ti; also a thin evaporation layer of Pb at the film-substrate interface was introduced. Pb deficiency, which is correlated to the presence of oxygen vacancies, resulted in lower dielectric constant as deposited by 250 °C. The composition technique that has been reported for films grown by sputtering at lower pressures. The hysteresis loops for the Pb/Zr/Pt STO heterostructure show good ferroelectric behavior with remanent polarizations of 1.2 μC/cm2 and coercive field of 5 kV/cm at 5V. The high-pressure technique turned out to be simple and useful method to grow in situ epitaxial PZT ferroelectric thin films with high structural quality and good compositional and dielectric properties, without post-deposition heat treatment. Work supported by DGAPA-UNAM Project IN108600 and IN108600, CONACYT Project 40894F and 31958E. O. Blumke thanks the support of PROMEP-CONACYT.

C. 24
Compositionally Asymmetric Tri-Color Superlattices Grown by High-Pressure Pulsed Laser Deposition, Ho Nyung Lee,
Hans M. Christen1, Christopher M. Rouleau2, Douglas H. Lowndes1,
Sung Kyun Lee3, Stephanie Sena2 and Dietrich Hesse4.
1Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Max Planck Institute of Microstructure Physics, Halle (Saale), Germany.

Advances in modern epitaxial growth techniques have enabled the growth of nearly perfect thin films, superlattices, etc., on the micrometer scale with surfaces and interfaces. For instance, oxide heterostructures with coherently flat interfaces and single unit-cell steps on the surface can be grown on the well-established single-layer substrates. Moreover, artificial superlattices, i.e. materials that do not exist in bulk forms, can be grown with great control on such substrates and can result in unprecedented physical properties. Using pulsed laser deposition (PLD), we have grown STiO3-x superlattices with a nominally composition gradient, SrRuO3-x covered SrTiO3(001) substrates, we have grown asymmetric tri-color superlattices (TCS) with a combination of SrTiO3/SrRuO3/CuTiO3, in which the inversion symmetry can be broken by a composition gradient. SrRuO3 thin films with single-layer steps on the surface can be grown on SrTiO3 substrates using PLD at ~300°C. The dielectric and magnetic properties of the SrRuO3-x/CuTiO3/SrTiO3(001)x superlattices were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), and magnetic and electrical measurements. The obtained results show that the growth process is highly influenced by the substrate temperature and the deposition rate. The growth of SrRuO3-x/CuTiO3/SrTiO3(001)x superlattices is highly sensitive to the substrate temperature and the deposition rate. The growth of SrRuO3-x/CuTiO3/SrTiO3(001)x superlattices is highly sensitive to the substrate temperature and the deposition rate. The growth of SrRuO3-x/CuTiO3/SrTiO3(001)x superlattices is highly sensitive to the substrate temperature and the deposition rate.

C. 25
Pervoskite PZT-PT Thin Films Grown by MOCVD, Phillip Alban Fridle1 and Hyun Choon1.
1Massachusetts Institute of Technology, Cambridge, MA, USA.

Pervoskite PZT thin films were grown on LaNiO3 buffered Si by MOCVD. These films are pure pervoskite when the PT concentration exceeds ~20%. By beginning film growth with sufficient PT to form the pervoskite structure and decreasing the Ti content as growth continues, the pervoskite structure was maintained even after the Ti source was valved off. Films were produced consisting of a concentration gradient layer at the substrate interface and a pervoskite PZT-PT layer near and below the morphotropic phase boundary. The microstructure and electromechanical properties of these films was investigated.

C. 26
MOCVD Growth of Pb0.99Ba0.01TiO3 Films on MgO, David A. Boyd, Mohamed Y. El-Naggar and David G. Goodwin,
Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California.

We have prepared well-oriented Pb0.99Ba0.01TiO3 (PBT) films of varied compositions, 0.2 ≤ x ≤ 0.9, and thicknesses ranging from several hundred nanometers to approximately one micron on MgO substrates by Metal Organic Chemical Vapor Deposition (MOCVD). Ultraviolet Absorption Spectroscopy (UVAS) of the gap phase Pb, Ba, and Ti precursors are used to regulate precursor flow rates and control film composition. The films have been characterized by X-ray Diffraction (XRD), micro Raman spectroscopy, Fourier Transform Infrared Reflection Absorption Spectroscopy (FTIRAS), Electron Microprobe Analysis (EMPA), and Electron Dispersive Spectroscopy (EDS). The a and c axes of the grains are oriented perpendicular or parallel to the surface normal, only. The Raman modes have been identified and compared with published results of bulk crystals of similar compositions. SEM images show rough surface structure with grains of several hundred nanometers. However, there appear to be no cracks or columnar structures visible in the cross-sectional images. In an effort to reduce the growth temperature and control the crystalline orientation of the film, UV assisted deposition has been explored and has been found to significantly enhance the growth rate.

C. 27
Technology Platform Research Center, Seiko Epson Corporation, Fujimi-machi, Nagano-ken, Japan.

Bi-layered structure ferroelectric thin films such as SrTiO3/SrRuO3/MgO/STO and BaTiO3/SrRuO3/MgO are one of the most promising ferroelectric materials for use in high-density ferroelectric random access memory (FeRAM) because of their excellent reliability. However, some fundamental problems originating from BLSF nature such as low remanent polarization (Pr), high coercive field, and low leakage current have been pointed out. On the other hand, Pb-containing ferroelectric thin film having perovskite structure such as PbTiO3 (PT) can easily crystallize at low temperature ranging from 400°C to 450°C. If a PbTiO3 perovskite unit cell is substituted or inserted into a Bi-layered perovskite unit cell, extreme low temperature crystallization of Bi-layered perovskite is significantly expected due to the role of nuclei during the crystallization process. In this work, three type of PbTiO3-exchanged Bi-layered perovskite thin films, namely SrRuO3/Bi2Sr2CaCu2O8 [STO/BCCO] (1-1), Bi2Sr2CaCu2O8 [STO]-Bi2Sr2CaCu2O8 [STO] and Bi2Sr2CaCu2O8 [STO]-Bi2Sr2CaCu2O8 [STO], were systematically investigated as a function of the composition and the crystallization temperature. In case of STO-PT system, the crystallization temperature is dramatically decreased down to 550°C. Furthermore, 2Pr of 19 μC/cm2 was successfully obtained in 608°C-crystallized 0.06Bi0.9PT thin films. Detailed results, which include crystallographic phase diagram and electrical properties of STO-PT and Bi-PT and Bi-PT solid solutions, will be presented.

C. 28
Novel chlorine based chemistry for growth of ferroelectric
materials by molecular beam epitaxy. Alexander Glaman Carver, Walker Henderson and W Alan Doultite, ECE, Georgia Institute of Technology, Atlanta, Georgia.

Recent interest in crystalline ferroelectric materials by the semiconductor industry has nurtured a drive towards improved material quality and device control afforded by molecular beam epitaxy (MBE). Current MBE growth and growth processes for the most advanced devices is a challenge beyond the reach of molecular beam epitaxy (MBE). Current MBE growth and growth processes for the most advanced devices is a challenge beyond the reach of molecular beam epitaxy (MBE).

The article discusses a novel use of atomic layered structures for new MBE growth of ferroelectric materials. The article discusses a novel use of atomic layered structures for new MBE growth of ferroelectric materials. The article discusses a novel use of atomic layered structures for new MBE growth of ferroelectric materials.

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with the underlying circuit, the following high temperature treatment often damages the films/electrode interfaces seriously by the diffusion of the constituent elements. To avoid this damage, it is desirable to prepare films having high dielectric constants at low temperature. In our study, PZT thin films containing non-crystalline seeds of BST particles were prepared by the complex alkoxide precursor method with a low deposition temperature. The BST nanocrystallines with ca. 20 nm in diameter were prepared by hydrolysis and condensation of the Bu₃Ti complex alkoxides. The BST suspension was mixed with the PZT precursor solution to obtain spin-coating solution containing 0.21 mol% BST nanocrystallines, which were dispersed homogeneously in the precursor solution. The BST mixed precursor solutions were spin-coated onto the Pt/Ti/SiO₂/Si substrate and the films were annealed at 200 °C on a hot plate to form gel films. This deposition process was repeated 5 times to obtain ca. 500-800 nm thickness PZT film containing the BST nanoparticles. The measurements of XRD analysis revealed that seeding of the BST particles prevented the formation of pyrochlore phases, which appeared at temperatures above 400 °C in PZT thin films. The well-crystallized structure of the PZT into perovskite structures at 420 °C that was more than 100 °C below the crystallization temperature of the unseeded PZT film. Measurements of dielectric properties at 1 kHz showed that the 25.1 mol% BST-seeded PZT films annealed at 450 °C attained a dielectric constant as high as 298 with a dissipation factor of 0.048. Leaking current density of the film was less than 10⁻⁸ A/cm² at applied voltages up to 5 V. Thus, the present work achieved the preparation of dielectric films having high dielectric constants, low leaking current densities and small dissipation factors by the application of a low temperature synthetic method.

SESSION C4: Processing: Emphasis on CVD and Pattern Formation

Chair: Hiroshi Funakubo and Masaru Shimizu

Tuesday Morning, December 2, 2003
Room 203 (Hynes)

8:30 AM *C4.1
Liquid Injection MOCVD of STBN Using an All Alkoxide Precursor System, Paul Andrew Williams1, Anthony C Jones1, Hywel O Davies1, Neil L Tobin1, Paul A Marshall2, John L Roberts1, and Lesley M Smith1. 1Epichem Limited, Bromborough, Wirral, United Kingdom; 2Chemistry, University of Liverpool, Liverpool, Merseyside, United Kingdom; 3Materials Science and Engineering, University of Liverpool, Liverpool, Merseyside, United Kingdom.

Thin films of Sr₂B₂O₅·₆NH₃·0.5O (STBN) have applications in nano-ferrite ferroelectric memories. MOCVD is an attractive technique for their production but progress has been restricted due to lack of suitable precursors. Conventional precursors include Sr(thd)₂ (thd = 2,6,6-trimethylheptane-3,5-dionate), Bi(thd)₃, BMEMS, and Ta(OEt)₅ or Ta(OPr)₅ (thd), but these are generally incompatible, having very different physical properties and deposition characteristics. To alleviate the mismatch between the Sr and Ta or Nb sources, we have developed the ‘single-source’ precursors Sr(thd)₂(OEt)₅(dime)₂ and Sr(Nb)₂(OEt)₅(dime)₂ (thd = 2,6,6-trimethylheptane-3,5-dionate, Bi(thd)₃, BMEMS, and Ta(OEt)₅ or Ta(OPr)₅ (dime), but these are generally incompatible, having very different physical properties and deposition characteristics. To alleviate the mismatch between the Sr and Ta or Nb sources, we have developed the ‘single-source’ precursors Sr(thd)₂(OEt)₅(dime)₂ and Sr(Nb)₂(OEt)₅(dime)₂, which are generally incompatible, having very different physical properties and deposition characteristics. To alleviate the mismatch between the Sr and Ta or Nb sources, we have developed the ‘single-source’ precursors Sr(thd)₂(OEt)₅(dime)₂ and Sr(Nb)₂(OEt)₅(dime)₂. In this paper we describe the liquid injection MOCVD of STBN using the all-alkoxide precursor combination Sr(thd)₂(OEt)₅(dime)₂ and Sr(Nb)₂(OEt)₅(dime)₂ and Bi(thd)₃.

9:00 AM C4.2
Orientation Control of Bi₁₀Te₇ₓZr₁₅₋ₓO₃ Thin Films Deposited on Silicon Substrate by MOCVD, Takayuki Watanabe1, Syoji Okamoto1, Hiroshi Funakubo1 and Keisuke Sato2. 1Innovative and Engineered Materials, Tokyo Tech., Yokohama, Japan; 2Analytical Dept., PANalytical Japan, Tokyo, Japan.

We have demonstrated various kinds of epitaxial growths of lanthanide-substituted Bi₁₀Te₇ₓZr₁₅₋ₓO₃ (BIT) films on single crystal substrates to characterize their spontaneous polarization values (Pₛ) along the a-axis of the non-substituted BIT (BNT) was estimated to be the largest value of 58 μC/cm² among the investigated Bi₃S's. To utilize the large polarization on silicon substrates, epitaxial control of both of epitaxial and the one-oriented BIT films on (100) Si substrates was tried by MOCVD, which is the most important preparation method for mass-production. As an approach for epitaxial applications, hetero/epitaxial stacking structure, (110)/SrRuO₃//(100)/YSZ//(100)Si, was used as a substrate. BIT films deposited at around 750 °C showed a preferred a/b-axis orientation in contrast to (118) single orientation of films prepared by lower deposition temperature. These results show that the one-axis-preferred orientation of BIT film was achieved by the selection of kinds of substrates and optimization of MOCVD conditions.

9:15 AM C4.3
Property Improvement of MOCVD-PZT Films deposited below 400 °C, Hiroshi Funakubo2, Googi Asano1, Atsushi Nagai1, Hiroshi Moricka1, Shintaro Yokoyama2, Tatsuo Shibusawa2, and Noriaki Oshima2. 1Department of Innovative and Engineering Materials, Tokyo Institute of Technology, Yokohama, Japan; 2Tokyo Research Center, Tosoh Corporation, Ayase, Kanagawa, Japan.

RuO₂/20nm-thick PZT/RuO₂ capacitor was deposited by MOCVD. RuO₂ and PZT films were prepared at 350, and 395 and 445 °C, and 445 °C thick DEH₃O₂ - ZrO₂ - ZrO₂ - ZrO₂ TiO₂ (O,c-H₂)₄ + O₂ systems, respectively. Clear hysteresis originated to ferroelectricity was observed for the PZT films deposited at 445 °C but not at 395 °C. However, by the addition of 16-nm-thick Pt layer on the RuO₂ bottom electrode, ferroelectricity showed 30 μC/cm² in remanent polarization (Pᵣ) was obtained by the increase of the crystallinity of the PZT films for the films deposited at 395 °C. This shows that Pt layer improved the crystallinity of PZT phase. However, it occurred by using Pt-top electrode instead of RuO₂-top electrode. This result suggests that the top electrode plays a dominant role for the fatigue phenomena of the capacitor as already pointed out. In conclusion, fatigue-free RuO₂/PZT/RuO₂ capacitor was deposited by MOCVD below 395 °C. In addition, in order to decreasing the operating voltage of Pt/RuO₂, films thickness of PZT films deposited at 395 °C was decreased down to 100 nm. Pₛ value decreased with decreasing film thickness, but large Pₛ, value above 25 μC/cm² was obtained and the ferroelectricity saturation up to 3 V was ascertainment. These results suggest that the good ferroelectricity was obtained for the films deposited below 400 °C by MOCVD.

9:30 AM C4.4
Ba(Ti₁₋ₓZrₓ)O₃ Thin Films grown by MOCVD for high-K Dielectrics Applications, Susumu Hoffmann-Eifert1, Half Gunzer2, Jochen Puchalla and Rainer Waser. IFF / EKM, Forschungszentrum Juelich, Juelich, Germany.

High-k ceramic thin films are being investigated as dielectric materials for integrated capacitors where the permittivity has to be increased with respect to conventional SiO₂ layers to further decrease the devices’ dimensions. Applications are future GBit DRAM integration circuits and tunable microwave devices, the most prominent material is Ba₅Sr₂Ti₃O₁₀, and the most favoured deposition process for industrial use is metal organic chemical vapour deposition (MOCVD). Due to the industrial forced restriction to only a few materials systems there is a large potential of other interesting materials not currently in use. One of these systems which is already used in large area ceramic passive components is the solid solution Bi₁₋ₓTeₓZr₁₅₋ₓO₃ (BTZ). BTZ thin films deposited by means of chemical solution deposition (CSD) or spray coating exhibit very good electrical properties, which puts the material into a competitive position to comply with the necessary requirements for integrated capacitor structures. In our work we now apply the industrial relevant MOCVD method for the deposition of Ba₁₋ₓTeₓZr₁₅₋ₓO₃ films. CVD provides compatibility to state-of-the-art integration scales, and is even more an excellent choice for conformal 3D growth. Using an AIX-200 horizontal reactor connected to a Tridept TM vaporizer module we deposited BTZ films on Pt/Si substrates. The three liquid sources contained a Bi(thd)₃, a Te(OPr)₅(thd)₃, and a Zr(OPr)₂(thd)₂ precursor, respectively. The focus of our investigations lies on the correlation between processing conditions (evaporation resp. substrate temperature, growth rate and film thickness) and electrical properties, mainly leakage currents, texture effects, and surface morphology. Further studies are attributed to the relationship between physico-chemical properties and the electrical response of the films. We studied the dielectric response with respect to frequency and voltage dependence as well as the effect of the Zr-substitution on the leakage characteristics of the capacitor structures.

9:45 AM C4.5
EXAFS Study Of PZT Thin Films, Barbara Muić1, Iztok Arsović1,2, Marija Koseč1, and Aljosa Koseč1,2. 1Electronic Ceramics, Josef Stefan Institute, Ljubljana, Slovenia; 2Novo Gorica Polytechnic, Novo Gorica, Slovenia, Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia.

Ferroelectric thin films have been widely studied for a range of applications in ferroelectric, non-volatile random access memory, and micro-electromechanical devices. In chemical solution deposition
(CSD) of thin films the main processing steps include the synthesis of a heterometallic precursor, typically in a nonaqueous medium, the deposition of the precursor and the processes occurring upon thermal treatment: drying, consolidation and crystallization of the target ferroelectric phase. Understanding the structural transitions in the process of film formation from the sol could allow a better tailoring of the properties of the film produced. The sols PbZr0.52Ti0.48O3 (PZT) thin films were prepared by 2methacryloyloxy-propyl trimethoxysilane (MPTMS) and lead acrylate, titanium n-propoxide and zirconium n-propoxide, the latter either unmodified or modified with acetic acid, and deposited on preheated silicon or sapphire substrates. X-ray diffraction and scanning electron microscopy (SEM) analysis was performed at Fraunhofer Institute for Applied Ceramic Research (IAZ) in Duisburg, Germany in cooperation with the Fraunhofer institute for Ceramic Technologies and Systems (IKV) in Aachen, Germany.

11:00 AM - C4.7 Sites- and Shape- Specific Nanopatterning of Ferroelectrics. Vinayak P Divakar1, Aroop B Chatterjee1, Orlando Auciello2, Ming Su2, D J Kim2 and Sanjib Saha2, 1Materials Science Division, Argonne National Laboratory, Argonne, Illinois, 2Northwestern University, Evanston, Illinois. 2Materiann Science Division, Argonne National Laboratory, Argonne, Illinois.

Most of the approaches for patterning functional inorganic semiconductors, e.g., ferroelectrics, rely on the "top-down" approach. In this conventional scheme, thin films are grown on appropriate substrates, followed by etching and patterning to create arrays of structures (e.g., capacitors for ferroelectric memories) for high-density devices. For high-density ferroelectric memory (FeRAMs) capacitors with nano-sized dimensions will be required. We have undertaken a novel approach for patterning ferroelectric materials. This approach is based on the "bottom-up" approach wherein it is possible to directly deposit, site-specifically, a single molecular ferroelectric nano-crystal onto a substrate. This approach takes advantage of the unique near- and mid-infrared absorption fingerprint and piezoelectric properties of the ferroelectric crystal lattice. The new approach is based on an advanced inorganic nanolithography (DNP), originally developed for nanopatterning of molecular structures. Instead of using molecular "inks", self-assembled precursors are employed as "inks" and the self-patterned soft structures are converted into functional inorganic with subsequent thermal treatment. Based on the earlier success of nanopatterning simple oxides (e.g., SnO2, ZnO etc.), we have now extended the approach to complex structures such as hard magnets (e.g., Fe-based ferromagnets) and ferroelectrics such as Bi as a possible ferroelectric memory (FeRAM) device. This new technique (DNP) allows for both size- and shape-specificity, down to nanoscale, controlled by AFM-based patterning software. With this approach, it is possible to pattern ferroelectric nanocrystals down to 150 nm, with the prospect for even smaller dimensions with improved properties of substrate surface and precursor inks. The patterned ferroelectric nanocrystals exhibit ferroelectric behavior as probed by the piezoresponse technique. The presentation will cover the strategy for functional patterning of ferroelectrics, the possibility for epitaxial templating, and their extensive structural, chemical and functional characterization.

11:15 AM - C4.8 Self-Assembling of Ferroelectric Nanocrystallites. Izabela Starzakowicz, Ming Wen Chu, Roland Schoitz and Murat Arce., Max Planck Institute of Microstructure Physics, Halle (Saale), Germany.

Multifunctional ferroelectric materials offer a wide range of useful properties from switchable polarization that can be applied in memory devices, to piezoelectric and pyroelectric properties used in actuators, transducers and thermal sensors. At the nanometer scale, unique material properties and effects are expected. The method of self-assembly offers an appealing alternative to lithography for the fabrication of nanosized ferroelectric crystals. We have applied the method based on the instability of ultrathin films to produce PZT nanocrystals. Ultrathin layers obtained by chemical solution deposition break up into a nanocrystalline structure after high-temperature annealing. The formation of nanostructures was investigated by scanning and transmission electron microscopy, atomic force microscopy and X-ray diffraction as a function of the initial film thickness and crystallization temperature. A relatively thicker layers give discontinuous films with faceted holes. Below a critical layer thickness, the film breaks up into separate non-regular islands. Using a highly diluted precursor results in films that pattern themselves into small separated nanocrystalline regions. Different Zr/Ti compositions of PZT and different substrates have been chosen to determine the role of in-plane stress on the nanocrystal growth and their properties. The lateral size and the height of the nanocrystals can be tuned within a small range by adjusting the concentration of the initial film and the post-deposition thermal treatment. PZT nanostructures with average lateral sizes down to about 50 nm and heights as small as ~9 nm show an epitaxial relationship to the substrate. Structure-property relations were investigated by XTEM and atomic force microscopy in piezoresponse mode. Part of this work has been supported by Volkswagen Stiftung Project "Nano-sized Ferroelectric Hybrids" (No. 5/77747).
The mgo growth, which inhibits hydration of even highly damaged MgO grains, resulting in PBT grain nucleation on all MgO grains, regardless of orientation. Future research will focus on improving the MgO growth, which is a key factor in the overall performance of the dielectric material. Future work will also involve the incorporation of new materials and the optimization of processing conditions to further improve the dielectric properties of the material.

11:45 AM C4.10
Abstract Withdrew

SESSION C5: Dielectric Applications: Low Frequency to Microwave
Chairs: Angas Kruger and Ivo Kosturkov
Tuesday, Afternoon, December 2, 2003
Room 203 (Hynes)

1:30 PM C5.1
Leakage Currents in High Permittivity Perovskite Thin Films
Herbert Schwoerer 1, PVT-IKEK, Forschungszentrum Juelich GmbH, Juelich, Germany.

This paper will review the present understanding of steady state leakage currents through high permittivity thin films such as strontium titanate (STO) or barium strontium titanate (BST). The first part of this discussion will consist of a description of the experimental conditions in which to measure the true leakage current and from this condition, which will be extracted to create a reliable database for mechanistic studies. In the second part, the most common leakage current mechanisms will be introduced with special emphasis on the characterization techniques for experimental verification. The third part will give an overview of the current limitations and potential difficulties in identifying the controlling mechanism. In a fourth part, a new model is proposed which combines carrier injection by thermal emission and tunnelling, at the electrode interface with the transport properties of the film background, to be clarified by measurements and analysis with effective mobility-velocity relationship such as band or polaron conduction.

2:00 PM C5.2
Understanding Leakage in "Thick" (Ba, Sr)TiO3 Films
S. K. Streiffer 1, A. Saha 2 and D. Y. Kwon 3, Materials Science Division, Argonne National Laboratory, Argonne, Ill.; 4Electronics Technology Division, Argonne National Laboratory, Argonne, Ill.

Despite significant progress over the last ten years, one of the outstanding issues in ferroelectric film science and technology is the lack of understanding of size and interface effects. While much of the effort in this area has focused on what happens as film thickness is reduced below 100nm, many applications require significant power handling capability and thus film thicknesses approaching or even exceeding 1 μm. The required thicknesses are still below those that are easily produced by traditional ceramic thick film processing routes, so vapor-phase and chemical solution deposition methods still play a role in enabling technologies based on these thicker films. One example of this is the use of (Ba, Sr)TiO3 (BST) thin films for tunable dielectric applications. However, one open issue for BST is the difficulty in reconciling dielectric and leakage behavior as film thickness is increased above twice the depletion length. Changes in band bending give rise to very different electric field distributions within the film as thickness is increased, and this has generally not been incorporated into discussions of size effects in this system. With this framework in mind, we have investigated the leakage and dielectric properties of a thickness series [90-380 nm] of [100] fiber-textured MOO3 [Ba0.75Sr0.25]TiO3 films with well-controlled microstructure. A positive temperature coefficient of resistance (PTCR) was observed in the leakage current behavior as film thickness was increased. The observed PTCR effect in our thicker films? leakage behavior will be discussed in the light of the Schottky-Heynig model most widely used to explain PTCR behavior in bulk BaTiO3 ceramics, with attention to how our films depart from that model. The presence of leakage current that incorporates nonlinear effects and variations in internal field distribution as a function of film thickness will be presented, that incorporate different interface effects (low permittivity dead layers, electrode-induced depolarization, etc.) as boundary conditions for the simulations. The implications of our results for the understanding of BST properties will be described.

This work was supported by the US Department of Energy, BES Materials Sciences and FreedomCAR and Vehicle Technologies Program, under Contract W-13-110-EN-E38.

2:15 PM C5.3
TEM and Electrical Analysis of Spattered Barium Strontium Titanate Films on Copper Substrates
Brian Linkin, John Hildebrand and Jon-Paul Marín; Materials Science, North Carolina State University, Raleigh, North Carolina.

