

SYMPOSIUM T
Ferroelectric Thin Films XIII

November 27 - December 1, 2005

Chairs

Ramamoorthy Ramesh

Dept. of Materials Science & Engineering
University of California-Berkeley
Berkeley, CA 94720
510-642-2347

Jean-Paul Maria

Dept. of Materials Science & Engineering
North Carolina State University
Research Bldg. 1, Rm. 322
Raleigh, NC 27695-7919
919-513-2843

Marin Alexe

Max-Planck-Inst of Microstructure Phys
Weinberg 2
Halle (Saale), D-06120 Germany
49-345-5582-705

Vikram Joshi

IC Intelligence Corporation
PO Box 993
Palo Alto, CA 95302
650-861-2341

Proceedings to be published online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume **902E**
of the **Materials Research Society**
Symposium Proceedings Series.

This volume may be published in print format after the meeting.

* Invited paper

TUTORIAL

FTT/U/W: Smart Materials – Fundamentals and Applications
Sunday November 27, 2005
9:00 AM - 12:30 PM
Room 200 (Hynes)

This tutorial will focus on the broad range of inorganic and organic functional materials that are being studied for applications as “Smart Materials,” including piezoelectrics, multiferroics, and electroactive polymeric materials. The tutorial aims to give the attendee a broad perspective of the various materials and their fundamental science, and then finish up with a summary discussion of their applications. Each segment will include background information, a description of the method, the current state of the art, new trends, and unique advantages and limitations (e.g., for fabrication of particular materials or devices, scalability, unusual geometries, and integration in multistep hybrid device fabrication schemes). The intention of the tutorial is to give the attendee a fundamental background on each method, the strengths of each technique, the ease/difficulty/cost of setting up, and future directions.

Fundamentals of Piezoelectric Materials – Trolier-McKinstry
Multiferroics – Viehland
Electroactive Polymers – Cheng
Applications and Examples – Madden

Instructors:
Z. Y. Cheng
Auburn University

John Madden
University of British Columbia

Susan Trolier-McKinstry
The Pennsylvania State University

Dwight Viehland
Virginia Tech

SESSION T1: Piezoelectrics
Monday Morning, November 28, 2005
Back Bay D (Sheraton)

8:00 AM *T1.1
Abstract Not Available [L. E. Cross](#)

8:45 AM *T1.2
Giant Piezoelectricity on Silicon for Integrated Sensors and Actuators. [Chang-Beom Eom](#), Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Smart materials that can sense, manipulate, and position are crucial to the functionality of micro- and nano-machines. Integration of single crystal piezoelectric films on silicon offers the fabrication of high performance piezoelectric microelectromechanical systems (MEMS) incorporating all the advantages of large scale integration on silicon substrates with on-board electronic circuits, in a manner which may radically improve performance at significantly lower cost. We have fabricated heterostructures with the highest piezoelectric coefficients ever realized on silicon substrates by synthesizing optimally oriented, epitaxial thin films of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) on vicinal (001) Si wafers using an epitaxial (001) SrTiO_3 template layer. The longitudinal (d_{33}) and effective transverse ($-e_{31}$) piezoelectric coefficients of the films are over 1200 pm/V and -29 C/m², respectively. These are highest values that have ever been reported for any piezoelectric films. These epitaxial heterostructures can be used for multilayered high performance MEMS devices that function with low drive voltage, high frequency ultrasound transducer 2-D arrays for medical imaging, micro-fluidic control, and capacitors for charge and energy storage. This work has been done in collaboration with D.M. Kim, R.R. Das, V. Vaithyanathan, N. B. Gharb, Y.B. Chen, H.P. Sun, J. Ouyang, V. Nagarajan, S. Trolier-McKinstry, R. Ramesh, D.G. Schlom, X.Q. Pan, S.K. Streiffer.

9:15 AM T1.3
Non-Linear Dielectric and Piezoelectric Response in {111} and {100} Oriented $0.5\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-}0.5\text{PbTiO}_3$ Thin Films. [Nazanin Bassiri Gharb](#)¹, [Dragan Damjanovic](#)² and [Susan Trolier-McKinstry](#)¹; ¹Materials Science and Engineering Department and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; ²Ceramics Laboratory, Ecole

Polytechnique Federale de Lausanne, Lausanne, CH-1015, Switzerland.

In this work, the nonlinear dielectric and piezoelectric response of {111} and {100} oriented thin films of 0.5 lead ytterbium niobate-0.5 lead titanate are reported as a function of AC electric field using a Rayleigh approach to separate reversible and irreversible contributions to the properties. The dielectric and piezoelectric properties of {100} oriented films show higher irreversible Rayleigh coefficients than {111} oriented films. The ratio of the irreversible to reversible coefficients is also higher in the {100} oriented films, showing a higher contribution to the dielectric permittivity and piezoelectric coefficient due to the irreversible component (movement of the domain walls) in these films with respect to the {111} oriented films. The nonlinear dielectric behavior of the films was also studied as a function of frequency (20Hz to 200kHz) and temperature (15K to 635K). The Rayleigh parameters showed a logarithmic dependence on frequency, as predicted for phenomena caused by the motion of the domain walls. The Rayleigh parameters decreased at lower temperatures, indicating a thermal dependent origin of the extrinsic contributions. Typically, the nonlinearity in the piezoelectric response that results from high field drive has been attributed to motion of non-180° (ferroelastic) domain walls. Here, we show that there are circumstances under which the field dependence of the piezoelectric coefficients can be due to largely reversible motion of domain walls, even if the only mobile walls in the system are not ferroelastic. The resulting piezoelectric coefficients follow a Rayleigh Law for the field dependence. This effect is experimentally confirmed in {100} oriented $0.5\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-}0.5\text{PbTiO}_3$ thin films. One distinguishing feature of this type of nonlinearity is a large second harmonic response in the strain response to an applied electric field.

9:30 AM T1.4
Surface Micromachining Approach to Ferroelectric MEMS Devices. [Jennifer Lynn Ruglovsky](#)¹, [Matthew Dicken](#)¹, [Kenneth Diest](#)¹, [Mohamed El-Naggar](#)², [Rongjing Zhang](#)², [Guruswami Ravichandran](#)², [David Goodwin](#)² and [Harry A Atwater](#)¹; ¹Applied Physics, California Institute of Technology, Pasadena, California; ²Mechanical Engineering, California Institute of Technology, Pasadena, California.

The realization of free-standing ferroelectric thin film devices compatible with CMOS processing is a priority in achieving sophisticated MEMS systems. To release an active film from a silicon substrate with a back-etch technique requires the removal of hundreds of microns of the substrate as well as a suitable and robust mask for the device layer. A more flexible and process compatible technique is surface micromachining. We present work utilizing a XeF_2 etch process for surface micromachining silicon with a resistant patterned oxide layer to create free-standing ferroelectric MEMS structures. With surface patterning, we are able to realize both bridge and cantilever geometries. Bridges are of interest because the tensile stress resulting from CTE mismatch in the layers promotes the switching of not only 180° but also 90° domains during device actuation, whereas cantilevers enable characterization of the linear piezoelectric effect. Both barium titanate and lead titanate thin films, grown by MBE and MOCVD, respectively, will be discussed. Each material has been synthesized in three different thin film microstructures: 1) poorly oriented, 2) fiber textured, and 3) biaxially textured. The latter two microstructures require a template layer, but otherwise the device structures employ similar layer thicknesses, electrodes, etc. Thus device performance may be correlated with chemical composition and microstructure. Materials characterization using both Piezoresponse Force Microscopy for the quantification of micro-scale ferroelectric properties and a ferroelectric tester utilizing a Sawyer-Tower circuit to measure polarization hysteresis over larger, device-scale areas enables micro-scale displacement to be correlated to macro-scale mechanical behavior. Cantilever displacement with applied voltage was measured using an AFM optical cantilever detection apparatus. Bridges were tested by measuring voltage induced forced displacement via load tips.

10:15 AM *T1.5
Engineering Elastic Domain Structures in Epitaxial Films. [Alexander Roytburd](#), Materials Science and Eng.Dept, University of Maryland, College Park, Maryland.

Non-180° domains in epitaxial ferroelectric films very often serves as elastic domains minimizing misfit energy. Three systems of 90° domains are formed to relax misfit stress in films of tetragonal ferroelectrics on cubic substrates. The number of necessary domains can be decreased by selection of special orientations of a substrate or by film patterning. Transfer from a three-domain state to a two-domain one results in the increase of mobility of domain walls and can dramatically enhance piezoelectric and dielectric film properties. Theoretical analysis and experimental results for PZT films will be presented to support above statements.

10:45 AM T1.6

A real-space non-local phase-field model of ferroelectric domain patterns in complex geometries. Kaushik Dayal and

Kaushik Bhattacharya; Engineering, California Institute of Technology, Pasadena, California.

Ferroelectric perovskites are used in various MEMS devices due to the strong coupling between electric field and strain. They also have large nonlinear responses to optical excitation for which they have been proposed as an element of photonics devices. In these applications, ferroelectrics are machined to have complex geometries with a complex arrangement of patterned electrodes. It is important therefore to understand the domain patterns that form in these complicated geometries. However, available phase field models assume periodicity or unrealistic electric boundary conditions, and do not lead to useful results in these contexts. Therefore, we develop a real-space non-local phase-field model to address this issue. The key issue is to resolve not only the dipole-dipole interactions in the ferroelectric but also stray or induced fields in the surroundings in a computationally efficient manner. We do so by using a boundary element method to account for the non-local electrostatic contributions, and this makes the modeling of free surfaces computationally tractable. The model is constructed by identifying the total energy consisting of Landau, domain wall and electrostatic contributions. We calibrate the method by simulating AFM topography measurement experiments, and use this to test different hypotheses of closure domains at the free surfaces of ferroelectric crystals. We also simulate PFM experiments in an accurate and consistent manner, by modeling the charged tip and calculating the response to the PFM taking into account nonlinear effects, such as large fields near the tip, and local switching. We also use the method developed to study the behavior of a ferroelectric crystal with patterned electrodes, a geometry that is of interest in the design of electronic devices with ferroelectrics. The ability of the boundary element method to handle free surfaces also allows us to study the nature of closure domains in ferroelectrics and the interplay between elastostatic energy and electrostatic energy. We also study configurations that are of interest in building photonics devices with barium titanate.

11:00 AM *T1.7

High Permittivity Barium Titanate Films and Their Patterning by Micro-contact Printing. Hajime Nagata¹, Susan

Trolier-McKinstry¹, Clive Randall¹, Pascal Pinceloup², James Beeson², Daniel Skamser², Michael Randall² and Azizuddin Tajuddin²; ¹The Pennsylvania State University, University Park, Pennsylvania; ²KEMET Electronics, Greenville, South Carolina.

Barium titanate (BaTiO₃, BT) thin films were prepared by chemical solution deposition on nickel foils, in the absence of chemical barrier layers. The films were sintered in a high temperature reducing atmosphere so that nickel oxidation is avoided. All thermal processing is performed at relatively low temperature (800 - 1100 °C) as compared with ceramic processes. Subsequent lower-temperature, higher oxygen pressure anneals were used to minimize oxygen point defects. These films showed a single phase perovskite structure with random or (100) orientation depending on the pretreatment of the nickel foils and the annealing conditions used. Homogeneous and very fine grains of >100nm in size were observed by SEM. High permittivities ($\epsilon_r \sim 3000$) were obtained in >200 nm thick BT films with loss tangents under 3% and with temperature coefficient of capacitance in X8R classification from 25 °C to >150 °C. Integrating BaTiO₃ films on nickel foil represents an important step towards high capacitance density passive components. The next important step for achieving high capacitance density passive components is to assemble these thin layers into a multi-layer capacitor configuration. Photolithography is routinely available, but is prohibitively expensive, especially for large numbers of layers. Consequently, it is important to consider inexpensive, manufacturable approaches to making multilayer samples on a basis that will fulfill world-wide demand for capacitive passive components into the next several decades. In this work, micro-contact printing was employed to pattern bulk dielectrics (BaTiO₃) and electrodes (LaNiO₃). Polydimethylsiloxane (PDMS) was used as the stamp for this experiment. After an oxygen plasma treatment of PDMS surface in order to render it hydrophilic, BT solution was coated on the PDMS by spinner with 2000-4000 rpm. Once coated, BT solutions were transferred to SiO₂/Si, Al₂O₃ substrates and Ni foils. Transferred BT features have 100-300 nm height. The height of the feature increased with increasing solution concentration and decreasing spinning speed. Edge resolution of better than 5 μm and a thickness uniformity of about 10 nm were achieved in micro-contact printed features. We believe that the quality of this feature will permit the assembling of ultra-thin multi-layered passive components. A prototype multilayer capacitor was built using this approach.

11:30 AM *T1.8

Lead-Free Ferroelectrics and Piezoelectrics. T. Zhao,

Department of Physics and Department of Materials Science and Engineering, University of California, Berkeley, California.

A challenge and, at the same time, an opportunity for the materials science community, especially the ferroelectric community, is to develop a new lead free ferroelectric/piezoelectric material to replace the currently used lead-based materials for a non-volatile, high speed, low power consumption, and high density ferroelectric memory cell and/or a high efficient piezoelectric transducer. The requirements for such a material, e.g. coercive field, fatigue, retention, etc. and a comparison among different ferroelectric materials will be discussed. The current progresses on a promising candidate for the lead free ferroelectric material, BiFeO₃ (BFO), will be presented. BFO thin films, in a thickness range from 2.8nm to 400nm, were prepared by pulsed laser deposition, sputtering, and chemical vapor deposition on SrTiO₃ and SrTiO₃/Si wafers with orientations of (001) and (111). The ferroelectricity and piezoelectricity were studied by RT-6000 ferroelectric probe station and piezoelectric force microscopy (PFM). A square-like ferroelectric hysteresis loop, a ferroelectric polarization and an out-of-plane piezoelectric coefficient (d_{33}) comparable to the values of a Ti-rich PbZrTiO₃ were achieved. A tunability of the coercive field and leakage current of the BFO films was realized by suitable chemical doping. The ferroelectric domain structure and its evolution with film thickness were studied by PFM; a stress-induced structure change from rhombohedral-like to tetragonal-like was observed in thin BFO films. The problems needed to be solved for this material to be used in a ferroelectric memory cell will also be discussed. This work is supported by an ONR MURI program.

SESSION T2: Ferroelectric Thin Film Processing Science

Chair: M. Alexe

Monday Afternoon, November 28, 2005

Back Bay D (Sheraton)

1:30 PM *T2.1

Nano-ferroelectrics. James F. Scott, Cambridge University, Cambridge, United Kingdom.

I summarize recent work on ultra-thin (65-nm) single crystals of SrTiO₃ and BaTiO₃ and show which finite size effects are intrinsic and which are extrinsic. I also discuss lateral sizes and show that the coercive field dependence upon ramp rate is quite different for capacitors of submicron width than for larger cells; the Landauer-Young-Drougard theory of switching, which neglects nucleation, describes the large cells well, but the submicron devices require the nucleation model of Pulvari and Kuebler. Detailed data are presented for Samsung 0.19 square micron lead zirconate-titanate (PZT) 32-Mb FRAM (random access memory) cells. Some data are also shown for nano-domain structures in SBT (strontium bismuth tantalate) nanotubes, along with our attempts to utilize these for ink-jet print heads and liquid drug delivery systems. Finally I show what occurs chemically when a nano-diameter filamentary short occurs in PZT and bismuth titanate films: The PZT phase separates into both alpha- and beta-PbO (from which estimates of the pressure and temperature inside the short can be made) and rutile TiO₂ but not anatase. In contrast, the bismuth titanate loses oxygen and bismuth and converts in part to pyrochlore.

2:15 PM T2.2

A superlattice approach to the synthesis of ferroelectric SBT thin films using liquid-injection-MOCVD. Richard J. Potter¹,

Ahmed Awad¹, Paul R. Chalker¹, Peng Wang¹, Anthony C. Jones^{2,3}, Timothy C. Q. Noakes⁴ and Paul Bailey⁴; ¹Engineering, The University of Liverpool, Liverpool, Merseyside, United Kingdom; ²Department of Chemistry, University of Liverpool, Liverpool, Merseyside, United Kingdom; ³Epichem Ltd, Bromborough, Merseyside, United Kingdom; ⁴CCLRC Daresbury Laboratory, Warrington, Cheshire, United Kingdom.

The low temperature synthesis of SrBi₂Ta₂O₉ (SBT) and SrBi₂(Ta_{1-x}Nb_x)₂O₉ (SBTN) thin films have been investigated using a superlattice approach. SBT films were deposited at 500°C using liquid injection MOCVD of a "single-source" Sr-Ta heterometal alkoxide precursor, Sr[Ta(OEt)₅(dmae)]₂ (dmae=OCH₂CH₂NMe₂) together with a separate Bi source, Bi(mmp)₃ (mmp=OCMe₂CH₂OMe). Thin films were deposited on silicon by independent injection of each source to produce Bi₂O₃/SrTa₂O₅ superlattices. This approach promotes the controllable incorporation of Bi and Sr in the films whereas co-deposition has previously been shown to result in a rapid suppression of Sr incorporation as Bi(mmp)₃ injection rate was increased [1]. The effect of the superlattice interlayer thickness was investigated and the results indicate that surface reactions during the growth process were responsible for the suppression of Sr incorporation. Optimization of

the SL interlayer thickness' has enabled the deposition of the required Sr: Ta: Bi ratios. The effects of post-deposition annealing have been investigated using medium energy ion scattering (MEIS) to depth profile the super lattices and measure the interlayer interdiffusion as a function of temperature. X-ray diffraction and Raman spectroscopy have also been used to characterize the conversion of the superlattices. Post-growth annealing the optimized superlattices converts the distinct layers of Bi₂O₃ and SrTa₂O₅ containing some interfacial pyrochlore, into a single layer of the perovskite SBT phase. The prospects for depositing ferroelectric SBT and SBTN films at low temperatures without the need for post-growth annealing will be discussed. [1] P.R. Chalker, R.J. Potter, J.L. Roberts, A.C. Jones, L.M. Smith, M. Schumacher, *Journal of Crystal Growth*, **272**, 778-784 (2004).

3:30 PM *T2.3

Synthesis and Properties of Barium Titanate Thin Films Deposited on Copper Foil Substrates. Jon Ihlefeld¹, Seigi Suh², William Borland² and Jon-Paul Maria¹; ¹Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; ²DuPont Electronic Technologies, Research Triangle Park, North Carolina.

Barium titanate thin films have been deposited on copper foils in the absence of interfacial layers via a chemical solution process. The dielectric - base metal stacks have been processed in reductive atmospheres such that substrate oxidation is avoided while allowing the perovskite film phase to crystallize. This accomplishment has facilitated the pursuit of a new embedded capacitor technology offering compatibility with polymer printed wiring boards and capacitance densities in excess of 2.5 $\mu\text{F}/\text{cm}^2$. This represents a distinct improvement beyond conventional foil-based capacitor strategies. Finally, three critical phenomena will be discussed: (1) the effect of grain size on the dielectric properties of barium titanate thin films (2) the effect of B-site substituents Zr and Sn on the lattice, microstructure, and dielectric properties and (3) the importance of cation stoichiometry. Most importantly, high processing temperatures have allowed for microstructural and dielectric properties similar to well-prepared bulk ceramics, including average grain diameters greater than 0.1 μm , relative permittivities in excess of 2000, and coercive fields below 10 kV/cm. These properties will be discussed in the context of bulk ceramic and thin film reference data and with regard to integration into printed wiring boards.

4:00 PM *T2.4

Multiferroic Characteristics and Giant polarization of BiFeO₃ Thin Films. Masanori Okuyama, Kwi-Young Yun and Dan Ricinschi; Dept. of Systems Innovation, Grad. School of Eng. Sci., Osaka University, Toyonaka, Osaka, Japan.

BiFeO₃ (BFO) films have been deposited on Pt/TiO₂/SiO₂/Si substrates at temperature as low as 450°C by pulsed laser deposition. The XRD shows that the film deposited at 50 mTorr consists of perovskite single phase. Dielectric constant and loss tangent are 146 and 0.03, respectively, and show a slight decrease with decrease of temperature and gradual decrease with probe frequency. Dielectric constant shows a good butterfly-shape hysteresis. Polarization hysteresis is observed at RT and the remanent polarization (Pr) is 102 $\mu\text{C}/\text{cm}^2$. Piezoresponse-Force-Microscopy domain maps show a nucleation-growth switching. The memorized polarization has been well maintained during a standard retention measurement. Moreover, the film shows a well-saturated weak ferromagnetic hysteresis loops at RT and the saturation magnetization is 40 emu/cm³ for a maximum magnetic field of 10 kOe due to canting of the spins. The piezoelectric coefficient is 66 pm/V, which is comparable to Ti-rich PZT film. Decreasing the temperature down to 90 K allowed us to obtain giant ferroelectric polarization such as Pr of 146 $\mu\text{C}/\text{cm}^2$ and a saturation polarization of 158 $\mu\text{C}/\text{cm}^2$ with a coercive field of 120 kV/cm at 20 V maximum applied voltage. This hysteresis loop has little change with the scanning frequency above 100Hz. These polarization values are the highest ever-measured in ferroelectric materials and have shown good reproducibility. The first-principles calculation of various BFO structures has been carried out by using density-functional theory. Electronic band structure of rhombohedral phase shows finite band gap, but those of tetragonal and cubic phases show some quasi-metallic states. Spontaneous polarization calculated using Berry phase is 97 $\mu\text{C}/\text{cm}^2$ in the rhombohedral phase but that using Born Effective Charges in cubic phase can be as high as 133 $\mu\text{C}/\text{cm}^2$. These calculations suggest that the measured giant ferroelectric polarization in BFO is consistent with theoretical values.