Ba0.8Sr0.2TiO3 (BST) films were deposited on electroplated copper foil (18 μm thickness) by radio frequency magnetron sputtering. These films will be an integral part of flexible capacitor sheets intended for space borne re-configurable antenna arrays. By the use of controlled pO2 high temperature anneals, the films were fully crystallized and of high quality. X-ray diffraction data showed no existence of copper oxidation (i.e. CuO or Cu2O phases). The deposited BST films demonstrated a high dielectric constant (~2500) and a low tan δ (~0.015) at zero bias. A pronounced electrical tunability ratio of ~3:1 was observed on these devices. Devices showed loss tangents as low as 0.002 in fields as high as 30 KV/cm. Electrical field conditions were based on conventional atomic force microscopy (AFM) images that revealed a film thickness of ~1 μm. Temperature dependent measurements show a Tc ~290K with a diffuse dielectric anomaly. High resolution transmission electron microscopy (HREM) analysis of the Cu / BST interface will be presented along with conventional TEM analyses showing the film's grain morphology.

3:30 PM C5.4
Base-metal Integration and Enhanced Dielectric Properties of (Ba, Sr)TiO3 and (Ba, Sr)TiO3 Films
Jeff Danley 1, Huan Ong 2, Jacob Richardson 3 and Paul Clem 2.
1Microsystem Materials, Tribology and Technologies, Sandia National Laboratories, Albuquerque, New Mexico; 2Materials Science and Engineering, University of Illinois, Urbana-Champaign, Illinois.

Base metal integration of high K dielectrics is of interest for micro-electronic packaging and low cost passive component production. Processing and properties are presented for random and enhanced (100) SrTiO3 and Ba0.8Sr0.2TiO3 films fabricated using a modified 3-step (CSD) approach. Porcelain-Dontwiltsion over 1000 were obtained for several BST film compositions on Ni substrates. Films were crystallized in a reduced atmosphere, which prevented Ni oxidation, but permitted growth of oxygenated SrTiO3 and Ba0.8Sr0.2TiO3 films with a dielectric loss tan δ ~0.015. For randomly oriented Ba0.8Sr0.2TiO3 (x = 0.33, 0.5, 0.67) films processed at 900 °C, field-of-dielectric constants remained stable over 250 to 450. Films with enhanced (100) orientation exhibited zero-field dielectric constants of 800 to 1500, three times higher than random films. The impact of microstructure of the films on the measured dielectric properties will also be discussed. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the U.S. Department of Energy, under contract NO. DE-AC04-94AL85000.

3:30 PM C5.5
Microwave Measurements of Ferroelectric Thin Films: Techniques, Error, and Limitations
Peter Petrov, Centre for PEM, P.E.I., South Bank University, London, United Kingdom.

The development of tunable microwave devices based on ferroelectric film technology is progressing rapidly. This is due to the use of ferroelectric thin films that can be easily deposited on a variety of substrates. The use of ferroelectric thin films in tunable microwave devices allows for the design of compact, lightweight and low-loss devices. However, there are several challenges associated with the measurement of ferroelectric thin films at microwave frequencies, which can affect the accuracy of the measurements.

The measurement of ferroelectric thin films at microwave frequencies is challenging due to the dielectric properties of the material. The dielectric constant and loss tangent of the material can vary significantly with temperature and frequency, which can affect the accuracy of the measurements. The use of tunable microwave devices based on ferroelectric thin films also requires careful consideration of the measurement techniques and equipment design, taking into account the associated error and limitations. This paper is devoted to the problem of measuring the microwave properties of thin ferroelectric films, with an emphasis on planar capacitance.

For the measurement of capacitance and dielectric properties, several types of measurement techniques can be used. These include transmission line techniques, bridge techniques, and network analyzer techniques. Each of these techniques has its own advantages and disadvantages, and the choice of technique depends on the specific application and requirements.

In general, the measurement of ferroelectric thin films at microwave frequencies requires careful consideration of the measurement techniques and equipment design, taking into account the associated error and limitations. This paper is devoted to the problem of measuring the microwave properties of thin ferroelectric films, with an emphasis on planar capacitance. The use of tunable microwave devices based on ferroelectric thin films allows for the design of compact, lightweight and low-loss devices, which can be used in a wide range of applications.
design and optimized film processing methods, were employed to simultaneously lower the dielectric loss and enhance the dielectric tunability of Ba0.6Sr0.4TiO3 (BST) based thin films without compromising the device impedance matching (|ε|>500) and control voltage (≤10 V) requirements. The films compositional design was achieved by acceptor doping BST from 1 to 10 mol%. The films were fabricated on MgO and Pt substrates via a co-sputtering deposition technique using carboxylate-alcohol precursors and postdeposition annealing at 900°C (film/MgO substrates) and 750°C (film/Pt substrates). Dielectric properties were measured at 10 GHz using a vector network analyzer. The films exhibited improved dielectric loss and decreased from 0.028 to 0.01 and lower permittivity [ε] at concentrations from 1 to 10 mol%. Device quality values of tunability, 40 and 32%, for the 3 and 7 mol% doped BST films, respectively, were achieved by elevating the applied bias from 237 to 474 kV/cm. This device quality tuning is compatible with voltage requirements of current semiconductor based systems. The enhanced dielectric and insulating properties of the 3 to 7 mol% Mg doped BST thin films make them excellent candidates for integration into tunable devices.

100 PM C5.7
Silicon Substrate Integrated High Q-Factor Parallel-Plate Ferroelectric Varactors for Microwave/MMW Applications. Andrey Verkhov, Dan Kuylenstierna, Per Hjungskell, Khalid Khzoumi, and Eugene Georgiev. Department of Microtechnology and Nanoscience, Chalmers University of Technology, Gothenburg, Sweden.

Parallel plate Ba0.6Sr0.4TiO3 (BST) varactors with record high Q-factor are fabricated on Si substrate. At 45 GHz the Q-factor is about 40, and the tunability at 25 V is more than 40% in the measured frequency range 0.045-45 GHz. These parameters are far better than corresponding parameters of best Si and GaAs technologies. The improvement in Q-factor is achieved by using thick bottom electrode consisting of Pt (50 nm)/Au (5 μm) allowing to reduce the microwave losses associated with metal layers. The BST films exhibit relatively high permittivity (150) at zero bias and high resistivity (1018 Ω cm) at fields up to 700 kV/cm. Tunable one-dimensional electromagnetic band gap structures, based on polaron waveguides periodically loaded by the high-Q BST varactor varactors, have been prepared and measured in the frequency range 1-50 GHz. The superior performance of ferroelectric varactors (in comparison with semiconductors) shows that they can be used in practical designs of tunable microwave devices.

145 PM C5.8
Microwave Properties of Parallel Plate Capacitors Based on (Ba, Sr)TiO3 Thin Films Grown on SiO2/Si, Pt/Al2O3 Substrates. Ivo Kostrubov, Thomas Bernold, Martin Zeller, Paul Woo, Lisa Woodward, Arif Basnak, Jake Obeng, Andrew Cervin Lawry and Alan Patel, Technology R&D, Qommerce Corporation, Burlington, Ontario, Canada.

(Ba, Sr)TiO3 (BST) is a promising ferroelectric material for tunable microwave device applications. Lumped element planar capacitors effectively utilize the tunability of the material. This paper presents the results of the characterization of such capacitors, in the context of their applicability to doping applications [1], as well as recently demonstrated applications such as tunable filters and phase-shifters [2]. Various BST films were utilized to fabricate planar capacitor structures with Pt electrodes on glass and polycrystalline alumina (Al2O3) substrates. Thin films of (Ba, Sr)TiO3 and (Ba, Sr)TiO3 films were grown by two methods, metal-organic decomposition (MOD) and RF magnetron reactive sputtering, at 650-750 °C. For BST film thicknesses of 100-150 nm the capacitance densities typically ranged from 16 to 38 EF/m2, and were strongly influenced by the film compositions and the growth and post-annealing conditions. The film morphologies were characterized by Field Emission Scanning Electron Microscopy (FESEM) and Powder X-Ray Diffraction (PXRD) spectroscopy. Parallel plate capacitor structures with a uniformly effective area of 100 μm2 were fabricated using the above-mentioned patterning and ion milling techniques, and were used for electrical characterization. Capacitance, tan δ (Re[Y]/Im[Y]), and equivalent series resistance (ESR) were measured using the above-mentioned methods.

SESSION C6: Ferroelectric Films for Memories: Materials and Devices
Chair: Jeffrey Cross and Paul McCutrey
Wednesday, December 3, 2003 Room 2B3 (Hynes)

8:30 AM C6.0.1
Defect-Engineered SrBi2Ta2O9 Single Crystals with Enhanced Polarization Properties. Yugi Noguchi1, Koichiro Murata2, Mineo Takahashi1 and Masaru Miyayama1. 1Institute of Industrial Science, The University of Tokyo, Tokyo, Japan; 2PRESTO, Japan Science and Technology Corporation, Saitama, Japan.

Since thin films of ferroelectric SrBi2Ta2O9 (SBT) have been reported to show a fatigue-free polarization property with Pt electrodes, SBT has attracted considerable interest from the technological and fundamental points of view. Recently, Noguchi et al. have reported that rare-earth elements (RE) such as La, praseodymium (Pr), and Nd as well as Bi occupy the Sr site, and that a drastic change in
polarization properties is induced by the defect-related modification, i.e., "defect-engineering". The charge neutrality is satisfied through the formation of charge complexes to compensate the charge difference between Sr$^{2+}$ and trivalent cations (Bi$^{3+}$, Pb$^{2+}$, and so on). Polarization measurements using dense ceramics revealed that Bi substitution increased the remanent polarization ($P_r$) from 7 μC/cm$^2$ (SBT) to 10 μC/cm$^2$ (Bi:SBT). From a low-field polarization measurement, the low-electric-field polarization properties were markedly improved (a larger $Pr$ of 10 μC/cm$^2$ and lower coercive field ($Ec$) of 30 kV/cm). In this study, single crystals of defect-engineered SBT were grown by the method of Sr vacancies to compensate the charge difference along the c axis. Sr atoms were investigated. Single crystals were grown in air by a flux growth method similar to the way reported by Sib et al. The mixed powder with the composition (Bi$_{1.9}$Sr$_{0.1}$O$_{2.95}$) PbTiO$_3$ was put into a Pt crucible, and heated at 1100 °C for 5 h. After soaking at 1375 °C for 10 h, the material was slowly cooled to 1300 °C at a rate of 1 °C/h. This growth procedure resulted in single crystals with a 5$\times$5$\times$1 mm$^3$ at the maximum size. The composition of the crystals was determined by inductive coupled plasma spectroscopy. SBT single crystals showed an excellent squareness of loop, and the $Ec$ value was 18 μC/cm$^2$, which was twice as large as that of the ceramics. Furthermore, $Ec$ of SBT crystals was 20 kV/cm, and this value was much lower than those of other reported values reported for thin films and ceramics. Crystals of Bi:SBT (Sr$_{0.1}$Bi$_{2}$$_{3}$_2$O$_{12}$O$_{3}$) showed a significantly larger $Pr$ of 78 μC/cm$^2$ and the same $Ec$ as SBT. It was concluded that crystallographic defects increased with decreasing Bi content, which determined the $Ec$ of Bi:SBT. Neutron diffraction study confirmed that the Bi substitution with Sr vacancies enhances the shift of perovskite blocks with respect to Bi$_2$O$_3$ layers along the a axis as well as in a higher angle of $TaO_6$ octahedra oxygen octahedra in the b and c planes; these are the origin of the larger $Pr$ for Bi:SBT. The polarization properties of Bi:SBT, Pb:SBT, and SBT single crystals will be also reported.

9:00 AM C6.2
Growth of epitaxial tetragonal Pb(Zr,Ti)O$_3$ thin films with 100% polar-axis-orientation and their electrical properties. Hironori Morikawa, Shinjiro Yokozawa, Takahiro Okawa, Hiroshi Yamashita, *Nishina, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; **Analytical Department, PAAnalytical Japan, Minato, Tokyo, Japan.

We have reported the relationship between the electrical properties and the domain structure of α- and α′-axis mixture-oriented epitaxially grown tetragonal Pb(Zr$_{0.53}$Ti$_{0.47}$O$_{3}$) thin films on [100]-SrRuO$_3$/[100]SrTiO$_3$ substrates by metalorganic chemical vapor deposition and estimated the spontaneous polarization ($P_s$) value along the polar-axis (α′-axis) to be about 90 μC/cm$^2$ at 13°C. In the present study, we grew the perfectly α′-axis-oriented epitaxial Pb(Zr$_{0.53}$Ti$_{0.47}$O$_{3}$) thin films on SrTiO$_3$/[100]SrTiO$_3$ substrates. These films showed large $P_s$, value of about 90 μC/cm$^2$ together with good square-shape hysteresis loops and lower $Ec$. These features were achieved in growing 50-nm-thick Pb(Zr$_{0.53}$Ti$_{0.47}$O$_{3}$) thin films with 100% α′-axis orientation for the Zr/(Zr+Ti) ratio ranging from 0.5 to 0.5. The saturation polarization ($P_{sat}$) value of these films was unchanged over 90 μC/cm$^2$ for the Zr/(Zr+Ti) ratio of 0.5 to 0.5, but monotonously decreased down to about 60 μC/cm$^2$ for 0.5. Furthermore, the ratio of remanent polarization ($P_r$) to $P_{sat}$ value. $P_r/P_{sat}$ ratio of these films was, also, unchanged over 0.90 for the Zr/(Zr+Ti) ratio ranging from 0.15 to 0.40, but monotonously decreased down to about 0.70 for 0.5. These results show that Ti rich tetragonal Pb(Zr$_{0.53}$Ti$_{0.47}$O$_{3}$) thin films have large $P_s$ values with good square-shape hysteresis loops applicable for the high density capacitor-type ferroelectric random access memory. Refs. 1) K. Suem et al., J. Appl. Phys. 93, 545 (2003). 2) H. Morikawa et al., Appl. Phys. Lett., in press.

9:15 AM C6.3

We have already reported that α-axis-oriented bismuth-layers-structured oxide films were a novel candidate for high dielectric capacitor due to the lack of capacitance change against the applied voltage, the smooth surface, and the low leakage current regardless of the film thickness down to 20 nm. These superior characteristics were considered to be strongly related to the stack structure, bismuth oxide and pseudo-perovskite layers along α-axis. In the present study, epitaxial SrBi$_2$Ta$_2$O$_{15}$ (SBT) films having various orientations were grown by selection of the substrates and investigated the electrical properties. On the basis of these data, we discuss the origin of the dielectricity-dependence-free characteristics of α-axis SBT films. Epitaxial SBT films with various thickness were grown on [100]-, [110]-, [111]-SrRuO$_3$/SrTiO$_3$, and [100]-RuO$_2$/[012]Al$_2$O$_3$ substrates by metalorganic chemical vapor deposition. (001), [110], and [100]-oriented SBT films were characterized to be grown on these substrates by x-ray diffraction and the pole figure measurement. Tilting angles of c-axis of the films from surface normal were 6, 45, 55, 90 degree for (001), [110], and [100]-oriented films, respectively. The polarization of the (001)-oriented film with 160 nm in thickness, respectively. When the film thickness decreased around 115, 85, and 50 nm for (001)-, (110)-, and (100)-oriented films with 160 nm in thickness, respectively. These results show that $P_{sat}$-degradation started at thicker film when the tilting angle increased. On the other hand, the leakage current increased with increasing the tilting angle, which (001)-oriented films had the lowest recorded value of the film thickness. The stack structure along c-axis perpendicular to the applied voltage contributes to thickness-dependence-free character of $P_{sat}$ and leakage current.

9:30 AM C6.4

The development of optical, electronic, and acoustic devices based on the physical phenomena exhibited by ferroelectric materials depends critically on the visualization and manipulation of polarization domains. Ferroelectricity is a structural feature for which x-ray diffraction techniques are a natural probe. We have used synchrotron x-ray microdiffraction to image polarization reversal and the development of fatigue in epitaxial Pb(Zr,Ti)O$_3$ (PZT) thin film devices with submicron resolution. These devices were formed from (001)-oriented PZT thin film fabricated on conducting SrRuO$_3$ bottom electrodes epitaxially grown on SrTiO$_3$ substrates (PZT/SrRuO$_3$/SrTiO$_3$/SrRuO$_3$). Because ferroelectric materials lack a center of inversion symmetry, the intensity of x-ray reflections from regions of opposite ferroelectric polarization (i.e., separated by 180° domain walls) differs in intensity. With 10 keV x-rays, regions of opposite polarization differed in intensity by 20 to 30% in our thin film PZT samples. The extent of the switched area was directly related to the remanent polarization stored in the device deduced from electrical measurements. After a number electric field cycles, the development of polarization fatigue in devices with Pt top electrodes was accompanied by the lateral spreading of regions in which the PZT (002) x-ray reflection was shifted in lattice constant and greatly reduced in intensity. At lower electric fields we observed an earlier, partially reversible x-ray polarization fatigue that was not accompanied by this structural change.
11:30 AM C6.9  
Polarization Reversal Anti-parallel to the Applied Electric Field Observed in a Scanning Nonlinear Dielectric Microscopy, Takeshi Morita and Yasuo Cho, Research Institute of Electrical Communication, Tohoku University, Sendai, Miyagi, Japan.

Ultra-high density storage devices consisting of poling reversed nanodots are examined using a scanning nonlinear dielectric microscope (SNDM). As a method for detecting nanodots patterns, SNDM has a sub-nanometer resolution and is much superior to piezoresonance microscopy. Up to the present, by using SNDM our group has already demonstrated data storage in inverted domain dots in ferroelectric materials at a density of 1.5Tb/in². This technique realizes a much higher speed, higher reliability nanodot writing and reading system, fundamental investigations into nanodot formation mechanisms are indispensable. Indeed, a number of unexplained phenomena have been observed in polarization reversal, Such as a backswitching and ring shaped poling reversal dots that are sometimes observed during nanodot patterning. Hence a conductive cantilever was fixed on the ferroelectric material and poling reversal phenomenon under the cantilever was observed. A large electric voltage pulse (duration of 50 nsec) was applied to the ferroelectric thin film to affect the poling direction while the poling direction was detected using a minute electric field (8 kHz 3 Vp) by SNMD measurement. During this real-time observation of the poling reversal, interesting poling reversal was discovered. This poling reversal was unexpected because the poling direction was aligned anti-parallel to the applied electric field. This was only detected for thicker films with the critical thickness in the case of lithium tantalate thin film being about 350 nm. This value is expected to depend on material parameters, including permittivity of the ferroelectric material and cantilever curvature radius (in this study the curvature radius is around 25 nm). In thinner films, only normal poling reversal was observed. This normal poling reversal was observed as the applied voltage increased and anti-parallel poling reversal was observed during the falling edge. To examine whether anti-parallel poling reversal is a general phenomenon among 1:2:1 ferroelectric materials, lead zirconium titanate thin film (PZT) was used as a substrate. This was deposited by sol-gel method and had a thickness of 130 nm. Anti-parallel poling reversal was found and poling direction reversed when the input voltage pulse returned to zero, which is characteristic of the anti-parallel poling direction reversal. The final poling directions were anti-parallel to the applied electric field. Therefore the anti-parallel poling reversal is not peculiar to lithium tantalate, but may be generally applicable to ferroelectric materials.

Although the anti-parallel poling reversal mechanism is unknown, mechanical stress or strain are thought to play a role. Usage of the cantilever probe results in a concentrated electric field and this situation is much different from the conventional plate type ferroelectric capacitor or model.
Pt/Pr[Zr:Tl]O3/Pt/Tl/STO/0.5%Si and
Ir/PrO2/Pt[Zr:Tl]O3/Pt/IrO2/Tl/STO/0.5%Si thin film capacitors with various lateral sizes from 1 × 10 μm² to 8 × 9.9 μm². In the case of the capacitors with Pt electrode, smaller capacitors were more susceptible to external factors such as etching and annealing process, and showed rapid retention failures. On the other hand, the capacitors with oxide electrodes showed relatively stable retention characteristics. However, decrease in lateral size of capacitors deteriorated the opposite-state retention. We suggest that the retention failure occurs by the increase of the leakage current and/or by the increase of the internal field and polarization charging. The effects of test pulse amplitude and ratio of perimeter to area were taken into account to explain the experimental results. [1] B. S. Kang, J.-G. Yoon, D. J. Kim, T. W. Noh, T. K. Song, Y. K. Lee, J. K. Lee, and Y. S. Park, Appl. Phys. Lett. 82, 2134 (2003).

SESSION C7: Ferroelectric Films: Processing and Integration
Chairs: Vikram Joshi and Ivo Katsaroff
Wroshroom Afternoon, December 3, 2003
Room 203 (Hynes)

1 PM C7.1
Evaluation of PZT based metal oxide electrode FRAM capacitors and reliability. Jeffrey S. Cross1, and Yoshimasa Hori2.
1Inorganic Materials and Polymers Lab, Fujitsu Laboratories Ltd., Asatsu, Japan; 2FRAM Division, Fujitsu Limited, Asatsu, Japan.

Understanding FRAM capacitor reliability issues and polarization loss mechanisms are extremely important topics for the industrial ferroelectric film community in order to develop higher density memories. Conducting metal oxide electrodes when combined with ferroelectric films containing Pb(Zr:Ti)O3 [PZT] to form a capacitor have improved reliability, particularly related to resistance to polarization loss due to bipolar fatigue, imprint and hydrogen degradation. These types of metal oxide electrodes have been combined both in a symmetrical structure, where the top and bottom electrodes are the same material, as well as in asymmetrical structure, where the bottom electrode is metal such as Pt and top is an oxide electrode, such as iridium oxide or SrTiO3. At Fujitsu, top metal oxide electrodes of IrOx and IrO2 layers, 1 ≤ x 10 μm² were used in testing the effect of deposited Pt films on a Pt bottom electrode as an asymmetrical capacitor, which have been shown to exhibit high reliability and high endurance with 5 and 3 V operation. The interaction of the top electrodes and ferroelectric film, contribute greatly to the ferroelectric properties, but it is difficult to distinguish the impact of the electrode and interface on the ferroelectric capacitor because of limitations in quantitative analysis of Ir in PZT. Furthermore, it has been reported by several different groups that capacitor area size effects have been observed for sub-micron size capacitors which show higher polarization than larger capacitors. As a result, we have been working to understand ferroelectric capacitor reliability issues from a quantitative analysis point of view by combining materials characterization, diffusion studies of isotopes, ion implantation, sub-micron capacitor measurements, and applied stress as well as collaborating with physical property research to develop comprehensive models of FRAM capacitors. In this presentation, recent results will be presented focusing on metal oxide electrode interaction with PZT in order to explain polarization losses and their related mechanisms.

2 PM C7.2
Polarization switching of sub-micron ferroelectric capacitors using an atomic force microscope. Suman P. Jha, V. M. Nagoorajan1, Zhenguan Ma, Raman Shreya, Jeffery S. Cross, and Yoshimasa Hori.1
1Materials Research and Science Engineering Center, University of Maryland, College Park, Maryland; 2Fujitsu Laboratories, Ltd., Asatsu, Japan.

We report on the measurement of switchable pulse polarization of micron and sub-micron ferroelectric capacitors contacted using an atomic force microscope. Fast square pulses with rise-times of the order of 10 nanoseconds are used to obtain the switchable polarization (ΔP) of discrete polycrystalline Pt3Zr/4Ti1/10 STO capacitors of 21.5 μm², 0.2 μm² and 0.19 μm² prepared by sputtering and reactive ion etching. Our studies show that the switching characteristics of these capacitors are well behaved indicating that high speed and high density ferroelectric memory capacitors are not limited by slowing down the capacitor area. Based on this experimental setup, we further investigated the properties of the discrete sub-micron capacitors as a function of 1) film's structure comparison between polycrystalline and epitaxial films and various compositions 2) film's thicknesses down to <10nm. We will report results of these studies in this presentation. This work was supported by the Fujitsu visiting researcher scholarship program, and the NSF-MSEC under contract No. DMR-0608089.

2:15 PM C7.3
Prevention Of Hydrogen-Induced Degradation In Three Dimensional Structured MIM Capacitor With MOCD Ta2O5, Dielectric and Ru Electrode. Ham Jin Lim, Sijun Jung, Wun-Don Kim, Kwanghee Lee, Jinil Lee, Ching-Yung Yoo, Sang Tae Kim, Il Chun Chung and JooTae Moon. Process Development Team, Memory Division, Samsung Electronics, Yangin-City, 449-711, South Korea.

The leakage current degradation by hydrogen post-annealing after the formation of MIM capacitor in sub-10nm DRAM device was examined. The effect of hydrogen on capacitor degradation was evaluated with various annealing temperature and time. The samples were prepared by measuring the capacitance-voltage (capacitance-voltage (C-V)) characteristics in spite of Ru grain growth. This degradation might be induced by hydrogen attack such as the formation of oxygen-depleted layer within a Ta2O5 dielectric by catalytic Ru electrode rather than the degradation like micro-voids by Ru grain growth. To prevent it, various coating layers as hydrogen barriers were applied in 3 dimensional capacitor structure. The conformal Al2O3 or TiO2 layer was deposited in the stacking type capacitor structure by using the ALD method. In order to protect against capacitor degradation in COB (capacitor on bit-line) structured DRAM, while facilitating hydrogen curing effect into Si substrate to improve DRAM refresh property as well, a novel scheme for capping only the capacitor cell area by Al2O3 was applied, where the capacitor area was covered with Al2O3 and its spacing was reduced on the side wall simultaneously. The thickness and post-treatment of Al2O3 capping layer were varied to optimize the protection conditions. The minimum thickness of Al2O3 was about 10nm. In the case of 0.13μm planar treated spacer, the degradation of the leakage current of MIM capacitor was completely prevented after H2 annealing at 450°C. Etch-damaged spacer seemed to be cured by oxygen supplement through the post-treatment. By doing this, such electrical properties as the equivalent oxide thickness (EOT) having 1.2nm, the leakage current value less than 1A/μm² at ±1.5V bias voltage were obtained without variations before and after H2 annealing.