4:30 PM T2.5

PZT and PLZT thin films on Cu substrates for dielectric and piezoelectric applications: Effect of processing atmosphere and film strain. Angus Ian Kingon, Sudarsan Srinivasan and Taeyun Kim; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

PZT and PLZT thin films on Cu foil substrates are of interest for embedded applications, as they can be embedded into printed wiring boards to produce both high value capacitors as well as additional functionality within the low-cost board. The copper substrate is attractive due to its low cost and very low resistivity. We have previously demonstrated the possibility of processing PZT thin films on copper substrates through tight control of oxygen partial pressure during processing. In this research we first isolate the effect of reduced oxygen partial pressure processing on properties by direct comparison of films processed on Cu with those processed on Pt foils under a wide range of oxygen partial pressures. We show that over this wide range, there is a relatively small impact on properties, and discuss the reasons for these observations. The study is then extended to PLZT films, with the composition range including both ferroelectric phases (for piezoelectric applications) and paraelectric phases (for dielectric applications). We show that for the ferroelectric films there is a strong dependence of properties on the film strain (induced simply by thermal expansion mismatch with the copper substrate and by sample bending). We have used the (PFM) piezo force microscope) to characterize the piezoelectric response and the domain structure. We show that film strain induce by bending has a large impact upon the domain structure, and the increased density of ferroelastic domain walls has in turn an substantial impact on ferroelectric, dielectric and piezoelectric properties. The implications are discussed: they may be viewed as an additional complexity, or alternatively as a new opportunity for introducing useful functionality into microelectronic systems based on printed wiring boards.

4:45 PM T2.6

Dielectric property control using crystal structure anisotropy in bismuth layer-structured dielectric. Muneyasu Suzuki¹, Kenji Takahashi¹, Takayuki Watanabe¹, Tadashi Takenaka³ and Hiroshi Funakubo^{1,2}; ¹Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Japan; ²PRESTO, Japan Science and Technology Agency, Saitama, Japan; ³Electrical Engineering, Tokyo University of Tokyo, Noda, Japan.

Bismuth layer-structured dielectrics (BLDs) have a strong anisotropy in the electrical properties due to their stacking crystal structure of bismuth oxide layer and pseudo-perovskite layer along *c*-axis. Following this crystal anisotropy, we found promising low leakage current density, low bias dependence of relative permittivity and constant relative permittivity independent of the film thickness and applied field. In the present study, we reports on the unique temperature dependence of the dielectric characteristics using epitaxial SrBi₄Ti₄O₁₅ (SBTi) with various *c*-axis tilting angles from the surface normal direction. SBTi has ferroelectricity along *a*-axis, but no ferroelectricity along *c*-axis due to the alignment of the BO₆ octahedron having a mirror plane. SBTi thin films with film thickness from 150 to 200 nm were prepared by MOCVD from Bi(CH₃)₃, Ti(O-*i*-C₃H₇)₄, Sr(C₁₁H₁₉O₂)₂ (tetraene)_{*x*}, and the O₂ gas. (001), (110), (105)/(015) and (100)/(010) oriented ones were grown on (100)SrRuO₃/(100)SrTiO₃, (110)SrRuO₃/(110)SrTiO₃, (111)SrRuO₃/(111)SrTiO₃ and (101)RuO₂/(110)Al₂O₃ substrates, respectively. The tilting angles of *c*-axis respective correspond to 0, 45, 55 and 90 degree for (001), (110), (105)/(015) and (100)/(010) oriented films. The temperature dependence of the dielectric properties from 80 to 400 K was measured at 100 kHz. The temperature coefficient of the capacitor (TCC) was respective 690 and 1370 ppm/K for the (110) and (105)-oriented one between 230 and 400 K. These positive values are explained by the ferroelectricity of SBTi with high Curie temperature, 803 K. On the other hand, the negative value, -105 ppm/K was observed for the (001) oriented one. These data shows that the TCC can be design by selecting ions and the number of BO₆ octahedra in pseudo-perovskite layer in BLDs thin films, because we indeed ascertained to various TCC value from positive to negative for various BLDs thin films.

SESSION T3: Poster Session I
Chairs: M. Alexe, V. Joshi, J.-P. Maria and R. Ramesh
Monday Evening, November 28, 2005
8:00 PM
Exhibition Hall D (Hynes)

T3.1

Transverse piezoelectric coefficients of {100}-textured PZT films with PbTiO₃ and PbO seed layers. Jian Zhong^{1,3}, Hui Han², Xiuyu Song¹, Periaswamy Padmini¹, Sushma Kotru¹ and Raghvendra Kumar Pandey¹; ¹Department of Electrical and Computer Engineering, The University of Alabama, Tuscaloosa, Alabama; ²Department of Physics and Astronomy, the University of Alabama, Tuscaloosa, Alabama; ³Material Science Program, the University of Alabama, Tuscaloosa, Alabama.

Lead zirconate titanate (PZT) film is one of the candidate materials for microelectromechanical systems (MEMS) due to its large piezoelectric response. Recent experimental and theoretical results show that {100}-textured PZT film with a composition close to morphotropic phase boundary (MPB) in rhombohedral side has the highest piezoelectrical coefficient. One of effective ways to obtain {100} texture is to deposit a proper seed layer on Pt/TiO_x/SiO₂/Si(100) substrate. Here PbTiO₃ (PT) and PbO were chosen as seed layers. PbZr_{0.52}Ti_{0.48}O₃ thin films with 1 micrometer thickness were then prepared on seed layer by using sol gel technique. As for PbTiO₃ seed layers, both sol gel-derived PbTiO₃ and pulsed laser-deposited (PLD) PbTiO₃ with a thickness of about 20 nm were used. Effect of pyrolysis temperature of sol gel-derived PbTiO₃ seed layer on PZT film texture was studied. Effect of annealing temperature of PLD-prepared PbTiO₃ seed layer on PZT film texture was studied. The PbO seed layer was obtained by annealing Pb-containing solution. The crystalline structure and texture of PZT films were studied by using x-ray diffraction (XRD) and the morphology of films were studied by using scanning electron microscopy (SEM). Dielectric constant, dissipation factor were measured by using a LCR meter. The polarization-electric field hysteresis loop were measured by using Virtual Ground system. A cantilever deflection setup were used to measure the transverse piezoelectric coefficient e_{31} of PZT films, all of which were first poled by using pulse voltage at 250 KV/cm. The results show that the optimized seed layer will improve the {100} texture of PZT films and increase further the value of transverse piezoelectric coefficients.

T3.2

Crack-Free Thick PZT Film by Microstructural Control. Chee-Sung Park, Gun-Tae Park, Jae-Wung Lee and Hyoun-Ee Kim; Materials Science and Engineering, Seoul National University, Seoul, South Korea.

Microstructural evolution of lead zirconate titanate (PZT) films deposited on a platinized silicon substrate by using a combination of the sol-gel and RF-magnetron sputtering methods was monitored. Regardless of deposition methods, microstructure of the PZT film was strongly influenced by grooving and thickness of the film. When the grain morphology such as grain shape, grain size, and the distribution of grain size was controlled, maximum thickness of the film without any crack increased markedly.

T3.3

Enhanced Ferroelectric Properties of PZT Film by Inducing Permanent Residual Stress. Jae-Wung Lee, Gun-Tae Park, Chee-Sung Park and Hyoun-Ee Kim; Materials Science and Engineering, Seoul National University, Seoul, South Korea.

The effects of residual compressive stress induced during cooling after annealing on the ferroelectric properties of PZT film were investigated. PZT films were deposited on a tensile side of elastically bent silicon substrates by rf-magnetron sputtering method by using a single oxide target. Compressive stress was induced on the film by removing the substrate from the holder after annealing. The compressive stress effectively compensated for the inherent tensile stress developing during cooling after annealing. The ferroelectric properties were enhanced markedly by the residual stress; the remnant polarization (Pr) and the saturation polarization (P_{sat}) increased by 35% and 24%, respectively, and the coercive field (Ec) showed a similar tendency.

T3.4

Preparation of piezoelectric BaTi₂O₅ nanowires by a simple two-step hydrothermal method. Jian Yu and Mitsuru Itoh; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

One-dimensional (1D-) metallic and semiconducting nanostructures (nanowires, nanorods, and nanotubes) have attracted considerable attentions due to their striking fundamental properties and potential applications in nano-scale electronic devices including field-effect transistors, opto-electronic devices, sensors, and light-emitting diodes. In the recent years, 1D-piezoelectric/ferroelectric nanostructures are also stimulating more researches for fundamental finite size effects and potential applications in such as nanoactuators, nanoelectromechanical systems. In contrast to the template-assisted preparation of polycrystalline ferroelectric 1D-nanostructures, we will report one two-step hydrothermal route to synthesize lead-free high Curie temperature piezoelectric BaTi₂O₅ single crystalline nanowires through monitoring nucleation and growth processes by means of controlling the shape of nucleus. For a typical case of BaTi₂O₅ nanowires prepared at 90°C for 1 h with titania nanotubes prepared at 170°C for 17.5 h as titanium resource, BaTi₂O₅ nanowires exhibited a diameter between 20-500 nm and length of 1-10 μm. The thermal stability and influence of hydrothermal parameters on formation of BaTi₂O₅ were also investigated. At last, the formation

mechanism of BaTi₂O₅ nanowires was briefly discussed from the viewpoint of lattice structure. This method does not require any template, membrane, surfactant or applied external field to create anisotropic nanoparticle or to control their growth orientation, which enables the growth of ferroelectric titanate nanowires at large-scale and very low temperatures.

T3.5

Piezoelectric Properties of Lead Zirconate Titanate Films Prepared by Arc Discharged Reactive Ion-Plating Method. Masahiro Akamatsu¹, Yoshiaki Yasuda¹, Masanao Tani¹ and Takashi Iijima²; ¹Research & Development Center, Stanley Electric Co., Ltd., Yokohama, Kanagawa, Japan; ²Structural Health Monitoring Group, Research Institute of Instrumentation Frontier, AIST, Tsukuba, Ibaraki, Japan.

It is necessary to develop a fabrication process of Pb(Zr_xTi_{1-x})O₃ (PZT) films with fast deposition rate to apply piezoelectric actuators and sensors in micro electromechanical system (MEMS). An arc discharged reactive ion-plating (ADRIP) method could prepare good-quality PZT thick films, typically 1 to 10 μm in thickness, with fast deposition rate. The apparatus is comprised of the plasma gun to generate a dc arc plasma and the three metal evaporation sources (Pb, Zr and Ti). Due to the effect of the high-density oxygen radical species in the plasma, perovskite single-phase PZT films were deposited with the deposition rate up to 5.6 μm/h at the substrate temperature of 550 degrees. Since those films exhibited a piezoelectric displacement, it is possible to apply piezoelectric actuators for MEMS devices. As an example of applications for micro actuators, we succeeded to fabricate the micro laser projector composed of the micro scanner which was moved with the optical angle of 26 degrees at 17kHz for the horizontal scan and 30 degrees at 77Hz for the vertical scan at the driving voltage of 24V. In order to elucidate the piezoelectric properties of the PZT films prepared by ADRIP, the piezoelectric coefficient, d₃₁, was estimated from the analysis of the cantilever unimorph actuators. In the process of the cantilever, the 2.4 μm thick PZT film with the composition ratio x=0.4 was prepared on SOI wafer with the Pt and Ti electrodes (Pt/PZT/Pt/Ti/SiO₂/SOI) at the deposition rate of 2.4 μm/h. The dielectric constant and loss factor were $\epsilon=610$ and $\tan\delta=2.1\%$, respectively. The PZT film exhibited the well saturated P-E hysteresis loop with the remanent polarization of 30.8 μC/cm² and the coercive field of 113kV/cm. The unimorph actuators were fabricated by using bulk micro machining processes. The PZT film was patterned by photolithography and reactive ion etching, and the SOI wafer was etched by deep reactive ion etching. The unimorph cantilever has the dimension of 2 to 5mm long, 300 to 500 μm wide and 30 μm thick. The tip deflection of the cantilever was measured by a laser interferometer with the applied voltage at the frequency of 100Hz. The typical tip deflection of the actuator with the dimension of 5mm long, the 300 μm wide and 30 μm thick was -10 μm at the voltage of 10V. According to the analysis of a unimorph actuator proposed by Q. Wang et al., a piezoelectric coefficient, d₃₁, could be estimated from a tip deflection. At the voltage of 10V which is under the coercive field, the value of d₃₁=-31 pC/N was evaluated. Since this value is smaller than that of a bulk ceramics, it is considered that an electric poling treatment improves the piezoelectric property. In addition, the control of the crystal orientation may promote the increase of d₃₁. We are investigating the electric poling treatment and the texture control by using preferentially oriented PZT seed layers prepared by chemical solution deposition method.

T3.6

Determination of the d₃₁ piezoelectric coefficient of PZT thin film using dedicated microelectromechanical systems.

Cedric Ayela¹, Eric Cattani², Caroline Soyer³, Christian Bergaud³, Martine Pugnieri² and Liviu Nicu¹; ¹Laboratoire d'analyse et d'architecture des systemes, CNRS, Toulouse, France; ²Centre de Pharmacologie et Biotechnologies pour la sante, INSERM, Montpellier, France; ³Laboratory for integrated micro-mechatronic systems, CNRS / University of Tokyo, Tokyo, Japan; ⁴Institut d'electronique de microelectronique et de nanotechnologie, CNRS, Lille, France.

In recent years, resonant biosensors such as quartz crystal microbalance (QCM) have been accepted as powerful techniques to monitor adsorption processes at bio-chemical interfaces. As an alternative, we develop arrays of resonant micromachined silicon-based biosensors using the microgravimetric effect (the resonant frequency is related to the sensor mass variation). Each biosensor can be individually addressed for integrated actuation and detection through a PbZr(x)Ti(1-x)O₃ (PZT x=0.54) thin film. Because of elaboration of materials technological variations, characterization of material properties is necessary and an important one is the piezoelectric coefficient d₃₁ to determine optimal working conditions[1]. Different methods[2,3] are used and we developed two methods using microcantilevers and micromembranes to determine

this coefficient under different bias voltage conditions. Microcantilevers and micromembranes have been fabricated by standard micromachining techniques starting with a Silicon-On-Insulator (SOI) wafer. Membranes are circular shaped with a total radius equal to $150\ \mu\text{m}$ while the PZT layer radius varied from 45 to $105\ \mu\text{m}$ with a $30\ \mu\text{m}$ step and the cantilevers width was $30\ \mu\text{m}$ while the length varied from 305 to $505\ \mu\text{m}$ with a $50\ \mu\text{m}$ step. The $900\ \text{nm}$ PZT 54/46 film was deposited by RF magnetron sputtering. We have measured static deflection under different bias voltage conditions on both dedicated microstructures using a Fogle dual-beam interferometer. The measured deflections were implemented in two different analytical models in order to calculate the d_{31} coefficient, one for microcantilevers and the other for micromembranes. The model established for micromembranes takes into account their two parts (the inner circular region and the outer annular region), their multi-layer composition and in-plane stresses. The analytical model used for microcantilevers needs the determination of an equivalent Young's modulus with the moment of inertia product using their frequency response. Resonant frequencies were measured using the optical beam deflection (OBD) technique. Measurement of static deflection allowed to evaluate the influence of DC voltage on the piezoelectric coefficient d_{31} . Results show a hysteresis-like cycle for both structures, microcantilevers and micromembranes. d_{31} values varied from $45\ \text{pm/V}$ for the positive saturation of polarisation to $-45\ \text{pm/V}$ for the negative saturation with a positive peak of $300\ \text{pm/V}$ around 0V when voltage was decreasing and a negative peak when voltage was increasing. These results confirm that the value of the piezoelectric coefficient d_{31} of PZT thin film depends on level of the DC voltage with a strong influence of the way it is applied. [1] M-A Dubois, P Muralt, D V Taylor and S Hiboux, *Int Ferroelectrics*, 22, 535 (1998) [2] A J Masys, W Ren, G Yang and B K Mukherjee, *J Appl Phys* 94 1155 (2003) [3] P Muralt, A Kholkin, M Kohli, T Maeder and N Setter, *Microelectron Ing* 29, 67 (1995)

T3.7 **Modelling of Electromechanical Ferroelectric Fatigue.** Santiago A. Serebrinsky¹, Irene Arias² and Michael Ortiz¹;

¹Graduate Aeronautical Laboratories, California Institute of Technology, Pasadena, California; ²Departamento de Matematica Aplicada III, Universitat Politcnica de Catalunya, Barcelona, Spain.

We develop a model of electro-mechanical ferroelectric fatigue based on a ferroelectric cohesive law that couples mechanical displacement and electric-potential discontinuity to mechanical tractions and surface-charge density. Coupled with a criterion for fatigue damage nucleation, the model is applied to a simple test configuration consisting of an infinite slab acted upon by an oscillatory voltage differential across the slab and otherwise stress free. We compare the results of the simulations with available experimental results. The simulations capture the existence of a threshold nominal field for the onset of fatigue, and the dependence of the nominal fatigue threshold on the size of the component, i.e., the size effect.

T3.8 **Deposition and Characterization of Graded Ferroelectric Pb(Zr,Ti)O₃ Films for Micromechanical Application.** Panya Khaenamkaew^{1,2}, Supasarote Muensit² and Andrei L. Kholkin¹;

¹Dept. of Ceramics and Glass Engineering / CICECO, University of Aveiro, Aveiro, Portugal; ²Dept. of Physics, Faculty of Science, Prince of Songkla University, Hat yai, Thailand.

Graded ferroelectric materials has been of great interest during last several years because of the ability to create new functionality and to alleviate several problems related to stress concentration and polarization discontinuities near the interfaces. This is especially important for piezoelectric applications, where the mechanical fatigue due to stress concentration and microcracking is essential. Another motivation is to tailor the piezoelectric coefficients of graded ferroelectrics and to increase the degree of poling. In this work, we report on the deposition and characterization of graded $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films with variable composition across their thickness. The films were prepared by the widely used methoxyethanol sol-gel route allowing for the composition variation in layer-by-layer deposition sequence. Zr concentrations x in the range from 0.3 to 0.7 were used with various deposition sequences. Detailed structural and microstructural investigation showed the absence of second phases and the pronounced dependence of microstructure on the deposition sequence and processing conditions. Ferroelectric, dielectric and piezoelectric properties will be reported with the special emphasis on micromechanical applications.

T3.9 **Effect of Diameter on Longitudinal Displacement in Disk Shape 10- μm -thick Lead Zirconate Titanate Films.**

Takashi Iijima¹, Satoko Osone¹, Yoshiro Shimojo¹, Hirotake Okino² and Takashi Yamamoto²; ¹Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and

Technology, Tsukuba, Japan; ²Dept. of Communications Engineering, National Defense Academy, Yokosuka, Japan.

Lead zirconate titanate (PZT) films are in demand for applications in many fields like memories, sensors and actuators. Combining the preparation technique for ferroelectric films with a Si micro machining process is an effective way to fabricate microelectromechanical systems (MEMS), such as piezoelectric micro devices for electrical and medical fields. Therefore, thick films with thickness varied from 5 to $100\ \mu\text{m}$ were required. On the other hand, piezoelectric film devices are usually operated with a substrate such as Si, so that the piezoelectric response of the thick films is affected by clamping of the substrate. From these reasons, it is necessary to clear the clamping effect for the thick films and evaluate the clamped piezoelectric response of the thick films. We investigate preparation process of PZT thick films using chemical solution deposition process and successfully prepare more than $10\text{-}\mu\text{m}$ -thick PZT films with dense microstructure. In this study, $10\text{-}\mu\text{m}$ -thick PZT films were deposited onto $2\ \text{inch}$ Pt/Ti/SiO₂/Si substrate with automatic coating system to materialize micro machined piezoelectric film devices. Pt top electrode and PZT layer were etched by reactive ion etching (RIE) process, and 100 to $20\text{-}\mu\text{m}$ -diameter PZT thick film disks were fabricated to investigate effect of disk diameter on the piezoelectric response of PZT disks fabricated on the Si substrate. A ferroelectric polarization-field ($P - E$) hysteresis curve and a longitudinal displacement were dynamically measured by an atomic force microscope (AFM) connected with a ferroelectric test system. In the case of bipolar measurement, with decreasing the PZT disk diameter, $P - E$ hysteresis curves did not show remarkable difference, while longitudinal butterfly shaped displacement increase, and amount of the displacement was saturated at a diameter of 30 and $20\ \mu\text{m}$. To calculate AFM measured longitudinal piezoelectric constant, AFM d_{33} , unipolar driven longitudinal displacement was measured at 20V that was lower than coercive field, E_c , of the PZT film disk. AFM d_{33} increased with decreasing the disk diameter, and the value showed saturation at about $169\ \text{pm/V}$ when the disk diameter was smaller than $30\ \mu\text{m}$. Moreover, the disk samples were poled at 100V for 10min . AFM d_{33} of before and after poling process were 65 and $94\ \text{pm/V}$ for $80\ \mu\text{m}$ -diameter film disk, and 153 and $315\ \text{pm/V}$ for $20\ \mu\text{m}$ -diameter film disk, respectively. The value of poled AFM d_{33} for $20\ \mu\text{m}$ -diameter film disk was comparable to bulk PZT ceramics. We consider these results suggest that decrease of the disk diameter reduces the clamping effect of the substrate and facilitates domain reorientation in the poling process.

T3.10 **Stress and Piezoelectric Activity of ZnO Thin Films.** Raegan L. Johnson¹, Robert J. Weber¹ and Max A. Noack²; ¹Electrical Engineering, Iowa State University, Ames, Iowa; ²Microelectronics Research Center, Iowa State University, Ames, Iowa.

In an attempt to fabricate MEMS piezoelectric cantilevers, an investigation to determine a correlation between film stress and film piezoelectric activity was performed. Piezoelectric ZnO thin films were deposited by RF magnetron sputtering. Films with various deposition parameters were deposited and characterized. In this study, the films were deposited on silicon substrates coated with silicon nitride and aluminum or gold. The various deposition conditions included oxygen concentrations of $20\text{-}70\%$ oxygen, temperature range of $44\text{-}300^\circ\text{C}$, RF power of $50\text{-}250$ Watts, chamber pressure of $5.4\text{-}20$ mtorr, and annealing temperatures of $300\text{-}400^\circ\text{C}$. XRD scans were performed on the films examining the quality of the (002) peak and an estimate of the stress in the film was calculated by looking at the lattice plane spacings. The piezoelectric activity of the film was then determined by fabricating a bulk acoustic wave microstrip resonator and performing RF scattering parameter measurements using a network analyzer. The response of a Mason Model equivalent circuit was then compared to the response of the actual film. The piezoelectric coupling coefficient was extracted from the modeling data as a measure of the amount of piezoelectric activity of the film. Further measurements are currently being performed to examine a correlation between piezoelectric activity and the amount of stress measured in the film. Any correlation between stress and piezoelectric activity will be reported. The dependence of stress and piezoelectric activity on deposition parameters will also be discussed.

T3.11 **Structural and Electrical Characterization of PZT on Gold for Micromachined Piezoelectric Membranes.** Michelle C. Robinson, Phillip D. Hayenga, Jeong Cho, Dylan Morris, C. D. Richards, R. F. Richards and D. F. Bahr; Washington State University, Pullman, Washington.

Incorporating piezoelectric thin films into MEMS based devices such as sensors and actuators allows a user to tailor the material to achieve imposed device requirements without changing the structure of the device. Often the piezoelectric material is sandwiched between two

metals in a capacitor configuration in order to collect the charge produced when the piezoelectric material is strained, either in the so-called 33 or 31 modes. Many research groups have utilized platinum bottom electrodes with an adhesion layer of titanium on a substrate of Si/SiO₂. The drawbacks to using platinum as a bottom electrode is that it introduces a large tensile effective residual stress of 800 MPa in membranes upon annealing and to achieve optimized membrane performance the platinum must be patterned. The easiest method of patterning platinum in a laboratory environment is using a lift off technique, which involves several processing steps. A few research groups have attempted to utilize gold as a bottom electrode with a chromium adhesion layer because this bottom electrode introduces only a 30 MPa effective residual stress to the membrane and it can be patterned using a simple wet etchant. The fabrication process for solution deposited lead zirconate titanate (PZT) based piezoelectric materials often involves heating of the sample to 650-700 degrees for crystallization, depending on the type of PZT. This temperature allows for the chromium to diffuse through the gold so that visually the gold surface turns from metallic to dull and with this surface change the piezoelectric material exhibits poor electrical properties. With this drawback, research groups have relied on platinum based bottom electrodes for several years despite the increased number of processing steps. This paper will discuss how ferroelectric PZT thin films have been fabricated that incorporate a gold bottom electrode with an adhesion layer of titanium-tungsten (10:90 wt%) and discuss the ferroelectric properties inherent to these films. Each PZT thin film was crystallized by RTA heating to 650 degrees. Typical results have found that for a solution deposited acetic based PZT with a Zr:Ti ratio of 40:60 the average piezoelectric coefficient, e_{31} , for the film is negative 4.3 C/m², with a relative dielectric constant of 814 at 200 Hz. Microstructural characterization with SEM found that the PZT structure remains columnar on both platinum and gold bottom electrodes. These results will be compared to acetic-based PZT at the morphotropic phase boundary. In addition, residual stresses after processing will be discussed, as will ferroelectric and piezoelectric fatigue results on this electrode system.

T3.12

The Influence of Substrate Miscut on Phase Purity and Piezoelectric Response of Epitaxial Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ Thick Films on Silicon. Dong Min Kim¹, Rasmi R. Das¹, Chang Beom Eom¹, V. Vaithyanathan², N. B. Gharb², S. Trolier-McKinstry², D. G. Schlom², Y. B. Chen³, H. P. Sun³, X. Q. Pan³, J. Ouyang⁴ and R. Ramesh⁴; ¹Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; ²Department of Materials Science and Engineering, Korea Institute of Science and Technology, University Park, Pennsylvania; ³Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ⁴Department of Materials Science and Engineering, University of California-Berkeley, Berkeley, California.

Single crystal relaxor ferroelectric Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) has significantly higher piezoelectric response than conventional ferroelectrics. Major challenge is to prepare these materials in epitaxial thin film form in between epitaxial metallic oxide electrodes, and integrate them on the silicon wafer to use their superior piezoelectric properties in MEMS devices. However, the growth of epitaxial PMN-PT films with good electromechanical properties is known to be difficult due to poor thermodynamic stability of the perovskite phase compared to the pyrochlore phases. We have fabricated piezoelectric heterostructures with phase pure epitaxial PMN-PT thick films up to 4 μm by using miscut (001) Si substrates with epitaxial (001) SrTiO₃ template layer. According to four-circle x-ray diffraction with a two-dimensional area detector 4 μm thick PMN-PT films on 4 degree miscut (001) Si substrates show phase pure perovskite epitaxial films. The longitudinal (d_{33}) and effective transverse ($-e_{31}$) piezoelectric coefficients of the films are over 1200 pm/V and -29 C/m², respectively. These are highest values that have ever been reported for any piezoelectric films. In contrast, PMN-PT films on exact (001) Si substrates found to contain high volume fraction of pyrochlore phases and unwanted second phases. This behavior may be attributed to the variation in terrace length with miscut angle. As the miscut angle increases, so does the concentration of ledge and kink sites on the surface. Volatile species, such as lead in the case of PMN-PT, are expected to be more tightly bound at ledge and kink sites than atop a terrace. Thus, the role of substrate miscut may be to maintain film stoichiometry by decreasing the propensity for volatile species to desorb. These epitaxial heterostructures on miscut Si substrates can be used for multilayered high performance MEMS devices that function with low drive voltage, high frequency ultrasound transducer 2-D arrays for medical imaging. We will discuss of the microstructure of the both PMN-PT films on miscut and non-miscut (001) Si wafers.

T3.13

Highly-Oriented Ferroelectric Pb_xBa_{1-x}TiO₃ Thin Films on

MgO and Si-based Substrates for High Strain Applications: Synthesis, Characterization, and Domain Structure.

Mohamed Y. El-Naggar, David A. Boyd and David G. Goodwin; Engineering and Applied Science, California Institute of Technology, Pasadena, California.

Pb_xBa_{1-x}TiO₃ (PBT) thin films of various thicknesses (200-1000nm) were deposited by MOCVD on single crystal MgO as well as Si₃N₄/Si substrates. Biaxially textured MgO, grown using ion beam assisted deposition (IBAD), was used as a growth template on the Si-based substrates. Film composition, 0.2 ≤ x ≤ 1, was controlled throughout the growth by a precursor delivery system that allowed for real-time spectroscopic closed-loop control of the gas phase stoichiometry during deposition. The ferroelectric films were highly oriented on both types of substrates, but detailed characterization using x-ray pole figures, electron backscatter diffraction, and cross-sectional TEM revealed microstructural differences resulting from the underlying substrate. Films on single crystal MgO had larger grains that contained 90° domain boundaries, while films on the biaxially textured templates consisted of smaller single-domain grains. We attribute the difference to the smaller grains of the underlying biaxial MgO template, characteristic of the IBAD process. High temperature XRD was used to monitor domain changes and indicated large changes in the domain fractions with temperature for PBT films on single crystal MgO. The large changes with temperature are consistent with the evolution of the domain structure to minimize the total energy of the system and act as a strain-accommodating mechanism. No such changes were observed for the films that lacked 90° domain boundaries on Si-based substrates. Potential application of domain switching in such highly textured ferroelectric thin films to achieve high strains will be discussed alongside integration efforts into micromechanical testing structures (e.g. cantilevers and bridges) using both traditional and lattice-matching oxide electrodes to maintain texture.

T3.14

Theory for Effective Piezoelectric Coupling Factors for Barium Titanate and Lead Titanate Polycrystalline Films. Jennifer Lynn Ruglovsy¹, Kaushik Bhattacharya², Jiangyu Li³ and Harry A. Atwater¹; ¹Applied Physics, California Institute of Technology, Pasadena, California; ²Mechanical Engineering, California Institute of Technology, Pasadena, California; ³Engineering Mechanics, University of Nebraska, Lincoln, Nebraska.

Piezoelectric displacements and other electromechanical constants are easily quantified for single crystal materials, but most traditional thin film growth methods result in polycrystalline films. We therefore consider the effect of the grain-scale mosaic spread in the crystallographic texture and orientation on the device-scale piezoelectric coupling factor achievable in thin film devices of tetragonal 4MM materials. Our method enables the effective electromechanical properties to be obtained for a polycrystalline film. The grain orientations in a ferroelectric polycrystal can be described by rotations by Euler angles relative to a single crystal. The grain orientation distribution is assumed to be described by a Gaussian distribution when considered at the device scale, with texture ranging from that of a single-crystal to completely isotropic polycrystalline film. We can also develop coupling factors for biaxially textured films by extension of this theory. The effective electromechanical properties, characteristic of piezoelectric materials and governed by constitutive equations for stress and electric displacement of such an aggregate of grains, can be modeled using a self-consistent approach. The essence of the self-consistent approach is to use the electromechanical field for a single grain embedded in a matrix –with yet-to-be-determined uniform effective moduli– to simulate the electromechanical field in a grain at a particular orientation in the film. The total effective properties are found via numerical iteration over all grain orientations. We also propose a new figure of merit for piezoelectric performance in polycrystalline films. Traditionally piezoelectric displacement is used as a figure of merit for piezoelectric device performance. However this value gives little insight to the robustness of the film and its support of electric fields. We propose instead that the primary figure of merit for performance of a polycrystalline thin film device should be the piezoelectric coupling factor, defined as the stored mechanical energy per unit input electrical energy. From our theory, the elastic stiffness, piezoelectric displacement, and the dielectric constant tensors may be combined in a meaningful way to yield this single, dimensionless value.

T3.15

High Aspect Ratio Ferroelectric Structures for High Frequency Ultrasound Transducers. Ioanna Gavriel Mina¹, Bharadwaja S. N. Srowthi¹, Sungkyu K. Park², Hyunsoo Kim², Kyunsoo Choi³, Richard L. Tutwiler⁴, Insoo Kim³ and Susan Trolier-McKinstry¹; ¹Materials Science and Engineering and Materials Research Institute, Penn State University, University Park, Pennsylvania; ²Electrical Engineering Department, Penn State University, University Park, Pennsylvania; ³Computer Science and Engineering, Penn State University, University Park, Pennsylvania;

⁴Applied Research Laboratory, Penn State University, University Park, Pennsylvania.

High frequency ultrasound imaging (>50 MHz) is useful in imaging tissue, the eye, live cells and nondestructive evaluation of microelectronics devices. In this work, we are utilizing high aspect ratio ferroelectric structures to create a two dimensional array of transducers that will be interconnected to analog transmit and receive electronics. The output of the analog subsystem will be interfaced to a multi-channel data acquisition system which in conjunction with digital beamforming electronics will enable focusing and beam steering for the ultrasound system. A height:width aspect ratio of at least two is required for each element in this application. Fabrication of high aspect ratio structures of perovskite materials using infiltration of porous silicon templates, and coating of Cu posts is reported in this work. Water based LaNiO₃ and 2-methoxyethanol based PbZr_{0.52}Ti_{0.48}O₃ (PZT) sol-gel precursor solutions were used to deposit films in Si molds by vacuum infiltration assisted dip coating. It was found that the deposition rate was 39 nm/infiltration with a 0.7M PZT solution and 20 nm/infiltration with a 0.3 M LaNiO₃ solution. Pyrolysis and crystallization were then performed. The Si molds were subsequently removed by XeF₂ gas phase etching. A 1M molar PZT solution was employed for mist coating the Cu posts. In both cases aspect ratios of >6 were obtained. This paper will describe optimization of the processing, including the phase development of the crystalline structures with heat treatment. In addition, the integration of these structures into ultrasound transducers will be described.

T3.16

Microstructure of Epitaxial

0.67Pb(Mg_{1/3}Nb_{2/3})O₃-0.33PbTiO₃ Films Grown on Miscut (001) Si and SrTiO₃ Substrates. X. Q. Pan¹, Y. B. Chen¹, H. P. Sun¹, D. M. Kim² and C. B. Eom²; ¹Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ²Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Epitaxial thin films of relaxor ferroelectric Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) and its solid solution Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) have received considerable attention for its significantly high electromechanical coupling coefficient, high dielectric constant and diffuse phase transition, which can be used as microelectromechanical (MEMS) and electronic devices. However, little detailed information has been reported concerning the microstructures of PMN-PT films which are important to understand their physical properties. In this work, the microstructure of epitaxial 0.67Pb(Mg_{1/3}Nb_{2/3})O₃-0.33PbTiO₃ films with an epitaxial SrRuO₃ bottom electrode, which were grown on 4 degree miscut (001) SrTiO₃ substrates (001) Si substrates with an SrTiO₃ buffer layer, was characterized by transmission electron microscopy (TEM). It was found that atomic steps on the (001) Si surface, resulting from the miscut, induce a large number of anti-phase boundaries in the SrTiO₃ layer. These antiphase boundaries propagate into the SrRuO₃ bottom electrode and the epitaxial PMN-PT film. Similar defects were not observed in the epitaxial PMN-PT films grown on 4 degree miscut (001) SrTiO₃ substrates. All PMN-PT films grown on 4 degree miscut substrates are free of pyrochlore phases. The different effects of vicinal cutting on the microstructure of PMN-PT films will be discussed with growth model(substrate surface-terrace induced defects) where the conservative and non-conservative antiphase boundaries can be formed.

T3.17

Thin film dielectric Research for embedded, wireless, multifunctional, and Si-compatible applications. Jon-Paul Maria, Mark Losego, Jon Ihlefeld, Dipankar Ghosh, Spalding Craft, Brian Laughlin and Seymen Aygun; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Recent efforts at NCSU to develop methods for preparing device quality ferroelectric thin films that overcome several long-standing cost and complexity issues will be presented. We focus on compositions from the barium strontium titanate (BST) and lead zirconate titanate (PZT) solid solution families deposited on low cost substrates like base metal foil and ceramic aluminum oxide. The foil-based devices are targeted towards embedded capacitors, while the materials prepared on aluminum oxide are intended for tunable microwave circuit elements. We will also show results aimed at compatibility between complex oxides and semiconductor substrates. This will include investigations of lanthanide oxides on Silicon and rocksalt oxide solid solutions on GaN. The focus of this work is achieving process compatibility as it pertains to thermal expansion and chemical reactivity, and the pathways to success involve a fundamental understanding of processing science. Our methods for chemical solution deposition of BT and PZT on Cu will be discussed, with specific attention to the achievement of permittivity values in excess of 2500 in film thicknesses less than 0.6 microns. Similarly we

will demonstrate that low loss tunable dielectrics can be prepared on copper by sputtering, with dielectric quality factors in excess of 300 in the absence of any chemical barrier layers. Finally, we will show recent results for MBE growth of oxide materials on Si and GaN in some cases achieving heteroepitaxy at room temperature.

T3.18

InSitu X-ray Studies of Zr Incorporation during MOCVD PZT Growth. Ruey-Ven Wang^{1,2}, S. K Streiffer^{1,2}, G. B.

Stephenson^{1,2}, D. D. Fong^{1,2}, F. Jiang¹, P. H. Fuoss¹, J. A. Eastman¹, K. Latifi³ and C. Thompson³; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²The Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; ³Department of Physics, Northern Illinois University, DeKalb, Illinois.

Pb(Zr,Ti)O₃ (PZT) is an attractive model compound for use in investigating the formation of compositionally-complex oxide heterostructures. In order to extend our studies of the ferroelectric transition in ultrathin PbTiO₃ films grown by metal-organic chemical vapor deposition (MOCVD) to PZT, we need to understand the growth of 1- to 50-nm-thick alloy films with spatially uniform Zr/Ti ratios and well-defined strain states. However, this is challenging since several mechanisms can lead to composition gradients in a growing PZT film. At the simplest level, metal-organic transport into the reactor can, under certain circumstances, be a function of the deposition system history. A more interesting question is whether the incorporation of Zr for given metal-organic flow conditions is a function of the film strain state, and whether incorporation efficiency changes when strain begins to relax as the film thickness exceeds the critical thickness. Alloy growth can also drive a surface morphological instability, where surface roughening is linked to lateral compositional heterogeneity. Combining grazing incidence synchrotron x-ray scattering and fluorescence techniques, we have monitored the evolution of the Zr composition and the film structure *in situ* during the MOCVD of PZT onto (001) SrTiO₃. In addition, surface roughness of samples at various stages of the growth process was evaluated using scanning probe microscopy. We will describe results on the interrelationship between local Zr composition and strain relaxation processes, and on the thickness-dependent evolution of surface roughness as a function of Zr-dependent lattice mismatch between the PZT and the SrTiO₃ substrate. Work supported by the US Department of Energy, Office of Science, Basic Energy Sciences under contract W-31-109-ENG-38

T3.19

Growth and Characterization of Epitaxial PZT Thin Films on Ag Buffered Si(001) using RF Sputtering. Chun Wang¹, David

E. Laughlin² and Mark H. Kryder¹; ¹Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²Materials Science and Engineering Department, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Much research has been performed to grow epitaxial Pb(Zr,Ti)O₃ (PZT) (001) thin films on Si substrates using a variety of buffer layers. Here we report on the growth of epitaxial thin films of PZT (001) with a Pt bottom electrode on Si(001) single crystal substrates using a Ag buffer layer. PZT samples were deposited at room temperature and post-annealed at temperatures ranging from 600°C to 700°C using Rapid Thermal Annealing (RTA). Under these conditions, both PZT (20/80) and PZT (53/47) samples were shown to consist of a single perovskite phase and to have the (001) orientation. Film crystallinity was evaluated by θ - 2θ , Φ and ω X-ray diffraction scans. The orientation relationship was determined to be PZT(001)[110]—Pt(001)[110]—Ag(001)[110]—Si(001) [110]. The full width at half maximum height of PZT(001), Pt(002), Ag(002) peaks were 3.2, 1.08 and 0.95 degrees, respectively, obtained from the rocking curves. Atomic Force Microscopy studies showed that the surface roughness of PZT was 1.7nm after annealing. The microstructure of the multilayer was studied using transmission electron microscopy (TEM). The electron diffraction pattern also confirmed the epitaxial relationship between each layer. The measured remanent polarization P_r and coercive field E_c of the PZT(20/80) thin film were 26 μ C/cm² and 110kV/cm. For PZT(53/47), P_r was 10 μ C/cm² and E_c was 80kV/cm.

T3.20

Chemical Solution Deposition of Ferroelectric Thin Films and Nanotubes. Konstantin Anatolievich Vorotilov¹, Alexander Sergeevich Sigov¹, Olga Michailovna Zhigalina², Elena Dmitrievna Mishina¹ and Vladimir Alexandrovich Vasiljev¹; ¹Electronics, MIREA, Moscow, Russian Federation; ²Institute of Crystallography, Russian Academy of Sciences, Moscow, Russian Federation.

We discuss CSD techniques of BST and PZT thin films and nanotubes, as well as some new results in characterization techniques of such structures. BST as a high-k dielectric is the most promising candidate for 4 Gbit 65-nm generation of DRAMs, MMICs, as well as

for microwave phase shifters of electronically erasable antennas. BST films with different Ba/Sr content (Ba/Sr = 50/50, 60/40, 70/30) were prepared by CSD from alkoxide solutions modified by 2-ethylhexanoic acid. The films were deposited on Si-SiO₂-Ti-Pt, MgO, Al₂O₃, LaAlO₃ substrates. Microstructure of BST thin films is examined by TEM, electrical properties by CV and IV. It is shown that crystallization process of BST films is realized by nucleation in the bulk and on the interface, that is sufficiently differ from PZT films where dominant crystallization process is nucleation on the bottom electrode. Possible ways to change crystalline structure of BST films from polycrystalline tens nm to 50-80 nm columnar grain sharp (100) texture are discussed. Templating of a material into a nanoporous membrane is a new technique, that allows one to fabricate nanostructures with pre-defined size and shape of nanoparticles (tubes, rods, etc.). We report on fabrication and characterization of PZT nanostructures templated into porous alumina membranes with diameter within the range of 50...200 nm. The structure of the obtained nanomaterials was characterized by AFM, TEM, and SEM. To distinguish between paraelectric and ferroelectric phases, optical second harmonic generation (SHG) was applied: phase is centrosymmetric and does not produce dipole-type SHG in the bulk of the material, while the ferroelectric phase is noncentrosymmetric and produces a very strong SHG signal.

T3.21
BiFeO₃ Doped PZT Thin Films for Embedded FeRAM Devices. Seung-Hyun Kim¹, Chang Young Koo¹, Jung-Hoon Yeom¹, Jong-Hyeon Cheon¹, Hyun-Jung Woo¹, Jowoong Ha¹, Suk-Kyoung Hong² and Hyunjung Shin³; ¹R&D Center, INOSTEK Inc., Ansan, Gyeonggi, South Korea; ²R&D Division, Hynix Semiconductor, Gyeonggi, South Korea; ³School of Advanced Materials Sci. and Eng., Kookmin University, Seoul, South Korea.