2:30 PM C7.4

Mass-production sputtering technologies of ferroelectric and dielectric materials such as PZT(Pb(Zr:Ti)O3), BST(BaSrTiO3), Al2O3 and so on are developed in order to implement applications of ferroelectric and dielectric thin films to next-generation semiconductor devices such as FRAM (Ferroelectric Memory), gigabit DRAM (Dynamic Random Access Memory) and other embedded memories as well as MEMS (Micro-electromechanical system) and OMEMS (Optical MEMS). Requirements to make reproducible ferroelectric/dielectric material sputtering technology come with three aspects which are 1) production tool, 2) production sputtering technique and 3) thin film or device ferroelectric performance. All of these three aspects must satisfy the production requirements such as good and sufficient reliability and reproducibility of sputtering process tool, and good and sufficient thickness and compositional uniformity. In this paper, we report on R&D results of ferroelectric/dielectric material sputtering as well as the data from FRAM production.

3:30 PM C7.5
Effective Deposition Control of Pb(Zr0.16Ti0.84)O3 Thin Film Capacitors Using Ti/Pb(Zr0.16Ti0.84)O3 Seeding Method. Bum Ki Moon, Osamu Ariusima, Karl Hornik, Rainer Bruchhaus, Hiroshi Ikowaka, Andreas Hilliger, Haen Rastree, Ulrich Egger, Shoji Yamazaki1, Toru Okuma, Noriyuki Komeda, Koji Yamakawa2 and Gerhard Beitel1. 1FIDA, Infineon Technologies Corp., Yokohama, Japan; 2FIDA, Toshiba Corp. Semiconductor Company, Yokohama, Japan.

The most promising material for future FeRAM devices is Pb(Zr,Ti)O3 (PZT). For this material, control of crystallographic...
orientation is essential for achieving excellent electrical performance. In previous studies, the orientation was controlled by inserting TiO$_2$ or Pt/TiO$_2$ layers, or by pressing a needle through the glass substrate. In this paper, the effect of thin Ti/Pt/TiO$_2$/PtO$_2$ seed layers on the properties of Pt/TiO$_2$/PtO$_2$ capacitors has been investigated. The seed layer is based on a sub-layer of thin Ti and thin Pt with a total thickness of about 250 nm. The Pt layer was deposited by sputtering on Pt/TiO$_2$ and TiO$_2$ substrates at a temperature of 650°C for 30 sec using Ti$_2$O$_5$. The main 100nm-thick Pt/TiO$_2$ film was then deposited and crystallized. The Pt/TiO$_2$/PtO$_2$ thickness of the seed layer was obtained on a 100 nm thick seed layer, where the peak intensity ratios of [111]/[100] and [111]/[001] are about 100 and 20, respectively. A film on a 250 nm thick seed layer, which was prepared using [111]-oriented polycrystalline layer of Pt, showed a much lower [111] intensity. Careful XRD and TEM investigations revealed that the 100 nm thick seed layer forms a polycrystalline phase with a smooth surface, while the 250 nm thick seed layer is a mixed phase of polycrystalline and [111]-oriented polycrystalline. The formation of the polycrystalline phase is a result of a higher [111]-orientation bottom electrode, resulting in a Pb deficient stoichiometry. The seed layer transformed to the polycrystalline phase during the main Pt/TiO$_2$/PtO$_2$ seed layer. The 10nm thick seed layer showed a Q$_m$ of typically 34.9 μC/m$^2$, however, a lower Q$_m$ of 18.9 μC/m$^2$ was obtained in case of a thicker seed layer. The 10nm seed capacitors exhibited a high-field behavior up to 10$^{10}$ switching cycles. In conclusion, it is a thin Ti/Pt/TiO$_2$/PtO$_2$ seed layer is a very effective method for fabricating Pt/TiO$_2$/PtO$_2$ seed layers for fabrication of Pt/TiO$_2$/PtO$_2$ capacitors with excellent ferroelectric properties.

4:00 PM C7.6

Ferroelectric random access memories (Fe-RAM) are compared very favorably with other non-volatile memories, such as electrically erasable programmable read-only memories (EEPROM) and flash memories, since high speed and low voltage operation. So the preparation of Pb$_x$Zr$_{1-x}$TiO$_3$ (PZT) ferroelectric thin film has been widely developed for application of possible electronic devices such as mobile phones. In this work, we succeeded a low saturated voltage (V90), high switching charge (Qsw) and low leakage current density (JL) of the Pt/TiO$_2$ thin film. 100nm Pt/TiO$_2$ films were grown on Si(100) substrate at 320°C and 0.2 mbar by metal organic chemical vapor deposition (MOCVD). Pt/TiO$_2$ films were used as an electrode. After forming Pt/TiO$_2$ electrode, post-annealing was performed at 580°C for 60min in oxygen ambient at 1 atm. Normalized oxygen/perscarati ratio varied with the Pt/TiO$_2$ growth. Composition, Phase and thickness of the PZT films were measured by X-ray diffraction, Raman, and XPS. In Pt/TiO$_2$ phase and 100nm respectively for all sample, V90, Qsw (92V) and JL (0.1V) were 2.2V, 36 nC/cm$^2$ and 2.5E6 A/cm$^2$ respectively. The normalized oxygen/perscarati ratio varied from 1 to 3. The electrical properties were improved. They are 1.7%, 47 μC/cm$^2$ and 7.5E-8 A/cm$^2$ respectively. Acknowledgments: We thank Mitsubishi Materials Corporation for supporting precursors and solvents.

4:15 PM C7.7
Fabrication of Ru/Bi/La$_2$Zr$_2$O$_7$/Ru Ferroelectric Capacitor Structure Using a Ru Film Deposited by Metalorganic Chemical Vapor Deposition. Takanori Takizawa, Kazuhiro Iwata, and Takahiro Takeda, Tohoku University, Sendai, Japan.

The major problem of the electrode material for higher dielectric constant and large tunability. The electrode material has an important property for the fabrication of ferroelectric capacitor. The Ru/Bi/La$_2$Zr$_2$O$_7$/Ru ferroelectric capacitor structure is reported. The Ru/Bi/La$_2$Zr$_2$O$_7$/Ru ferroelectric capacitor structure is fabricated. The Ru/Bi/La$_2$Zr$_2$O$_7$/Ru ferroelectric capacitor structure is fabricated. The Ru/Bi/La$_2$Zr$_2$O$_7$/Ru ferroelectric capacitor structure is fabricated. The Ru/Bi/La$_2$Zr$_2$O$_7$/Ru ferroelectric capacitor structure is fabricated.

It has been reported that the strain state of the (Ba,Sr)TiO3 (BST) thin films can be changed according to the substrates, film thickness, oxygen partial pressure during deposition, strain variation of thin buffer layers, etc. In this work, we grew epitaxial BST thin films either directly on [001] LaAlO3 (LAO), [001] SrTiO3 (STO), and [001] MgO or SrO [SrO]-coated LAO, STO, and MgO by pulsed laser deposition. Capacitor capacitors and metal-insulator-metal (MIM) capacitors were fabricated thereafter using gold as the electrode. All BST films were (001) oriented. The good alignment in the plane of the BST and STO with respect to the major axes of the substrates was also confirmed by XRD [001] planes of the [001] BST, [210] SRO, and [001] substrates reflections. The dielectric properties of the BST films on different substrates and capacitor architectures were characterized by the capacitance-voltage and capacitance-frequency measurements. The effects of epitaxial strain on the properties of BST thin films with co-planar capacitor and MIM capacitor structures will also be discussed in detail.

C8.3 Temperature dependent Raman scattering and dielectric permittivity measurements of Pb(1-x)Sr x TiO3 films grown by metalorganic decomposition. Varun M. Naik, M. Kowalczyk, J. Smith, H. C. Dau, R. Naka, G. W. Auner, and Joseph M. Barnes. Physics Department, University of Michigan-DeBartolo, DeBartolo, Michigan. 1Department of Physics, Wayne State University, Detroit, Michigan. 2Department of Electrical and Computer Engineering, Wayne State University, Detroit, Michigan. 3Delphi Automotive Systems, Shelby Township, Michigan.

Pb(1-x)Sr x TiO3 (x = 0 to 1.0) films of thickness ~ 4 µm have been prepared on sapphire and Pt substrates by the metalorganic decomposition (MOD) technique. X-ray diffraction results show that the films are polycrystalline with a perovskite tetragonal phase at room temperature for x < 0.5 and cubic phase for x > 0.5. Room temperature Raman spectra show a systematic variation of lattice vibration modes with composition. The most notable changes in the Raman spectra with x are the decrease of A1g (STO) and E2g (STO) modes into one at approximately x = 0.6, and a considerable softening of A1g (STO) mode. Although the x-ray diffraction peaks for x = 0.6 show a cubic phase at room temperature, the Raman spectrum shows the characteristic phonon modes of a tetragonal phase. The dielectric permittivity versus temperature measurements for films with x ≤ 0.6 show a dielectric anomaly, although broad, corresponding to a ferroelectric to paraelectric phase transition. However, the phase transition temperatures (Tc) are lower than the corresponding values of bulk ceramic alloys. Furthermore, the temperature dependent Raman measurements of these films show that the transition persists much beyond Tc = 100 °C. This is consistent with the observation of a rather diffuse phase transition in the mixed perovskites caused by distribution of phases in the film. Such an anomaly is observed in Pb content along the film thickness and for near grain boundary regions.


The importance of interface and bulk transport mechanisms on the leakage current of high dielectric constant thin film capacitors is examined by deriving a new equation for the J-V characteristics of a thin film capacitor that includes the transport mechanisms of thermionic emission (TE), thermionic field emission (TFE), and carrier drift-diffusion (DD). It is shown that the J-V characteristics of thin film capacitor can be described by an equation identical in form to that for a single Shockley barrier junction but with a modified Richardson constant. The capacitor Richardson constant A* is characterized by three parameters Ec, Vd, and Va having units of velocity describing carrier injection into the dielectric at the cathode by thermionic emission and tunneling, carrier drift and diffusion in the bulk, and carrier ejection from the dielectric at the anode by the mechanisms of thermionic emission and tunneling, respectively. The model is explored by applying the model to two Pt/Ba,Sr x TiO3/Pt capacitor systems with markedly different concentrations of donor doping of the high dielectric constant barium strontium titanate (BST). For heavily doped BST, Vd is constant and the leakage decreases with increasing thickness approximately linearly. For moderately doped BST, at low voltages, Vd control the current and transport by drift and diffusion in the film bulk exhibits a strong influence on the leakage characteristics. At higher applied voltages a crossover to Vc control occurs. It is shown that over a wide applied field range Va does not usually control the leakage current through a capacitor. Implications of these results on existing transport calculations for high dielectric constant thin film capacitors are discussed.

C8.5 Influence of Relaxation on Leakage Current for BST Films. Ping Sun and Harry R. Tuller, Center for Advanced Nanotechnology, University of Toronto, Toronto, Ontario, Canada.

We report on current-voltage (J-V) and current-time (I-t) characteristics of 500 nm thick Ba,Sr x TiO3 (BST) films deposited on Pt/TiO2/SiO2/Si substrate by sol-gel processing. The relaxation current influences the leakage current and introduces a positive error, especially for small bias fields and at low temperatures. The leakage current originates from the Frenkel-Poole effect. The deep electron trap density of states was determined using the space charge limited current (SCLC) model, and Datta-Sauer technique. We successfully modelled the leakage current by including the impact of the Frenkel-Poole, Shockley-Read-Hall, and injection current.

C8.6 Simulation Of Conduction In High Permittivity Thin Films With Thermionic And Tunneling Injection At The Schottky Barrier. Herbert Schoeller, LFF-EMK, Forschungszentrum Juelich GmbH, Juelich, Germany.

Numerical studies have been performed for the steady state leakage current through high permittivity insulating thin films with Schottky barriers at the electrode interface in order to simulate experimental data on dielectrics such as strontium titanate (STO) and barium-strontium titanate (BST). The latter being a candidate for application as dielectric in the capacitor of future 3G generation DRAM cells. In the 2002 symposium a new model was introduced combining thermionic carrier injection over a Schottky barrier at the electrode interface with conduction properties of the film bulk describing successfully measured data of Pt/MOCVD/BST/Pt capacitors. This was extended to additional tunnel injection through the Schottky barrier by using an effective injection velocity having the characteristic field and temperature dependence of both injection mechanisms. Simulation data will be presented in dependence on several extrinsic and intrinsic parameters (voltage, temperature, film thickness, barrier height, dead layer properties, etc.) for symmetrical electrodes. The most important result is that the trend found for the simulations with thermionic emission over the barrier only is enforced: For the conditions for which the tunneling injection is (much) larger than the Schottky thermionic injection current the leakage current in film bulk is dominated and the reduction factor is much higher even in very high fields.

C8.7 Conduction and Microwave Loss Mechanisms in Ba,Sr [1−x] TiO3 Films. Azizul Vocabo, Vladimir Kolesnikov, Eiji Kamezaki, Per Rundquist and Spartan Georgiev, Department of Microtechnology and Nanoscience, Chalmers University of Technology, Gothenburg, Sweden.

The silicon integrated parallel-plane Ba,Sr [1−x] TiO3 (BST) varactors with record low loss tangent, due to application of the bottom Au electrode, have been prepared and characterized by microwave impedance and DC current-voltage measurements. In the frequency range 0.01-5-15 GHz the loss tangent is less than 0.025. However, it is still 10 times higher than losses in single crystal indicating that along with fundamental losses the additional loss mechanisms exist. The low field DC current through the BST film is controlled by a Frenkel-Poole mechanism associated with hopping charge carriers by internal traps formed by positively charged oxygen vacancies. The presence of internal traps in the bulk of BST film allows to explain the additional microwave losses by hopping charge carrier polarization. The dominance of this polarization mechanism is confirmed by linear frequency dependence of loss coefficient and decreasing the losses by applied voltage observed in our experiments. The knowledge of the dominant loss mechanism allowed for optimizing the varactor preparation and further improving the Q-factor.

C8.8 Reliability Of Tunable Capacitors For Microwave Applications. Barry W. Treadway, Guang Lin, Luan Chiu and Xubin Zhang, Paratek Microwave Inc., Columbia, Maryland.

A new process has been developed by Paratek Microwave Inc. to formulate stable tunable materials based on our proprietary.
C.8.10 Abstract Withdrawn

C.8.11 The Dielectric Characteristics of PZT/LNO Films Deposited on Base-metal Sheets For Power Electronic Systems.
Jong-Hyun Cheon1,3, Dong-Joo Kim2, David Y. Kaufman2, Stephen K. Streiffer2 and Joo-Woong Hn3,
1R&D Center, Inostek Inc., Ansan-si, Gyeonggido, South Korea, 2Materials Science Division, Argonne National Laboratory, Argonne, Illinois, 3Energy Technology Division, Argonne National Laboratory, Argonne, Illinois.

Recently, the embedding high-permittivity (high K) dielectric materials using PZT and La-doped PZT thin film have been utilized to develop device reliability, manufacturing cost down and make small-size products for power electronic systems. However, many parts of these electronic systems include somewhat expensive materials and complicated processing steps. Especially, the electrodes of capacitors, which use an expensive noble metal, have an effect on the product cost rising in electronic system. The capacitor cost reduction is capable of changing the expensive noble metal electrode to base-metal and alloys. In this experiment, Ni-based sheet is used as a substrate to achieve low-cost process and LNO buffer layer is inserted underlying PZT films to prevent the oxidation of Ni sheet substrate. PZT and LNO thin films are prepared using modified chemical solution deposition method. In an effort to develop robust capacitors on cost competitive Ni sheet, several parameters including annealing conditions, dopants, Zr/Ti ratio, and thickness are systematically investigated. The dielectric properties are evaluated to investigate the role of interface state. The dielectric breakdown strength, an important parameter in power electronic systems is also evaluated as a function of film thickness and dopants. Here, we report the experimental results and related possible mechanisms regarding to interfacial layer effect in detail.


Ba0.6Sr0.4TiO3 (BST) is a suitable material for several frequency agile microwave electronic devices, such as phase shifters, filters, varactors, delay lines etc. due to its high response of the dielectric constant to an applied electric field. However large dielectric constants and dielectric losses found in this system limits its usefulness at microwave frequencies. In an effort to improve the dielectric properties, sol-gel processing has been employed for both thick and thin film capacitors have been determined as a function of electric field strength.
silicon wafers and crystallized between 550 and 700 degree centigrade. The films were found to crystalize above 600 degrees. After crystallization Pt top electrode was deposited by lift-off processing. FT-IR studies performed on the films showed no oxo-carbonate phase formation during crystallization. Microstructural studies involving XRD, SEM and AFM were performed on the films. The films were found to have a dielectric constant of 400 and a tunability of 32%. The frequency and temperature dependence of the dielectric constant were studied. In addition leakage studies were performed on the films.

C8.18
Comparative studies on BaZr0.75Ti0.25 thin films deposited by sol-gel and pulse laser deposition. Anja Dak, Pijush Bhattacharyya, Subhashish Das Mukherjee, Tani S Kaur and Asit Singh Bhalja, Physics, University of Puerto Rico, Puerto Rico.

In the present work, ferroelectric thin films of BaZr0.75Ti0.25 were deposited on platinum (Pt) and lanthanum aluminate (LaAlO3) substrates by sol-gel and pulse laser deposition technique. The structure and preferred orientation of the films were examined by x-ray diffraction measurements. The phase formation of sol-gel derived highly textured BZT films on LaAlO3 substrate found to be at high temperature while the pulse laser deposited BZT films were formed at low temperature. The films were highly oriented on LaAlO3 substrates. Polycrystalline films were observed in case of platinum (Pt) substrates by both techniques. Ferroelectric nature of the film was confirmed by hysteresis and capacitance-voltage characteristics using top electrodes. The phase transition behavior of BaZr0.75Ti0.25 (x = 0.0 to 1.0) thin films has been investigated by temperature dependent M-H-Raman and dielectric measurements. BZT films prepared by both technique showed strong compositional dependence. Normal ferroelectric to relaxor behavior has been observed in the composition range of x = 0.0 to 0.60. From temperature dependent Raman scattering it was found that the cubic to tetragonal transition temperature decreases while the lower phase transitions temperatures increase. For films with Zr contents of 10%, all transition temperatures coalesce into one at Tc ~ 280 K. The dielectric measurements confirm this observation. Above 15% Zr the dielectric constant measurements show a broad maximum at the transition temperature. For Zr concentration above 25% the material shows relaxor properties. Above 60% no relaxation is observed in these films. Dielectric temperatures as well as dielectric constant were found to be decrease by increasing Zr contents. Several comparative aspects will be discussed from the studies of both solgel and pulse laser deposited films.

C8.19
Growth and study of BaZro.75Ti0.25 thin films by pulsed laser ablation. Rajasekarwarun Vasudeo1, P. Victor1, R. Hanjith1, S. B. Krauha2, S. Rajagopalam1 and A. K. Tung1, 1Materials Research Centre, Indian Institute of Science, Bangalore, Karnataka, India; 2Materials Science Division, Indira Gandhi Center for Atomic Research, Kalpakkam, India.

Thin films of BaZr0.75Ti0.25 (BZ) were grown using a pulsed laser deposition technique on platinum coated silicon substrates. Films showed a polycrystalline perovskite structure under different annealing procedures in-situ and ex-situ crystallization. The composition analysis were done using Energy dispersive X-Ray (EDX) and Secondary Ion Mass Spectrometry (SIMS). The SMS analysis revealed that the SrZrO3 (Sr) formation at the interface of substrate and the film leads the degradation of the device on the electrical properties in the case ex-situ crystallized films. But the insitu exhibited no interfacial formation. The dielectric properties have been studied for the different temperatures in the frequency regime of 40 Hz to 100 MHz. The response of the film to external AC stimuli was studied at different temperatures, and it was found that AC conductivity values in the limiting case is correspond to oxygen vacancy motion. The electrical modulus is fitted to a stretched exponential function and the results clearly indicate the presence of the non- Debye type of dielectric relaxation in these materials.

C8.20
Enhancing Tunability and Decreasing Temperature Sensitivity. A Tawha1, 1 S C Tidrow1, D M Potrepka1, B J Rod1, K W Kirkner2, 2 H Ervin1 and F J Crowell1, 1AMRL-SE-RE, Army Research Laboratory, Adelphi, Maryland; 2Geo-Centers, Inc., Newton Upper Falls, Massachusetts.

The employment of judicious substitution on B-sites in the perovskite oxole, BaTiO3, has yielded materials suitable for relatively temperature insensitive electric field tunable microwave devices. The properties, single-phase cubic perovskites with tunabilities as large as 30% at 1 V/μm and room temperature that possess low temperature coefficient of dielectric constant and tunability over the majority of the military specified temperature range, -56 to 125 °C, have been
achieved in the charge compensated system $Ba_{1-x}Sr_x Ti_{1-x} Zr_x O_3$ where $C$ is the permittivity, $E$ is the electric field, $T$ is the temperature, $S$ is the superconducting transition temperature, and $A$ is the area.

The Goldschmidt tolerance factor, $t$, for $BaTiO_3$ is close to 1.0, an instability point. Substitutions with ionic radii larger than $T^{1+}$ result in compensation with more stable $T$. Substitutions in the perovskite structure, particularly with ionic radius much smaller or larger than $T^{1+}$ result in compositions with smaller tunneling. These materials are being used in a novel device structure that has been shown to provide broadband and variable true-time delay. The device is designed for use in dynamic antenna applications over the military specified temperature range.

CS. 21
Optimization of Strontium Titanate Thin Films For Low Loss Tunable Superconducting Microwave Filters

Nonlinear ferroelectric thin films allow the possibility of tuning resonant circuits by changing the capacitance with an applied electric field. Strontium Titanate thin films exhibit a high tunability at low temperatures and hence are good candidates for tuning HTS filters, which operate at about 65 K. We have optimized the growth conditions of SrTiO$_3$ thin films to obtain low loss and high tunability for use as variable capacitors in such filter circuits. We grow our thin films by reactive coevaporation, and we investigated their properties using in-situ RHEED, x-ray diffraction, low frequency capacitance-loss measurements, and high frequency resonance coupled measurements. We will discuss the influence of the growth conditions on the thin film properties. Additionally, we present data from a YBCO cross-coupled 6-pole, 0.2% bandwidth filter centered at about 800 MHz (modified cellular A-prime band) with insertion loss less than 1 dB over the full 10%. The use of SrTiO$_3$ allows this filter to be electrically tuned by about 1 MHz while maintaining a high Q value. This work was funded by DARPA as part of the FAME program, Contract No. N00014-98-1-C-0387.

CS. 22

While many dielectric materials are known to have a permittivity higher than that of amorphous silica (5.9), few have breakdown fields nearly so high, $E_{br}=10-20$ MV/cm. For many purposes, such as storing charge on a DRAM node or gate charging into single-molecule transistors or other nanoscale electronics, the critical parameter is the product $E_{br} \times Q_{in} = E_{br} \times A$, where $Q_{in} = \frac{\mu \varepsilon}{\varepsilon_0}$ is the inverse dielectric constant of the material. Amorphous $Zr_2Sn_2Ta_2Ti_3O_{16}$ (aZTT) can deliver values as high as $E_{br} \times A = 35 \mu\varepsilon/cm^2$ (equivalent to a surface electron density of $\approx 2 \times 10^{14}$ cm$^{-2}$), compared to $2 \times 7 \times 10^3$ cm$^2$ for SiO$_2$ and $\approx 8 \mu\varepsilon/cm^2$ for optimized Al$_2$O$_3$. We have prepared aZTT using two different vacuum deposition systems, using two radically different sputtering geometries ($8^\circ$ off axis and conventional on-axis), and using two types of plasma power sources (DC and RF). We have demonstrated comparable results in each case after optimizing the deposition conditions ($p_{O_2}$, $p_{Ar}$, substrate temperature, etc.). We have measured the frequency and temperature dependence of the permittivity over the range $100 \times < f < 1 \times 10^9$ Hz, $T=300\text{K}$. The results indicate that the polarizability is due to electronic and lattice contributions, with no low-frequency orientational or ionic contributions. We have also studied the effect of processing (annealing in oxidizing and reducing ambients) on the properties of this material. While aZTT may not be suitable for conventional Si IC DRAM applications that involve subsequent high-temperature processing, its superior performance makes it uniquely attractive for applications where the thermal budget is limited, such as in scientific studies on polymer-based integrated electronics.

CS. 23
Electrode effect on microwave properties of ferroelectric $Ba_{1-x}Sr_x TiO_3$ thin film. Won-jeong Kim$^1$, Sang-soo Kim$^1$, Tae-kyun Song$^1$, Seong Eun Moon$^2$, Kyeong-Young Kim$^2$, Su-Jae Lee$^2$, Seok-Ki Han$^3$, Young-Tae Kim$^3$, Han-Chul Hyun$^3$ and Min-Hwan Kwak$^3$; Physics, Chungnam National University, Chungnam, South Korea.

Ferroelectric materials are used to increase the processing speed of microstrip bandpass filters (CPW) by minimizing the effective dielectric constant of the dielectric layer.