Ferroelectric random access memories (FeRAMs) are well known to have a number of distinct properties such as fast programming, high write endurance, low voltage operation and low power read/write properties that make them most attractive candidates for standard non-volatile technologies. For realization of embedded FeRAM devices, the requirements for the ferroelectric capacitor became stringent. The requirement includes higher remanent polarization ($P_r > 25$ micro C/cm² at 2.5V) in order to compensate for the small amount of charge due to the reduced size of capacitors and integration-related degradation of the P_r . To solve these drawbacks, it is highly required to achieve high quality ferroelectric films having sub-100 nm thickness at low annealing temperature. However, due to size effect and high leakage current density of very thin films, it has been serious obstacles to realize embedded FeRAM devices. In addition, scaling-down films have shown serious long term stability problems such as imprint and opposite state retention. Recently, we have fabricated high-quality BiFeO₃-tetragonal symmetry PZT thin films using newly developed chemical solution preparation techniques. Sub-100 nm thin films are investigated. All processes are performed below 600 oC for 2 min. using RTA systems. In this research, it is found that remanent polarization, leakage current density and long term stability of BiFeO₃-tetragonal symmetry PZT thin films are reasonably good due to the fundamental role of Bi in the ferroelectric instabilities and Fe ion doping effect in PZT system. In this research, the influence of thickness scaling of these films and the composition effect of BiFeO₃-tetragonal symmetry PZT thin films on the ferroelectric performance are also investigated. Our results suggest that with stringent process control, well-prepared sub-100 nm BiFeO₃-tetragonal symmetry PZT thin films can be achieved excellent ferroelectric performance and provide the possibility to realize embedded FRAM devices. *This work was supported by National Research Laboratory program and System IC 2010 project.

T3.22
Growth characteristics of metal-organic chemical vapor deposited Pb(Zr,Ti)O₃ films on SrRuO₃ electrodes. Sim Joon Seop, Jin Shi Zhao, Hyun Ju Lee, Woo Young Park and Cheol Seong Hwang; Seoul National University, Seoul, South Korea.

It has been reported that SrRuO₃ (SRO) thin films have several merits as the electrodes for ferroelectric Pb(Zr,Ti)O₃ (PZT) thin films, such as similar lattice structure, lower coercive voltage, better polarization saturation property, and excellent polarization retention. However, such improvements are realized only when the SRO has a good crystalline quality which requires a quite high film growth temperature (~ 600°C). Such a high growth temperature may cause several problems in the fabrication of ferroelectric memory devices. Therefore, in this study, chemical and structural interactions between sputter-deposited SRO electrode grown at a low temperature (350°C) and PZT film grown by metal-organic chemical vapor deposition (MOCVD) are investigated. PZT thin films were grown by liquid-delivery MOCVD on SRO/Ir/IrO₂/SiO₂/Si at 570°C. SRO films were deposited by DC sputtering method on Ir (100nm)/IrO₂(50nm)/SiO₂/Si at 350°C under Ar ambient. Some of

the SRO electrodes were annealed at 600°C for 30min under oxygen and nitrogen atmosphere, respectively. PZT films were also deposited on Ir and Pt electrodes under the same conditions for comparison. It was found that the PZT films deposited on SRO electrodes shows a higher Zr concentration than those deposited on Pt and Ir electrodes from XRF measurement. In addition, the measured Zr concentration of the film on SRO substrate decreases with increasing film thickness. XRD measurement showed that PbTiO₃ (PT) phase, instead of PZT, were grown on the as-deposited SRO electrode although PZT films were deposited on the Pt and Ir electrode under the same PZT film deposition conditions. Neither PTO nor PZT peak was detected from the film grown on the O₂ and N₂ annealed SRO electrodes. Additionally, it was observed that the Zr3d_{5/2} peak positions in the XPS spectra from the film grown on the as-sputtered SRO electrodes are different between the 5-min- and 20-min-deposited PZT films. These results suggest that Zr component may be incorporated or react with SRO at initial step of deposition which affect the properties of the consecutively deposited PZT films. Detailed analysis results and the electrical measurement data of the PZT films grown on the various electrodes will be shown.

T3.23
Deposition of Highly (100) Oriented PZT Film using Lanthanum Nitrate/Nickel Acetate Buffer Layer. Jong-Jin Choi^{1,2}, Byung-Dong Hahn¹, Joo-Hee Jang³, Woon-Ha Yoon¹, Dong-Soo Park¹ and Hyoun-Ee Kim²; ¹Department of Future Technology, Korea Institute of Machinery and Materials, Chang-Won, Gyeong-Nam, South Korea; ²School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; ³Division of Materials Science and Engineering, Pukyong National University, Busan, South Korea.

Highly oriented Pb(Zr,Ti)O₃ [PZT] films were fabricated using lanthanum nitrate/nickel acetate double layers as a buffer layer. The orientation of the PZT thin film were analyzed by X-ray diffraction (XRD), electron beam back-scattered diffraction (EBSD) and high resolution transmission electron microscopy (HRTEM), and the results showed that the film had nearly 100% of (100) preferred orientation regardless of Zr/Ti ratio or substrates. The film deposited on the buffer layer had this orientation, regardless of the other deposition conditions, such as the pyrolysis temperature, pyrolysis time, annealing temperature, and heating rate. The buffer layer was also acted as a very effective diffusion barrier against Pb-Si interdiffusion, thus allowing for the direct deposition of PZT films on Si, SiO₂/Si, and glass substrates. Using this buffer layer, highly oriented PZT film was fabricated stably and reproducibly, regardless of the coating conditions and substrate materials, including various ceramics and metal plates. This strong orientation was attributed to the formation of a crystalline intermediate phase between the PZT and lanthanum nitrate during annealing. The lanthanum nitrate/nickel acetate double layers became lanthanum nickel oxide (LaNiO₃), which shows good electrical conductivity, after an annealing process at 650oC. The nature and the role of lanthanum nitrate buffer as a layer for the growth of highly (100) oriented PZT films have been studied. The dielectric, ferroelectric, piezoelectric and electrooptic properties of the highly (100) oriented PZT films with a lanthanum nitrate/nickel acetate buffer layer were measured and compared with the values measured from the (111) and (100) oriented PZT films deposited without buffer layer.

T3.24
Characterization of PbxPty alloy formation during deposition of Pb(Zr,Ti)O₃ thin films by liquid delivery metal-organic chemical vapor deposition. HyunJu Lee, Jin Shi Zhao, JoonSeop Sim, DongYeon Park and CheolSeong Hwang; Seoul National University, Seoul, South Korea.

Pb(Zr,Ti)O₃ (PZT) film capacitors with Pt electrodes attract much interest because of their good ferroelectric properties and low leakage current. However, the PbxPty alloy formation between the PZT film and Pt electrode during the metal-organic chemical vapor deposition (MOCVD) has hindered the adoption of Pt bottom electrode along with the fatigue issue related with the Pt electrode. Therefore, the PbxPty alloy formation in MOCVD of PZT is carefully investigated in this study. The influence of Pt bottom electrode microstructure on the alloy formation was also studied. PZT films were deposited on Pt(50nm)/TaOx(20nm)/SiO₂/Si and Pt(150nm)/TaOx(20nm)/SiO₂/Si substrates by liquid-delivery MOCVD at temperatures ranging from 475°C to 570°C. In order to understand the mechanism of PbxPty alloy formation, the processing parameters such as temperature, oxygen flow rate, and precursor input ratio, were changed. The alloy formation was confirmed by X-ray diffraction (XRD) and transmission electron microscopy. When the PZT film was deposited at 475°C no PbxPty alloy was formed. The relative XRD peak intensity ratio of the alloy phase and Pt (IPbxPty/IPt) shows a maximum value at 550°C and monotonically decreases with increasing temperature. PbxPty formation is also

affected by the oxygen flow rate. PbxPty alloy formation was suppressed with increasing O2 flow rate even at 550°C. It is considered that the PbxPty alloy was formed in the early stage for PZT deposited on Pt substrate. However, when the precursor input ratio (Pb/(Zr+Ti)) was < 0.45, the PbxPty alloy was not detected in XRD measurement. When the precursor input ratio was > 0.5, the PbxPty alloy peak begins to emerge. We also found that the relative intensity of IPbxPty/IPt decreases with increasing deposition time due to the out-diffusion of Pb from PbxPty alloy to PZT film during deposition. From above results, it was understood that the PbxPty alloy formation is due to the diffusion of metallic Pb occurring mainly along the Pt grain boundaries during the PZT film deposition. Since the Pt grain size decreases with decreasing Pt film thickness, the PbxPty alloy formation on Pt (50nm) is more active than on Pt (150nm). The effect of PbxPty alloy on electrical property of PZT films will also be reported.

T3.25
Enhancement of Dielectric Constant of BaTiO3 Thin Film by Hydrothermal Treatment. Won-Hoon Song, Sung-Taek Lim, Soo-Hyun Lyoo, Hyun-Ju Jin, Hyung-Dong Kang and Yul-Kyo Chung; Samsung Electro-Mechanics, Suwon, South Korea.

Most of BaTiO3 and other perovskite thin films have been prepared by sol-gel or vapor phase methods. (e.g., pulsed laser deposition, metal-organic chemical vapor deposition, and sputtering). After preparing thin films, for increasing permittivity of films, they were thermally treated at relatively high temperature to crystallize the amorphous layer. In this case, although thin films with high dielectric constant could be obtained, a high temperature process which limit the material selection of substrates is inevitably needed. Our interest is the fabrication of high permittivity BaTiO3 thin films using hydrothermal synthesis. It is a technique that involves the growth of oxides directly from aqueous solutions, generally at elevated temperatures (~100-400°C) and pressures (~0.1-15MPa). BaTiO3 thin films have been successfully deposited on Ti foil by hydrothermal synthesis at 250 °C and for several hours. In this work, amorphous TiO2 layers were formed by sol-gel spin coating on the Pt/Ti/SiO2/Si. BaTiO3 thin films were hydrothermally synthesized in Ba-containing solution. Hydrothermally synthesized BaTiO3 thin films were composed of grains with size about 100nm and their thickness of the dielectric layers was about 215nm. The dielectric constant of BaTiO3 thin films was enhanced by controlling of various hydrothermal treatment conditions.

T3.26
Effect of Post-Annealing on Electrical Properties of PZT Thick Films Formed by Aerosol Deposition Process. Byung-Dong Hahn¹, Jong-Jin Choi^{1,2}, Kwan-Ho Ko³, Woon-Ha Yoon¹, Dong-Soo Park¹ and Doh-Yeon Kim²; ¹Department of Future Technology, Korea Institute of Machinery & Materials, Changwon-shi, KyungNam, South Korea; ²School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; ³Division of Materials Science and Engineering, Pukyong National University, Pusan, South Korea.

Pb(Zr,Ti)O3[PZT] thick films with thickness over 10µm were deposited on various substrates by aerosol deposition process at room temperature. The films showed fairly dense microstructure without crack. Only a perovskite single phase was observed in the films. However, PZT thick film formed by aerosol deposition generally shows very small grain size (<100nm), which may have adverse effects on the electrical properties of the film. In this study, post-annealing process was employed to induce grain growth of the as-deposited thick films and to improve the electrical properties. After deposition, the films were annealed in air at temperatures up to 1000°C. Annealing time at a given temperature was varied from 1h to 10h. Effects of post-annealing process on the microstructural evolution were observed using a field-emission scanning electron microscope and a high resolution transmission electron microscopy. The dielectric, ferroelectric and piezoelectric properties of the annealed film was characterized using impedance analyzer, Sawyer-Tower circuit and laser interferometer, respectively. The annealed film with large grain size showed markedly improved electrical properties in comparison with as-deposited film.

T3.27
Abstract Withdrawn

T3.28
Epitaxial Growth of CaxBa1-xNb2O6 thin film on (001) MgO by pulsed laser deposition. Paul F. Ndonge, Mounir Gaidi, Roberto Morandotti and Mohamed Chaker; INRS ENERGIE MATERIAUX ET TELECOMMUNICATIONS, UNIVERSITE DU QUEBEC, Varennes, Quebec, Canada.

Calcium barium niobate (CBN) CaxBa1-xNb2O6 crystals, like

Strontium Barium Niobate (SBN) SrxBa1-xNb2O6 crystals belong to the class of ferroelectric materials with a tetragonal tungsten bronze type structure. There is a wide range of work performed on SBN, which demonstrates how these material are ideal for photonics applications thanks to their high electro-optic, pyro and piezoelectric coefficients. However, those properties are somehow limited by the difficulty of growing high quality homogeneous single crystals, by their significant cost and by the difficulty of integrating such crystals in a single chip for the fabrication of miniaturized optical devices. Hetero-epitaxial growth of ferroelectric materials can be considered as a viable alternative to cristal fabrication. For example, SBN exhibit one of the highest electro-optic coefficient ever measured on thin film (844 pm.V-1) and for this reason, a series of techniques have been used to grow high quality hetero-epitaxial SBN film on differents substrates. Among those, one can quote metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), sol-gel synthesis, radio frequency magnetron sputtering and pulsed laser deposition (PLD). The last technique is also ideal for growing various multicomponents oxides such as CBN because it enables to reproduce in the thin film the same composition of the target. In this paper, we report, for the first time in our knowledge, a parametric study of epitaxial CBN growth. The effect of the oxygen deposition pressure and temperature on the crystalline quality of the films has been systematically studied by way of X-ray diffraction, rocking curve, phi scan analysis and atomic force microscopy. In addition, the refractive index and extinction coefficient of the CBN film have been obtained by using variable angle spectroscopic ellipsometry.

T3.29
Characteristic Comparison Between Epitaxial PZT and PMN-PT Thick Films Grown by MOCVD. Shintaro Yokoyama¹, Satoshi Okamoto¹, Keisuke Saito², Takashi Iijima³, Hirotake Okino⁴, Takashi Yamamoto⁴ and Hiroshi Funakubo¹; ¹Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Japan; ²Application Laboratory, Bruker AXS, Yokohama, Japan; ³Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; ⁴Department of Communications Engineering, National Defense Academy, Yokosuka, Japan.

We have demonstrated the systematic growth of epitaxial Pb(Zr_{1-x}Ti_x)O₃ [(1-x)PbZrO₃-xPbTiO₃, PZT] and (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ (PMN-PT) thick films with good ferroelectricity and piezoelectric response.^{1,2} In the present study, we investigated the relationship between the electrical properties and the crystal structure of (100)-/(001)-oriented epitaxial PZT (about 2 µm in thickness) and PMN-PT films (2-3 µm in thickness) with wide range of PT content (x) grown on (100)cSrRuO₃//(100)SrTiO₃ substrates by metalorganic chemical vapor deposition (MOCVD) and compared these characteristics with those of PZT sintered bodies and PMN-PT single crystals. The constituent phase with mixture of rhombohedral (or pseudocubic) and tetragonal phases was estimated from x-ray diffraction reciprocal space mapping analysis and their x ranges were found to be from 0.40 to 0.60 for PZT films and from 0.40 to 0.55 for PMN-PT films. These x range of mixture phase were different from the reported ones for PZT sintered bodies³ and PMN-PT single crystals⁴ and were expanded for the films compared with the bulks in both systems. In addition, it shifted to higher x region for PMN-PT films. Longitudinal field-induced strain (Δx₃₃) measured by scanning probe microscopy with ferroelectric tester and transverse piezoelectric coefficient (e₃₁) measured using unimorph cantilever with laser Doppler meter of the films had maximum around x=0.50 for PZT films corresponding to the middle composition of mixed phase region, while x=0.40 for PMN-PT films the rhombohedral (pseudocubic) side edge of mixed phase region. The maximum e₃₁ for PZT and PMN-PT films were -8.9 C/m² and -11.0 C/m², respectively, and were larger than that of PZT sintered bodies and PMN-PT single crystals. This could possibly be due to the effect of substrate clamping. From these results, the crystal structure against the x value of the films was different from the bulks because of the strain from substrates and the relationship between piezoelectric response and crystal structure in film form was suggested. Refs. ¹) S. Yokoyama *etal.*, Appl. Phys. Lett. **83**, 2408 (2003). ²) S. Yokoyama *etal.* (unpublished) ³) Ragini *etal.*, J. Appl. Phys. **92**, 3266 (2003). ⁴) B. Noheda *etal.*, Phys. Rev. B **66**, 054104 (2002).

T3.30
Preparation of Ir and IrO2 Electrodes by MOCVD Using a New Ir Precursor. Hironori Fujisawa¹, Naoya Iwamoto¹, Masaru Shimizu¹, Hirohiko Niu¹, Taishi Furukawa^{2,3}, Kazuhisa Kawano^{2,3} and Noriaki Oshima^{2,3}; ¹University of Hyogo, Himeji, Hyogo, Japan; ²Tosoh Corp., Ayase, Kanagawa, Japan; ³Sagami Chemical Research Center, Ayase, Kanagawa, Japan.

Ir-based thin films are promising electrode materials for PZT capacitors in non-volatile ferroelectric random access memory. For the

realization of high-integrated FeRAM with 3D capacitors, it will be required to prepare both ferroelectrics and electrodes by MOCVD due to its high conformal growth. We have already developed MOCVD technique of Ir, IrO₂ and Ir/IrO₂ electrodes using liquid precursors, Ir(EtCp)(COD) and Ir(EtCp)(CHD). Fabrication of 3D PZT capacitors with Ir-based electrodes has also been reported. However, there have been several drawbacks in MOCVD using these precursors, such as difficulty in preparing IrO₂ electrode with a smooth surface and oxidation of underlying Ti-based barrier metals during the deposition of IrO₂. One of reasons for these difficulties may be the relatively high decomposition temperature for the use of these precursors as MOCVD precursors due to the rigid chemical structure. In this study, we report on preparation of Ir and IrO₂ electrodes by MOCVD using a newly developed Ir precursor, Ir(EtCp)(C₂H₄)₂ ((Ethylcyclopentadienyl)bis(ethylene)iridium), which has a much lower decomposition temperature, 220°C, than those of previous liquid precursors (370°C for Ir(EtCp)(COD) and 300°C for Ir(EtCp)(CHD)). Ir(EtCp)(C₂H₄)₂ (m.p.2°C) was vaporized at 55°C by the conventional bubbling method. Ir and IrO₂ films were prepared on SiO₂/Si at 200-400°C. The partial pressure of oxygen was changed from 0 to 3Torr. When Ir(EtCp)(C₂H₄)₂ was used, nucleations as high as 8×10²μm⁻² were observed at the initial growth stage of Ir thin films. This nucleation density was much higher than those using previous liquid precursors. Due to this high nucleation density, both Ir and IrO₂ films prepared using Ir(EtCp)(C₂H₄)₂ showed very smooth surface with surface roughnesses of 1-2nm and 3-4nm, and low electrical resistivities of 9-20 and 150-180μΩ-cm, respectively. Applications of Ir-based electrodes by MOCVD using Ir(EtCp)(C₂H₄)₂ to PZT capacitors will be also discussed.

T3.31
Microstructure and ferroelectric properties of ultrathin PbTiO₃ films by MOCVD. Hironori Fujisawa¹, Masaru Shimizu¹, Hirohiko Niu¹, Yasutoshi Kotaka² and Koichi Honda²; ¹University of Hyogo, Himeji, Japan; ²Fujitsu Lab. Ltd., Atsugi, Kanagawa, Japan.

The critical thickness in ferroelectric thin films has long been studied from the viewpoint of not only finite size effects but non-volatile memory applications. However, it still remains unknown due to difficulties in sample preparations of high-quality ultrathin films and detection of ferroelectric polarization switching. Recent theoretical studies have predicted stable ferroelectric polarizations in PbTiO₃ films with several unit cells. Experimentally, on the other hand, the presence of ferroelectric stripe domains was proved in 1.2nm-thick PbTiO₃ films by synchrotron x-ray study. However, it is quite difficult to directly detect ferroelectric polarization switching because of an increase in leakage and/or a decrease in ferroelectric signal. We have already reported that high-quality epitaxial PbTiO₃ and Pb(Zr,Ti)O₃ films can be obtained on SrRuO₃/SrTiO₃(100) by MOCVD, and that PZT films thinner than 10nm had ferroelectricity by CR-PFM (contact-resonance piezoresponse force microscopy) which had a higher sensitivity than that of conventional PFM. In this study, microstructure and ferroelectric properties of ultrathin PbTiO₃ and Pb(Zr,Ti)O₃ films on SrRuO₃/SrTiO₃(100) and SrTiO₃(100) substrates by MOCVD were investigated in more detail. Thicknesses of PbTiO₃ films were determined from cross-sectional HR-TEM observations and X-ray reflectivity measurements. Microstructure of ultrathin PbTiO₃ films was investigated by AFM, HR-TEM and HAADF (High Angle Annular Dark Field)-STEM. PbTiO₃ films thinner than 5nm with an atomic step were successfully grown on insulative SrTiO₃(100) and conductive La-doped SrTiO₃(100). Cross-sectional TEM observations revealed that PbTiO₃ films had well-defined microstructure throughout the thickness and that the interface between PbTiO₃ and SrTiO₃ was very sharp. Polarization switching in a 2.7nm-thick PbTiO₃ thin film on La-doped SrTiO₃ were investigated by CR-PFM and KFM (Kelvin probe force microscopy). When two 1×4μm² regions were scanned by the SPM tip with DC voltages of +2.5 or -3V, respectively, different contrasts were observed for these two regions by CR-PFM and KFM. The different contrasts suggest the formation of the switched domains with downward and upward polarizations, that is, stable ferroelectric states in the 2.7nm thick PbTiO₃ film.

T3.32
(S)TEM studies of Epitaxial PbTiO₃/SrTiO₃ Ferroelectric Thin Films. A. T. J. van Helvoort¹, Oystein Dahl², Bjorn G. Soleim¹, Randi Holmestad¹ and Thomas Tybell^{2,3}; ¹Dept. of Physics, Norwegian University of Science and Technology (NTNU), Trondheim, Norway; ²Dept. of Electronics & Telecommunications, Norwegian University of Science and Technology (NTNU), Trondheim, Norway; ³NTNU Nanolab, Norwegian University of Science and Technology (NTNU), Trondheim, Norway.

Ferroelectric perovskite materials are interesting for use in a variety of applications ranging from non-volatile memories to micro/nano electromechanical devices. In thin film electronic devices,

understanding and controlling the interface between the ferroelectric material and the electrode is important. The detailed structure at the interface can influence the macroscopic physical properties. Here, an in-depth analysis of the interface, based on TEM investigations, of epitaxial thin films of (001)-oriented PbTiO₃, grown on (001)-oriented SrTiO₃ substrates using off-axis radio frequency magnetron sputtering, will be presented. High angle annular dark-field scanning TEM (ADF STEM) displayed atomically sharp interfaces between film and substrate. Low-angle ADF-STEM revealed an out of plane strained layer at the PbTiO₃ / SrTiO₃ interface, having a strain vector parallel to the polarization direction. The width of the strained interfacial layer was found to be ~1.5-3 nm, depending on the electrode environment [1]. The low energy loss spectrum, as well as the mean-free-path, of the bulk of the film was different from the interfacial region. In the bulk of the film, the lattice parameters were constant, as confirmed by convergent beam electron diffraction. However, at the interface the TEM data is consistent with an evolution of the lattice parameters. [1] A.T.J. van Helvoort, O. Dahl, B.G. Soleim, R. Holmestad and T. Tybell, Appl. Phys. Lett. 86 (2005) 092907.

T3.33
Iridium Electrodes for Ferroelectric Capacitors Deposited by Liquid-Delivery MOCVD. Marco Lisker, Yves Ritterhaus and Edmund P. Bulte; University of Magdeburg, IMOS, Magdeburg, Germany.

Thin Ir films are needed as electrode material for ferroelectric capacitors made of SBT (SrBi₂Ta₂O₉) or PZT (Pb(Zr_xTi_{1-x})O₃) as dielectric material. The PZT based non-volatile ferroelectric random access memories show better fatigue characteristics if platinum is replaced by iridium as the electrode material. Metalorganic chemical vapor deposition (MOCVD) was used for the deposition because of the superior step coverage of three-dimensional structures compared to the conventional physical vapor deposition processes of metal layers. Particularly in memory fabrication, good step coverage is essential. The Ir films were deposited on different substrates at temperatures of 300-500 C by liquid-delivery MOCVD. The precursor Ir(EtCp)(1,5COD) [iridium(ethylcyclopentadienyl)(1,5-cyclooctadiene)] was dissolved in toluene (0.1 M concentration) for the deposition experiments. The Ir films were deposited onto TiO₂/SiO₂/Si-, SiO₂/Si-, and Si-substrates to compare the Ir film properties on different substrates. The growth conditions oxygen flow, growth temperature, and reactor pressure were varied. The growth rates were in a range between 0.05 and 4.6 nm per minute. We found that the growth rates were highly influenced by the oxygen flow and the substrate material. The oxygen supported the decomposition of the precursor, and the carbon and hydrogen of the organic source were oxidized, which suppressed its incorporation into the iridium layer. Annealing in air at temperatures above 700 C resulted in an increased oxidation of the films as proved by XRD analyses. The resistivity of the films was determined by the van-der-Pauw method. Low resistivities of 5.7 - 70 E-6 Ohm*cm were obtained for the as-deposited iridium films.

T3.34
Growth of Ferroelectric PbZr_xTi_{1-x}O₃ (PZT) Thin Films by Liquid-Delivery Metalorganic Chemical Vapor Deposition. Serhiy Matichyn, Marco Lisker and Edmund Bulte; Institute of Micro and Sensor Systems, Otto von Guericke University Magdeburg, Magdeburg, Germany.

In this study lead zirconat titanat (PZT) thin films were deposited using direct liquid injection metal organic chemical vapor deposition (DLI-MOCVD). Tetraethyl lead - Pb(C₂H₅)₄, Zirconium tetr-butoxide - Zr[OC(CH₃)₃]₄ and Titanium isopropoxide - Ti[OCH(CH₃)₂]₄ diluted in toluene were used as Pb, Zr and Ti precursors respectively. Each precursor was delivered into the reactor separately to prevent the formation of the unwanted pyrochlore phase. Nitrogen and oxygen were used as transport and reaction gas respectively. CZ-Si (100) 150 mm wafers covered, before PZT deposition, with electrode structure Ir/TiO₂/SiO₂ were used as substrates. The substrate temperature was varied from 350 to 550 C and the deposition pressure were from 3.5 to 15 mbar. The deposition rate of PZT films were investigated as a function of the deposition temperature, pressure and injection parameter. For the electrical characterisation of the PZT films, metal-ferroelectric-metal (MFM) capacitors were fabricated using deposition of an Ir-electrodes through a shadow mask. The chemical states and stoichiometry of PZT-films was characterized by employing X-ray photoelectron spectroscopy (XPS). The crystal structure of the films were investigated using X-ray diffraction (XRD). The surface composition was Pb : Zr : Ti = 1.05 : 0.52 : 0.48, which indicates that the deposited films had a stoichiometric PZT composition. 130 nm thick PZT films deposited on Ir showed <110> preferred orientation. The main role for formation of the perovskite PZT films plays content of the lead in the deposited films. Lead deficient caused formation of the pyrochlore

phase with poor electrical properties. In the films with significant excess of lead a second PbO phase appeared that can be observed even with naked eye. Negligible excess of lead can be reduced by post-deposition annealing at 500-600 °C. The Ir/PZT/Ir capacitor showed large value of the remanent polarisation about 60 $\mu\text{C}/\text{cm}^2$ at applied voltage of 3 V. So high value of the remanent polarisation can be induced by structural stress in the films. After ten switch impulses the value of the remanent polarisation have significant decreased that probably is concerned with relaxation of crystal cells.

T3.35

The Properties of ferroelectric domain of PLT thin films Prepared by RF Magnetron Sputtering. Hong Liu, Dingquan Xiao, Jiagang Wu, Zhaohui Pu, Jiliang Zhu and Jianguo Zhu; Materials Science, Sichuan University, Chengdu, Sichuan, China.

Ferroelectric Lanthanum-modified lead titanate (PLT) thin films were fabricated by the multi-target magnetron sputtering system on Pt/Ti/SiO₂/Si(100) substrates. The x-ray diffraction (XRD) patterns of the PLT films showed that the pure perovskite structure was formed in the PLT thin films. The SEM observation shows the crystal grain was small and well-distributed. The Piezoresponse Force Microscopy (PFM) was used for determining the domain structure of these films. It was found that the 180° domain was the main domain structure of PLT thin films. The pyroelectric property of PLT thin films have been examined and discussed. The experiment results show that the PLT thin films prepared by RF sputtering exhibit good electrical characteristics.

T3.36

Electroacoustic properties of piezoelectric ZnO and PZT films for FPW devices. Sang Hoon Yoon, Jung Hyun Park and Dong-Joo Kim; Materials Engineering, Auburn University, Auburn, Alabama.

Piezoelectric property of ZnO and PZT has attracted much attention for many applications such as acoustic wave devices, gas sensors, and chemical and biological sensing devices. Among the chemical and biological applications, Flexural Plate Wave (FPW) sensor can allow to be operated at relatively low frequency and in liquid and gas phases, which are important in device fabrication. To launch the acoustic wave in the membrane, ZnO films are required to have c-oriented textured structure, and, furthermore, the stable dielectric constant, high resistivity, and low dissipation factor for both ZnO and PZT films are needed for this application. ZnO films were fabricated onto silicon substrates by RF magnetron sputtering while chemical solution deposition (CSD) method was used for preparing PZT films. Both ZnO and PZT films are optimized by studying process parameters, for example deposition temperature, pressure and sputtering gases for sputter deposition, and the precursors and thermal treatment for CSD. The electroacoustic properties of ZnO and PZT films were investigated to determine the performance of the sensor, and to understand the relationship between film structures such as surface roughness and microstructure and acoustic properties. The comparison between experimental results and simulation will also be discussed in detail.

T3.37

Influence of the lead-source on PZT 30/70 thin film orientation. Mira Mandeljc, Barbara Malic and Marija Kosec; Electronic Ceramics Department, Jozef Stefan Institute, Ljubljana, Slovenia.

Ferroelectric lead zirconate titanate (PZT) thin films have been investigated for a wide range of applications, such as piezoelectric, pyroelectric, electro-optic and ferroelectric devices. Among various deposition techniques chemical solution deposition (CSD) enables high purity, large deposition area, easy composition control, low processing temperatures. CSD method usually involves the deposition of the PZT sol onto the substrate followed by a post deposition annealing process. For optimizing CSD processing conditions, such as decreasing the annealing temperature and control of the film orientation, the mechanisms involved in the nucleation and growth of the perovskite phase should be understood. PZT 30/70 thin films, deposited on platinized silicon substrates by spin-coating, were prepared by the 2-methoxyethanol route in which lead acetate and lead oxide were used as the lead-source. By a careful control of solution chemistry and annealing conditions pure perovskite phase is obtained at as low as 400 °C, while at 375 °C the perovskite phase coexists with the amorphous phase. Generally, the crystallization of the amorphous PZT precursors both in bulk and thin film form occurs via the pyrochlore-type phase, however, the range of its stability reported to be above 450/500 °C. The direct transition of the amorphous to perovskite phase has been reported for lead titanate thin films on Pt/Si substrates, but in the case of PZT 53/47 thin films only when deposited SrTiO₃ (100) substrate which exhibits a good agreement of lattice parameters. It is possible that in the case of PZT thin film heated at 375 °C the pyrochlore-type phase is not a stable phase;

this could explain the rarely encountered coexistence of amorphous and perovskite phases. The lead source has got a major impact on the orientation of the thin films, namely by using lead oxide we obtain the (111) and with lead acetate the (100) orientation, respectively. In the case of the PZT film prepared from lead oxide the decomposition of the organic, that is alkoxide, groups, causes within the bulk of the film strongly reducing atmosphere, which as a consequence, allows a partial reduction of Pb(II) species to metallic lead, which further forms a transient PbPt_x phase at the interface PZT/Pt. The PbPt_x phase acts as a nucleation layer for the (111) orientation of PZT. The PbPt_x phase has been confirmed by XRD and SEM analyses. In contrast, in the case of the lead-acetate based PZT films, the thermal decomposition of the functional groups, i.e. acetate and alkoxide, yields a less reducing atmosphere, as a consequence PbPt_x phase is formed in a lesser extent and in a narrower temperature/time range and cannot act as a nucleation layer. Therefore lead-acetate based PZT films crystallize in (100) orientation.

T3.38

A Novel Iridium Precursor for MOCVD. Kazuhisa Kawano^{1,2}, Taishi Furukawa^{1,2}, Mayumi Takamori^{1,2}, Ken-ichi Tada¹, Tetsu Yamakawa¹, Noriaki Oshima^{2,1}, Hironori Fujisawa³ and Masaru Shimizu³; ¹Sagami Chemical Research Center, Ayase, Kanagawa, Japan; ²Tosoh Corporation, Ayase, Kanagawa, Japan; ³University of Hyogo, Himeji, Hyogo, Japan.

Ir, Ru, their oxides and Pt have been investigated as capacitor electrodes of next generation memory devices including FeRAMs. Among them, Ir and IrO₂ are promising electrode materials for FeRAMs because they have thermal resistant character and are effective for the improvement of fatigue loss of PZT capacitors. For the realization of future high density FeRAMs with a 3D structure, MOCVD technique is indispensable because of its highly conformal growth, high growth rate and compatibility with LSI process. There have been many reports on Ir and IrO₂ deposition by MOCVD using various kinds of Ir precursors. For example, (ethylcyclopentadienyl)(cyclooctadiene) iridium, Ir(EtCp)(COD), had been intensively investigated as a liquid Ir precursor for MOCVD. Ir(EtCp)(COD) with rigid structure was very stable under the MOCVD conditions and had fairly high vapor pressure. However, it had some disadvantage such as long incubation time, low nucleation density at an initial growth stage and difficulty of conformal film deposition. IrO₂ thin films with high crystallinity were not obtained using this precursor. (Ethylcyclopentadienyl)(cyclohexadiene) iridium, Ir(EtCp)(CHD), showed better properties than those of Ir(EtCp)(COD); shorter incubation time, higher nucleation density and better surface morphology. However these properties were not sufficient enough as a MOCVD precursor. In the present work, a novel Ir precursor, Ir(EtCp)(C₂H₄)₂, was synthesized and examined its physical properties. Crystalline properties of Ir films deposited by MOCVD using this novel precursor were also investigated. The structure of this precursor was identified by proton NMR, carbon NMR, IR and mass spectrometry. The melting point, the vapor pressure and the viscosity of Ir(EtCp)(C₂H₄)₂ were 2C, 0.1 Torr/55C and 5.5cP/r.t., respectively. Thermal properties were analyzed by TG and DSC. TG measurement was carried out in inert atmosphere (Ar). Ir(EtCp)(C₂H₄)₂ vaporized stably and was more volatile than Ir(EtCp)(CHD) and Ir(EtCp)(COD). DSC of Ir(EtCp)(C₂H₄)₂ measured under N₂ atmosphere showed lower thermal decomposition temperature (220C) than those of Ir(EtCp)(CHD) (300C) and Ir(EtCp)(COD) (370C). Growth behavior of MOCVD Ir films using Ir(EtCp)(C₂H₄)₂ was also investigated. Numerous nuclei were observed at an initial growth stage of deposition and highly conformal films were grown. Moreover, both metal Ir and IrO₂ films were successfully prepared on various substrates.

T3.39

Growth Mechanism of c-Axis-Oriented Epitaxial Bismuth Layer-Structured Dielectric films. Kenji Takahashi¹, Muneyasu Suzuki¹, Mamoru Yoshimoto² and Hiroshi Funakubo^{1,3}; ¹Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Japan; ²Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; ³Japan Science and Technology Agency, Saitama, Japan.

High-dielectric constant materials with good stability against the applied electric field, film thickness and the temperature are highly desired for various capacitor applications. We have previously proposed that c-axis-oriented bismuth layer-structured dielectrics (BLDs) films are a novel candidate for high dielectric capacitor application due to the low capacitance change against the applied voltage and the low leakage current independent of the film thickness down to 20 nm, corresponding to 8 unit cells. ¹) BLDs grow 2-dimensionally due to their large crystallographic anisotropy. This is an advantage for fabrication of thin film devices having smooth surface irrespective of film thickness. Although it is critical to investigate the growth mechanism of thin film of BLDs, the research

on the growth at the initial stage has been hardly reported in spite of the fact that the thickness must be decreased for higher capacitance. In the present study, we grew *c*-axis-oriented epitaxial SrBi₂Ta₂O₉ (SBT) films on atomically-flattened SrRuO₃ and SrTiO₃ substrates and investigate the growth mechanism at the initial stage, especially below a few molecular-layers. *c*-axis-oriented epitaxial SBT films with various thickness were grown by pulsed metalorganic chemical vapor deposition (MOCVD). Atomically-flattened (100)SrTiO₃ single crystals were used as substrates. Atomically-flat SrRuO₃ layers were also grown on these SrTiO₃ substrates by MOCVD. Surface of the resultant films were observed by atomic force microscope and found to be a lot of grain islands having a constant height corresponding to half-unit-cell of SBT (~1.2 nm). Nucleation density of the island depended on the deposition temperature; it decreased with the increase of deposition temperature. Completely filled SBT layer was laid under the incompletely grown half-unit-cell island layer, suggesting the Frank-van der Merwe growth mode in the initial stage of SBT film growth on SrTiO₃ substrates. Extremely-small lattice mismatch between SBT film and SrTiO₃ substrate, -0.18 %, may contribute for this growth mode. Height of steps and width of terraces perfectly agreed with those of SrTiO₃ substrate were observed on SBT film surface, indicating the propagation of the information of patterns on SrTiO₃ surface. There are a high potential barrier, Ehrlich-Schwoebel barrier, and potential minimum at edge of upper and lower terraces, respectively. Therefore, adsorbed species on the terrace migrate to step or kink and are incorporated to them, and climbing up to a next terrace hardly occurred. However, in-plane growth of half-unit-cell SBT islands climbing over the step wall was observed. It was considered to be a special phenomenon for *c*-axis-oriented BLD films owing to their several times larger out-of-plane parameter than that of single step height of SrTiO₃. 1) T. Kojima *et al.*, Mater. Res. Soc. Symp. Proc. 748, U15.2.1 (2003).

T3.40 **Abstract Withdrawn**

T3.41
Morphotropic Phase Boundaries in Pb-Free Systems.
Daniel Scott Tinberg and Susan Trolier-McKinstry; Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Pulsed laser deposition was used to deposit BiScO₃-BaTiO₃ thin films on LaAlO₃, SrRuO₃, and Pt-coated Si substrates. This novel ferroelectric system was predicted to show a morphotropic phase boundary, based on a tolerance factor approach. In addition, the lone pair on the Bi³⁺ ion may also facilitate high permittivity values. The perovskite structure was found to be stable for compositions of 20-40 mol% BiScO₃ in both epitaxial and polycrystalline films. Dielectric measurements demonstrate that these films show relaxor like behavior and have permittivities in the range from 200 to 400, with loss tangents of ~0.05. Hysteresis measurements show the films have a coercive field around 200 kV/cm with a modest remanent polarization near 5 μC/cm². The films exhibit a tunability of ~25% at fields of ~500 kV/cm. Additionally, the films exhibit a small change of permittivity (~25%) between room temperature and 250°C.

T3.42
Depth-Dependent X-Ray Study of PbTiO₃ Thin Films.
Gustau Catalan¹, Arjen Janssens², Oliver H. Seeck³, Guus Rijnders², Dave Blank² and Beatriz Noheda¹; ¹Materials Science Center, University of Groningen, Groningen, Netherlands; ²MESA+, University of Twente, Nijmegen, Netherlands; ³Hasylab, DESY, Hamburg, Germany.

Grazing angle synchrotron radiation has been used to study the in-plane crystallography of epitaxial films of PbTiO₃ (PTO), grown layer-by-layer on insulating and conductive substrates. The results show that the top layers of PTO films are different from those towards the interior of the films. In particular, we observe i) an evolution of the diffraction angles consistent with a depth gradient of in-plane lattice parameters, and ii) surface structures different from those inside the bulk of the film. We believe that the strain gradient and the surface reconstruction may be closely related to the recently observed stability of ferroelectric polarisation in ultra-thin films of PTO.

T3.43
Ferroelectric and Piezoelectric Properties of the Lanthanum-Substituted Epitaxial BiFeO₃ Films on Si Substrate. Ying-Hao Chu¹, Tong Zhao¹, Qian Zhan¹, Florin Zavaliche¹, Maria P. Cruz¹, Seung-Yeul Yang¹, I-Nan Lin² and R. Ramesh¹; ¹Department of Materials Science & Engineering, UC Berkeley, Berkeley, California; ²Department of Physics, Tamkang University, Tamsui, Taiwan.

With the worldwide booming interest in data storage, transducers, and MEMS applications, materials with superior ferroelectric and

piezoelectric responses are of great demand. The drawback of a popular ferroelectric system, Pb(Zr_xTi_{1-x})O₃ (PZT), is its relative toxicity accruing from lead. Recently, perovskite BiFeO₃ (BFO) has attracted attention because of its superior ferroelectric and piezoelectric properties in both epitaxial and polycrystalline thin films. Therefore, BFO provides an alternative choice as green ferro/piezoelectric material which is environmentally preferable. However, the BFO films on Si substrate show a ferroelectric coercive field of 250 kV/cm, which is too large for memory device applications. Lowering the coercive field to below 100 kV/cm has become a key issue. By substituting Lanthanum ions into the positions of Bismuth ions, both Curie temperature and lattice parameters will be decreased with increasing Lanthanum concentrations, providing a potential approach to reduce the coercive field of BFO-based materials. In this study, Epitaxial (La_xBi_{1-x})FeO₃ films were grown by pulsed laser deposition on STO and Si substrates with a SrTiO₃ template layer. We will present the effect of La-substitution on the structure and ferro/piezoelectric properties.

T3.44
Raman Study of Phase Evolution in High Zr Content PZT Films. Chi Yat Yau and Relva C. Buchanan; Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio.

High Zr content ferroelectric PZT has potential applications for uncooled thermal infrared sensor and low power consumption electronic memories. The ferroelectric properties of the PZT thin films vary with composition, especially in the high Zr content range, and are sensitive to stress and defect state conditions. In this study, the Zr content effect in metalorganic derived 0.5-1.0 micron PZT films with Zr content varying between 90 and 97 %, were investigated using Raman scattering technique and hysteresis loop measurements. The resulting microscopic lattice dynamical changes were correlated to the macroscopic dielectric properties via the Lyddane-Sachs-Teller (LST) equation. A deviation of the phonon mode frequencies at 95 % Zr content from the LST equation was observed, coincident with the onset of the ferroelectric-antiferroelectric (FE-AFE) phase transition, signified by the double hysteresis-loop features. This coincidence of phase boundary shift can be attributed, therefore, to stress relaxation caused by interfacial defects introduced during film synthesis.

T3.45
Electrical Properties of Au/Bi_{4-x}La_xTi₃O₁₂ Thin Film/Si Structures and Reduction of Interface States. Atsushi Kohno and Hiroyuki Tomari; Department of Applied Physics, Fukuoka University, Fukuoka, Japan.

Sub-100nm-thick polycrystalline Bi_{4-x}La_xTi₃O₁₂ (BLT) thin films have been formed on silicon substrates by sol-gel and spin-coating techniques. The analysis of X-ray diffraction profile shows that the BLT films consisted of the grains of sub-100 nm size on the average and the size depended on the crystallization temperature. By pole-figure measurements it was confirmed that the preferred orientation in the BLT films depended on the crystallization temperature and time. Clockwise hysteresis was observed in capacitance-voltage (C-V) characteristics for Au/BLT/p-Si structures. The hysteresis voltage width for the C-V curves was related to the preferred orientation in the BLT film. The frequency dispersion of the C-V curve was caused by a large amount of interface states at BLT/Si interface. As the film was crystallized at 550°C for 2 h the maximum interface state density was ~3.4x10¹¹ cm⁻²ev⁻¹ at 1 kHz. Also, the negative gate-voltage shift of the C-V curve from the ideal curve and the gate-bias dependence of the flat-band voltage were observed, resulting in the presence of undesirable positive charges in the film. By post-annealing of the device at 400°C in oxygen atmosphere, the interface state density was reduced to a third of the initial value and also the positive charge was significantly diminished.