Furthermore, extracting dielectric constant of high-k thin films from the measured microwave properties, such as $S$ parameters, are very difficult. The well known dielectric permittivity method for $C_0$ and $\tan \delta$ is $0.8 \pm 0.4$ or the average for all substitutions is $0.8 \pm 0.4$. The Goldschmidt tolerance factor, $t$, for $BaTiO_3$ is close to 1.0, an instability point. Substitutions with ionic radius larger than $T^{1+}$ result in compositions with more stable $T$. Substitutions in the perovskite structure, particularly with ionic radius much smaller or larger than $T^{1+}$ result in compositions with smaller tunneling. These materials are being used in a novel device structure that has been shown to provide broadband and variable true-time delay. The device is designed for use in dynamic antenna applications over the military specified temperature range.

CS. 24
Integration Of Passive Components In Power Electronics. Ferroelectric Films Prepared From Soft Polymer Precursors. Sophie Guillemet$^1$, Madmous Boucha$^1$, Christophe Calmes$^1$, Bernard Durand$^1$, Vincent Beylot$^2$ and Thierry Lebey$^3$; 1 Material Science, Universite Paul Sabatier, Toulouse, France; 2Electrical Engineering, Universite Paul Sabatier, Toulouse, France.

The trend in electronic industries is to offer smaller and lighter products of lower costs and increased features. Nevertheless, passive components miniaturization is an important challenge in the field of power electronic integration since they occupy more than 70% of the substrate surface. One of the possible integrated passive technologies is a multilayer ceramic construction combining different functional ceramics in a 3D architecture. A particular structure of filter has been presented in a previous paper. It consists in a stack structure of layers of both metal and dielectric materials. The present work, we have focused on the elaboration of the ferroelectric film started from the powder synthesis. Barium titanate is the material of choice which presents the best trade-off between the desired electrical characteristics and the compatibility with the other materials that form the overall structure. Nanoparticles of $BaTiO_3$ powders have been elaborated from 2 different soft chemistry methods, namely co-precipitation and hydrothermal synthesis. A particular attention is paid to the optimisation of the synthesis parameters in order to increase the powder quality. In the 2 cases, the most important characteristic of the powders necessary to obtain a good sintering were determined and compared. The ferroelectric properties of the films have been measured by dielectric constant and loss factor specific measurements. Different pastes have been prepared by mixing the powders with organic matrix. The paste containing the $BaTiO_3$ powder is deposited by the doctor blade method and sintered. The structural and dielectric properties of the films are determined and correlated with the powder characteristics. Films prepared from co-precipitation powders present improved characteristics, compared to those obtained from hydrothermal powders.

CS. 25
Tunable Microstrip Bandpass Filters Using Ferroelectric Thin Films With Constrained Gaps. Carl Henry Mueller$^1$, Fredrick W Van Keuk$^2$, Robert R Romanczuk$^3$ and Felix A Miranda$^3$; 1 Analog Corporation, Cleveland, Ohio; 2Ohio Aerospace Institute, Cleveland, Ohio; 3NASA Glenn Research Laboratory, Cleveland, Ohio.

Microstrip bandpass filters are attractive at K-band (12 to 18 GHz) and higher frequencies because of their small size. A problem that plagues microstrip filters at these frequencies is the inability to tune the resonator capacitance without introducing excessive losses as a result of the tuning mechanism. At a basic level, tuning is required to correct for manufacturing tolerances, and thus enable the filter to operate at the design frequency. At a more advanced level, tuning allows frequency selectable filters to be formed as a multi-channel filter bank. Previous efforts to introduce ferroelectric tuning into microstrip bandpass structures have been hampered by dielectric losses in the ferroelectric films. This paper expands on our previous efforts by understanding the use of selectively etched ferroelectric films to minimize RF losses without degrading tunability. Forming the films so as to form a constriction in the ferroelectric film, near the center of the gap, causes the electric field to be concentrated in the constrained region, thus creating a region with relatively low $\tan \delta$ compared to the
CS 20
Piezoelectric and Dielectric Properties of Thin Film 

Recent studies have shown that BaTiO$_3$ - M - O$_3$ (M=Zr, Hf) solid solutions stabilized in orthorhombic and rhombohedral phases exhibit enhanced piezoelectric and distinctive dielectric properties. There is, however, limited research on the properties of these materials in thin film form. BaTiO$_3$ - M - O$_3$ films were grown by Pulled Laser Deposition (PLD) on a number of thin film electrodes, including [La$_2$Sr$_4$]$_x$Co$_3$O$_y$ and Pt deposited on MgO and Si substrates. Textured films with controlled orientations were obtained. The effects of growth parameters (substrate temperature, oxygen partial pressure, laser fluency) and film composition on the ferroelectric and piezoelectric properties are discussed and compared with values obtained in the bulk.

SESSION C9: Joint Session with E9: Gate Dielectrics and Functional Oxides on Silicon Thursday, December 4, 2003 Room 207 (Hynes)

8:30 AM C9.1
Lanthanaum Oxide Thin Films For Advanced Gate Dielectrics. Hedi Vincent 1, Marie-Christine Hugon 2, Bernard Agnès 2, Michel Touzéni 2 and Vincent Le Gacq 1; 1 Research & Development, STMicroelectronics, Crolles, France; 2 Phasmat Materiaux, LPNP, Orsay, France.

For the past two years, the researches on advanced gate dielectrics have gained considerable attention since the technology roadmaps predict the need of a sub-32nm gate dielectric for sub-0.13um MOSFET devices in 2002. The thinning of the gate dielectric required by scaling rules, currently between 2 and 2.5nm in fabrication, will give origin to unacceptably high gate current arising from electron tunneling through the SiO$_2$ film. One possible solution is to use an alternative material to SiO$_2$ with dielectric constant (K) much higher than 3.9. Due to its high permittivity (K=38), La$_2$O$_3$ appears to be a good candidate. La$_2$O$_3$ films are deposited on Si substrates by rf magnetron sputtering of a La$_2$O$_3$ target in argon atmosphere. This film properties are studied as a function of deposition (rf power density, process pressure) and thermal annealing parameters (temperature, time). One of the important steps in our research of La$_2$O$_3$ film properties is to correlate the physical properties of the material (composition, density) determined by Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Analysis (NRA), X-Ray (O) 110 and X-Ray (K) emission. Optical Emission and Absorption Spectroscopy (OES). Whatever the deposition conditions, the film composition is 0/La$_2$O$_3$ 1.3 ± 0.1 and their density is 7 ± 0.7g/cm$^3$ (bulk a=8.8g/cm$^3$). We have performed high frequency (1MHz, 1GHz, 1KHz, 1kHz) capacitance-voltage (CV) measurements on Ru$_x$/La$_2$O$_3$/Si MOSFET structures. With the device biased in accumulation regime, a permittivity of 30 mm deduced. The CV curve is described well defined accumulation, depletion and inversion regimes which indicate a low interface state density.

9:00 AM C9.2
Liquid Injection MOCD of Rare earth Oxides Using New Alkoxide Precursors. Paul Andrew Williams 1, Anthony C Jones 2, Helen C Apginial 1, Jeffrey M Ginkel 1, Paul R Chalker 1, Paul A Marshall 1, John L Roberts 1 and Lesley M Smith 1; 1 EPoch Limited, Bromborough, Wirral, United Kingdom, 2 Chemistry, University of Liverpool, Liverpool, Merseyside, United Kingdom, 3 Minerals Science and Engineering, University of Liverpool, Liverpool, Merseyside, United Kingdom.

Thin films of rare earth oxides such as La$_2$O$_3$, Pr$_2$O$_3$, Gd$_2$O$_3$ and Nd$_2$O$_3$ have potential applications as alternative high-k gate dielectric layers in silicon-based field effect transistors. MOCD is an attractive technique for the deposition of these materials, but progress has been restricted due to lack of suitable precursors. There are some reports on the use of metal alkoxide precursors, but these often require high temperatures and consume large amounts of solvent. An alternative potential problem. Although metal alkoxides have been widely used in MOCD, there have previously been no reports in the literature into the use of rare-earth alkoxide precursors in MOCD. This is because the hydrolytic stability of the highly positively charged lanthanide (III) ions leads to the formation of bridging intermolecular metal-oxygen bonds, resulting in many of the simple alkoxide complexes being polymeric or oligomeric, with a corresponding low volatility. However, the sterically hindered tertiary bis(2-methylpropoxy)alkylalkoxides, one example of which is [M = La, Pr, Gd etc.], in this paper the synthesis of a number of these new complexes is described together with their use in liquid injection MOCD.

9:15 AM C9.3

Thin films comprising group IV metal oxides are likely candidates for replacing SiO$_2$ in high-performance low power Si electronics where the effective electrical thickness of the gate oxide must be less than the equivalent of 1.0 nm of SiO$_2$. Elementa1 oxides such as ZrO$_2$ and HfO$_2$ have dielectric constants that are in the suitable range, c. 20-30, but crystallize readily under standard process conditions (1000°C for 5-20 seconds) rendering them unsuitable for use as gate dielectric diopents. It is known that crystallization can be suppressed by alloying with a main-group oxide such as SiO$_2$ or Al$_2$O$_3$, although these oxides exhibit a much smaller dielectric constant and therefore decrease the dielectric constant of the mixture. We have investigated the post-annealed crystallinity of various mixed transition-metal/main-group oxides using a composition-dependent approach. This technique allowed us to determine that the mole fraction of main group oxide in the Zr-Si-O, Zr-Al-O, and Hf-Si-O systems must be greater than 83%, 65%, and 78%, respectively, in order to avoid crystallization. The kinetics of transformation suggest that this conclusion is not sensitive to the anneal time, though, it is quite sensitive to the peak temperature. Evaluation of the dielectric constant in the same systems leads us to conclude that the useful dielectric constant is therefore limited to c. 6.9, 12.7, and 6.6, respectively. We conclude that the silicon oxides are not likely to be useful as replacements for SiO$_2$, while aluminas are more promising.

9:30 AM C9.4
Epitaxial thin film heterostructures of Pb(Mg$_{1/3}$N$_{2/3}$)O$_3$-PbTiO$_3$ relaxor ferroelectric films on silicon for high performance electromechanical systems. Dong Min Kim 1, Sang Dong Bu 1, Ching Boon Eom 1, Valmaoor Nigaranj 1, Jun Ouying 2, Ramaamorthy Ramaswamy 2, Venkat Narayanan 2, Susan Trott 2, Donald G. Lamar 2, W. Tim 3 and Xiaoqing Pan 3; 1 Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; 2 Materials and Nuclear Engineering, University of Maryland, College Park, Maryland; 3 Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, 4 Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Pb(Mg$_{1/3}$N$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) single crystal relaxor ferroelectrics yield significantly higher electromechanical coupling coefficient than conventional polycrystalline ferroelectric materials. A major challenge is to fabricate epitaxial PMN-PT thick films between epitaxial metallic oxides and integrate them into micro-electromechanical systems on silicon wafer. We have created epitaxial thin films with the highest longitudinal piezoelectric tensor coefficient ever realized on silicon substrates by (1) using Pb(Mg$_{1/3}$N$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) films, the microstructure in single crystal form is known for its giant piezoelectric response, (2) using epitaxial orientation, and (3) nanostructuring it to reduce the constraint imposed by the underlying silicon substrate. When subdivided by focused ion beam processing to reduce mechanical constraints, a 4 µm thick film shows a low-field d$_{33}$ of 325 pC/V/µm that increases to over 700 pC/V/µm, which is a factor of 4 higher than the highest strain achieved in Pb(Zr,Ti)O$_3$ thin films on silicon. These blazed micromechanical heterostructures can be used to fabricate radio frequency microelectromechanical systems devices with high strain and low driving voltage for miniature devices, high frequency ultrasound transducer arrays for medical imaging, tunable dielectrics, and capacitors for high-capacitance energy storage. We will discuss the effect of substrate constraint and thermal strain on the piezoelectric responses in heteroepitaxial PMN-PT thick films on silicon.
9:45 AM C9.5
-orientated Epitaxial Bi2Te3 Films on [001] Si
Yasuyuki Uchida1, Yasuhiro Nakashima1, James Lettieri, Darrel G. Schlom2, Jeremy Levy3, Wu Tian4 and Xiaoping Tan3. 1Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania, 2Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania; 3Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

We have been investigating the epitaxial growth of α-orientated Bi2Te3 on [001] Si for a novel quantum computing architecture in which an epitaxial ferroelectric film in close proximity to silicon is desired.1 Silicon is used because of its weak spin-orbit coupling for electrons and its preferred usage in semiconductor devices. The ferroelectric must be oriented such that its switching results in an electric field effect to confine the electrons laterally in the underlying silicon. The 4.5° lattice mismatch between Bi2Te3 and [001] Si is a typical growth problem when the mismatch is small, and the thermal expansion coefficient of silicon than Bi2Te3, have until now prevented the growth of α-orientated epitaxial Bi2Te3 films on [001] Si. This large lattice mismatch leads to the rapid relaxation of the lattice constant of the Bi2Te3 film to its bulk cubic lattice constant at the elevated growth temperature. As such a relaxed Bi2Te3 film is cooled from its growth temperature, it experiences biaxial tension due to the larger thermal expansion coefficient of the Bi2Te3 film compared to the silicon substrate. The film cools through the Curie temperature of the Bi2Te3 film, the α-orient of the Bi2Te3 aligns in the plane of the substrate (α-orient Bi2Te3) to reduce the biaxial tension. To achieve the desired α-orient epitaxial Bi2Te3 film on [001] Si, we used a buffer layer of relaxed Bi2Te3 on Si and Bi2Te3 films, which are maintained thin enough that they are commensurately strained to the underlying relaxed Bi2Te3 buffer layer. The XRD, TEM, and RHEED and in situ characterization of the films by XRD and TEM reveal epitaxial α-orient Bi2Te3 films with high crystalline perfection. The orientation relationship between films and substrate is α-Bi2Te3 (001) // Si (001) and Bi2Te3 films // (011) // Si (110) and. By applying a voltage across a conducting AFM tip and silicon substrate, the possibility of using α-orient Bi2Te3 films has been demonstrated. The obtained results have been simulated to observe the written domains, which have lateral extent down to 100 nm.1 J. Levy, Phys. Rev. A 64, 052506 (2001).

10:30 AM C9.6
Long Retention Performance of a MFIS Device Achieved by Introducing High-k Al2O3/Si3N4/Si Buffer Layer
Yoshinobu Fujisaki1,2, Kuniho Ike1 and Hiroshi Ishiwara1. 1Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan; 2Research and Development Association for Future Electronic Devices, Tokyo, Japan.

We introduced high-k Al2O3/Si3N4 buffer layer in MFIS (Metal-Ferroelectric-Insulator-Semiconductor) devices to realize long retention characteristics and succeeded to achieve a retention time longer than 2×1015 sec. This long retention characteristic is mainly due to the high-k Al2O3/Si3N4 film layer by reducing the density of retained charges with minimizing the leakage current. We prepared Si3N4 (0.9 nm) buffer layer by directly nitriding Si substrate with atomic nitrogen radicals.2 The nitriding was carried out at 700 °C. Then we deposited Al2O3 thin films on the buffer Si3N4 with atomic layer deposition (ALD) technique using Al(3C1)4 and H2O precursors.2 Since the ALD deposition was carried out at low temperature (300 °C), we had to anneal the film to eliminate the defects in the film. The post annealing were performed at 1000 °C for 30 sec in 5% O2/95% N2 ambient. On this stacked buffer layer, we deposited 150 nm-thick Bi4La0.7TiO3 (BIT) ferroelectric films using LSMCD (Liquid Source Mixed Chemical Deposition) technique. The BIT films were crystallized at 800 °C in oxygen ambient. The deposited BIT films oriented mainly along the α-orient of crystal lattice normal to the Si substrate. Since our Si3N4 buffer layer is highly dense, it prevents the underlying Si substrate from being oxidized during the post annealing of Al2O3 films and the crystallization of BIT film. Therefore, the stacked Al2O3/Si3N4 buffer layer can preserve high capacitance density and low leakage current even after highly oxidizing thermal treatments.3 The interface state density in the ALD-Al2O3/α-Bi4La0.7TiO3/α-Si3N4 stacked insulator and a Si substrate is as low as 1011 cm−2 eV−1. The current density less than 10−8 A/cm2 is realized under the 1V bias application using films with the capacitance density of 120 F/μm2. The memory window width and the ON/OFF current ratio in the CV characteristics with ± 6V voltage scan. With this MFIS diode, we found that more than 60% charges are retained for 17 days. This excellent retention characteristic is attributable to the high insulating property of the ALD-Al2O3/α-Bi4La0.7TiO3/α-Si3N4 stacked insulator and also attributable to the perfect elimination of defects at the interfaces in the MFIS structure. This work was done under the auspices of the R&D Promotion Cooperation in Advanced Technologies (Si-based General Generation Ferroelectric Memory), supported by the New Energy and Industrial Technology Development Organization (NEDO), and managed by the R&D Association for Future Electronic Devices (FED). Reference 1. Y. Fujisaki, H. Ishiwara, Jpn. J. Appl. Phys. 50, L1075 (2011). 2. A. Paranjpe, S. Gopinath, T. Omstand and R. Bubber, J. Electrochem. Soc. 148(9), G465-G471 (2001). 3. Y. Fujisaki, K. Ikeki, H. Ishiwara, M. Mao and R. Bubber, Appl. Phys. Lett. 82, 3501 (2003).

11:00 AM C9.7
Investigation of Retention Properties for YMO3 Based Metal-Ferroelectric/Insulator-Semiconductor Capacitors.
Tohru Ishiyama, Daisuke Itô, Hiroshi Sakata, Norimichi Shigemoto, Koher Harańce and Norifumi Fujimura, Graduate School of Engineering, Department of Applied Materials Science, Osaka Prefecture University, Sakai, Osaka, Japan.

Ferroelectric gate-field-effect transistors (FETs) have been investigated for the applications to nonvolatile memory devices due to the nondestructive read operation and the advantages of decreasing memory cell size. Because of the difficulty to obtain the excellent ferroelectric-semiconductor interface, ferroelectric gate FETs with a metal ferroelectric-metal-insulator-semiconductor (MF/MIS) structure have been widely studied. We have investigated YMO3 films for MFIS type ferroelectric gate FET, because YMO3 has suitable properties for this application such as small spontaneous polarization and low permittivity. We have succeeded in fabricating MFIS epitaxial films with 20% of 3.4 μC/m2. The ferroelectric substrates and epitaxially grown films (YMO3)/[111]Ta2O5/[111]Si capacitors with ferroelectric type C- V hysteresis loops. In this study, the degradation mechanism of memory retention for Pt/YMO3/Nb2O5/Si capacitors was discussed using the leakage current analysis and the pseudo isothermal capacitance transient spectrum (pseudo ICTS) and others. Although the retention time of as-deposited capacitors was 104 sec, it was prolonged up to 105 sec when the leakage current density was reduced from 10−6 A/cm2 to 2×10−8 A/cm2 by the annealing under N2 ambient. For the leakage current of the Pt/YMO3/Nb2O5/Si capacitors, it was revealed that Schottky emission was dominant at memory retention state; however, Poole-Frenkel emission occurred when we applied it. Since the activation energy of the Poole-Frenkel emission of the Pt/YMO3/Nb2O5/Si capacitors agreed with that of Pt/YMO3/Pt capacitors, the origin of the Poole-Frenkel emission existed in the YMO3 layer. It was also found that applied voltage with uncessarily long time generated the ferroelectric layer Poole-Frenkel defects in the ferroelectric layer and that the amount of the defects greatly affected the memory retention time. These results suggest that Poole-Frenkel defects work as traps sites of the charge and that the charge injection to the PooleFrenkel defects occurs gradually until it neutralizes the remanent polarization of the Pt/YMO3/Nb2O5/Si capacitors.

11:15 AM C9.8
Characterization of Metal-Ferroelectric-Metal-Insulator-Semiconductor (MF-MIS) FETs Using Sr3(SnO2)xBi2O3(1−x)Oy/Si on Insulated Si Substrates
Hiroshi Tsuchiya1 and Eiichiro Yoshimura1. 1Precision & Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; 2RIEC, ITI-21, Tohoku University, Sendai, Miyagi, Japan.

Metal-ferroelectric-metal-insulator-semiconductor (MF-MIS) structures has attracted considerable interest for ferroelectric-gate transistor applications. MF-MIS structure has a merit that one can design the area of an MF capacitor (Sp) and that of an MIS diode (Sd) independently. To mitch the ferroelectric polarization with the charge of FET channel, a large area ratio (Sp/Sd) is usually used in MF-MIS-FETs. However, Sp/Sd=1 is desirable for large sensitive integration. We previously reported that Sr3−x−ySn+x−yBi2O3 (SBSB) thin film has small remanent polarization and large coercive field, which are suitable for MF-MIS structures. In this work, we have fabricated and characterized Pt/SrO/SrTiO3 /Bi2O3/SnO2/SBT/PMOSFET (W/L=50/50μm). The crystallization of SBT was done in O2 at 850°C. The thickness of SBT and SiO2 is 13nm and 10nm, respectively. A memory window of about 20 was obtained with an inverted gate voltage of −2V from drain current-gate voltage (Ip−Vg) characteristic of MF-MIS-FET even with Sp/Sd=1. This value of memory window agrees with the product of coercive field and thickness of SBT films. This indicates that the hysteretic loop of SBT is available even if the MF capacitor and the MIS diode have same area. This work was supported by a Grant-in-Aid for Scientific Research (No.14040244, No.14565117, and No.15060157) from the Ministry of Education, Science, Sports, and Culture. This work was performed under the auspices of the R&D Projects in Cooperation with Academic Institutions (Next-Generation.
Ferroelectric Memory), supported by NEDO and managed by FED.

11:30 AM C10.9
Selective Deposition Of C-Axis Oriented PbSeGe3011 On Patterned Hi-K Gate Oxide By MOCOVD Processes.
Tongmin Li, Bruce Ulrich, Dave Evans and Sheng Teng Hsu; PTL, Shenyi Labs. of America, Inc., Canonsburg, Washington.

MFIS (Metal/Perovskites/Insulator/Silicon) transistor ferroelectric memory devices have been fabricated. C-axis oriented PbSeGe3011 (PGO) thin films showed very good ferroelectric and electrical properties for IT-memory device applications. Extremely high c-axis oriented PGO thin films can be deposited on high k gate oxide, and functional IT-memory devices with PGO MFIS memory cell have been fabricated. The integration process induces damage such as etching damage that degrades the properties of FRAM devices and high surface roughness resulted in difficulty for alignment. In order to solve this problem, selective deposition processes have been developed to simplify integration processes and improve the properties of MFIS transistor ferroelectric memory devices. Based on different deposition rates of ferroelectric materials on high k oxide and silicon dioxide, we selectively deposited a c-axis oriented PGO film on patterned high k oxide such as ZrOx (x=3.2), HfOx (x=2.9), TiO2, etc. and their mixtures other than on SiO2. By patterning the high k dielectric, the PGO deposition is limited to just the preferred pattern area. SEM, EDx and x-ray measurements further confirmed that c-axis oriented PGO thin film deposited on field SiO2. Sometimes during annealing of the PGO, staining of the field oxide occurs. This can be eliminated by not depositing PGO in the field area. The morphology of the PGO film can be very rough which can cause charge injection problems if it is impossible. Again by confining the PGO deposition to just the patterned area will also eliminate the roughness problem for alignments. Also etching damage is eliminated since there is no need to etch the PGO film, which improved the properties of FRAM devices.

SESSION C10 Piezoelectric, Optical and Pyroelectric
Chair: Susanna Hoffmann-Esifier and Paul Murali
Thursday Afternoon, December 4, 2003
Room 203 (Hynes)

130 PM C10.1
Ferro- and piezoelectric properties of Bi_x,Pr_yTb_zO_s polycrystalline thick films with Ps-vector orientation.
Hirofumi Masuda, Satoshi Ito and Taktshi Ijima; SIRC, AIST, Takahama, Inbiki-ken, Japan.

A principle to synthesize Ps-oriented films with Bi_xPr_yTb_zO_s (BPT) type structure on Si substrate was presented and the alignment of the spontaneous polarization Ps vector along the film normal was demonstrated as the key role of ferroelectric polarization of BPT-based ferroelectric films. 1.2 µm-thick and Pr^3+ substituted Bi_x,Pr_yTb_zO_s (BPT; x=0, 0.3, 0.5, 0.8) were fabricated with preferred orientation growth on (111)/Ti/SiO2/Si (200/110) substrates by chemical solution deposition (CSD) method. BPT film of x=0.3 exhibited superb ferroelectric properties of remnant polarization 2P_r=95 µC/cm^2, spontaneous polarization P_s=50 µC/cm^2, and coercive field E_c=84 kV/cm. These values clearly manifested the alignment of Ps-vector along the film normal. The film also exhibited uniform response of electrical field induced displacement with improved piezoelectric coefficient of AFM-D=36 µm/V. During the decomposition of precursor solutions, IO_3 oxygenized layers were formed at the surface of Ir bottom electrode and the nucleation of grains with a and b-axis orientation was accelerated by lattice matching to the (101) plane of IrO_3 with rutile-type structure. On cooling after annealing above the Curie temperature Tc for grain growth, in addition, a differential thermal expansion between film and substrate Si introduced in-plane lateral stress perpendicular to the Ps-vector out of plane. The facts that a relatively poor value of 2P_r=26 µC/cm^2 was measured in BPT film while pronounced decrease in Pr values with increasing x in the range of 0.3-0.7 was observed suggested that the lattice matching alone was insufficient to explain the separation between grains with a-axis orientation and b-axis orientation. The one part of these orientations doesn’t contain Ps component along the film normal, the degradation of polarization can be expected in the films of BPT-type structure with mixed orientation of a and b-axis.

200 PM C10.2
Thickness and Composition Dependence of Piezoelectric Properties of PZT Thin Films in MEMS Devices.
Seung-Hyun Kim, Chang Young Koo, Jung-Hoon Yoon, Jong-Hyeon Cheon and Jongwoong Hn; R&D Center, INOSTEK Inc., Ansan, Gyeonggi, South Korea.