T3.46
Epitaxial Growth of Strontium Bismuth Tantalate/Niobate on Buffered Magnesium Oxide Substrates. George H. Thomas^{2,1}, David B. Beach¹ and Ziling B. Xue²; ¹Chemistry, Oak Ridge National Lab, Oak Ridge, Tennessee; ²Chemistry, University of Tennessee, Knoxville, Tennessee.

An all-alkoxide route was employed for the synthesis of epitaxial films of SrBi₂Ta₂O₉ (SBT) and SrBi₂Nb₂O₉ (SBN) on LaMnO₃ (LMO) buffered MgO [100] substrates. LMO layers, approximately 50 nm thick, were deposited via rf-magnetron sputtering from an oxide target in the presence of Ar/4%H₂ and H₂O on an MgO single-crystal substrate that had been heated to 700C. Films of SBT and SBN were deposited via spin coating, and then crystallized at 900C in the presence of air for twenty minutes. Individual layers were approximately 60 nm thick and films as thick as 0.5 micrometer were deposited by multiple depositions steps. Electron and surface probe microscopy revealed that the films were smooth and featureless. Following the deposition and heat treatment of the final layer, the

sample was post-annealed for one hour at 900C to maximize film crystallinity. X-ray characterization was used to structurally characterize the films. $\theta/2\theta$ scans showed only (h00) peaks for both the buffer and the SBT or SBN layers, indicating the films were c-axis aligned. Pole figures indicated that the films were aligned in the plane as well. The full-width-at-half-maximum (FWHM) of the out of plane rocking curves and in-plane phi scans were less than 1 degree.

T3.47

Effects of Thickness and La Substitution on Microstructure of BiFeO₃ Thin Films. Qian Zhan¹, R. Yu², T. Zhao¹, Y. H. Chu¹, U. Dahmen³ and R. Ramesh¹; ¹Department of Materials Science and Engineering and Department of Physics, University of California, Berkeley, Berkeley, California; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; ³National Center for Electron Microscopy, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Recently, BiFeO₃ (BFO) has attracted considerable interest due to its excellent ferroelectric and piezoelectric properties which make it a promising candidate for lead-free ferroelectric memory cells and piezoelectric sensor devices. Since structure strongly influences properties, the microstructural changes of epitaxial BFO films with different thicknesses and different lanthanum-substitution levels were systematically investigated at nanometer and atomic scales using high-resolution transmission electron microscopy in conjunction with diffraction contrast analysis. For thick pure BFO films, the crystal structure is bulk-like (rhombohedral). Domain structure is developed in such films. For ultra thin films, a change to a tetragonal structure is induced by the lattice-mismatch between the film and the substrate. The effect of different La substitutions on the microstructure of BFO films was also studied. For films with higher La substitutions, the crystal structure changed and different domain structure is formed, which lead to a significant change of ferroelectric and piezoelectric properties.

T3.48

Enhanced Pyroelectric Property of PZT Films Deposited on Oxide/Pt Hybrid by Chemical Solution Deposition. Hui Han¹, Xiyu Song², Jian Zhong^{2,3}, Sushma Kotru³, Padmini Periaswamy³ and R. K. Pandey³; ¹Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama; ²Materials Program, University of Alabama, Tuscaloosa, Alabama; ³Department of Electrical and Computer Engineering, University of Alabama, Tuscaloosa, Alabama.

Pb(TixZr1-x)O3 (PZT) thin films are considered to be a good candidate for the fabrication of uncooled IR detectors because of its good ferroelectric, dielectric, pyroelectric properties and relatively low crystallizing temperature. It is well known that the built-in electric field (self-polarization) in PZT layers can enhance the pyroelectric effect, and there have been many reports on how to set up this built-in electric field during depositing PZT films. The methods include using seed layer; adjust the excess degree of lead in sol-gel solution, etc. Perovskite oxides, such as LaNiO_{3-y} and La_{0.5}Sr_{0.5}CoO_{3-y}, have a variable oxygen composition (y value), and it depends on the atmosphere during annealing. Oxygen vacancies introduced during reduced atmosphere annealing can downgrade the conductivity of these oxides, and make the oxides transit from metallic conductor to semiconductor. When PZT films were deposited on these unfully oxidized electrodes, a shift hysteresis loop, that is imprint, will be observed. This means that there will be an internal electric field result from the oxygen vacancies exist in the PZT layer. For memory application, it would be harmful since it may cause the asymmetric coercive fields and polarization states. However, this phenomenon maybe contributes the pyroelectric and piezoelectric property of PZT. In this paper, we report using perovskite oxide electrode (LSCO, LNO) annealed in reduced atmosphere by rapid thermal annealing (RTA) to improve the pyroelectric property of PZT. Simple, Low cost chemical solution deposition was applied to deposit the oxide electrode layer and PZT ferroelectric layers.

T3.49

Electric-Field-Induced Displacements in Pt/PZT/Pt/SiO₂/Si System Investigated by Finite Element Method. Hirotake Okino¹, Masahiro Hayashi¹, Takashi Yamamoto¹, Takashi Iijima², Shintaro Yokoyama³, Hiroshi Funakubo³ and Nava Setter⁴; ¹Dept. of Communications Eng., National Defense Academy, Kanagawa, Japan; ²Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; ³Dept. of Innovative and Engineered Materials, Tokyo Institute of Technology, Kanagawa, Japan; ⁴Ceramic Laboratory, Materials Institute, College of Engineering, Swiss Federal Institute of Technology-EPFL, Lausanne, Switzerland.

Currently, several techniques such as atomic force microscope (AFM), laser Doppler vibrometer and laser interferometer have been employed

to evaluate the electric-field-induced displacements. Among them, double-beam laser interferometer (DBI)[1] has been the most precision technique; however it has needed a well-skilled operator and some sample processing. Recently, AFM has been widely used to measure field-induced strains, because AFM is easy to operate and has sufficient sensitivity. Nevertheless, there has been some doubt whether piezoelectric constant d_{33} evaluated simply from AFM-measured strains has been intrinsic d_{33} or not. In this paper, Electric-field-induced displacements of PZT film capacitor Pt/PZT/Pt/SiO₂/Si(100) were calculated by finite element method with changing parameters of sample geometry and material constants of PZT. Sample geometric parameters were the diameter of top electrode ϕ_{TE} ranging from (0.2-1000 μ m), PZT film thickness t_{PZT} (0.5-10 μ m) and whether PZT film was continuous or side-etched. The thickness of the substrate t_{PZT} was 300 μ m. Surface longitudinal displacements and net longitudinal displacements of the PZT film were computed out, which corresponded to strains measured using AFM and DBI, respectively. Five types of effects that prevent measurement of the intrinsic d_{33} using AFM were clarified and discussed: (1) substrate-bending effect[1] (observed under the condition of $0.5 \times t_{PZT} < \phi_{TE}$), (2) local backside displacement ($t_{PZT} < \phi_{TE}$), (3) in-plane clamping by the substrate ($t_{PZT} < \phi_{TE}$), (4) in-plane clamping by the continuous film ($\phi_{TE} < 20 \times t_{PZT}$) and (5) edge-clamping effect ($\phi_{TE} < 0.5 \times t_{PZT}$). The substrate-bending effect and the local backside displacement were negligible, if the displacements were measured by DBI. Side-etch treatment was effective to eliminate the in-plane clamping by the continuous film and the edge-clamping effect, although it had no effect for larger ϕ_{TE} ($20 \times t_{PZT} < \phi_{TE}$). In order to measure the intrinsic d_{33} , both smaller ϕ_{TE} (comparable to t_{PZT}) and side-etch treatment were essential; however this condition is difficult to be satisfied experimentally. Under usual experimental conditions with larger ϕ_{TE} ($20 \times t_{PZT} < \phi_{TE}$), AFM-measured d_{33} (and DBI-measured d_{33}) depended on not only intrinsic d_{33} but also d_{31} , s_{11} , s_{12} and s_{13} of PZT, which was qualitatively described by the Lefki-Dormans's equation[2]. Because d_{31} is mostly proportional to d_{33} , these measured (effective) d_{33} values are still small even if the intrinsic d_{33} is relatively large. Thus, it was suggested to measure transverse piezoelectric properties using another method (ex. by measuring the tip displacement of unimorph cantilevers) and to perform simulation and fitting to evaluate intrinsic d_{33} and d_{31} , simultaneously. [1] A. L. Kholkin, Ch. Wüthrich, D. V. Taylor, and N. Setter, Rev. Sci. Instrum. **67**, 1935 (1996) [2] K. Lefki and G. J. M. Dormans, J. Appl. Phys. **76**, 1764 (1994).

T3.50

Optical and Structural Properties of Patterned Regions of Thin Single-Crystal Films of LiNbO₃ Fabricated by Localized He⁺ Ion-Implantation. Djordje Djukic¹, Ryan M. Roth¹, Richard M. Osgood¹, Kenneth Evans-Lutterodt², Hassaram Bakhru³ and Sasha Bakhru³; ¹Microelectronics Sciences Laboratories, Columbia University, New York, New York; ²National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York; ³Department of Physics, SUNY at Albany, Albany, New York.

Metal-oxide crystals, such as LiNbO₃, are known for their superior optical properties, and have been widely used in a variety of active photonic devices. However, these devices have utilized mostly bulk crystals or thick wafers, since growth of single-crystal thin films of metal-oxides still presents a considerable challenge. We have developed a thin film technology based on exfoliation of single-crystal thin films of metal-oxides from a bulk single crystal sample. This technique involves high energy ion implantation followed by thermal processing and wet chemical etching to release thin crystal sheets off the entire surface of a bulk material, resulting in a freestanding thin film. Film thickness can be controlled by varying the implanted ion energy, and typically yields 10-3 μ m thickness for freestanding thin crystals. We report the use of ion-beam patterning to fabricate patterned thin ($\leq 1\mu$ m) film regions on a LiNbO₃ wafer by using localized ion implantation. This approach allows generation of very thin local films regions mechanically supported by the bulk wafer; it also provides an air-gap region for high-refractive-index confinement or a channel for microfluidics applications. Instead of implanting the entire crystal surface, in this case, the implantation was done through a thick photoresist mask, which was defined by optical lithography. In the subsequent CIS steps only the implanted areas are undercut, which results in formation of a membrane structure - a thin film of LiNbO₃ suspended over a submicron airgap. These structures were found to provide sufficient mechanical support for fabrication of extremely thin LiNbO₃ films. In order to examine the effect of ion implantation on the thin surface layer of the crystal forming the membrane structure, a series of measurements comparing the properties of the thin membrane films and bulk material were performed. Membrane optical quality, in membranes as thin as 1-2 μ m, was verified by performing optical waveguiding measurements; these measurements showed excellent guided wave properties and multimode interference. Additional characterization of local optical

response was done using IR microscopy. Spatially resolved synchrotron X-ray microdiffraction measurements were done to characterize the membrane crystal structure and examine the stress distribution in implanted vs. unimplanted crystal regions. A systematic study of the sensitivity of the optical and structural properties of thin film membranes to varying ion-slicing process conditions, such as thermal processing and etch chemistry, has also been carried out and related to crystal implant dose and thin-film stress due to residual He. ¹ Work supported by NSF (DMR-0405145) and ONR (N00014-03-01-0984)

T3.51

InSitu Measurements of Macroscopic Stress in Thin Film $Pb_xBa_{1-x}TiO_3$. David A. Boyd, Mohamed Y. El-Naggar and David G. Goodwin; Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California.

A great deal of theoretical and experimental efforts have focused on the formation of polydomain structures as a strain-relief mechanism in ferroelectric films, and x-ray methods are used in particular to study the microstructure. Macroscopic wafer curvature can be related to the average wafer stress through Stoney's equation. Curvature measurements are complimentary to x-ray measurements and require no knowledge of the microstructure or the mechanical properties of the film. Coherent Gradient Sensing (CGS) has been used to measure, *insitu*, the macroscopic curvature in thin films of $Pb_xBa_{1-x}TiO_3$ (PBT) ($0.2 \leq x \leq 1.0$) on single crystal MgO (001). The films were grown by metal organic chemical vapor deposition (MOCVD) and were found from x-ray diffraction (XRD) to be well-oriented, having volume fractions of a and c domains that are oriented either perpendicular or parallel to the surface normal only. The presence of polytwin domains was verified by XRD pole figures and electron backscatter diffraction. Successive curvature measurements were made during growth, cooling, and subsequent thermal cycling of the PBT films. For $x=1$, very small changes in the stress during growth were found, and upon cooling from the growth temperature, 650 °C, all the films are found to be in be in compression with stress values on the order of several hundred MPa. Near T_c , pronounced changes in the slope of the curvature with temperature are observed and attributed to the evolution of the domain structure, which is confirmed by XRD. We also compare these results with the Landau-Ginzburg-Devonshire (LGD) calculation of the a and c domain volume fractions.

T3.52

Enhanced Electrical properties in Mn-doped $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films. Sushil Kumar Singh, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan.

Bismuth titanate-based thin films are considered to be candidates for the memories applications such as NvFeRAM, because of their large polarization, high fatigue endurance limit and lead-free chemical composition. $Bi_4Ti_3O_{12}$ (BTO) belongs to a class of Aurivillius phases with layered intergrowth structures, which consist of alternate stacking of perovskite-like ($Bi_2Ti_3O_{10}$) and fluorite-like (Bi_2O_2) layers. From consideration of the structural chemistry of the Aurivillius phases, site-engineering (substitution technique) is important factor to improve the properties of the materials. The influences of the Bi_3+ site substitution by equal valent La^{3+} , Nd^{3+} cations and Ti_4+ site substitution by high valent V^{5+} , W^{6+} , Mo^{6+} cations on ferroelectric properties of BTO were reported in the literature. It was shown that the Bi 's side substitution can increase the polarization as well as coercive field. However, in case of Ti side substitution, the polarization may increase whereas the coercive field decreases. Ti -side substitution by high valent cations is functional to the decrease in oxygen vacancy. $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) films prepared by chemical solution deposition show either with (117) or (001) preferred orientation, depending upon the various processing conditions. Due to the highly anisotropic ferroelectric properties of BLT films, it is important to understand the crystallization behavior of these films. We have observed that the grain morphology of doped BLT films, besides the ferroelectric properties, is also dependent upon the orientation of the film. Mn^{5+} doping at Ti_4+ site in BLT shows modification in structure, which affects the microstructure and ferroelectric properties of BLT films. Small amount of Mn in BLT films influences the ferroelectric properties of the films that is, it enhances the remanent polarization and reduces the coercive field. We have observed large plate-like grain morphology with small rod-like grains were increased initially but substitution more than 2% was modified the morphology of the BLT films.

T3.53

PZN-PT Thin Films Derived from MOD Process for MEMS Application. A. L. Ding and X. Y. He; The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

The relaxor ferroelectrics, $Pb(Zn_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ (PZN-PT), has attracted attention for MEMS application due to its excellent dielectric, ferroelectric and electromechanical properties [1]. PZN-PT single crystals exhibit very high dielectric permittivities and high piezoelectric coefficients along the [001] direction [2]. The perovskite PZN-PT thin films with preferred orientation would be promising candidates for numerous integrated device applications, such as ferroelectric random access memories and piezoelectric micro-actuators. However, it is difficult to obtain the PZN-PT thin films with pure perovskite phase because the pyrochlore phase existent [3]. The key to realize MEMS application for PZN-PT thin film is to restrain and eliminate pyrochlore phase in preparing process. In this study, influences of some key process parameters on the phase structure of the PZN-PT thin films were investigated and analyzed. $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$ - $xPbTiO_3$ (PZN-xPT) thin films were prepared by a metal-organic decomposition (MOD) process on the Pt/Ti/SiO₂/Si and Pt/TiN/Si substrates, respectively. The crystallization behavior and the development of the perovskite structure in the films were investigated in terms of PT content x ($x=0.4\sim 0.7$). Two precursor routines were selected to examine the effect of precursor solution characteristics on film crystallization. Perovskite PZT(53/37) thin films were used as a buffer layer to promote the formation of perovskite phase in the PZN-PT thin films. About 81% perovskite phase in the PZN-0.4PT film was induced out from the complete pyrochlore phase due to the buffer layer. Highly (111) and (100) oriented PZN-PT (30/70) thin films were obtained by the substrate induction effect. The ferroelectric and dielectric properties of the above two films were reported. The study has showed that the PZN-PT films can be realized applications in MEMS.

T3.54

Effect of Composition and Structure on Ferroelectric Response of Bi_4 - $xSm_xTi_3O_{12}$. Maharaj S. Tomar, Ricardo Melgarejo, Sandra Dussan and Ram S. Katiyar; Physics, University of Puerto Rico, Mayaguez, Puerto Rico.

Bismuth titanate ($Bi_4Ti_3O_{12}$) is an electroceramic within the Aurivillius phase material with weak ferroelectric memory. However, the partial substitution of Bi ion by a trivalent rare earth tilts TiO_6 octahedra towards Bi_2O_2 interlayer, have resulted in improved the ferroelectric polarization. In order to demonstrate this effect, we synthesized Bi_4 - $xSm_xTi_3O_{12}$ by a solution chemistry route and thin films were deposited by spin coating on Pt (Pt/TiO₂/SiO₂/Si) substrate. X-ray diffraction studies of the films showed a stoichiometric solid solution for the composition $x < 1$. The c-axis growth films showed ferroelectric polarization $P_r = 18$?C/cm² for the composition $x < 0.7$. Bi_4 - $xSm_xTi_3O_{12}$ ceramic thin films could be a potential candidate for nonvolatile ferroelectric memory devices. The films showed low leakage current at room temperature, showing the possibility of lead free ferroelectric devices.

T3.55

Metalorganic chemical vapor deposition of lead-free ferroelectric $BiFeO_3$ films. Seung-Yeul Yang^{1,2}, F. Zavaliche², Y. J. Lee², Y. H. Chu², M. P. Cruz², Q. Zhan², L. Mohaddes-Ardabili^{1,2}, T. Zhao², V. Vaithyanathan³, D. G. Schlom³ and R. Ramesh²; ¹Materials Science and Engineering, University of Maryland, College Park, Maryland; ²Materials Science and Engineering, University of California, Berkeley, Berkeley, California; ³Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

There is currently significant interest in the field of ferroelectric thin film materials and devices, with a strong focus on non-volatile memory (FeRAM) applications. It is quite desirable to have a ferroelectric material system that has the large polarization properties and low temperature processability of the PZT system with the chemical 'benign-ness' of the SBT system. Recently, perovskite $BiFeO_3$ (BFO) has attracted great attention due to its large ferroelectric polarization and smaller dielectric constant, which makes to be an interesting replacement candidate for Pb -based ferro/piezoelectrics. It is, however, imperative that a viable, manufacturable process be available for the deposition of the ferroelectric layer. Epitaxial BFO thin films were grown by metalorganic chemical vapor deposition (MOCVD) equipped with liquid delivery system on $SrTiO_3$ (STO) (001) and STO / Si (001) covered with an $SrRuO_3$ (SRO) electrode layer using $Bi(thd)_3$ and $Fe(thd)_3$ as precursors. A systematic study on deposition process control such as stoichiometric composition, structure change and growth temperature was carried out. The film composition and phase equilibrium are sensitive to the $Bi:Fe$ ratio in the precursor. In the optimized condition, an epitaxial single perovskite phase thin films were obtained. Electrical measurements using both quasi-static hysteresis and pulsed polarization measurements confirm the existence of ferroelectricity with a switched polarization of 110-120 °C/cm², $\Delta P (= P^* - P)$. Out-of plane piezoelectric (d_{33}) measurements using

an atomic force microscope yield a value of 50-55 pm/V. This work has been supported by the ONR under a MURI program.

T3.56

Characterization of La, Ti and La/Ti -Codoped Bismuth Ferrite Thin Films by Chemical Solution Deposition Method. Chia-Ching Lee and Jenn-Ming Wu; National Tsing Hwa University, Taiwan, R.O.C., Hsinchu, Taiwan.

Pure and doped BiFeO₃ (BFO) thin films were prepared using Bi acetate and Iron acetylacetonate as starting material and were coated on Pt/Ti/SiO₂/Si(100) substrate by Chemical Solution Deposition (CSD) method. The pure perovskite phase of BiFeO₃ thin films was formed at low temperature (~350 degee C) without impurity phase accompanied. Effect of dopants such as La (BLFO), Ti (BFTO) and the codopants of La/Ti (BLFTO) on the microstructure and electrical properties of BFO were investigated. X-ray photoelectron spectroscopy indicated that the Fe ions were trivalent without chemical fluctuation. Changes of film direction was observed on the La-doped and La/Ti-codoped films and the change depended greatly on the dopant content. In contrast, Ti-dopant affected microstructure of BFO films. The leakage current density and P-E (polarization vs electric field) hysteresis loops of BLFO, BFTO and BLFTO were improved. Leakage current density of BLFTO films was three orders of magnitude lower than pure BFO films, The P-E hysteresis loops curves of La-doped, Ti-doped, and La/Ti-codoped BFO films were lws leaky than pure BFO films. Remnant polarization (Pr) values of optimal La-doped, Ti-doped and La/Ti-codoped BFO film were 46, 176 and 20 $\mu\text{C}/\text{cm}^2$ respectively under an applied field of 800 KV/cm.