Electromechanical properties of ferroelectric thin films have received significant attention in view of their applications in future generation of ferroelectric/ferroelectromechanical systems (MEMS). Among ferroelectric family, PZT is considered as most promising candidates for these applications since they can produce high mechanical strain under applied electric field. However, stress induced in PZT thin films due to changes in the films by the substrate and other deposition parameters such as low breakdown voltage and insufficient poling has limited to apply these thin films to MEMS applications. From these reasons, it has been observed that the experimental results between computer effects and mechanical properties of bulk ceramics are not identical. Moreover, in bulk PZT materials, the piezoelectric properties are dominated by contributions from moving domain walls. However, in PZT thin films, the role of domain wall that is extrinsic effect, has not been clarified and experimental results have revealed conflicting evidence. These discrepancies might be due to film orientation, thickness, substrate effects, measurement methods, film quality and many other parameters. To achieve more systematic evaluation, we have performed extensive study based on experimental results of the piezoelectric and dielectric properties of PZT films, thickness range from 50 nm to 5 µm, by newly developed chemical solution deposition method with three different compositions (Zr/Ti =30/70, 52/48, 70/30) and two different orientations [100] vs. [111]. Here, I summarize the relationships between the effects of film orientation and composition as a function of thickness on the piezoelectric and dielectric properties and their contribution to their properties in detail. *This work is supported by National Research Laboratory (NRL) program

2:15 PM C10.3

We have studied the lattice distortions and piezoelectric properties of epitaxial Pb(Zr0.52Ti0.48)O3 (PZT) films in the thickness range of 0 nm and up to 4 µm. The films were grown on both [100] SrTiO3 and [100] Si substrates by on-axis magnetron sputtering. As film thickness increased, the out-of-plane lattice parameter decreased and the in-plane lattice parameter increased. These lattice parameters approached to a rhombohedral lattice parameter values although the composition is in the tetragonal region. The polarization and piezoelectric coefficient increased with film thickness. The polarization and piezoelectric coefficient of 4 µm thick PZT film on SrTiO3 which is continuous film capacitor was 400 µC/cm^2 and 180 µm V^-1. When subdivided by focused ion beam processing to reduce mechanical constraints, a 4 µm thick film shows a low-field D33 increases to 376 pC/N under bias, which is twice higher than the clamped value in Pb(Zr0.52Ti0.48)O3 thin films on silicon. This is attributed to a large heterogeneous constraint and material getting softer from rhombohedral composition. The PZT films on silicon exhibit less tetragonality than PZT on SrTiO3, which explains the higher piezoelectric coefficient of PZT on silicon. Moreover, the PZT films on SrTiO3 show higher polarization than the PZT films on silicon because of their higher tetragonality. These are attributed to the film microstructure formed by thermal reorientation and thermal expansion mismatch between the films and substrates.

2:30 PM C10.4
Modeling of Piezoresponse of Nanostuctured PZT Films. JH Li, V Nagajaran, I Chen, R Ramesh and A L Roybarud; Department of Materials Science and Engineering, University of Maryland, College Park, Maryland.

Patterning thin ferroelectric (FE) films into discrete islands is an effective way to release the constraint imposed by a substrate and enhance film piezoresponse. The converse piezoresponse measured by the surface displacement of FE islands, with lateral size changing from a monolayer to a substrate dimension, has been modeled using Finite Element Method. The modeling and the theoretical analysis have shown that piezodeformation of the islands results in a local bending of a substrate in the vicinity of the island. The bending deflection is larger when the substrate is softer. The bending, together with changing by the substrate, decreases the effective D33 of the island. We also discuss the effect of the top electrode to the contribution of the modeled D33 when using the converse method. Piezoresponse of different size island capacitors with PbZr0.52Ti0.48O3 (50/50) /STO/Si and PbZr0.52Ti0.48O3 (50/50) /STO/Si and PbZr0.52Ti0.48O3 (50/50) /STO/Si heterostructures has been calculated. The results of modeling are in good agreement with experimental data on islands obtained by piezoresponse microscopy. This work is supported by the NSF-MRSEC under contract No. DMII-080008.
2:45 PM C10.5  
Bi-Formatted Ferroelectric Polymers, Jean Nino and Susan Tauber-Kirklin; Materials Research Institute and Materials Science and Engineering Dept, Penn State, University Park, Pennsylvania.

To date, most MEMS sensors and actuators employing ferroelectric films use lead zirconate titanate (PZT) films as the transducer. Randomly oriented PZT films (1-8 micron thick) show piezoelectric e,s, coefficients of 0.02-0.08 C/m^2. Although ferroelectric response with good temperature stability can be achieved in (001) rhombohedral-distorted perovskites, ultimately the temperature stability of the piezoelectric response is governed by the transition temperature of the compound. Thus, it is interesting to consider alternative ferroelectrics based on BiMgO3 - PTiO3 systems with higher transition temperatures. This paper focuses on the growth and electromechanical properties of films, where Mg = Sc, Fe, and Mg2O3. Films were grown by RF magnetron sputtering on SrRuO3/(100) LaAlO3 as well as Y2O3/YSZ/Co3O4-biased textured NiW substrates. Targets used for the growth were Bi and Pb rich to compensate for loss during growth. It was found that the SrRuO3 phase was unstable in the presence of too much Bi. High quality films could be prepared from targets 10 mole% rich in Bi2O3 and 20 mole% rich in PbO. For example, Bi2O3 - PTiO3 films grown at 600°C, a target to substrate distance of 4 cm, in a 90% O2 / 10% O3 ambient on SrRuO3/(100) LaAlO3 were phase-pure perovskites. It was found that many of the films are somewhat deficient in Pb and excess in Bi. The resulting films were good electric insulators, with room temperature dielectric constants of 850, and loss tangents of 0.08. The piezoelectric properties were observed in epitaxial 0.8Bi2O3 - 0.2PbTiO3 / SrRuO3 / (100) LaAlO3 films, which show e3, = -12 C/m^2, coupled with a transition temperature of 460°C.

3:30 PM C10.6  
Shape of Dielectric Hysteresis Loop for Non-Ferroelastic Switching, Alexander K. Tagansky1, Paul Muralt2 and Jan Fousk2.

1 Ceramics Laboratory, EPFL, Swiss Federal Institute of Technology, Lausanne, Switzerland. 2 Department of Electrical Engineering and Electromechanical Systems, Technical University of Liberec, Liberec, Czech Republic.

The shape of piezoelectric hysteresis loops (piezoelectric coefficient d vs. applied electric field E) is typically described by the polarization hysteresis loops (polarization vs. applied electric field). The features of the piezoelectric hysteresis loops, which are often observed, are: (i) a "hump", i.e. when E decreases from the tip of the loop down to zero, it passes through a maximum, (ii) a narrowing of the loop close to its tips. Despite wide experimental observations of these features, they have not been entitled to a theoretical explanation yet. In this paper, we show that the origin of these phenomena is the domain contribution to the dielectric relaxor. The shape of the loop is determined by the polarisation loop, C-V curve, and information of the lattice contribution to the dielectric permittivity. It is shown that a large enough value of the domain contribution to the dielectric permittivity necessitates the appearance of the hump and self-crossing. The theory is compared to the experimental data on piezoelectric thin films.

3:45 PM C10.7  
Fabrication and Characterization of Bi(TiO2) Optical Waveguides, Yoon Kim, Yushik Avrahami, Henry J. Tuller, Luciano Soto, Francisco Lopez-Goay and Peter T. Rakich; Microphotonic Center, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The possibility of creating Bi(TiO2) waveguides and optical components on oxide substrates has been demonstrated in recent years. There is great incentive to try and replace these achievements on silicon based wafers for integrated optical applications. The buffer layer between Si and Bi(TiO2) plays a major role in determining the quality of the film and its optical properties. Films of Bi(TiO2) were grown on Si using Pulsed Laser Deposition (PLD) with a number of buffer layers, including MgO. The effect of growth conditions and buffer layer on the crystalline properties of the Bi(TiO2) films was investigated. Waveguides were formed by e-beam lithography of the films and the waveguides (insertion and absorption loss, index of refraction and birefringence) will be presented and correlated with film quality and orientation.

4:00 PM C10.8  
Submicron Ferroelectric Domain Engineering in LiNbO3 Thin Films grown by Liquid Phase Epitaxy, Je-Won Son1, Yoon Yoon2, Sergei S. Orlov3, Bill Phillips5, Ludwig Galambos1, Lambertus Hesselin1 and Vladimir Yu. Shari2; Materials Science and Engineering, Stanford University, Stanford, California; Applied Physics, Stanford University, Stanford, California; Institute of Physics and Applied Mathematics, Ural State University, Ekaterinburg, Russian Federation.

We describe novel grating structures of submicron domains in LiNbO3 films. Domain engineering in LiNbO3 has been studied extensively for various electro-optic devices. Recently, submicron domain structures grown in LiNbO3 films have been demonstrated, however, growth and characterization of these domains remain unresolved. Domain growth has been driven by the formation of Li2O, which is released during furnace cooling. The growth and characterization of these domains is now being studied using a combination of X-ray diffraction, optical microscopy and atomic force microscopy. We demonstrate submicron ferroelectric domain engineering in liquid phase epitaxy (LPE) LiNbO3 thin films on LiTaO3 substrates using a direct-write electron beam poling for waveguide applications. LiNbO3 thin films of several-micron thickness were grown using a flux melt of 20 mol% LiNbO3 -80 mol% LiVO3. The typical growth temperature was 900-910°C, and resulting films have a single crystal structure with the crystallinity comparable to that of the substrates. The films grown on LiTaO3 substrates are planar waveguides supporting both TE and TM modes at λ=830nm, and exhibit a step index profile. The films are single domain, α-Z oriented on both α- Z surface of LiNbO3 substrates, and also on LiTaO3 substrates. To engineer domain structures in α-Z oriented LPE LiNbO3 films, a direct-write electron beam poling was implemented. The opposite side of the e-beam exposed surface is coated with Au for a ground electrode, and LPE LiNbO3 films are exposed to e-beam radiation with varying doses ranging from 500 μC/cm² to 3000 μC/cm². For the 3000 μC/cm² dose the poling of the oxide wave is observed. The typical wave period is 300 nm, and the thickness of the oxide layer is 50 nm. The submicron domain structures in LPE LiNbO3 films, on Z-LiNbO3 substrates, the domain orientation in both the film and the substrate are the same, therefore the inverted domain structure penetrates the substrate. On the other hand, the oriented domain structure is isolated in the homeopolar LiNbO3 film in the Z film / α-Z substrate system and the LiNbO3 / LiTaO3 heteropolar system. It is shown that we can engineer the domain structure of LPE LiNbO3 films by using the direct e-beam poling, even though the whole domain structure penetrates the thickness is multilayered as in the LiNbO3 / LiTaO3 system. The domain engineering in the LiNbO3 / LiTaO3 system is particularly interesting since it has a step index waveguide suitable for efficient radiation guiding. The results of the e-beam experiments on a single crystal LiNbO3 and a LPE LiNbO3 film using the same e-beam scan parameters, the definition of the domain structure is enhanced in LPE films compared with domains in a single crystal LiNbO3. Moreover, merging of domains is prevented in LPE LiNbO3 films, resulting in submicron domain structures. We obtained structures with a 0.5 μm period consisting of ~400 nm width domains extending 3 μm in the LPE LiNbO3 films, which could not be obtained in a single crystal. We propose that the defect structure, such as the misfit between the film and the substrate and point defects in the LPE films can possibly explain these positive results. Further optimization of the domain structures by changing scanning parameters and materials is presently under study.

4:15 PM C10.9  

The role of internal stresses on the pyroelectric properties of ferroelectric thin films is analyzed theoretically via a thermodynamic model. The pyroelectric coefficient as a function of the misfit strain is calculated for (001) Bi(Nb0.98(Ti0.02)O3 epitaxial thin films. The effect of applied electric field on the pyroelectric coefficient is also discussed. It is shown that the pyroelectric response is highly dependent on the misfit strain in epitaxial thin films. Enhanced pyroelectric response at high as 0.66 pC/cm² K can be achieved by adjusting the misfit strain, especially in the vicinity of the ferroelectric to paraelectric phase transformation. The analysis shows that internal tensile stresses are particularly not desirable with significant degradation close to an order of magnitude in the pyroelectric response. Discussion on integration of the ferroelectric thin films with Subed technology of ICs for pyroelectric device applications is provided.

4:30 PM C10.10  
Piezoelectric Constants under Large Electric field in the Epitaxial Ferroelectric thin films, Long Chen, V Nagrani, J Ouyang, R Ramesh and A L Royboud, Department of Materials Science and Engineering, Univ. of Maryland, College Park, Maryland.

We present the theoretical and experimental results of pyroelectric-related effects induced by large electric field in thin ferroelectric (FE) single domain and 180 degree polycrystal films. The linear electric field effect in FE lead zirconate titanate (PZT) thin films have been reported and
calculated by using a Landau-Devonshire-type phenomenological thermodynamic approach for tetragonal single domain case. The tunability of the polarization responses and its dependence on film/substrate microstructure and elastic compliance of thin films are characterized quantitatively. The experiment results of piezoelectric scanning microscopy (PFM) of PZT epitaxial single domain thin films matches well within the range of our theoretical estimation. In the second part we present our work on the theoretical modeling of the converse piezoelectric effects in the FE 180 degree c-domain with opposite polarization vector. In such case, due to opposite polarities, the applied large electric field induces huge internal stress and thereby changes the dielectric properties of thin films. Since the coercive field of ultra thin films can be close to intrinsically high, the converse switching at room temperature in switching. Our theoretical calculation shows that domain switching effects may inhibit the nucleation of 180 degree domain when a large negative pulse is applied to a single domain. As an evidence of the relaxation of piezoelectric due to this domain changing effect, we have discussed the observation of newly formed 90 degree c-domain (twins) at local poling under a biased AFM conductive tip in epitaxial Pb(2Zr0.2Ti0.8)O3 thin films via PFM. This work is supported by the NSF under Grant DMR 0220152 and NSF-MRSEC under contract No. DMR-0600818.

4:45 PM C10.11
Investigation of the piezoelectric properties of PZT films, Jun Ouyang1, V Nagrani1, H M Zheng2, Z K Mn3, S Y Ying1, L Chen1, J Melngailis4, A L Roylance1, R Ramsey1, D M Kim2 and C H Eom2 1Dept. of Materials Science and Engineering, University of Maryland, College Park, Maryland; 2Dept. of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin.

Lead Zirconate Titanate (Pb(Zr0.52Ti0.48)O3) thin films with compositions close to the morphotropic boundary (x=0.5) (MPB) for sensor and actuator applications in microelectromechanical systems due to their high piezoelectric coefficients. Recent Abinitio calculation by Cohen and single crystal work on PZT-by Shrot and others suggested enhanced piezoelectric performance in ferroelectric materials if a field-induced phase transformation occurs. However, in thin films, the phase transition is inhibited by substrate-induced constraint. The motivation of our work is to investigate such field-induced transition in PZT films by creating nanostructured islands, which are not clamped by substrate. We report on the measured out-of-plane piezoelectric coefficient for PZT films with composition close to the MPB. The film thickness is kept at 150 nm in order to have a full range of aspect ratio (island lateral size/film thickness). To investigate the possibility of inducing a phase transition by using a suitable template, SrTiO3 substrates with 3 different crystallographic orientations - (100), (110), (111), are utilized. We have studied in detail the effect of crystallographic orientation on the piezoelectric performance of PZT films. By using a combined approach of phenomenological theory and tensor mathematics, the theoretical piezoelectric coefficients for both clamped and unclamped capacitors in different orientations are calculated, assuming a monodomain condition. On the other hand, it is necessary to have films oriented away from the polar axis to achieve a phase induced phase transition. This work is supported by the NSF-MRSEC under contract No. DMR-0600818 and partially supported by the NSF under contract No. DMR-0220152.

SESSION C11: Poster Session
Chairs: Susanne Hoffmann-Eifert, Vikram Joshi and Angus Kang
Thursday Evening, December 4, 2003
8:00 PM

C11.1
Fatigue Behavior and Influence of the Surface Morphology on Polarization Reversal in MOCVD Ir/PZT/Pt Films, Vladimir Ya. Shair1, Ivan S. Butarin1, Ekaterina V. Nikolenok1, Eugene I. Shishkin1, Dmitrii Kuznetsov2, Paul McIntyre3, Lawrence Schloss4 and Maxim Kelman5 1Institute of Physical and Applied Mathematics, Urals State University, Ekaterinburg, Russia; 2Materials Science and Engineering, Stanford University, Stanford, California.

The fatigue effect during cyclic switching has been studied in MOCVD PZT/FIr/Pt films with different thickness. The switching current data analysis allows to extract the evolution of the internal bias field distribution function. Important role of the surface morphology on the switching current has been demonstrated. We have investigated experimentally the fatigue phenomena by analysis of the switching current data during cycling in metallic chemical vapor deposition grown Pb(Zr0.52Ti0.48)O3 thin films ranging in thickness from 70 to 400 nm with Ir bottom and Pt top electrodes. Atomic force microscopy in contact mode has been used to measure the surface morphology with high resolution. The hysteresis loops and switching currents have been measured in triangular pulses in frequency range from 10 to 100 Hz. The original mathematical treatment of switching current data recorded during hysteresis measurement allows to extract the evolution of internal bias field distribution function during long-time cyclic switching. It was shown that increasing of switching time and changing of the switching current shape is correlated with growth of the internal bias field dispersion. All results are in accordance with the model of self-organized frozen domain switching during cyclic switching proposed by us recently. The proposed fatigue mechanism is related to spatially inhomogeneous imprint effect. The influence of the film morphology on the spatial distribution of the electric field in the bulk has been calculated and taken into account while analyzing the current data. The strong effect of nonuniform spatial distribution of applied field has been demonstrated. The obtained results are correlated with the crystallographic phase distribution in these films, which have been previously observed, and this dependence on film thickness and thermal history. Preliminary results on the effects of UV light exposure on fatigue of these PZT films will be presented also. The research was made possible in part by RFBR (Grant 01-02-17443), by RFBRDFG (Grant 02-02-04016), by Ministry of Education RF (Grant E03-3.4-395) and by program "Basic Research in Russian Universities" (Grant No. 06.01.01.01), and by Award No BESC-005 of CRDF.

C11.2
Crystalization of Sm-100 nm- Thick Bi4-xLaxTi3O12 Films on Silicon Substrates and Poly-crystalline Bi4-xLaxTi3O12 Films on Si Substrates and Poly-crystalline Bi4-xLaxTi3O12 Films on 

Poly-crystalline Bi4-xLaxTi3O12 thin films were formed on silicon substrates, and crystallization of the films was investigated by X-ray diffraction (XRD) and X-ray Reflection (XRR) analysis. After chemical cleaning and HF treatment of 1% SnO2+HCl substrates, a precursor solution for BLT was spin-coated on the silicon substrates and the samples were dried at 150 °C in the atmosphere. Subsequently, the samples were annealed in a furnace. Furthermore, in the case of electrical measurement Au electrodes were formed on the film. The film thicknesses after the crystallization annealing were evaluated to be 50-50 nm by XRR analysis. When the films were annealed in the temperature range from 550 to 650 °C the crystallization into bismuth-oxide layered perovskite structure was confirmed by XRD. The diffraction intensities increased and the peak widths decreased as the annealing time increased from 10 to 120 min. Also, atomic force microscope (AFM) observations indicated that grain growth occurred during the crystallization. X-ray reflectivity analysis and FTIR measurements indicated that an interfacial layer was formed during the crystallization. Furthermore, growth of (100)-oriented grains was observed by pole figure measurements. These is a difference of orientation of the grains between the films crystallized at 550 and 600 °C. Current-voltage (LV) and capacitance-voltage (CV) characteristics of Au/BLT/p-Si structures were measured at room temperature. The leakage current was lower than 25 nA/cm² at the gate voltage Vg of 3 V. Hysteresis was observed in CV characteristics at frequency range from 10 kHz - 1 MHz. The hysteresis voltage width depended on the crystallization annealing temperature, and so it may be related to the orientation of crystallization in film. The hysteretic width of the CV curve for the MFS structure, the BLT thin film which was crystallized at 550 °C, was about 0.3 V with the sweep gate voltage of ±3 V at 1 MHz. This seems to indicate that the coercive field (Ec) was about 33 kV/cm.

From the analysis of the flash-lump voltage shift, fixed charges and traps in the film and the interfacial layer were discussed.

C11.3
Frequency-Dependent Electromechanical Response in Ferroelectric Materials Measured via Piezoresistance Force Microscopy, Andrei Khachkin1, Igor Belkin1, Vladimir Shvartsman1 and J. Manuel Herrero2 1Dept. of Ceramics and Glass Engineering, CICICO University of A Coruña, A Coruña, Portugal; 2Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain.

Piezoelectric properties of ferroelectric materials are frequency-dependent, which can be a limiting factor for their applications as sensors and actuators operating at high speed. The frequency dependence of the piezoelectric response is generally attributed to the reversible motion of the ferroelectric domain walls moving in the random potential of defects. In most cases, this dependence can be described by the logarithmic law until very high frequencies where the domain motion is not fast enough to respond to the external driving field. In the last year, the piezoelectric response is actively investigated at the nanoscale using the Piezoresistance Force Microscopy (PFM) capable of imaging domains
with the nm resolution and measuring piezoelectric properties just under the PFM tip, i.e., over distances comparable with the domain wall width. In this paper, we will also discuss recent findings related to the frequency-dependent piezoelectric response measured using PFM setup where the properties of the individual domain walls can be, in principle, accessed. Several materials have been tested such as piezoelectric titanates thin films [lead zinc titanate doped with La] and piezoelectric single crystal. The mechanical properties of the PFM cantilevers in the contact with the piezoelectric media will be taken into account. It will be shown that the frequency dependence of the piezoelectric effect is strongly influenced by the mechanical resonances in the PFM. It will be shown that, using stiff cantilevers, the frequency dependence of the piezoelectric response in ferroelectric materials can be determined. It will also be demonstrated that the electrostatic interaction that frequently masks the piezoelectric response in PFM can be eliminated by using stiff cantilevers and sharp tips.

C11.4 Ferroelectric Domain Studies In PZT Thin Films With Different Compositions By PFM. Aiyong Wu, Paula Vilariño, A Khodkin and Isabel Salvador, University of Aveiro, Aveiro, Portugal.

Due to growing field of applications of ferroelectric thin films it is of great interest to study the ferroelectric properties of thin films on a nanometer scale. The integration of ferroelectric thin films into microelectronic devices requires substantial improvement in the understanding of the materials. The physical properties of ferroelectric materials at the submicron level, as well as an implementation of new tools suitable for in situ testing ferroelectric thin films structures. Piezoresponse Force Microscopy (PFM) has been recently used in the field of ferroelectric materials due to its powerful capabilities for monitoring domain features and investigating electrical properties locally at a nanoscale level. The use of PFM to characterize the domain behavior of ferroelectric thin films is of importance from both the technological and scientific point of view. Successful experiments have been performed to non-destructive ferroelectric thin film, such as domain structure and switching behavior. However, the PFM studies in the PZT system have been mainly concentrated near the morphotropic phase boundary compositions and a few of them in the tetragonal region. In the current work, PFM based technique is applied to analyze the domain behavior as a function of film composition in a systematic way. Polycrystalline PZT thin films were deposited on a commercially available Pt/Ti/SiO2/Si substrate via sol-gel technique. Ferroelectric domain structure, symmetric domain switching, polarization distribution and piezoelectric non-linearity by PFM are studied in ferroelectric PZT thin films with different compositions (from PZT20/80 to PZT60/40), which cover the tetragonal to rhombohedral crystallographic symmetry. The stability of the local piezoelectric response of the PZT thin films of different composition is presented and discussed in terms of grain size, annealing temperatures, presence of defects and charge accumulation. Simultaneously, the microscopic electrical characteristics of the films are analyzed. The dependence of the domain structure and electrical response at a nanoscale provided by PFM with the macroscopic electrical properties is presented and discussed.

C11.5 Kinetics of phase transformation of PZT thin film by sol-gel method using Scanning Force Microscopy. Bangli Lee1, Changleteck Bae2, Seunghyun Kim3 and hyunjung Shin1; advanced material engineering, Korea university, seoul, South Korea; 2Inosite Inc, seoul, South Korea

Lead zirconate titanate (PZT) thin films are prepared by sol-gel techniques onto platinum Si substrates (Pt/Ti/SiO2/Si). The sol-gel process draws much technological attentions because of its unique advantages on changing compositions and easiness to dope with impurities, and ability to make large coatings. Understanding the mechanisms of the nucleation and growth in ferroelectric PZT thin film will be of considerable importance in optimizing the sol-gel process. Scanning Force Microscopy modified to detect the piezoelectric response from ferroelectric thin films is used in this study. We have investigated the piezoelectric response of sol-gel PZT (52/48) thin film with 300nm in thickness. The PZT film was annealed in commercial tube furnace at 430°C to 470°C with holding time of 10–60min. Isothermal ferroelectric phases were found in the surroundings of phase diagram upon heating between 430°C and 470°C. The amount of phase change to perovskite characterized by SFM found to increase rapidly with annealing time and to be saturated. The kinetics process of growth was modeled using the Avrami equation. The Avrami exponent n was determined to be ~0.84. The activation energy will be determined. The results of the perovskite surface coverage taken from SFM are more reliable than other microscopic techniques, such as TEM or SEM, because of capability to obtain film from thin film in high resolution (~10nm in lateral). Moreover, kinetic studies of phase transformation from pyrochlore to perovskite are help to develop low-temperature processing.

C11.6 Dielectric anomaly in epitaxial strontium bismuth titanate thin films. Kenta Komiya, Iwao Kusugawa and Masahiko Tsuchida; Research Center for Superconductor Photonics, Osaka University, Suita, Osaka, Japan.

SrBi2Ta2O9 (SBT) has attracted much attention from the viewpoint of application to ferroelectric random access memory (FRAM) because of their high fatigue endurance, low coercive fields. Recently, it was reported that cation substitution for Sr2+ site and Bi3+ site strongly affects the ferroelectric and the dielectric properties of SBT. Meanwhile, most of the research have been done for polycrystalline SBT thin films on conductive Pt coated Si substrates for memory applications or polycrystalline ceramics for investigating fundamental properties. Therefore it is difficult to compare these results because of the difference in the quality and the orientation of each sample. We consider that it is important for understanding their properties to systematically measure the temperature dependence of the dielectric properties with epitaxial SBT thin films. In this study, we constructed measurement systems which can operate in wide temperature range from 290 °C to 600 °C, to measure temperature dependent dielectric properties of SBT thin films of different compositions using interdigital surface electrodes. We found that the peak of dielectric constant vs. temperature depend on frequency and dielectric peak shift from 275 °C to 307 °C when the measurement frequency changes from 100 kHz to 1 MHz. Such a behavior is typically seen in relaxor materials, and found with stoichiometric SBT for the first time. Our results suggest that the dielectric constant of SBT decreases with temperature. Moreover, the result shows that the dielectric constant remarkably decreases below 450 °C. These phenomena imply the presence of paraelectric phase in the low temperature region. The details of dielectric properties of epitaxial SBT thin films as a function of temperature and frequency will be discussed.

C11.7 Charge Retention Characteristics of PZT Thin Films For High Density FeRAM Devices. Jung-Hoon Yeom1, Seung-Hyun Kim1, Chang Young Koo1, Jong-Hyun Cheon2, Jwong Hsia3 and Cheol Seong Hwang4; 1Inosite Inc, Ansan-si, Gyeonggi-do, South Korea; 2School of Materials Science and Engineering, Seoul National University, Seoul, South Korea

Among the various reliability properties of the ferroelectric capacitors, ferroelectric fatigue, imprint and retention are the most important and consequently received most attention. Presently, fatigue and imprint are better understood and mechanisms can be explained. Retention of charge is overcome by using oxide electrode materials and dopants. On the other hand, the retention is significantly less understood and ill-defined. At present, various processes and mechanisms have been proposed for this failure mode but, however, it is difficult to distinguish between the possible degradation processes from standard electrical measurements. At approach to these potential serious problems there is a series of experiments designed to isolate specific sample characteristics, dopants, composition, and processing parameters. By identifying the influence of each in a systematic fashion, we hope to gain insight into potential solutions and explanations. In this research, we explore some state and opposite retention characteristics of PZT materials by five different variables: [1] donor dopant concentration, [2] Zr/Ti composition, [3] A-site (La) and Ba site (Nb) dopants, [4] invar dopants, and [5] film thickness. The purpose of this study is to better define, understand and describe how to overcome retention failure. Among numerous parameters affecting the charge retention characteristics, we have specially focused on the effect of oxygen vacancies. This work is supported by National Research Laboratory (NRL) program.

C11.8 T-site Substitution Using the Higher-valent Cations For Enhancing the Ferroelectric Properties of Neodymium-substituted Bismuth Titanate Thin Films. Hiroshi Uchida1, Seichiro Kodai2, Hirofumi Masuda2, Takashi Iji1, Takayuki Watase1, and Hiroshi Funakubo3; 1Department of Chemistry, Sophia University, Tokyo, Japan; 2Materials Structure Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 3Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Japan.

Thin films of neodymium-substituted bismuth titanate,
(Bi,Nd)4Ti3O12 (BNT), have excellent ferroelectric properties comparable with those of Pb-base ferroelectrics. In this study, we observed the effect of bismuth titanate (BTT) crystal on the perovskite structure of the BNT film. Ti-site ions in BNT thin films were substituted by other ions with higher charge valences in order to compensate the charge valence of oxygen vacancies in BNT crystal. Solution-grown single-domain thin films were prepared using bismuth nitrate, neodymium nitrate, and metallic Ti, V$_2$O$_5$, and 2-methoxyethanol as starting materials. The solutions were spin-coated on (111) Pt/Ti/SiO$_2$/Si substrates, followed by drying at 150°C for 3 min in air. After repeating these processes several times, the resulting films were heat-treated for crystallization at 750°C for 5 min in air. The films were fabricated from the spin-coating solutions with chemical compositions of Bi$_3.5$(Nb$_{0.5}$Ti$_{0.5}$)$_{0.7}$O$_{3}$, Bi$_3.5$(Nb$_{0.5}$Ti$_{0.5}$)$_{0}$O$_{3}$, Bi$_3.5$(Nb$_{0.5}$Ti$_{0.5}$)$_{-0.3}$O$_{3}$, and Bi$_3.5$(Nb$_{0.5}$Ti$_{0.5}$)$_{-0.6}$O$_{3}$. The results of XRD analysis indicated that all of the films consisted of single phase having Bi$_2$Ta$_2$O$_7$ crystal structure (m = 3) without preferred orientation. The films were deposited in an environment that those films had not incomparable with the structure with diameters of ~ 100 nm. These results suggested that Ti-site substitution did not affect both the microstructure and the crystal structure of the BNT films. V$_2$O$_5$-substitution enhanced the remanent polarization (PR) of films, and the relative low dielectric constant (k) up to 35 μC/cm$^2$ (x = 0.02), while both films possessed similar coercive field (E) of approximately 120 kV/cm. Leakage current density of the BNT film was suppressed by V$_2$O$_5$-substitution from ~ 10$^{-7}$ A/cm$^2$ (x = 0) down to ~ 10$^{-10}$ A/cm$^2$ (x = 0.02) at an applied field of 100 V/cm, which would be observed to the compensation of oxygen vacancies by Ti-site substitution using the higher-valent cation.

C11.9 Preparation, Microstructure and Physical Characteristics of Ferroelectric PbSbGeO$_3$ Thin Films for Memory Application, Yuxiang Liu*, Christine Caragiannis-Broadbridge, Ann Hein Lehmann, and Tao-Ping Ma
Department of Electrical Engineering, Yale University, New Haven, Connecticut, USA; Department of Physics, University of Connecticut, New Haven, Connecticut, USA; Facility for Electron Microscopy, Trinity College, Hartford, Connecticut.

Thin films have great potential for memory applications. The ferroelectric oxide thin films, such as lead zirconate titanate (PZT), use the number of domains in the memory cell to store data. These thin films are typically composed of a ferroelectric material that can be switched between two states of polarization. The switching is achieved by applying an electric field, which induces a change in the orientation of the dipoles within the material. This change in orientation results in a change in the phase of the electric field, which is detected by a readout device.

Ferroelectric thin films are also valuable for their potential for device applications. For example, they can be used as switches in memory devices, sensors, and data storage devices. In addition, ferroelectric thin films have potential applications in the field of non-volatile memory, where the data is stored permanently and can be accessed later.

In this study, we investigated the ferroelectric properties of PbSbGeO$_3$ thin films. We found that these films exhibited excellent ferroelectric properties, such as high remanent polarization and high dielectric constant. These properties make them suitable for use in memory devices and other electronic applications. We also investigated the microstructure and physical characteristics of these films, such as their grain size and orientation, to gain a better understanding of their properties.

C11.10 Novel PZTN Thin Film For High-Density FeRAM, Takashi Kijima, Hiromasa Miyama, Takao Atsumi, Noe Nakai and Toyoshi Shimoda
Research Center, SEIKO EPSON Corporation, Nagano, Japan.

Ferroelectric random access memories (FeRAMs) have attracted considerable attention due to the recent development of portable computer technology. However, fabrication of FeRAMs is still difficult, because of problems such as the ferroelectric film quality. In this study, we investigated Si-substituted films with spin coating. In this experiment, we tried to substitute 30% of Bi$^{2+}$ ions by Ti$^{4+}$ ions (PZT) to only Ni$^{2+}$. The crystallization temperature increased to 800°C. We obtained a only pyrochlore phase. Therefore, we added a 3mol% Ni$^{2+}$ in Zr$^{4+}$ in PZT at the same time. At last, we were able to obtain a highly oriented Bi$^{2+}$:Zr$^{4+}:Ti$^{4+}:Ni$^{2+}$ (PZTN) thin film with perovskite single phase lower than 60°C. Our new Si substituted 15nm-thick PZTN thin film has a good square-shaped hysteresis loops. The polarization is well saturated at an applied voltage of 1.5V. Additionally, it shows an excellent fatigue resistance, such as a high endurance voltage of 100 V.

The leakage current property of the Ni$^{2+}$-substituted PZT film, the leakage current decreased at least by 4-orders-of-magnitude in comparison with typical PZT, and it was less than 10$^{-9}$ A/cm$^2$ at 3V with high-breakdown voltage over than 200 V. Moreover, as THz radiation of the good imaging response, we showed that the shifted quantum of hysteresis loops were less than 3%. Therefore, we investigated a new more detailed structural change of the PZTN film quality using Secondary Ion Mass Spectrometry (SIMS). The oxygen deficient defects were reduced about 10% in comparison with one of PZT. The excess coordinate number of Nb with compensation of one of Ti was compensated for oxygen deficient precipitation. 1, T. Kijima and H. Ishihara, Jpn. J. Appl. Phys. 41(2002)2,716

C11.11 Ferroelectric memory in La doped Bi$_2$Ti$_2$O$_7$ thin films, F.E. Molgarejo, Mokarrar Singh Tomar and S. P. Singh, Physics, University of Puerto Rico, Mayaguez, Puerto Rico.

The recent demonstration of large ferroelectric memory in rare earth doped Bi$_2$Ti$_2$O$_7$ attracted a lot of research interest in this material. Bi$_2$-La$_2$Ti$_2$O$_7$ for different compositions (x = 0, 0.06, 0.56, 0.75, 0.85, 1.0 and 1.5) have been synthesized by sol-gel method and thin films were deposited using spin coating on Pt (Pt/TiO$_2$/SiO$_2$/Si) substrate. Thin films were post annealed at 700°C Structural studies based on X-ray diffraction and Raman spectroscopy shows well oriented films. The prominent effect of La substitution observed in low frequency Raman modes. Ferroelectric response shows high remanent polarization (P$_r$ = 48 μC/cm$^2$) for x = 0 and fatigue free response observed up to 10$^4$ switching cycles. The ferroelectric response for seven other compositions will be presented.

C11.12 Novel Ferroelectric Material For One Transistor Memory Application, Wee Sik Kim, Chang-Ki Lee, Jun-Kyu Yang and Hyung Ho Park
Ceramic engineering, Yonsei University, Seoul, South Korea.

The study of ferroelectric-gate controlled devices has been vigorously pursued since this device is expected to have numerous advantages such as very small memory cell size, non-destructive read-out, high-speed operation, and low-power consumption. However, there is no reliable memory device fabricated yet because of the difficulty in the complicated integration processes for one transistor memory device fabrication. Especially, annealing under O$_2$ atmosphere for the crystallization of ferroelectric material induces the formation and growth of interfacial layers such as silicon oxide and silicon nitride between insulator and silicon substrate. In this case, if the thickness of the interfacial layers is thick, because most of the applied voltage drop occurs across these layers, an effective field on the ferroelectric layer could not be enough for the polarization reversal. To overcome aforementioned problems, in this paper we synthesized the ferroelectric CeTi$_2$O$_7$ (CTO) by annealing under vacuum. CTO films were deposited on YZO/Si (100) by chemical solution method. The crystalline property of the film with annealed temperature was characterized and the ferroelectric and electrical properties were monitored by measuring the capacitance-voltage and current-voltage relations.

C11.13 A Comparative Study On The Ferroelectric Behavior In Metal-Ferroelectric-Insulator-Semiconductor Structure Using Various Ferroelectric Material, Wee Sik Kim, Chang-Ki Lee and Hyung Ho Park
Ceramic engineering, Yonsei University, Seoul, South Korea.

Ferroelectric-gate controlled devices, such as metal-ferroelectric-insulator-semiconductor (MFIS) FET, were studied especially for its high speed operation and low power consumption. However, conventional MFIS structure has many problems such as difficulty of deposition of ferroelectric thin films directly on silicon, increase of trap density, and diffusion of elements into silicon, etc. In order to avoid these problems, we fabricated metal-ferroelectric-oxide-insulator-semiconductor (MFIO) FET structure. In this study, we investigated the ferroelectric behavior in MFIS and MFIO structures using various ferroelectric materials. We found that the MFIO structure is the best candidate for FET applications. The MFIO structure consists of a series connection of capacitors, which can be switched on and off by applying a voltage to the gate electrode. The resulting voltage is then transmitted to the source and drain terminals, allowing the device to operate as an electronic switch.
permittivity and thickness of interfacial layers including ferroelectric layer itself. In this work, from a point of view described above, we fabricated MISFET structures using various ferroelectric materials such as Pb(Zr, Ti)O3, SrBi2Ta2O9, and Nd2Ti2O7 which have different permittivity and process condition, and discussed the relationship between the constitutional structure and the operating condition of field effect transistor.

C11.44 Abstract Withdrawn

C11.45 Structural And Electrical Investigations Of Ferroelectric Lead Strontium Titanate Thin Films And Ceramics. M. Jin3, P. Bhattacharyya1, Yu. I. Yuzuyk1, R. S. Kucyev2 and A. S. Blavats1 2
1Department of Physics, University of Puerto Rico, San Juan, PR, Puerto Rico; 2Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania.
SrTiO3 and PbTiO3 are known to form the solid solution in the entire range. The Curie temperature and lattice constants of Pb1-x SrTiO3 (PST) were found to depend on Pb/Sr ratio composition. PST x=0.3 is the paraelectric at room temperature and exhibit ferroelectric phase transition below room temperature. The properties like high dielectric constant and low leakage current densities of ferroelectric PST thin films are attractive for applications in dynamic random access memories. Lead strontium titanate (Pb1-x SrTiO3) (x=0.3-1.0) targets were prepared by the conventional powder processing method. Thin films of these compositions were deposited on various substrates like crystallized silicon, MgO etc by pulsed laser deposition technique. These films were characterized for their phase purity, surface morphology, dielectric, and leakage current characteristics. X-ray diffraction and surface microscopy were used for the structural characterization of these materials. The Curie temperature x-ray diffraction studies for x=0.3 indicated a stabilized cubic perovskite phase. Raman spectroscopy was used to study lattice dynamics of the bulk ceramics and thin films on different substrates. Soft mode behavior in films is discussed in comparison with the bulk data. The grain size of PST thin films was observed to be reduced with the increase in strontium contents. The room temperature dielectric constant decreased while the leakage current densities reduced with the increase in strontium contents of PST thin films. The changes in the thin film properties with varying composition were investigated and compared with the bulk properties.

C11.46 Ferroelectric Properties Of Pb0.95Sr0.05TiO3 Film Spun-Coated On Pt Bottom Electrode Using A La3Sr9Co2O8 Buffer Layer. JuHyun Kim1, Woong Kim Cho1 and Kyoung Shin Koh2 1Material Science and Engineering, KAIST, Taejon, South Korea; 2Chemistry, Chungang Univ., Seoul, South Korea.
We have studied ferroelectric properties of Pb0.95Sr0.05TiO3 [PZT (40/60)] films grown on Pt/TiO2/SiO2/Si bottom electrode using a La3Sr9Co2O8 (LSCO) buffer layer. It is approved that the conductive perovskite LSCO thin film (about 5nm thick) which consist with fine grain (less than 20nm) is grown on the Pt/TiO2/SiO2/Si substrate at relatively low temperature (450°C) by d.c. magnetron sputtering and shows the ohmic contact to the Pt bottom electrode. In order to investigate the ferroelectric properties of spin-coated PZT 40/60 films, we measured the P-V hysteresis loop vs. temperature. Different from the general increase of leakage current with temperature in the schottky or ohmic contact, it shows a very small increase up to 373K. Also, in fatigue test, it shows a smaller decrease in Pr up to 2x1014 switching cycle at 323K than 283K. We measured the J-V curves vs. temperature. Different from the general increase of leakage current with temperature in the schottky or ohmic contact, it shows a very small increase up to 373K. However, above 373K, the increase appears in different aspect. The current density is dependent on the square of the applied voltage and exponential of temperature. This is a new type of space charge limited conduction from the existence of the LSCO buffer layer.

C11.17 Hydrogen Effects in MFSET and MISFET with Pt/SrBi2Ta2O9/Si and Pt/SrBi2Ta2O9/Y2O3/Si Gate Structures. Jun Bin Shim1, Young Seok Kwon2, Seong-il Kim3, Yong The Kim1, and Jung Hee Park1 1systems technology division, Korea Institute of Science and Technology, Seoul, South Korea; 2Electronics Engineering, Korea University, Seoul, South Korea.
The single transistor type ferroelectric memory has many advantages over the capacitor type because of its nondestructive read operation and small cell size. Many kinds of attempts have been tried to fabricate metal ferroelectric semiconductor or metal ferroelectric insulator semiconductor field effect transistor (MFSET or MISFET). In this study, we have studied the hydrogen annealing effects on the single transistor type ferroelectric memory devices. It is well known that the hydrogen annealing degrades the ferroelectric properties but the leakage current and interface trap density are improved. The MISFET (Pt/SrBi2Ta2O9/Y2O3/Si) and MFSET (Pt/SrBi2Ta2O9/Si) were fabricated with direct etching process by using the indiffusively coupled plasma reactive ion etch (ICP-RIE) system. The memory windows of MISFET and MFSET were 0.74 V and 1.0 V at 7 V, respectively. Then, after hydrogen annealing at 400°C for 30 min, memory windows were degraded. But, the leakage current was reduced, which affected dielectric characteristic of the single transistor type ferroelectric memory. The threshold voltage was shifted toward positive bias, which resulted from the reduction of the interface trap density of the MISFET and MFSET. These results are well consisted with the electrical results of the MISFET and MISFET structures. The hydrogen annealing effects are more dominant in the MISFET than in the MISFET and MISFET structure.

C11.18 Characteristics And Calculation Of One Transistor Memory Devices. TingCheng Li, Sheng Ting Hsu, Bruce Uhrich and Dane Evans1, 2, P. T. T. Shaper, LuKah America, Inc., Carson, California.
One transistor memory devices with MFMPIS (M: Metal, P: Ferroelectrics, M: Metal, P: polysilicon, I: insulator, S: silicon) structure have been fabricated. The working functions of memory window, retention, imprint, switching characteristics, and thermal stability have also been measured and evaluated using various methods. One-transistor memory devices show excellent memory working functions. The typical one-transistor memory devices show memory windows around 2-3V. The memory windows are almost saturated from operation voltage of 3V. For the one transistor memory device, after writing on state (+5V), the drain current (ID) at VD of 0.1V and VG of 0, 0.5 and 1 V was about 2x10^-14 A. After writing on state (-5V), the drain current (ID) at VD of 0.1V and VG of 0, 0.5 and 1 V was about 1x10^-15 A. The on state current to the off state current ratio about 9 orders of magnitude. However, the one-transistor memory devices also show poor retention and switching properties, especially at higher temperatures. Compared with calculation data based on circuit modeling of flash memory device, most experimental results are consistent with the calculation data. The challenges for one-transistor memory devices are switching properties and retention properties at higher temperatures. The effects of depolarization field and leakage current on the retention properties at higher temperatures have also been calculated and discussed.

A long-term consideration in the application of ferroelectrics for device production is hydrogen-induced failures. Protection of the active ferroelectric layer through covering the device with a dense dielectric can mitigate these failures. However, the dielectric deposition temperature should be sufficiently low so as not to degrade underlying transistor plug layers, or react with the memory capacitor to degrade performance. Furthermore, the addition of elemental silicon in the base silicon process for construction of a barrier need to be minimized so that transistor properties remain reliably. In part, a design solution to this problem is to employ an aluminum oxide hydrogen diffusion barrier in the device structure. We have focused on MOCVD of the barrier layer using an array of precursors, including trimethylammonium and aluminum iso-propoxide, among others. The effects of RF plasma on deposition rate and film properties have been explored. We have successfully reduced the deposition temperature from 690°C to 50°C without sacrificing film quality and deposition rate. Produced films are uniform over 8” diameter wafers and are highly reproducible. Films are produced in a spin-CVD®8TM® chamber, an in situ low pressure MOCVD reactor. The electrical characterization and physical properties of these films will be discussed.

C11.20 Lead Barium Titanate Thin Film Based Positive Temperature Coefficient Coefficient of Resistance Thermistors. RaviPrakash Jageunay, and Susan Troller-Mckinstry, Materials research Institute, Pennsylvania State University, University Park, Pennsylvania.
Positive Temperature Coefficient of Resistance (PTCR) thermistors typically employ donor doped compositions of BaTiO3. The PTCR phenomenon is thought to be due to the formation and inactivating grain boundary barriers separating conducting grains. The barrier is
modulated by ferroelectric polarization and the dielectric permittivity of the material. In this work, (Bi, Pb)TiO₃ were investigated at high temperatures and pressures. Lead layers of 0.35μm prepared by a sol-gel technique showed a Tc of 340°C with around 50% lead content. XRD of these films indicates that the films do have a perovskite structure. The room temperature dielectric constant for the films was found to be around 400, with a dielectric loss of around 5%. A remanent polarization of 20 μC/cm² and a coercive field of 900 kV/cm was obtained. The PTCR characteristics of films based on this solid solution series will be reported.

C11.21 Magnetic and Ferroelectric Behaviors of Multi-Ferroic RMnO₃ (R: yttrium or rare earth ion) Thin Films
Noritsugu Fujimori, Hironori Sakai, Takashi Yoshidama and Hironori Shigemitsu, Graduate School of Eng., Osaka Prefecture Univ., Osaka, Japan.

Ferroelectric materials with magnetic properties have several advantages when the material is used for memory devices. Hexagonal yttrium and rare earth magnetic rare earths exist in low temperatures. We have demonstrated the YMnO₃ thin films show ferroelectric and antiferromagnetic behavior and demonstrate a relationship between carrier concentration and magnetic properties of YMnO₃ films. However, little interaction is observed between magnetic spin and dipole moment. Although YMnO₃ films exhibit antiferromagnetic magnetization behavior whereas the crystallographic orientation and the carrier concentration, Li doped sample displays paramagnetic ferromagnetic (weaker ferromagnetic) behavior. Substitution by Yb enhances the ferromagnetic interaction. This paper describes the effect of A-site substitution on the magnetic and ferroelectric properties of RMnO₃ films and also demonstrates electric field control of magnetic properties of the films.

C11.22 Characterization of layer-transferred single crystal BaTiO₃ thin film by H and He⁺ ions co-implantation
Young-Bae Park, Jennifer L. Ruglowesky, James M. Zalimer and Hary A. Atwater, Applied Physics, California Institute of Technology, Pasadena, California.

We have investigated ion-implanted layer transfer of BaTiO₃ thin films onto various substrates to obtain high quality single crystal ferroelectric thin films. We will report thermodynamic criteria for cavity nucleation and ferroelectric properties of transferred single crystal BaTiO₃ thin films. Bulk single crystal BaTiO₃ was processed by high dose H and He implantation. The implantation energy was around 100 keV and dose ranged from 1 x 10¹⁵ to 1 x 10¹⁶/cm² for H+ and He⁺, respectively. Ion implanted BaTiO₃ films were transferred onto various substrates (Si, Si₃N₄ and Al) at room temperature. To investigate cavity growth and layer transfer, xeroradiograms were performed in the range from 300 to 900 °C in various ambient and pressure environments. Single crystal BaTiO₃ films were transferred by using the area of 2 x 200 μm² were transferred onto Si₃N₄/Si substrates. Transferred layers exhibited single crystal like structure with tetragonal phase. Film stoichiometry did not change compared to bulk BaTiO₃ but transferred layer exhibited slight polycrystalline character change. RMS surface roughness of transferred layer was in the range of 30 nm. Ferroelectric domain size ranged from 1 to 2 μm and showed typical ferroelectric domain switching behavior with a coercive field ~ 20 kV/cm. Cavity nucleation before layer transfer was observed by optical microscopy and SEM. FRES analysis was conducted to obtain hydrogen depth profiles in the implanted region. AFM was used to characterize surface roughness and measured the size of surface blisters, cavity radius and height. Raman spectroscopy was used to measure structural and chemical disorder. Microstructural analysis was performed using plan view TEM. For the oxide layer stoichiometry, RBS was performed before and after layer transfer. TEM was used to investigate the ferroelectric domain and switching property. The initial stages of layer splitting were studied with thermodynamic modeling and prospects for large-area single crystal ferroelectric layer transfer onto various substrates will also be discussed.

C11.23 Deposition Of BaTiO₃ Thin Films And MgO Buffer Layers On Patterned GaAs Substrates For Integrated Optics Applications
Ding-Yun Chen, Timothy E. Murphy and Jamie D. Phillips, Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan.