T3.57

Switching Spectroscopy Mapping Piezoresponse Force Microscopy (SS-PFM) of Ferroelectric Materials and Nanostructures. Sergei V. Kalinin and Stephen Jesse; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The application of ferroelectric materials for electronic devices such as FeRAMs, ferroelectric gate FET, and data storage, necessitates the quantitative studies of local switching behavior, including imprint, coercive bias, remanent and saturation responses, and work of switching. Here we introduce Switching Spectroscopy Mapping Piezoresponse Force Microscopy (SS-PFM) as a tool for real-space imaging of switching properties on the nanoscale. In SS-PFM, local electromechanical hysteresis curves are acquired at each point in the image and are analyzed to yield spatially resolved maps of switching properties, thus allowing the relationship between switching behavior and microstructure and defects to be established on the nanometer length scales. The implementation and data analysis in SS-PFM are discussed in detail. Hysteresis loop formation mechanism is analyzed for the case when the tip is used as a top electrode in the thermodynamic and kinetic limits and the relationship between materials parameters and measured data is established. SS-PFM is used to image switching phenomenon in sol-gel lead zirconate-titanate (PZT) thin films and demonstrate enhanced pinning in the vicinity of grain boundaries in polycrystalline PZT. The effect of step edges and surfaces defects on switching behavior in nearly ideal PLD-grown epitaxial PZT thin films is demonstrated. The SS-PFM was also applied to ferroelectric capacitors and image formation mechanism in the top-electrode excitation case is discussed. We expect that this approach will further understanding of the relationship between material microstructure and polarization switching phenomenon on the nanoscale as well as provide a quantitative tool for ferroelectric material and device characterization.

SESSION T4: Ferroelectrics Processing
Tuesday Morning, November 29, 2005
Back Bay D (Sheraton)

8:00 AM *T4.1

Structural, Piezoelectric and Ferroelectric Properties of Self-Assembled PbTiO₃ Nanoislands Fabricated by MOCVD. Masaru Shimizu¹, Masaki Nagata¹, Hironori Fujisawa¹, Hirohiko Niu¹, Koichiro Honda², Yasutoshi Kotaka² and Minoru Osada³; ¹Dept. of Elect. Eng. & Comp. Sci., University of Hyogo, Himeji, Hyogo, Japan; ²Fujitsu Lab. Ltd., Atsugi, Kanagawa, Japan; ³National Institute for Material Science, Tsukuba, Ibaraki, Japan.

In the past several years, ferroelectric nanoisland structures have attracted considerable interest from the point of views of size effect and ultimate potential for ferroelectricity. There have been several reports on piezo- and ferroelectric properties of PbTiO₃, PZT and SBT nanostructures. However, crystalline structure and piezo- and ferroelectric phenomena in ferroelectric nanoislands with lateral sizes smaller than 50nm are not well understood. In this paper, crystalline

structure and piezo- and ferroelectric properties of self-assembled PbTiO₃ nanoislands fabricated on various substrates by MOCVD were investigated. Structural control and size dependence of piezoelectricity were also discussed. PbTiO₃ nanoisland structures were fabricated on Pt-covered Si and SrTiO₃ by self-assembly using MOCVD. On Pt-covered Si(100), the pyramidal-shaped islands were randomly distributed and the in-plane orientation was random, because the Pt was polycrystalline and had a random in-plane orientation. On the other hand, three types of nanoislands, pyramidal-shaped, triangular-prism-shaped and square-shaped, were fabricated on Pt-covered SrTiO₃(111), (101) and (001). Structural control of the shape and in-plane direction of PbTiO₃ nanoislands was successfully achieved due to epitaxial relationships. The width and height of nanoislands on Pt-covered Si were smaller than those on Pt-covered SrTiO₃. Piezo- and ferroelectric properties of nanoislands were investigated using piezoresponse scanning force microscopy (PFM). Piezoelectric hysteresis loops were observed for PbTiO₃ nanostructures on various substrates. At this stage, the minimum width and height of the PbTiO₃ nanoisland showing piezoelectric hysteresis loop were 27 and 1.2nm, respectively. Crystalline structure and microstructure were examined by Raman spectroscopy, X-ray diffraction and TEM. From Raman spectra measurement, island structures were found to have large residual stress and to show lower phase transition temperature than that of bulk. Crystalline structure and piezo- and ferroelectric properties of PbTiO₃ nanoislands were also compared with those of PbTiO₃ ultrathin films with thicknesses thinner than 10nm.

8:30 AM T4.2

The Effect of Nucleation and Growth on Strain and Symmetry in the Ferroelectric PbZrTi(1-x)O₃.

Arjen Janssens¹, Guus Rijnders¹, Dave H. A. Blank¹ and Beatriz Noheda²; ¹Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; ²Faculty of Mathematics and Natural Sciences and Materials Science Center, University of Groningen, Groningen, Netherlands.

An enhancement of the piezoelectric effect can be induced in PbZrTi(1-x)O₃ by lowering the symmetry. This can be achieved in, for instance, superlattices with different compositions of PbZrTi(1-x)O₃. This will artificially induce cation order and, subsequently, a lower symmetry. However, when dealing with such epitaxial heterostructures, strain due to the lattice mismatch with the substrate and/or the individual layers, becomes very important. Strain not only shifts transition temperatures but can also influence the symmetry of the superlattice. Here we present our study of the growth mechanisms, such as nucleation behaviour, and the related strain states. We investigated the growth by RHEED controlled PLD on substrates with different in-plane lattice parameters, such as SrTiO₃ and DyScO₃. In addition, we observed that the growth behaviour of PbTiO₃ (PTO) depends on the surface termination of the substrate, either A-site (for instance TiO₂-terminated SrTiO₃) or B-site (for instance SrO-terminated SrRuO₃). The first shows a layer by layer growth, the latter an island like growth which continues into a layer by layer growth after deposition of ~4 unit cell layers. The differences of this growth behaviour are studied, besides RHEED, by TEM and AFM and can be explained by PbO volatility.

8:45 AM T4.3

Pb(Zr,Ti)O₃/Electrode Interface Layer Engineering of Ferroelectric Random Access Memory Capacitors.

Ye (Mike) Chen and Paul C. McIntyre; Materials Science and Engineering, Stanford University, Stanford, California.

Ferroelectric fatigue, imprint and opposite-state retention failure are important phenomena which limit the reliability of ferroelectric random access nonvolatile memories (FeRAM / FRAM). Recent reports have suggested that these processes may be caused, at least in part, by the presence of a nonferroelectric interface layer (passive layer) between the ferroelectric film and the electrode. In this work, we have used x-ray photoemission spectroscopy (XPS) to determine that there is a Pb-rich surface layer on as-deposited, state-of-the-art, Pb(Zr,Ti)O₃ (PZT) films grown by metalorganic chemical vapor deposition. Angle resolved XPS showed that the surface layer is approximately one nanometer thick, but a wet-chemical etch was effective in removing it. Because little is known about the Pb-rich surface layer and resulting interface chemistry of electroded PZT films, a well-studied dielectric oxide, HfO₂, was deposited by atomic layer deposition (ALD) onto PZT films after the surface layer was removed by the wet-chemical etch. This ultrathin HfO₂ film behaves a passive layer with respect to polarization switching and allows a direct investigation of passive layer effects. Platinum top electrodes were deposited for electrical characterization. Preliminary results indicate that the ALD-HfO₂ film reduces the switchable polarization of the ferroelectric capacitors, as expected, while also reducing steady state leakage conduction. The effect of this modification of the PZT/metal interface on the switching reliability of PZT capacitors

will be discussed in detail.

9:00 AM T4.4

Control Factor of Squareness in *P-E* Hysteresis of MOCVD-PZT Films. Hiroshi Funakubo, Akihiro Sumi, Shoji Okamoto, Yoshihisa Honda and Shintaro Yokoyama; Tokyo Institute of Technology, Yokohama, Japan.

Squareness in *P-E* hysteresis [the ratio of the remanent polarization (*Pr*) to saturation polarization (*Psat*), $Pr/Psat$] of ferroelectric thin film is an important factor for FeRAM and MEMS applications. For example, rhombohedral PZT films have lower leakage current density and lower coercive field than tetragonal PZT films, but have a lower squareness in *P-E* hysteresis loops. This makes rhombohedral PZT films difficult to FeRAM applications, but useful for MEMS compared with tetragonal ones. However, the systematic research of the squareness in *P-E* hysteresis has not been investigated. In the present study, we systematically investigated the *P-E* hysteresis loops of the rhombohedral MOCVD-PZT films as a function of the temperature from 10 K to Curie temperature (*Tc*) by changing the film thickness (180-3200 nm), in-plane orientation (epitaxial and fiber-textured films) and out-of-plane orientation [(100) and (111) orientations], and the applied stress from the substrates (films on Si and on SrTiO₃ substrates). Room temperature *Pr/Psat* value for the films deposited on Si substrates was higher than that on SrTiO₃ substrates irrespective of the measured temperature for both of epitaxial and fiber textured (100)-oriented films. In addition, room temperature *Pr/Psat* value increased with increasing the *d* spacing of (200) diffraction peaks estimated from XRD θ -2 θ patterns. This suggests that the *Pr/Psat* value decreased with increasing the strain from the substrates. On the other hand, *Pr/Psat* was almost equal to unity when the measured temperature was as low as 10 K for (100)- and (111)- oriented epitaxial films grown on SrTiO₃ substrates. However it decreased with increasing temperature started at lower temperature for (100)-oriented epitaxial film than (111)-oriented one. As a result, the *Pr/Psat* value of (111) oriented film was lower than that of (100)-oriented one at room temperature. This can be explained by the highly strained states of (100)-oriented films compared with (111)-oriented one due to the lack of the strain relaxation mechanism. Taking account of the fact that the *Tc* value estimated from the temperature dependence of *Ec* was almost the same for all films, the strain applied from the substrates took an important role to define the *Pr/Psat* value. Indeed *Pr/Psat* value was ascertained to be increased with increasing the film thickness for epitaxial (100)-oriented films grown on (100)SrTiO₃ substrates due to the relaxation of the strain from the substrate.

9:15 AM T4.5

Processing and Properties of Vertically Aligned High Aspect Ratio Ferroelectric Pb(Zr_{0.52}Ti_{0.48})O₃ Tubular Structures.

Bharadwaja S. N. Srowthi¹, Xin Li², Hui Fang¹, Venkat Gopalan¹, Theresa Mayer², Fred Roozeboom³ and Susan Trolier-McKinstry¹; ¹Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; ²Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania; ³Philips Research Labs, Eindhoven, Netherlands.

Ordered array of high aspect ratio (> 30:1) ferroelectric structures have potential applications in areas such as tunable photonic crystals, biosensors and miniaturized transducers. In this work we report on the processing of high aspect ratio Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT) tubes (1.5 and 2 microns in diameter) with 2D hexagonal symmetry prepared using a vacuum infiltration technique of Si molds. Pre-patterned porous silicon templates were used to mold vertically aligned PZT micro tubes. These arrays were pyrolyzed at 300 °C for 2 min, followed by releasing the tube arrays using a combination of reactive ion etching and XeF₂ silicon etch. Removal of the Si prior to crystallization of the PZT reduces the chemical reaction between the Pb with the silicon templates. Subsequently the released structures were crystallized at 750°C for 1 min, using a rapid thermal annealing furnace. Pervoskite phase formation was confirmed by X-ray diffraction and high resolution TEM analysis. These tube arrays act as photonic crystals and exhibit a TE- mode band gap with no detectable TM- mode band gap between 4.0 and 4.4 microns, consistent with the theoretical calculations. For small signal dielectric and electrical characterization, coaxial tri-layer structures of (metallic LaNiO₃)/PZT/(metallic LaNiO₃) have been processed in a similar way. The electrical characterization setup and subsequent dielectric and electromechanical properties will be discussed.

10:00 AM T4.6

Ba Substituted Pb(Zr_xTi_{1-x})O₃ Thin Films Grown by MOCVD. Susanne Hoffmann-Eifert, Jochen Puchalla and Rainer Waser; IFF/ IEM, Research Centre Juelich, Juelich, Germany.

The most prominent ferroelectric material for integrated non-volatile memories is Pb(Zr,Ti)O₃. In this study we report on the modification

of PZT thin films by substitution of Pb against Ba in order to study the effects accompanied with incorporation of a bigger A-site cation in the PZT system. The polycrystalline (Pb,Ba)(Ti,Zr)O₃ films are grown on Ir(111)/TiO₂/SiO₂/Si as well as on Pt(111)/TiO₂/SiO₂/Si substrates at temperatures between 580°C and 650°C applying a liquid-delivery MOCVD technique. The precursor solutions of Pb(DPM)₂, Ba(DPM)₂, Zr(IBM)₄, and Ti(OiPr)₂(DPM)₂ dissolved in butylacetate were separately injected into the reactor using a TriJet™ vaporizer. A PZT (30/70) film of 150 nm thickness shows good ferroelectric properties with *P_r* = 35 μC/cm² and *E_c* = 90 kV/cm. In first randomly oriented films the Ba substitution was unfortunately not effective in lowering the coercive field. The (Pb,Ba)(Ti,Zr)O₃ films show improved phase stability and a more homogeneous morphology compared to the pure PZT films. In addition the dielectric losses in the PBZT films are as small as 0.025. The presentation will in addition deal with the Ba substitution effect in films with a preferred orientation of the grains, namely (111). Further studies address the formation of IrO₂ or PbPt_x interfacial layers, and the analysis of the ferroelectric and dielectric properties and the leakage currents in the Ba-doped PZT thin films.

10:15 AM T4.7

Atomic Layer Deposition of Multi Component Oxide Thin Films Using Liquid Delivery Source Injection.

Takayuki Watanabe¹, Susanne Hoffmann-Eifert¹, Cheol Seong Hwang² and Rainer Waser¹; ¹Institute of Solid State Research and CNI - Center of Nanoelectronic Systems for Information Technology-, Research Center Juelich, Juelich, Germany; ²School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

One major challenge in the integration of ferroelectric thin films like Pb(Zr,Ti)O₃ into future non-volatile memory devices is the reduction of the film thickness below 50 nm combined with the necessity for homogeneous, stoichiometric films on complex 3-D structures. Atomic layer deposition (ALD) is a surface reaction controlled process and by this gives the possibility to achieve homogeneity even on complex structures. We selected an ALD system equipped with a liquid source injection to prepare multi component oxide thin films. Due to the narrow selectivity of precursors for typical divalent cations such as Pb, Sr, and Ba, and their limited thermal stability of the low-vapor pressure β -diketonate-based precursors, *e.g.*, Pb(DPM)₂ and Sr(DPM)₂, liquid delivery source injection methods become attractive. Focusing on PbTiO₃ as a model material, each constituent cation oxide film, TiO_x and PbO_x, was prepared on Pt covered Si substrates in a sequential gas supply procedure at first. We used 0.1 M Ti(Oi-Pr)₂(DPM)₂ and Pb(DPM)₂ dissolved in ECH solvent as precursors (supplied by SAES Getters S.p.A), and water vapor as an oxidant. In Arrhenius plots in terms of the deposited film thickness vs. deposition temperature, a clear transition temperature, where the deposition mechanisms changed from ALD to CVD, was observed for both TiO_x and PbO_x films. For PbO_x films, the relative carbon incorporation in the films showed the maximum at the transition temperature. We successfully observed a typical ALD behavior for the TiO_x as well as for the PbO_x films, *i.e.*, the deposited film thicknesses per cycle saturated against injected precursor volume. Interestingly, the TiO_x films deposited at 300°C were amorphous whereas the PbO_x films deposited at 220°C were already crystalline. We subsequently combine the single oxide ALD processes to prepared PbTiO₃ and finally Pb(Zr,Ti)O₃ thin films.

10:30 AM T4.8

Influence of Crystal Phase and Orientation on Electro-Optic Effect of PLZT Epitaxial Films. Keisuke Sato^{1,2,3}, Masatoshi

Ishii^{1,2,3}, Masao Kondo¹ and Kazuaki Kurihara¹; ¹Fujitsu Laboratories Ltd., Atsugi, Kanagawa, Japan; ²Fujitsu Ltd., Kawasaki, Kanagawa, Japan; ³OITDA, Bunkyo-ku, Tokyo, Japan.

Lanthanum-modified lead zirconate titanate

((Pb_{1-3/2x}Lax)(ZryTi_{1-y})O₃, hereafter designated PLZT

(X/Y/100-Y), where X=100x, Y=100y) are of much interest in

electrooptic (EO) applications, because a large electrooptic coefficient has been reported on their transparent ceramics. A number of applications such as modulators and switching devices were proposed using this material. Assuming the epitaxial film with few defects such as the grain boundaries is desirable to obtain the PLZT film waveguide of a low loss. In addition, if PLZT film with small polarized light dependency, a small and efficient device can be obtained. In this paper, the crystal orientation dependency of the EO effect in PLZT epitaxial film with pseudocubic, rhombohedral and tetragonal crystal were investigated to clarify the mechanism of the polarized light dependence of the EO constant. The PLZT(8/65/35), PZT(70/30) and PZT (30/70) epitaxial films (film thickness about 2μm) were deposited using the sol-gel method on niobium doped SrTiO₃ single crystal substrates (Nb:1wt%) with (100), (101), and (111) orientation. Each composition was pseudocubic, rhombohedral and tetragonal as the PLZT bulk ceramics, respectively. The crystal structure and

orientation of the PLZT films were determined by X-ray diffraction (XRD). The refractive index and the EO coefficient were measured by the prism coupling method (wavelength: 1.55 μ m). nTM and nTE denote the refractive index perpendicular and parallel to the substrate, respectively. The formed films were confirmed to be the epitaxial by XRD. First, the relationship between polarized light dependency of the electrooptic effect and the film orientation was investigated. The polarized light dependency of the electrooptic effect of the film with (111) orientation is the largest in the other orientation. On the contrary, that with the (100) distribution is the smallest. These behaviors explained using the switching model based on the rhombohedral domain (or polar domain). Next, the relationship between polarized light dependency of the electrooptic effect and the crystal phase of the films was investigated. In the tetragonal PZT(30/70) film with (001) orientation, the birefringence (nTM-nTE) varied in proportion to the electric field. This behavior seems to be appearance of Pockels effects. Therefore, the polarized dependency of tetragonal epitaxial film with (100) orientation is slightly larger than that of pseudocubic or rhombohedral films. In summary, the PLZT epitaxial film with less polarized light dependency of electrooptic constant for ferroelectric optical wave guides can be successfully prepared by using the (100)-oriented pseudocubic or rhombohedral electrooptic crystal. This work was partly supported by the Next generation Energy Development Organization (NEDO) of Japan within the joint program "Electrically controlled optical switch for high speed and large throughput WDM node device".

10:45 AM T4.9

Ferroelectric phase transformation and dielectric losses of SrTiO₃ thin films on Pt electrodes. Steffen Schmidt, Jiwei Lu, Sean Keane and Susanne Stemmer; Materials, University of California, Santa Barbara, Santa Barbara, California.

SrTiO₃ exhibits a nonlinear, electric field tunable dielectric permittivity that is of interest for tunable microwave circuits. Wide spread application of ferroelectric thin films in tunable microwave devices has thus far not been realized due to unacceptably high dielectric losses in thin films. In this talk, we will discuss major contributions to the dielectric and electric properties of ferroelectric thin films for microwave tunable applications, using SrTiO₃ thin films on epitaxial Pt electrodes on sapphire substrates with carefully characterized microstructures as a model perovskite thin film system. In particular, the influence of film orientation, phase transformations, applied bias field, temperature and annealing atmospheres was studied. Control of the underlying epitaxial Pt electrode surface was used to control the SrTiO₃ film orientation. We show that epitaxial growth of (111) oriented SrTiO₃ films is promoted by thin Ti adhesion layers underneath the Pt electrode. In contrast, SrTiO₃ films that were grown under identical sputter deposition conditions on epitaxial Pt electrodes on sapphire without Ti adhesion layer were predominantly (110) oriented, although they also exhibited an epitaxial relationship with Pt. Epitaxial (111) oriented SrTiO₃ films showed a ferroelectric phase transformation at ~ 150 °K, whereas films that were predominantly (110) oriented films did not exhibit a phase transformation in the measured temperature range (100 °K - 300 °K). The difference in the phase transformation behavior was due to the different coupling of thermal mismatch strain with the different film orientations. We apply Landau-Ginzburg-Devonshire models to explain the different phase transformation behavior. Two major contributions to the dielectric losses were identified: a low temperature loss increase for the (111) oriented film, which could be suppressed by an applied bias field, and a loss peak at ~ 250 °K (at 1 MHz), which was strongly frequency dependent and likely associated with a relaxing defect. The low temperature loss mode was related to the appearance of a phase transformation and contributed to the dielectric losses even at temperatures that were more than 100 °K above the phase transformation. The results showed that film strain has an indirect effect on dielectric losses by shifting or inducing ferroelectric phase transitions and experiments should carefully distinguish this mechanism from the influence of point defects. Possible origins of the different loss contributions are discussed.

11:00 AM T4.10

Ion Modification for Improvement of Electrical Properties of Perovskite-based Ferroelectric Thin Films Fabricated by Chemical Solution Deposition Method. Hiroshi Uchida¹, Hiroshi Nakaki^{1,2}, Shintaro Yasui¹, Seiichiro Koda¹, Risako Ueno², Hiroshi Funakubo², Ken Nishida³, Takashi Katoda³ and Minoru Osada⁴; ¹Sophia University, Tokyo, Japan; ²Tokyo Institute of Technology, Yokohama, Japan; ³Kochi University of Technology, Kochi, Japan; ⁴National Institute of Materials Science, Tsukuba, Japan.