The integration of ferroelectric thin films with semiconductors is of high interest for integrated optics and optoelectronic integrated circuits (OEIC). Ferroelectric oxides such as BaTiO₃ are transparent in the visible and infrared and possess strong electro-optic coefficients making them attractive for active and passive optical components. Highly oriented BaTiO₃ thin films on GaAs have been previously demonstrated using MgO buffer layers. The MgO buffer layers for thin films have been problematic for integrated optics applications due to the inability to obtain thin MgO cladding layers for optical waveguiding and the presence of cracking in the thin films that are likely a result of thermal expansion mismatch. The films on MgO buffers on patterned GaAs substrates as an approach to achieve crack-free optical waveguiding structures. BaTiO₃ and MgO thin films were deposited by pulsed-laser deposition on pre-patterned GaAs substrates. The GaAs substrates were patterned into stripe geometries with widths ranging from 1 to 10 μm and depths of 0.1 μm using reactive ion etching to achieve vertical sidewalls. We observe cracking and peeling of the thin films on patterns with lateral dimensions exceeding several microns or with etch depths significantly less than the BaTiO₃/MgO film thickness (~0.5 μm). We observe crack-free thin films for patterns with lateral dimensions of a few microns and etch depths similar to the film thickness. We believe that the patterned features provide strain relief to prevent cracking due to thermal expansion mismatch during heating and cooling steps of the deposition process. The structures obtained are suitable for single-mode optical waveguiding structures, where optical characterization will be presented. Furthermore, we will report on the inclusion of Al₂O₃ buffer layers obtained through wet-exfoliation of AlGaAs prior to BaTiO₃/MgO deposition as a means of enhancing optical waveguiding.

C11.24 Parametric studies on Suppressing Secondary Phases in Lithium Niobate thin films deposited by Pulsed Laser Deposition
Ji-Won Seo¹, Sergei S. Orlova², Bill Phillips² and Lumbert Hesselink², ¹Materials Science and Engineering, Stanford University, Stanford, California, ²Electrical Engineering, Stanford University, Stanford, California.

We performed parametric studies to suppress secondary phases in lithium niobate thin films by pulsed laser deposition (PLD). A KrF excimer laser (λ = 248 nm) was used as a PLD source and co-sputtered sapphire and LiNbO₃ were used as substrates for waveguide applications. The main limitation in producing single phase LiNbO₃ films by PLD is that secondary phases such as a Li-deficient phase (Li₂NbO₄) or easily mixed. In our previous research, we deposited lithium niobate films on sapphire (0001) substrates in two different deposition geometries, on-axis and off-axis. Under the same growth conditions, it was found that the on-axis geometry was prone to produce a Li-deficient phase while the off-axis geometry produced single phase LiNbO₃. The main differences between the on and off-axis geometries are the growth rate and scattering of materials in the plume that reach the surface of the substrate. By reducing the growth rate and changing the ambient gas pressure in the on-axis geometry, we found that the main factor that can reduce the secondary phase is controlling the plume strength, rather than the growth rate. To investigate the reduction between the film plume and the plume strength, extensive parametric studies were performed by changing the oxygen ambient pressure, the target-substrate distance, and the Li content in the target. The film, phase and deposition of the films was investigated by XRD and XPS. It is shown that there is an optimal range of ambient pressure and target-substrate distance to produce single phase LiNbO₃ films. As the ambient oxygen pressure or target-substrate distance increases, i.e., the plume strength decreases, the phase of the lithium niobate films changes from Li-deficient mixtures of LiNbO₃ to the LiNbO₃ single phase. Further reducing of the plume strength passing through the optimum conditions, it changes the appearance of the Li-excess phase (Li₅NbO₄). The trend of the phase change is consistent in lithium niobate films produced by using either LiNbO₃ or Li-rich targets, but the Li-rich target has an optimized condition with a stronger than the LiNbO₃ target. From these results, we postulate that the main reason for the change in the composition of the film created by PLD is due to the chemistry of the film and the post-deposition. The surface morphology and structural evolution of single-phase films and Li-deficient phase mixed films are also studied by AFM and TEM, and related to the growth mechanism with a lattice misfit.

C11.25 Abstract Withdrawn

C11.26 Structural, Dielectric and Piezoelectric Properties of 0.5(0.75Pb₁/₄La₁/₄Nb₂/₄O₃-0.25PbTiO₃ Thin Films Prepared via Sol-Gel
Namtran Bui Gharch and Susan Trolles-McKenney, Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania.

[1-x]Pb₁/₄La₁/₄Nb₂/₄O₃-xPbTiO₃ (PZT-NPT) has one of the highest
Curie temperatures (~360 °C) near the morphotropic phase boundary (±0.5 °C) among the relaxor-Pt solid solutions. This should yield good piezoelectricity and low dielectric properties and a wide operating temperature range, which are promising for transducers and actuators. In this work, 0.5YbNi:0.5PPT thin films were deposited on platinum substrate by sol-gel processing. Films with strong [111] preferred orientation as confirmed by x-ray diffraction. The films exhibited good ferroelectric and piezo-electric properties. The dielectric permittivity was around 820 and 1160 and the dielectric loss around 4% and 2.5% respectively for the [111] and [001] films, respectively. The permittivity increased with increase in the deposition rate up to 1000 °C. The cell parameter near the surface for the [001] oriented film probably due to either a compression or stress gradient throughout the thickness of the film. An oscillating condition gradient was observed through the thickness of the films where alternating layers roughly 80 nm thick rich in Yb and Nb and depleted in Ti were followed by the reverse.


We have improved the hydrothermal method to deposit lead zirconate titanate (PZT) thick film from green PZT bulk substrate. The titanium substrate was hold on a stirring wheel which was installed in a autoclave to mix up a solution. The deposition rate depended on the rotation speed of the stirrer. By increasing the rotation speed, the deposition rate has increased 8 times longer than the previous method. We obtained 200 micron thick film and then measured the vibration characteristic in the piezoelectric film around 5 MHz. Hydrothermal synthesis for PZT film uses chemical reaction between a substrate of titanium and a solution which includes Pt, Zr and Ti ions in an autoclave. The process is carried out at the temperature around 120 degrees Celcius to 160 degrees Celcius and with KOH solution. The process has been improved during the passed decade for deposition applications such as sensors and actuator were reported. The major point of the passed investigation about the deposition process was chemical side such as temperature, KOH concentration and so on. However, the deposition speed was still very slow. It was around 2 micron per 24 hours for one synthesizer process. Therefore, it was required 50 times synthesizer process to obtain thick film of 100 micron for thickness mode transducer. We developed a high speed rotation substrate holder in autoclave. The stirrer rotation speed was raised up to 245 rpm. The holder moved at a velocity of about 0.8 m/s in autoclave. The higher deposition rate was obtained at higher rotation speed of the stirrer. As a result, we obtained the thickness of over 200 microns of hydrothermal PZT film by 15 times synthesizer processes. The element was deposited on one side of the Ti substrate. The element was 10 mm square. We have measured the frequency response of the element in the range of 1 to 10 MHz and higher. Due to the superior high intensity characteristics of the hydrothermal PZT film, the thickness mode transducer will be applicable to high intensity ultrasonic at high frequency.

C11.28 Melt Deposition of Micron-Thick Lead Zirconate Titanate Thin Films. Mark D. Loper 1, 2, S. Tholen-McKinstry 1, N. Basiri Ghareh, 1 and M. T. Flanagan 1, 2, Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; 2Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

A majority of the work published on liquid source misted chemical deposition (LSMD) has focused on the fabrication of thin ferroelectric films for random access memory (RAM) applications. However, the ability of LSMD to combine the characteristics of good stoichiometric control of a chemical solution deposition process with good film conformality, makes this a desirable technique for other applications, including micro Actuators and integrated passive components. In the LSMD process, each film deposition cycle is limited by its low throughput. This paper describes the feasibility of depositing micron-thick lead zirconate titanate (PZT) films using the LSMD tool. PZT films of 52/48 composition were deposited on both platinum and titanium-coated alumina substrates. The deposition temperature and the deposition geometry of the LSMD tool were identified as factors affecting the deposition rate at which micron-thick samples can be prepared. By switching to a focused nozzle delivery geometry and increasing the chamber temperature from room temperature to 60 °C, the total process time for 1 μm thick films can be reduced from 480 min to 80 min. In addition, piezoelectric hysteresis measurements indicated a polarization for PZT films deposited on platinum in alumina substrates (33 μC/cm²) compared to those deposited on platinum in silicon substrates (20 μC/cm²). The polarization loop for the silicon substrate sample was also tilted. These observations are explained by the fact that the stress gradients in the PZT films deposited on silicon substrates due to a larger mismatch in the thermal expansion coefficients of the film and the substrate.


A remarkable interest in electric-field-induced displacements in ferroelectric thin films has arisen for application and integration of ferroelectric microelectromechanical systems. Currently, several techniques such as atomic force microscopy (AFM), interferometry and direct methods have been employed to evaluate the electric-field-induced displacements. Among these techniques, AFM is the most effective technique for materials research, because AFM is easy to operate and has sufficient sensitivity. However, there have been few reports on sample geometry influence on electric-field-induced displacements in piezoelectric thin films measured by AFM. In this study, we report detailed investigation of electric-field-induced displacements calculated by finite element method (FEM), and compare the calculations with experimental results. 3-D FEM analyses were performed using a commercial software (Dynum Co., Ltd., PicoPLUS). Electric-field-induced displacements were calculated using electric field-dependent dielectric constants, in the case of applied field frequencies for AFM measurements (50 Hz–1 kHz) were sufficiently lower than the mechanical resonant frequencies of thin film specimens (MHz). Columnar FEM models consisted of 5 layers: Pt (1.1 μm)/PZT(52/48)/Pt(1.1 μm)/SiO2(1 μm)/Si(200 μm). The ratio of the whole FEM models were 10 times as long as the ratio of the tip electrodes (TE) ranging from 0.1 μm to 500 μm. Piezoelectric constant (d33 (A)), stiffness (cijkl), permittivity (eεij) and density of pure PZT/52/48 ceramics were calculated for these constants of PZT thin films. Here, d33 of PZT thin films was 225 × 10−12 m/V. After the FEM calculation, d33 (Part) was computed from displacement at the center of TE surface. d33 (Part) were also estimated from PZT thin film deformation at the center of the model. If the TE radius was longer than 200 μm, d33 (Part) became negative, while d33 (Part) still remains to be positive. As the TE radius decreased from 1 μm to 0.1 μm, d33 (Part) became to the bulk value rapidly. Therefore, necessary conditions to measure intrinsic d33 by AFM were shorter TE radius than the thickness of ferroelectric films and side etching treatment. [1] A. L. Khodkin, Ch. Wüthrich, D. V. Taylor, and N. Setter. Rev. Sci. Instrum. 67, 1305 (1996).

C11.30 The Synthesis and Structure of New Piezoelectric Materials (nodule-processed in MBE). Peter Wave Field, Haung Liu and Long Zou; State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, wuhan university of technology, wuhan, hubei province, China.

A new nodule materials B5LaIaxTixNh1-xO40, which could be a candidate of piezoelectric materials, were synthesized by doping Li4 in the system Ba0.5Ti0.2O2. Nb2O5 in millimeter wave field. XRD and scanning transmission spectroscopy (SEM) analysis were performed to study crystal structure and microstructure of reaction products. It was found that pure reaction products could be obtained at temperature 900 °C 8 min. The results of XRD showed the crystal phase of tetragonal structure with space group I4mm and cell parameter a=1.2512(2) nm, c=0.4088(5) nm. The reaction mechanism in millimeter wave field was analyzed based on the XRD quantitative data. The theoretical calculations are...
agreement with experiment data.

C11.31

Ferroelectric Properties of a Lead Zirconate Titaneate Film Deposited by a Hydrothermal Method. Takeshi Morigi1, Yasuo Watanabe1, Hiroshi Morigi1, Hiroshi Funakubo2, Nawa Seto1 and Yasuo Cho2. 1Institute of Industrial Science, University of Tokyo, Sendai, Japan; 2Tokyo Institute of Technology, Yokohama, Japan; 3Swiss Federal Institute of Technology, Lausanne.

Among various methods, a hydrothermal method is a unique method to deposit a ferroelectric thin film below 200 degrees Cezkis. Concerning a PZT thin film, a chemical reaction of solution containing lead, zirconium and titanium ions is utilized with high alkali concentration. Morigi et al. adopted a titanium metal as a substrate and policrystalline PZT thin film was successfully obtained [1] and this film was applied to a micro ultrasonic motor by T. Morigi et al. [2]. Alternatively, polarization phenomena indicated a fine crystal orientation, and can be thought to have good property due to direct synthesis under low temperature. Indeed, SEM photograph verified the deposited film consisted of cubic shaped crystals. A.T. Chien et al. have studied an epitaxial hydrothermal PZT films using a SrTiO3 single crystal 100 as a substrate. XRD measurements revealed film alignment of 001; although 100 peak was also detected. Electrical properties including a piezoelectric performance could not be measured because of non-conductivity of the SrTiO3 substrate. In this study, an epitaxial SrTiO3 thin film was sputtered on SrTiO3 100 as a bottom electrode. Then, a PZT thin film was deposited on SrTiO3 by a hydrothermal method. With a suitable heating method and suspending substrate condition, crystal quality was improved. A PE hysteresis loop was measured and grain induced ferroelectric effect could be measured. The polarization direction were measured using a nonlinear dielectric microscopy (SNMD) and it was confirmed that polarization directions were aligned parallel to the thickness direction during the deposition process without a poling treatment [1]. K. Shimomura, T. Tsurumi, Y. Ohba, M. Daimon, Preparation of lead zirconate titanate thin film by hydrothermal method, Jpn. J. Appl. Phys., vol. 36, pp. 2174-2177 (1997). [2] T. Morigi, M.K. Kuribayashi, and H. Tsuchiya, "A Cylindrical Shaped micro ultrasonic motor utilizing PZT thin film", Sensors and Actuators, vol. 83, pp. 226-230 (2000). [3] A.T. Chien, J.S. Speck, and F.P. Lance, "Hydrothermal Process of PbTiO3 and PbZr1-xTixO3 at 90-150 deg.C", J. Mater. Res., vol. 13, 5, 1176-1178 (1997).

C11.32

Local Hysteresis Behavior of Ferroelectric Thin Films of Sr1.05Pb0.45Ti0.55O3. Vignesh Raghunath Palikar1, M. Higgins2, S. C. Pandurangi1, R. Pisco3, and S. Bhattacharyya. 1Condensed Matter Physics & Materials Science, Tata Institute of Fundamental Research, Mumbai, Maharahtra, India; 2NEC Research Institute, Princeton, New Jersey.

2 Mole percent Sr1.05Pb0.45Ti0.55O3 thin films have been deposited on Pt/TiO2/Si/Si substrate by pulsed laser deposition technique. Polarization hysteresis loops are checked and ferroelectric loop trace is drawn. The ferroelectric properties are determined by using ferroelectric loop tracer. The piezo-response in various local regions on the film has been studied using Atomic Force Microscope (AFM) with a conducting tip. The tip current of the AFM instruments are simple square and polycrystallinity in nature. Saturated ferroelectric hysteresis loop and well-defined local piezoelectric loops obtained on different films demonstrate excellent properties equivalent to any other established ferroelectric material like PZT. Deflection, amplitude and phase images obtained by using AFM with conducting tip yield the following important conclusions. ● The first more fundamental conclusions that the structural defects especially spatially correlated ones such as grain growth are dominant pinning centers. These pinning centers are significantly more important than random point defects that may exist throughout the sample in both intra and inter-granular space. ● The second, more technically significant, conclusion is that the ferroelectric and ferroelastic properties of Sr1.05Pb0.45Ti0.55O3 are strongly dependent on N-V in FRAM the cell size should match with the grain size and for higher memory cell densities the grain size should be smaller. ● Sr segregates at the grain boundaries without affecting PbTiO3 matrix. Moreover, it restricts the grain growth. The optimization of Sr concentration could therefore help to control the grain size and achieve higher memory cell densities in N-V FRAM.

C11.33


Sr0.7Bi2.4Ti3O9 (SBT) layer with ≈40 nm thickness was introduced as an under layer for the phase formation of SBT thin films with the same chemical composition. The influence of seed layer on the phase formation characteristics of SBT thin films was investigated using x-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. Formation of pyrochlore as well as Aurivillius phase was observed in both the unseeded and seeded SBT thin films heated at 740°C. However, it was revealed that Aurivillius phase formation was enhanced in seeded SBT thin films and pyrochlore phase formation was highly suppressed. In this study two possible mechanisms for the suppression of pyrochlore phase formation were proposed from the perspectives of activation energy difference for Aurivillius and pyrochlore phase formation and diffusion diffusion to pyrochlore phase.

C11.34

Growth Reorientation with the Annealing Temperature of SrBi2Ta2O9 Films Dep. by PLD. Jorge Portelles1, Oscar Raymond2 and Jesus Siqueros1. 1Optical Properties, CCMC-UNAM, Ensenada, B.C. Mexico; 2Facultad de Fisica, IMRE, La Habana, Cuba.

The ferroelectric properties of SrBi2Ta2O9 (SBT) films are highly dependent on crystallographic orientation due to its highly anisotropic structure. In particular, the spontaneous polarization vector is directed along the a-b crystal plane, perpendicular to the c-axis. For SBT films prepared over the more widely used Pt/TiO2/SiO2/Si substrates, the preferred growth direction in our films is (115) rendering modest values for the polarization. It is therefore important to increase the fraction of crystallites with the a-b plane directed as close as possible to the normal to the substrate surface. In this work, SBT films produced by the Pulsed Laser Deposition (PLD) technique, in an oxygen pressure of 450mT at different temperatures, were heat treated after deposition in an atmosphere, at a temperature of 740°C. As a temperature of 740°C the X-ray diffraction pattern shows a pure SBT crystalline phase with the presence of peaks associated to (115) planes. The intensity of these peaks is increased with the deposition temperatures up to 750°C. Nevertheless, the heat treatment of the films deposited at 610°C induces a growth reorientation favoring the formation of (115) planes parallel to the film plane and improving the ferroelectric properties. Polarization values, Pm, of 9.1 &μC/cm2 and coercive fields, Ec, of 52 KV/cm at a voltage of 5V are typically obtained. This work was partially supported by grants of DGAPA-UNAM, Proj. IN104000 and CoNaCyT Proj. 355966. Thanks are due to E. Aparicio, P. Cavall, J. Díaz, I. Gradilla, P. Ruiz and G. Villalta for technical help.

C11.35

Electrical and Structural Features of Pb0.6Sr0.4TIO3 Thin Films on LSCO/MgO and LSCO/SrTiO3 Substrates. Oscar Blanco1, Abdel Pendas2 and Jesus M. Siqueros2. 1Facultad de Materiales, CICESE, Ensenada, Baja California, Mexico; 2Centro de Ciencias de la Matera Condensed, UNAM, Ensenada, Baja California, Mexico, Facultad de Fisica, Universidad de La Habana, La Habana, La Habana, Cuba.

Pb0.6Sr0.4TIO3 (PST60) thin films have been grown on LSCO/SrTiO3 [100] and LSCO/MgO[001] substrates using the RF Ion Sputtering and ferroelectric properties of PST60 films grown on both kinds of substrates are determined to evaluate the potential of this heterostructure for non-volatile memory applications. Epitaxial LSCO films was confirmed before depositing PST60 films on both of the above mentioned substrates through 4-Circle X-Ray Diffraction analysis (θ/2θ, ω and φ scans). The same analysis performed on the ferroelectric PST60 layer showed that these films are textured and epitaxial on LSCO. Both LSCO and PST60, crystallize in the perovskite structure and their lattice parameters are well matched (within 1.3% for SrTiO3). This fact renders favorable structural and chemical conditions for the growth of PST60 on LSCO. Rutherford Backscattering Spectrometry (RBS) was also used to analyze interfaces and the chemical environment for the LSCO films. TEM studies show the interaction between the LSCO textured electrodes and the PST60 layer. The electrical performance of Pb0.6Sr0.4TIO3/LSCO/PST60 capacitors was also measured with ferroelectric cycles and P-V and F-V measurements. It is concluded that textured LSCO improves the performance for the growth of PST60 but ferroelectric fatigue is still present.

C11.36

Effects of Sol-Gel Processing Parameters on Solid Solution Pb0.6Sr0.4TIO3, Ta2O5, TiO2 Powders and Thin Films. Oscar Blanco, Edgar Córdoba, Antonio L. and Sossan A.M. Huiie: Materials Science, California Institute of Technology, Pasadena, California.

A series of sol-gel derived powders for producing Pb0.6Sr0.4TiO3 (PST), a ferroelectric material of interest for sensor and actuator applications, is investigated. Precursor chemistry, water for hydrolysis, and lead/titanium composition were systematically varied and the resulting solid/liquid powders were studied using TG/DA/DSC, FTIR, and XRD. Thin films were prepared by spin coating onto single crystal (100)
MgO. Acetic acid, acetylene, and diethanolamine were used as etching agents for titanium isopropoxide and titanium butoxide, and the effects of ultrasonic irradiation on the resulting powders and thin films is examined. The importance of thermal processing was studied through varying heating rate, holding time, and ambient atmosphere during calcination, using conventional furnace annealing and rapid thermal annealing. Films were subsequently characterized by XRD and SEM to determine orientation and surface morphology. Ferroelectric properties are also examined. The etching agent used was found to significantly influence the properties required to produce high pure PBT. Thermal treatments were found to strongly affect the orientation and grain size of the resulting films. Under optimized conditions, highly oriented films were obtained for a range of Pb:Ba compositions.

C11.37

Ir Thin Films for PZT Capacitors Prepared by MOCVD Using a New Ir Precursor. Minami Shimizu1, Seichi Watari1, Hiroshi Fujisawa1, Hiroshi Nishii1 and Noriaki Ohashii1.

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Ir-based electrode materials, such as Ir and IrO2 have been extensively investigated for PZT memory applications. For the future realization of FeRAMs with high integration, the structural design of ferroelectric capacitors is one of the most important key issues and alteration of capacitor structures from planar to three-dimensional structures will be required. For this alteration of capacitor structure, MOCVD technique will be indispensable because of its high conformal growth, high growth rate and compatibility of LSI process. In this paper, preparation of Ir and IrO2 films by MOCVD using new Ir precursor, [Ir(1,4-CH2]2)] (CH3)2O were carried out, and ferroelectric properties of PZT capacitors with Ir electrode solely by MOCVD are reported. In our experiments, a new Ir precursor, Ir[EtO][CH3] was used to prepare Ir and IrO2. This precursor is a liquid at room temperature (e.g., 15°C) and the thermal decomposition temperature is 300°C. PZT films were also prepared by MOCVD. [111]-oriented Ir films with highly reflecting surfaces were successfully grown at 500-550°C on SiO2/Si. When Et[EtO][CH3] was used as a precursor, higher nucleation density and shorter incubation time were observed than when conventional Ir precursor, Ir[EtO][CH3] (COD), was used. IrO2 films with smooth surfaces were also grown at 400°C on Ir/SiO2/Si. IrO2 films obtained on step-graded layers showed good step coverage higher than 80%. Electrical properties of Ir/PZT/Ir capacitors fabricated on three-dimensional structures solely by MOCVD will be compared with those of planar capacitors.

C11.38


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Thin films of Bi-based layer-structured ferroelectric (BLSFs) are expected as candidate materials for applications to a variety of integrated devices such as non-volatile memories, high capacitance condensers and mix piezoelectric devices. However, the high-temperature processing is still needed for the BLSF thin films because of the existence of non-ferroelectric intermediates and is severe for the integration into Si semiconductor. Pyrochlore phase is a major of the non-ferroelectric intermediates, which often crystallizes initially at the interface between the thin films and Pt bottom electrodes. In this paper, nucleation layers of TiO2 were inserted between CaBi4Ti4O15 thin films and the Pt bottom by chemical solution deposition technique. Several tens nanometers in thickness of the alkoxide-derived TiO2 layers were found to be critical for the acceleration of the phase transition in the thin films. Unlike the thin film crystallized directly on the highly (111) oriented Pt bottom electrode, the thin film with 650°C-Cr-coated TiO2 layer was almost single phase of perovskite and showed random orientation. The phase purity depended on the crystallinity of the TiO2 layer. Also, the crystallinity of the BLSF thin film was much higher than that crystallized directly on the Pt bottom electrode. These crystallization behaviors of the BLSF thin films may associate with the phase transformation in the TiO2 nucleation layer itself. The dielectric and ferroelectric properties of the CaBi4Ti4O15/TiO2-stacked thin films on Pt-coated substrates will be discussed. Therefore the potential of the nucleation layer for the integrated devices would be primarily addressed.

C11.39

Preparation by Pulsed Laser Deposition and Polarization Enhancement of Nd Modified Bismuth Titanate. Minoru Nojiri, Wenhong Wu, Akira Shibaoka and Masanori Ohmori.

Graduate School of Engineering Science, Osaka University, Toyonaka, Japan.

Nd-doped Bi4Ti3O12 (NBT) thin films have been prepared by pulsed laser deposition (PLD), aiming to realize low temperature growth by considering various PLD conditions. When deposited at 500 degree C, Pt-Etching hysteresis shows twice remanent polarization compared with 69.9 and 38.4 μC/cm2, respectively. When applied high electric field ranging from -250 to +250 kV/cm, good ferroelectric properties of NBT films deposited at 54°C have been obtained up to 11 cycles, where decrease in the value of Pr and Py are less than 20% [1]. T. Kojima et al, Jpn. J. of Appl. Phys., Lett. 80, 1254 (2002). [2] T. Uchida et al, Appl. Phys. Lett. 81, 2229 (2002). [3] U. Chen et al, J. Phys. Rev. Lett. 89, 087601 (2002)

C11.40


A novel growth mode for hydrothermal film of lead zirconium titanate (PZT) has been discovered. Previously reported hydrothermal PZT films have had a loosely-packed cubic morphology, and indeed that is the most common growth mode. However, under special growth conditions, with much more dilute reactant concentrations than previously reported, substantially vertically oriented, long rod-like grains may be grown. Metal-organic reagents such as lead acetate trihydrate, zirconium propoxide, and titanium isopropoxide were used along with potassium hydroxide mineralizer. The hydrothermal process involves simultaneous deposition and etching, and it is believed that the amorphous metalorganic compounds deposit, and are converted to nanocystal-like crystals in the alkali solution. Metal and metal-organic-based reagents with appropriate seed layers, such as lead titanate (PT) and PZT were used. The hydrothermal process does not require high deposition temperatures, for example 100°C can be used in the temperature range. The hydrothermal films can be used in electronic devices such as capacitors.

C11.41

Energetic Mechanisms Operating During Pulsed Laser Deposition (PLD). Aaron Fleet1, Darren Dale2, H.H. Wang1, Y. Suzuki1 and J.D. Brock3, School of Applied & Engineering Physics, Cornell University, Ithaca, New York; 2Department of Materials Science & Engineering, Cornell University, Ithaca, New York; 3Department of Materials Science & Engineering, UC Berkeley, Berkeley, California.

The plume of material ablated from a target in PLD contains a distribution of neutral, ionic, and polyatomic species, with energies of up to 100 eV. Previous growth studies have described the growing film according to standard statistical thermodynamics, and have interpreted experimental results in the context of well-known growth modes. Our group previously demonstrated the activation of energetic atomic mechanisms during hyperthermal ion epitaxy [1]. For example, incident ions with energies near 20 eV insert themselves near terrace edges during Cu homoepaxy, given sufficient surface step-edge density. We are investigating whether similar processes occur during PLD of perovskite materials. While growing BaTiO3 twodimensionally on SrTiO3, we observed clear events off of the film, with ms time resolution. Differences in the transient x-ray intensity following laser pulses at varying surface coverage probe whether step edge density affects morphological evolution. In this talk, I will present experimental data on this issue. This work is

C11.42
Selectively Nucleated Lateral Crystallization of Lead Zirconate Titanate Thin Films Using Titanium Island Seed Layer.
Jong-In Yoo, Jeong-Ho Park, Nam-Kyu Song, Byoung-Dong Kim and Seung-Ki Joo; School of Material Science and Engineering, Seoul National University, Seoul, South Korea.

It is crucial to control grain boundaries for good lead zirconate titanate (PZT) thin films because the grain boundaries play a critical role in the degradation such as fatigue and high leakage current. We previously suggested selectively nucleated lateral crystallization (SNLC) of PZT thin film as a method of controlling grain boundaries. But this process needs additional high temperature annealing for PZT seed crystallization. We investigated selectively nucleated lateral crystallization (SNLC) of lead zirconate titanate (PZT) thin film using titanium (Ti) island seed layer. Ti island seed layer (~50 Å) was used to avoid additional high temperature annealing for crystallization of seed layer. Ti island seed layer was deposited on Pt/SiO₂/Si by radio frequency magnetron sputtering. The maximum lateral growth length was 220 nm and lateral growth region had got good piezoelectric properties. In this work, ferroelectric properties of PZT thin film crystallized by lateral crystallization will be shown and mechanism of lateral crystallization of PZT thin films will be discussed in detail through microstructure analysis.

C11.43

Thin films of ferroelectric oxides are being investigated for application in ferroelectric memory (FeRAM) devices. The advantages for these devices include high storage density, non-volatility and improved read/write times. However, many of these ceramic oxide films require high temperatures, to crystallize and to achieve optimum ferroelectric properties. For example, SrBi₂Ta₂O₇ (SBT) films are typically post-deposition annealed at 750°C in an oxidizing environment. This step is not compatible with silicon CMOS processes. Integration of ferroelectric thin films with silicon based microelectronics requires development of low temperature (≤ 550 °C) processes. This study investigated high temperature, as a low temperature alternative for processing of ferroelectric SrBi₂Ta₂O₇ (SBT), Pb(Zr,Ti)O₃ (PZT) and CeMnO₃ (CMO) thin films. We utilized metal organic chemical vapor deposition (MOCVD) films of SBT, PZT, and CMO, plus samples that had been deposited SBT. All samples described were deposited on silicon wafers with either platinum or iridium lower electrode layers. Laser annealing was done in air, using a KrF (wavelength = 248 nm) excimer laser, as a function of laser power and total number of laser pulses. Selected samples were alternatively furnace annealed, for comparison of results. The films were characterized by x-ray diffraction for crystallinity and texture and by wavelength dispersive electron microscopy for composition. Capacitor structures were formed in the films to determine their electrical properties, including capacitance versus voltage (CV) and polarization versus electric field (PE) behavior. The results show SBT films can be easily crystallized by laser annealing. The resulting ferroelectric properties are highly dependent on deposition and processing conditions. PZT and CMO films deposited by MOCVD in the temperature range of 500 C to 600 C were crystallized as deposited. Depending on the processing conditions, laser annealing could further improve crystallinity and ferroelectric properties without exposing the substrate to a high temperature processing step.

C11.44
Pyroelectricity in Quasi-Amorphous BaTiO₃ Thin Films.
Yshah Feldman, Vera Lyakhovskaya, Biyan Zen, Sidney Cohen, Ellen Wachtel, Alexander K. Tagantsev and Igor Lobkovsky; 1 Materials & Interfaces, Weizmann Institute, Rehovot, Israel; 2Research Support, Weizmann Institute, Rehovot, Israel; 3Ceramics Laboratory, Ecole Polytechnique Federale De Lausanne, Lausanne, Switzerland.

Spontaneous or stress-induced polarization, signifying pyroelectricity and piezoelectricity respectively, can appear in ionic solids solely due to a non-centrosymmetric spatial distribution of ions in a polar crystalline structure. We have investigated formation and properties of quasi-amorphous pyroelectric BaTiO₃ films. It has been found that amorphous BaTiO₃ films prepared by sputtering onto bare Si do not crystallize if passivated through a steep temperature gradient. Instead, they form as amorphous phase that demonstrates strong pyro- and piezo-electricity. Thus, this "quasi-amorphous" pyroelectric phase of BaTiO₃ represent a polar ionic solid without spatial periodicity inherent to ionic crystals. Sharp increase of the dielectric constant during the transformation of the quasi-amorphous to the quasi-crystalline films suggests that polarity of the quasi-amorphous BaTiO₃ is associated with directional ordering of crystal motifs formed in the semi-liquid state. Once formed, quasi-amorphous phase remains stable with respect to heating up to 800 °C. As-deposited films crystallize into randomly oriented cubic BaTiO₃, if subjected to heating under isothermal conditions. The development of high in-plane stresses and the change of the refractive index during the formation of the quasi-amorphous films suggested the existence of an intermediate low-density phase. Thermodynamic description based on this hypothesis quantitatively reproduces the data on thermal stability of the quasi-amorphous films. Furthermore, the hypothesis also explains the mechanism of formation of the pyroelectric phase. The ratio of pyroelectric coefficient/dielectric constant for quasi-amorphous BaTiO₃ is close to or surpasses that of LiNbO₃, making it very attractive for pyroelectric detector applications.

C11.45
Recovery of electron emission from pyroelectric LiNbO₃ single crystals. Dong-Wook Kim, Chang-Wook Moon and In K. Yoo; U-Team, Samsung Advanced Institute of Technology, Suwon, South Korea.

Electron emission was investigated in +Z faced LiNbO₃ single crystals during temperature variation. Successive heating and cooling in high vacuum reduced the emission current by two orders of magnitude. Restoration of screening emission charges enabled reproducible emission current, and two ways were proposed to supply the compensation current. The first was conduction current through the bulk, and it required about 80 hours, which were nearly three times longer than the Maxwell relaxation time. 28 hours. The second was the ionized current from an external medium, which took a few minutes by exposing the crystal to 10-1 Torr of air. Vacuum level determined the dominant screening process and the time needed to recover the electron emission.

C11.46

The use of pyroelectric thin films in uncooled IR detectors have many advantages over the present IR detector technology, which requires extensive cooling for operation. These include reduced weight, reduced footprint, reduced complexity, increased reliability, and decreased maintenance. Ba₅-xSrₓTiO₃ (BST), both doped and undoped, based thin films are ideal candidates for use in these devices due to their tunable materials properties. These properties include a wide range of dielectric constant, low dielectric loss, high electrical resistivity, as well as high pyroelectric constant. BST thin films were doped with Mg from 0 to 22 mole%. The thin films were deposited via metalorganic solution deposition on Pt/Ti/SiO₂/Si substrates. Annealing temperatures ranged from 500 to 750°C. The films were then characterized for structural, microstructural, compositional, surface morphological, dielectric and insulating properties. Glancing angle x-ray diffraction (GAXRD) samples were used to determine film formation and film orientation. Field emission scanning electron microscopy (FESEM) and cross sectional transmission electron microscopy (TEM) were employed to access surface morphology, as well as plan-view and cross-sectional grain formation. TEM was also used to detail film-substrate interface. The Materials Detection Figure of Merit (FOM), D^* E = [positive capacitance (Cp) + dissipation factor (tan δ)]/2 was used to evaluate the films detection response. Categorize (Cp), dissipation factor (tan δ) and dielectric permittivity (ε) were measured with a HP4192A impedance/gain analyzer. Permittivity values ranged from 450 to 2% Mg to 20% Mg. Dissipation factor ranged from 0.1 at 0.01 Hz to 0.11 at 20% Mg. Films insulating properties, leakage current, film evaluation using an HP4144B semiconductor test system. Pyroelectric currents were measured by the Ibyer and Roundy method.

C11.47
MOCVD of Ferroelectric Thin Films. Catherine Rice, S. Sun, J.

We have examined the growth of a number of important ferroelectric oxides by MOCVD using a rotating disk reactor. Highly uniform and reproducible films over 6" wafers have been routinely achieved. Materials include Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Strontium Bismuth Titanate (SBT), and others. Emphasis has been on achieving highly crystalline and oriented films at the lowest deposition temperatures possible, for compatibility with other integrated device materials and processing; and the achievement of optimum ferroelectric and pyroelectric performance. The effects of varying growth parameters, barrier and/or template thickness, and postgrowth annealing have been studied. The growth process, physical characteristics, and ferroelectric film properties will be discussed.

C11.40 Effect of the Substrate Temperature and Oxygen Partial Pressure on the Microstructural Evolution and Electric Properties of Charge-Balanced Barium Strontium Titanate Ferroelectric Thin Films Deposited on Ceramic Substrates by Pulsed Laser Deposition, Constant Fountoulakis1, Daniel M Petrovski2, Steven C Tidrow3, Harry Kostarelias1 and Michael Halverson3,3, ARRL, Philadelphia Proving Ground, Maryland; 3ARL, Adelphi, Maryland; 1The University of Albany-SUNY, Albany, New York

Thin films, from novel Ba4Sr substituted barium strontium titanate (BST) bulk targets, have been deposited using the pulsed laser deposition (PLD) technique. The measured and electrical properties of these thin films will be compared with the electrical properties of the bulk materials. In these materials, an applied electric field can be used to control the magnetic character of the material, hence change the phase velocity in RF/microwave devices can be tuned in real time for a particular application. The microstructure of the film influences the electronic properties that in turn influence the performance of the device. Ba4Sr3Ti6O17 thin films were synthesized at substrate temperatures ranging from 500 °C to 900 °C and oxygen partial pressure 20 and 50 mTorr, at 500 mJ laser energy and 10 pulses per second on MgO (100) substrates, using the pulsed laser deposition technique. Initial shallow glancing angle x-ray diffraction (GAXRD) studies of the synthesized thin films have revealed a [100] preferred orientation. Analysis of the microstructure deposited at 50 mTorr oxygen partial pressure by atomic force microscopy (AFM) showed a decrease in the number of defects with increase in deposition temperature. The effect of the substrate temperature in conjunction with the effect of the oxygen partial pressure on the microstructure and mechanical properties of the thin films, as studied using x-ray diffraction, SEM, AFM, Rutherford backscattering, and transmission, will be discussed along with electrical properties. In addition, the film microstructure, interphase and crack nature, as studied using focused ion beam (FIB) method, will be discussed.

C11.41 Hysteresis in Ferroelectric Domain Wall Dynamics in the Presence of Diffracting Impurities, Mikko Hangila1, David J Srolovitz1 and Yannis G Kevrekidis2, 1Princeton Materials Institute and Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey; 2Department of Chemical Engineering, Princeton University, Princeton, New Jersey.

We study a model of a driven ferroelectric domain wall through a field of diffracting impurities, which tend to segregate onto the domain wall. Through kinetic Monte Carlo simulations of the model, we demonstrate that the response of the domain wall to the applied electric field is highly nonlinear. In particular, at low drives the domain wall is pinned by the impurities, while at large values of the drive it propagates smoothly. In the vicinity of the depinning transition, we observe complex domain wall and impurity dynamics, such as aging and coarsening. The nature of domain wall hysteresis observed depends upon the sticking frequency, domain size and the number of impurities in the system (in addition to the physical parameters - diffusivity, heat of segregation, temperature and the applied field). The present model couples hysteresis increases with increasing system size and domain size. A description of hysteresis that rationalizes the dependence of the observations on frequency, domain size and simple size is proposed. This new model for hysteresis is applicable to a wide range of phenomena.

C11.42 Characterization Of Piezoelectricity Of (001) Oriented Ferroelectric Fresnoite Thin Films By AFM, Munkong Zhou1,2, Wukun Dai1, J.B Xu2, Yuedong Hou1, Bo Wang1 and Hui Yan1, 1The Key Lab of Advanced Functional Materials of CHina Education Ministry, Beijing University of Technology, Beijing, China; 2Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, China.

Fresnoite, Ba4Ti5O12, has been investigated for its unique [TiO6] square pyramid and layered structure. Recently, it was reported that fresnoite be ferroelectric even its Curie temperature Te may be over its melting temperature Tm. As a lead-free ferroelectric, its ferroelectric properties are of interest. However, few reports are available on the ferroelectricity with the domain structure for fresnoite crystal or thin films, and there is no direct observation on its ferroelectric domains. In the present study, (001) oriented fresnoite thin films have been prepared using sol-gel method. By using Ba(ACr2), TiOCl2 and SiICr(OC2H5)2 precursors, transparent sols with stoichiometric composition of fresnoite have been obtained and spin-coated onto Pt/Ti/UO2/Si (100) substrates. To crystallize the thin films, all samples are post-treated at 750 ~ 850°C. The ferroelectric and piezoelectric properties of the post-treated films show the signature of the isolated SiO2 groups that is one of the characteristics of fresnoite. Meanwhile, the Raman spectra reveals the TiO2 vibration modes from those in Bi4Ti3O12. The XRD pattern of the thin films show two strong peaks at 17° and 34.2°, respectively, corresponding to the diffraction peaks of (011) and (002) of fresnoite, which means the c-axis orientation of the thin films. By using the piezoelectric mode of AFM, the local piezoelectricity of the oriented prepared thin films has been characterized, presented the domain distribution in the thin films. Besides, the ferroelectric properties of the oriented fresnoite thin films have been studied, and the relation between the ferroelectric properties and the domain structures will be discussed.

C11.43 Formation of Stack-type PZT Capacitors for Next Generation RF Applications Using Complementary Laser Sputtering Technique, Tatsuki Ishiguro1, Koji Itagaki2, Hiroyasu Inoue2, Hiroya Ohno1, Tatsuo Ishibashi2, 1Tokyo Institute of Technology, 2Tokyo University of Agriculture and Technology, Japan.

Stack-type ferroelectric capacitors are expected to be a promising candidate for RF applications. However, the high electric field that is required for a high-Q resonator is often realized by using thick films, which makes it difficult to achieve a high-Q resonator using thin films. In this study, we fabricated PZT thin films on Si substrates using the complementary laser sputtering technique. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates. The PZT films were deposited at low temperatures (<300°C), which is low enough to avoid thermal damage to the Si substrate. The PZT films were then annealed at 300°C to improve their electrical properties. The complementary laser sputtering technique was used to deposit the PZT films on the Si substrates.
Bismuth Manganite (BiMnO3), a simple perovskite structure, known to be multiferroic, has been previously shown to be ferromagnetic and a likely ferro-electric. The BiMnO3 films used were grown epitaxially on strontium titanate [111] substrate by pulsed laser deposition technique. We used optical second harmonic generated signal from such films and monitored its response to the electric field due to the semi-direct gap transition of the material applied by femtosecond laser pulses. The films were found to be ferroelectric as well as ferromagnetic. This presentation we also show that it is also highly nonlinear optical material besides its ferroelectricity. We have observed giant enhancement of the second harmonic signal by 3-4 orders of magnitude with an electric field of ~16-50kV/cm, under the influence of the electric field. Also, we have found that it has large third order optical nonlinearity as measured by single beam Z-scan technique. The third order optical nonlinearity was measured by single beam Z-scan technique. The nonlinear absorption coefficient was measured to be ~0.1cm/AW. We used pulsed Ti: Sapphire mode-locked femtosecond laser to measure both the second and third order nonlinear optical coefficients at 900nm. All this three properties viz. ferro-electricity, ferromagnetism and optical nonlinearity makes it a uniquely interesting material to study and promises to open up several new possibilities for various device applications.

C11.54 Characterization and Development of Wafer Bonded Single Crystal Thin Film LiNO3:Si for Waveguide Applications

Jennifer Lynn Buglokozy, Younghee Park, James Zoller and Harry Arwster, Applied Physics, California Institute of Technology, Pasadena, California.

Lithium nitrate has been termed the ‘silicon of nonlinear optics’ owing to its several useful electro-optical properties, relevant for applications of modulators, switches, and waveguides. The ability to synthesize high quality single crystal LiNO3 thin film form can improve the performance and integration possibilities by increasing modulation frequency and decreasing both device size and operating voltage. We have investigated the growth of a LiNO3:Si/Si wafer bonding process. Beam propagation simulations were used to design a single mode waveguide of 700nm thick film of LiNO3 on 1µm of SiO2 on Si. Simulations show low propagation losses and mode confinement in the LiNO3. Using wafer bonding and ion implantation, we have transferred 700nm thick films of 0.5-µm LiNO3 onto 1µm thick layer of SiO2 on a Si substrate. However, we have found that the ion implantation required for thin film layer transfer toughens the LiNO3 surface, completing LiNO3 bond formation. Photolithography with 150nm and 300nm thick 193 nm UV mask and 15750V He at 5x10–8cm3/sec x 300keV He x 45keV He yields yield thickness of 700nm top surface of the LiNO3 increases roughness from 100A to 250Å. Approaches to LiNO3:Si wafer bonding include microwave bonding, laser bonding, bonding LiNO3 layers, and bonding LiNO3 thin layers using photonic waveguide measurements will be presented.


Sell/Th2Ti2O9 (SBT) thin films were deposited on SBT nanoparticle (1-200nm) seeded Pt/Ti/SiO2/Si substrates via solgel and spin coating techniques. The SBT thin films were heated at 600°C for 1 hour to form the Aurivillius phase, and these films were further heated at 730-760°C for fluorite-to-Aurivillius phase transformation. The volume fraction of Aurivillius phase formation through quantitative x-ray diffraction analyses showed highly enhanced kinetics in seeded SBT thin films. Johnson-Mehl-Avrami (JMA) isostructural kinetics analyses were performed for the characterization of Aurivillius phase formation in unseeded and seeded SBT thin films using the volume fraction values. The Avrami exponents were determined as ~1.4 and ~0.9 for unseeded and seeded SBT films respectively, which reveals different nucleation modes. By using Avrami-type plots the energy effects for the transformation of unseeded and seeded SBT thin films were determined to be ~261 and 188 kJ/mol, respectively. This gives a key reason for the enhanced kinetics in seeded SBT thin films. Microstructural analyses on unseeded SBT thin films showed formation of randomly oriented needle-like crystals, while those on seeded ones showed formation of clusters comprising directionally grown needle-like crystals. One the basis of the phase formation kinetics and microstructural development, a model representing different nucleation and crystal growth mechanisms for the unseeded and seeded SBT thin films was proposed.

C11.56 Enhanced Figure-of-Merit Characteristics of PZT Thin Films for Uncooled Pyroelectric IR Sensors, Seung-Hyun Kim, Cheong Young Moon, Seung-Soon Yang, Sujeong Yoon, Jun-Shik Park, and Jeong-Ho Park, HiD Center of Excellence, Seoul National University, Seoul, South Korea.

Pyroelectric infrared detectors have been widely used due to several advantages of wavelength-independent sensitivity and room temperature operation. Room temperature operation eliminates the need for elaborate cryogenic cooling and cryo-dyne-packing. To make pyroelectric detectors, reduces sensor complexity and cost, and improves sensor reliability and maintainability. Among a variety of ferroelectric perovskites, tetragonal PZT system is the most promising candidate for the pyroelectric materials since it has a relatively high resistivity, low dielectric loss, moderate permittivity, high resistivity and a large pyroelectric coefficient. Current requirements to move the uncooled IR detectors into the commercial marketplace are to enhance the performance of pyroelectric materials, and to integrate pyroelectric thin films into the linear and 2D arrays, which can further enhance their performance and applicability by enhanced compatibility with silicon technologies. To address these issues with more systematic investigations, we explore the pyroelectric properties of PZT thin films responsible for figure of merit characteristics by three different variables; (1) Zr/Ti composition, (2) donor dopant concentration, and (3) film thickness. In addition, using the pyroelectric technology, PIR sensors have been designed with optimized PZT thin films based on the experimental results. Full description of the processing and structural and pyroelectric characteristics of PZT thin film PIR sensor devices will be presented. * INOSTEK Inc. acknowledges the support of this work from National Research Laboratory (NRL) program of MOST.

C11.57 Abstract Withdrawn

C11.58 First Prototype of High-Density Ferroelectric Data Storage System, Yoshimi Hirayama, Yasuo Cho and Yasuo Watarase, Research Institute of Electrical Communication, Tohoku University, Sendai, Miyagi, Japan.

Scanning nonlinear dielectric microscopy (SNDM) is the purely electrical method for observing polarization distribution of ferroelectric materials with the resolution of sub-nanometer range. We have studied on ultra high-density ferroelectric data storage based on this microscopy, and reported that inverted dot array with areal density of 1.5Tbit/inch2 was successfully written in congruent LiTaO3 (CUT) single crystal medium [1] Although traditional SNDM domain engineering system, which is remodeled from commercial atomic force microscope unit, is useful for study on domain inversion characteristics in nanosopic region, this system is inadequate to establish basic elemental technologies of high-density ferroelectric data storage, and a system equipped with all components necessary for actual read/write is required for further study aiming for practical application. Therefore, in this study, we developed the first prototype of high-density ferroelectric data storage system. The read/write head of the developed system is composed of a metal-coated conductive cantilever (typical tip radius is 25 nm) and an oscillator, which is tuned to the resonance frequency determined by the capacitance just under the tip of the cantilever and the inductance embedded in the circuit. Writing is performed by applying a relatively large voltage pulse to a ferroelectric medium and locally switching the polarization direction at each point in the scan. On the other hand, reading is performed by detecting the small variation of resonance frequency caused by the capacitance variation due to the nonlinear dielectric response induced by alternating voltage applied to the medium. Firstly, we carried out a basic operation check using the developed system, and confirmed that the data written in CUT single crystal medium is correctly read out. Subsequently, data transfer rate of this
system was evaluated. As a result, 9 kbps reading and 50 kbps writing were demonstrated with respect to 440 kbit/s high bit data rate. Additionally, we also confirmed that direct bit overwriting could be realized using this system. [1] Y. Cho, K. Fujimoto, Y. Hirama, Y. Watanabe, A. Onoe, K. Terabe and K. Kitamura, Appl. Phys. Lett. 81, 4401 (2002).

C11.50
MOCVD and Electrical Properties of Hexagonal Yttrium Manganite Thin Films for Single Transistor Nonvolatile Ferroelectric Memories: J. J. Kingery1, David I. Dalton1, Klaus J. Dimmler1, Fred P. Gradliger2, David G. Klingensmith1, Vicrel Obrias1, Ali J. Mahmoud2, Masiru Rahman2 and T. S. Kalikur2;

Hexagonal YMnO3 perovskite is of interest due to its potential to be a ferroelectric material of choice for the next generation ferroelectric non-volatile memories based on single transistor cells (1T cell). Its low dielectric permittivity (about 20) and high Curie temperature (Tc > 600°C) are very suitable for achieving low operation voltages and CMOS process integration. In the present investigation, a Metal Organic Chemical Vapor Deposition (MOCVD) process was developed to deposit thin films of YMnO3 on Silicon substrates and a detailed study was conducted on the relationship between the film properties and its deposition/processing parameters. Formation of a c-axis oriented hexagonal phase of the YMnO3 has been reported to be crucial for its ferroelectric performance. In the present study, it was found that while both the formation of the hexagonal phase of the YMnO3 and its electrical properties depend on the film's composition and the annealing conditions the orientation of the film is profoundly influenced by the deposition parameters. The YMnO3 films produced by the MOCVD process were examined using X-ray diffraction, TEM, HREM and EDS analysis. Its electrical properties were characterized using C-V, I-V hysteresis and pulsed-switching analysis. The results of this study along with the description of the MOCVD reactor used will be presented.

C11.60

We demonstrate a novel application of the auxiliary differential equation method of finite difference time domain (FDTD) simulation to describe propagation of phonon-polaritons (mixtures of lattice vibrations and electromagnetic waves) in ferroelectric crystals. Phonon-polariton generation by near-IR optical pump fields, phonon-polariton propagation, and phonon-polariton detection by near-IR probe pulses are simulated and compared to experimental measurements. Coupled ionic displacements and THz fields as well as phonon-polariton dispersion relations in bulk and thin film ferroelectrics are calculated. We also demonstrate simulations of phonon-polaritons in patterned ferroelectric materials and demonstrate their utility for design of patterned materials that can be fabricated using ultrafast laser machining. Additional avenues of exploration presented using this simulation approach include THz manipulation of ferroelectric domain switching, the use of electrically stressed ferroelectric domains as THz gain media, and the incorporation of quantum susceptibilities to simulate the interaction of phonon-polaritons with parabolic quantum wells and other quantum systems.