Enhancing the electrical properties of perovskite-based ferroelectric films, including simple-perovskite oxides like Pb(Zr,Ti)O₃, BiFeO₃, and layered-perovskite oxides like SrBi₂Ta₂O₉, Bi₄Ti₃O₁₂, are required for developing the applications for nonvolatile memories, microactuators, etc. Although many researchers have carried out

related studies based on ion-doping techniques using various cation species, general strategy for controlling the electrical properties of perovskite-based materials have never been established: especially, it is remarkable that no promising candidate for the dopant species have been found for Pb(Zr,Ti)O₃ in the past works. Authors attempted the improvement of ferroelectric properties of certain perovskite-based films by ion modification at appropriate lattice sites in perovskite crystals using rare-earth cations. Strategy for enhancement of the electrical property is mainly based on two concepts, that is, (i) substituting the volatile cations such as Pb²⁺ and Bi³⁺, and (ii) controlling the crystal anisotropy of perovskite unit cell. In this study, the influences of ion-modification conditions (i.e., amount, species and occupying site of substituent cations) on the ferroelectric properties of perovskite-based films fabricated by a chemical solution deposition were investigated. Substituting volatile cations in simple-perovskite oxides, such as Pb²⁺ in Pb(Zr,Ti)O₃ and Bi³⁺ in BiFeO₃, with rare-earth cations [i.e., strategy (i)] enhanced the insulating properties of these films due to suppressing the generation of metal and / or oxygen vacancies. Similar phenomenon was also found in layered-perovskite oxides, such as Bi₄Ti₃O₁₂ films. For example, Nd³⁺-substituted BiFeO₃ and Bi₄Ti₃O₁₂ films exhibited well-saturated P-E hysteresis loops with excellent remanent polarization (Pr) values of approximately 50 and 30 μ C/cm², respectively, while distorted hysteresis loops due to degraded resistivity were observed at non-substituted BiFeO₃ and Bi₄Ti₃O₁₂ films. Also, crystal anisotropy of perovskite-based oxides was controlled by varying the species and the occupying site of substituent cations [i.e., strategy (ii)]; e.g., as for Pb(Zr,Ti)O₃ films, Ti- and Zr-site (B-site) substitution with rare-earth cations whose ionic radii locate on the smaller part of rare-earth series (such as Y³⁺, Dy³⁺) could promote the anisotropy of Pb(Zr,Ti)O₃ crystal, i.e., the ratio of the lattice parameters (c/a). Ferroelectric measurement on epitaxially-grown Pb(Zr,Ti)O₃ films indicated that spontaneous polarization (Ps) of Pb(Zr,Ti)O₃ along the polar [001] direction was enhanced from 71 to 84 μ C/cm² by Dy³⁺-substitution, which was based on the promotion of crystal anisotropy. We concluded that the strategy for enhancing the electrical property mentioned in this study would be applicable for a various kind of perovskite-based ferroelectric films.

11:15 AM T4.11

Fabrication of Aggressively Dimensioned Tunable BST Capacitors and the Understanding of Cu/BST Adhesion Issues. Brian James Laughlin, Dipankar Ghosh and Jon-Paul Maria; Materials Science, North Carolina State Univ., Raleigh, North Carolina.

Previous research has demonstrated the ability to grow high film quality sputtered (Ba_x, Sr_{1-x})TiO₃, BST, thin films on Cu foil substrates. Electrical characterization of these films routinely shows a permittivity of 650 with tunabilities of 4:1 and breakdown strengths in excess of 400 kV/cm in metal-insulator-metal, MIM, capacitor structures. Although these conventional foils are well suited to printed wiring board based embedded passive and RF applications, additional possibilities in the microwave regime can be realized if flexible tunable dielectric structures can be synthesized with capacitance values in the pF range. Such small capacitance values necessitate very fine capacitor dimensions given the large permittivity values associated with BST. Outlined in this presentation is a novel method of Cu foil substrate fabrication by evaporation. These Cu "Ultra-Foils" allowed for the patterning of MIM structures with critical dimensions on the scale of 3 μ m by photolithographic techniques when properly laminated on to silicon wafers. The challenge of adhering BST to smooth Cu surfaces was encountered, and interface engineering was needed to achieve BST films free of delamination defects. This adhesion was accomplished through Cu surface alloying. The results of sessile drop experiments between BST surface and Cu alloys will be presented to gain a phenomenological understand of adhesion in this system.

11:30 AM *T4.12

MOCVD and Process Integration of SBT Based FeRAMs. Solayappan Narayan, Symetrix Corporation, Colorado Springs, Colorado.

FeRAMs are gaining momentum in the non-volatile memory market and finding applications both in embedded and standalone products. Medium density products (> 1Mb) based on stack ferroelectric capacitor process is beginning to appear in the market. Both PZT and SBT based material technologies are being pursued by various companies around the world for current medium density and future high density products. This invited paper will discuss about SBT based FeRAM technology and its current status. First, metal-organic chemical vapor deposition (MOCVD), which is considered as an enabling technology for future high density 3-D cells and also for improved capacitor reliability, will be reviewed in detail for SBT including the tool behavior, long term repeatability results, capacitor reliability etc. Secondly, the performance of fully integrated MOCVD

based ferroelectric capacitors with a 1Mb, 0.25um based 3-level metal test vehicle will be presented. This discussion will include basic parametric data, reliability data such as fatigue and imprint, and signal distributions. Certain aspects of the process integration of the test vehicle will also be covered in this talk.

SESSION T5: Field Effects and Gate Dielectrics
Chair: D. Schlom
Tuesday Afternoon, November 29, 2005
Back Bay D (Sheraton)

1:30 PM *T5.1

Ferroc Tunnel Junctions. Hermann Kohlstedt¹, Nicholas Pertsev^{2,1}, Adrian Petraru¹, Alexander Kaiser¹ and Rainer Waser^{3,1}; ¹IFF-IEM and CNI, FZ Juelich, Juelich, Germany; ²Ioffe Physico-Technical Institute, St. Petersburg, Russian Federation; ³Institut fuer Werkstoffe der Elektrotechnik, RWTH Aachen University of Technology, Aachen, Germany.

We present the concept of ferroc tunnel junctions, in which two metal electrodes are separated by a nanometer-thick barrier made of insulating ferroelectric or multiferroic material. For ferroelectric tunnel junctions (FTJs), the current-voltage (I-V) characteristics are analyzed assuming that the direct electron tunneling represents the dominant conduction mechanism. First, the influence of converse piezoelectric effect inherent in ferroelectric materials is described. It is shown that the lattice strains of piezoelectric origin modify the I-V relationship owing to strain-induced changes of the barrier thickness, electron effective mass, and position of the conduction-band edge. Second, we analyze the influence of an internal electric field caused by imperfect screening of polarization charges by electrons in metal electrodes. For asymmetric FTJs with dissimilar electrodes, we found that this depolarizing-field effect may lead to a strong change of the barrier resistance after the polarization reversal (on/off ratio ~ 3). Moreover, the symmetry of the resulting I-V loop is different from that characteristic of the strain-related resistive switching. The crossover from one to another type of the hysteretic curve, which accompanies the increase of FTJ asymmetry, is described taking into account both the strain and depolarizing-field effects. In addition, we present an experimental method which enables us to distinguish the resistive switching of ferroelectric origin from other effects. Our method is based on the use of atomic force microscope with conducting tip-cantilever system and the simultaneous measurements of the current, capacitance, and piezoelectric coefficient as functions of voltage. A ferroelectric barrier may be also combined with ferromagnetic or superconducting electrodes to create a new type of tunnel junctions, in which a cooperative phenomenon exists in both the tunnel barrier and the electrodes. It is anticipated that the properties of magnetic and superconducting tunnel junctions may be considerably modified by the introduction of a ferroelectric barrier. Redistribution of conduction electrons screening the polarization charge (in the electrodes) and voltage-dependent strain effects (in the barrier) may alter the tunnel magnetoresistance effect (TMR) in magnetic tunnel junctions and the wave function coupling in Josephson tunnel junctions. Tunnel barriers made of multiferroic materials (e.g., BiFeO₃ or BiMnO₃) offer new opportunities. Conversely, the tunneling electrons can be used as an ultra-sensitive analytical tool to study ferroelectricity and magnetism at the nanoscale, provided that ferroc tunnel junctions can be really created. In other words, the powerful tool of electron tunneling spectroscopy may be employed to investigate several kinds of novel tunnel junctions with probably new and fascinating properties.

2:00 PM T5.2

First principles calculations on the interface properties of epitaxial LaAlO₃ and silicon. Clemens Foerst^{1,2,3}, Dmitri O. Klenov⁴, Susanne Stemmer⁴, Ju Li⁵, Sidney Yip¹, Karlheinz Schwarz³ and Peter Bloechl²; ¹Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Institute for Theoretical Physics, Clausthal University of Technology, Clausthal, Germany; ³Institute for Materials Chemistry, Vienna University of Technology, Vienna, Austria; ⁴Materials Department, University of California, Santa Barbara, California; ⁵Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio.

One of the most acute challenges of the semiconductor industry is the introduction of new so-called high-K gate oxides. Conventional SiO₂ based gate oxides need to be replaced in order to avoid quantum mechanical leakage currents through ultrathin oxide layers. High-k oxides films provide the characteristics of an ultrathin gate oxide layer at a larger thickness and thus avoid tunneling currents. The properties of thin films as well as their suitability for device applications are decisively influenced by the interface atomic and electronic structure. In this paper we extend our previous work on the growth and

interfacial properties of SrTiO₃ [1] to LaAlO₃ [2]. While LaAlO₃ is structurally identical to SrTiO₃, the interface structure and chemistry varies due to the different charge distribution in the oxide. We find that an electronically saturated interface is obtained only if dopant atoms segregate to the interface. These findings raise serious doubts whether LaAlO₃ can be used as an epitaxial gate dielectric. [1] Clemens J. Foerst et al., Nature 427, 53 (2004) [2] Clemens J. Foerst et al., submitted; preprint at arxiv.org/cond-mat/0505013

2:15 PM T5.3

Electrical Characteristics of Ferroelectric Field Effect Transistors (FeFETs) Incorporating Langmuir-Blodgett Films of a Vinylidene Fluoride Ferroelectric Copolymer. A. Gerber¹, M. Fitsilis¹, H. Kohlstedt¹, R. Waser¹, Timothy J. Reece², Stephen Ducharme² and E. Rije³; ¹Institute of Solid State Research (IFF), and CNI - Center of Nanoelectronic Systems for Information Technology, Research Center Juelich, Juelich, Germany; ²Department of Physics and Astronomy, Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska; ³Institute for Thin Films and Interfaces (ISG 1), and CNI - Center of Nanoelectronic Systems for Information Technology, Research Center Juelich, Juelich, Germany.

We report the electrical characteristics of a kind of non-volatile memory device consisting of a Field-Effect Transistor where the gate insulator includes a thin ferroelectric polymer film, producing a Ferroelectric-FET, or FeFET. Each device consisted of a p-type silicon substrate, with diffusion-doped source and drain contacts, an SiO₂ or HfO₂ dielectric layer, a ferroelectric Langmuir-Blodgett film of a 70% vinylidene fluoride-30% trifluoroethylene copolymer [1], and a gold gate electrode. The source-drain conductance showed hysteresis due to polarization reversal in the ferroelectric film as the gate bias voltage was cycled. A FeFET with a 35-nm thick ferroelectric film and a 10-nm thick passivated SiO₂ insulator exhibited a 1-V wide hysteresis as the gate voltage was swept repeatedly between ± 6 V. The data are in good agreement with device simulations using a mathematical, semi-empirical MOSFET model (BSIM3v3) [2]. State retention was approximately 5 minutes, possibly limited by polarization relaxation due to incomplete saturation of the ferroelectric polarization. The Fe-FET is a promising nonvolatile memory element that affords fast non-destructive readout. This work was supported by the USA National Science Foundation, the Nebraska Research Initiative and by Volkswagen-Stiftung. [1] S. Palto, et al., Ferro. Lett. 19, 65 (1995). [2] W. Liu, MOSFET Models for SPICE simulation, John Wiley & Sons, (2001).

3:30 PM *T5.4

Electric/Magnetic Field Control of the Interface Band Diagram in Rectifying Oxide Heterojunctions.

Harold Y. Hwang^{1,2}, Naoyuki Nakagawa¹ and Tomofumi Susaki¹;

¹Dept. of Advanced Materials Science and Dept. of Applied Physics, University of Tokyo, Chiba, Japan; ²PRESTO, Japan Science and Technology Corporation (JST), Saitama, Japan.

The nature of the electronic structure at oxide heterointerfaces is an emerging area of research focus. Modern growth and probe techniques present the possibility of studying the chemical and electronic environment of interfaces at the atomic scale. Furthermore, control of the interface electronic structure is central to the function and improvement of oxide device characteristics. Recent studies of rectifying oxide junctions have revealed a number of unusual features distinct from conventional semiconductor junctions. Our studies of rectifying manganite-titanate heterojunctions reveal a depletion layer that is tunable by applying an external magnetic field. This creates a large positive magnetocapacitance and an exponentially-enhanced differential magnetoresistance, occurring despite the absence of a spin filter. Although a detailed examination of the temperature dependence in zero magnetic field is roughly consistent with a conventional crossover from direct tunneling to thermally assisted processes, the behavior in an applied magnetic field shows significant departures from this model, indicating reconstruction of the interface electronic structure. Furthermore, the large electric field dependence of the permittivity of SrTiO₃ plays a significant role in the junction characteristics, as can be isolated and observed in metal Schottky junctions.

4:00 PM T5.5

Ferroelectric Gates for Modulation of 2D-gas at GaN/AlGaN Interfaces and Ferroelectric Nanolithography. Igor Stolichnov, Lisa Malin, Paul Murali and Nava Setter; IMX-LC, EPFL, Lausanne, Switzerland.

The concept of ferroelectric field-effect transistor is implemented using the GaN/AlGaN heterostructure with 2D electron gas at 20 nm below the interface. Pb(Zr,Ti)O₃ films with thickness of 100-300 nm deposited on top of this heterostructure was used as a ferroelectric gate. The processing conditions were optimized in a way to obtain

high quality textured Pb(Zr,Ti)O₃ films without destroying the 2D gas situated very close to the interface. Study of transport properties in this system demonstrates the possibility to modify the 2D gas by switching the spontaneous polarization in the gate. Concentration and mobility of electrons in the 2D gas were monitored using Hall effect and resistivity measurements in a wide temperature range from 4.2K to 300K. The polarization oriented in the direction from bottom to top provokes a depletion effect in the channel resulting in a conductivity decrease by factor 4 or stronger. A correlation between the depletion effect in 2D gas and the change of the spontaneous polarization with temperature has been observed. The depletion effect is found to be reversible so that the initial conductivity in 2D gas can be restored by inverting the spontaneous polarization in the gate. The polarization in the ferroelectric gate was controlled either by using a gate electrode or without any electrode through the tip of a scanning probe microscope. In the last case the technique of direct domain writing was successfully applied for making patterns with the line width of about 300nm with a good retention. These results suggest that ferroelectric gates integrated into systems with 2D electron gas may be potentially interesting for a number of experiments and applications as a flexible and nondestructive way of making rewritable nanopatterns for low-dimensional semiconductor structures.

4:15 PM T5.6

Combined PLD and MBE growth of perovskites oxides on Si(001). Andrea Cattoni¹, Matteo Cantoni¹, Mauro Riva¹, Luca Signorini¹, Riccardo Bertacco¹, Franco Ciccacci¹ and Gerd J. Norga^{1,2}; ¹L-NESS Center, Politecnico di Milano, Como, Italy; ²Formerly with Science and Technology Department, IBM Research GmbH, Rueschlikon, Switzerland.

Functional oxides with crystalline interfaces on silicon (e.g. ferroelectric oxide/Si; magnetic oxide/Si; semiconducting oxide/Si) represent interesting new materials systems, each with significant potential for novel device functionality. Using SrTiO₃ on Si (100) as a model system, we demonstrate the suitability of a combined oxide molecular beam epitaxy (MBE) / pulsed laser deposition (PLD) approach to screen functional oxide/Si heterostructures with atomically controlled, crystalline interfaces. MBE-grown, monolayer thin BSO is used as a template for topotaxy of SrTiO₃, deposited by PLD, in UHV. We show that due to the superior stoichiometry control afforded by PLD, this approach is excellently suited to explore the limits in device performance for high quality, low bulk defect content material. Using in situ XPS, we demonstrate that adequate oxygen incorporation in the as-deposited SrTiO₃ layer is essential to avoid interfacial reactions which would destroy the epitaxial structure of the interface during the UHV annealing step. Finally, we employ in-situ direct and inverse photoemission spectroscopy to study the evolution in electronic structure of interface and the magnitude of conduction and valence band offsets between Si and SrTiO₃ during growth and subsequent annealing steps.

4:30 PM T5.7

Resistive switching and I-V hysteresis of metal-ferroelectric-semiconductor-metal structures. Rene Meyer^{1,2}, Y. Chen¹, Paul C. McIntyre¹, Rob Oligschlaeger² and Rainer Waser²; ¹Materials Science and Engineering, Stanford University, Stanford, California; ²CNI, Center of Nanoelectronic Systems for Information Technology, FZ Juelich, Juelich, Germany.

Recently, bistable resistive switching of binary and ternary oxides has attracted particular interest in view of an application as storage element in a future generation of non-volatile random access memories (NVRAM). However, the nature to the resistance change is only poorly understood. Several mechanisms such as metal filamentary conduction, electrochemical reduction or Mott metal-insulator transitions are under discussion. In this paper, we report on numerical prediction and experimental observation of an I-V hysteresis in weakly conductive ferroelectric medial heterogeneous thin films. In contrast to the switching behavior mostly reported, a gradual change of the resistance of at least one order of magnitude is found around the coercive field. Model calculations of the quasi-static I-V response of a metal-ferroelectric-semiconductor-metal structure are performed by taking into account the P-E hysteresis of the ferroelectric. The resistance change originates from a redistribution of inner charge carrier upon polarization reversal. The simulation discloses a broadening of the ferroelectric switching caused by the depolarizing field in the ferroelectric layer. The broadening of the polarization switching around the coercive field leads to a continuous change of the layer resistance. Although the remnant polarization is reduced under the influence of the depolarizing field, different resistance states can be clearly distinguished to be due to a polarization reversal. Simulation results will be compared with experimental data obtained from polycrystalline PZT-based ferroelectric capacitors and epitaxial perovskite heterostructures. At the moment we cannot rule out a filamentary conduction mechanism in all systems. However, the excellent agreement between experiments and model calculations

suggest that measured resistive switching effects may be ferroelectric rather than of different nature.

4:45 PM T5.8

Electrical Properties of Ferroelectric/ZnO Heterostructures. Emine Cagin, Jeffrey J. Siddiqui, Dingyuan Chen, Song Chua, Vinay Alexander and Jamie D. Phillips; Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan.

Interfacing ferroelectric and semiconductor materials will allow the exploitation of unique properties associated with ferroelectrics for semiconductor device applications. The polarization of ferroelectric materials results in band bending at the ferroelectric/semiconductor interface and corresponding charge density in the semiconductor. The charge density can be modulated using an electric field, enabling control over the electrical properties of the semiconductor. The quality of the ferroelectric/semiconductor interface is critical for creating and maintaining a significant charge density. Chemical interactions between the two materials lead to a poor interface characterized by material defects degrading the charge density. Oxidation of the semiconductor is often a problem when using common semiconductors such as GaAs and Si in conjunction with ferroelectric oxides. We believe that a semiconducting oxide material such as ZnO would provide an excellent material for interfacing with ferroelectric oxides due to suppressed oxidation or reactivity at the ferroelectric/semiconductor interface. In this work, the characteristics of ferroelectric/ZnO heterostructures are reported, where (Pb,Zr)TiO₃ (PZT) is used as a prototypical ferroelectric oxide. The electrical properties of PZT on ZnO and ZnO on PZT heterostructures are investigated. The PZT and ZnO layers were grown using pulsed laser deposition. Isolated ZnO/PZT and PZT/ZnO capacitor structures were fabricated using standard metallic evaporation and photolithographic fabrication techniques. X-ray diffraction measurements indicate polycrystalline PZT with random orientation and predominant (0001) ZnO orientation for ZnO on PZT on Pt structures. For PZT on ZnO on Al₂O₃, preferred (110) and (0001) orientations for PZT and ZnO, respectively are observed. Polarization-electric field (P-E) measurements indicate a strong ferroelectric hysteresis with remanent polarization of greater than 15 uC/cm². The polarization and capacitance characteristics will be presented for these structures and related to crystalline quality and interfacial properties.

SESSION T6: Characterization I

Chair: J.M. Triscone

Wednesday Morning, November 30, 2005

Back Bay D (Sheraton)

8:00 AM *T6.1

Atomic and Electronic Imaging of Heterostructures. David A. Muller¹, N. Nakagawa² and Harold Y. Hwang²; ¹Applied Physics, Cornell University, Ithaca, New York; ²Department of Advanced Materials, University of Tokyo, Kashiwa, Chiba, Japan.

Electron energy loss spectroscopy (EELS) provides direct information on the local electronic structure of a material. In ionic systems, EELS measurements of formal valences give insight and place remarkable constraints on the structure and stability of heterointerfaces and defects. This is of considerable importance to the field of oxide electronics and ferroelectrics, where been the growth of atomically-abrupt heterointerfaces has been a central goal. However, when the interfaces are between polar and nonpolar layers, electrical and atomic abruptness turn out to be mutually incompatible goals. This is the bulk analogy of the surface reconstructions found in polar systems where a material terminated along a bulk polar plane has a net charge and a divergent surface energy. Unlike conventional semiconductors, for multivalent oxides, physical roughness is not the only option - atomically abrupt interfaces are allowed if electrons can be redistributed at lower energy cost than it takes to redistribute ions. These extra electrons are detectable by EELS. Recent work on SrTiO₃/LaAlO₃ [001] interfaces has found that Ti-La interfaces are conducting, but Sr-Al interfaces are insulating. Our EELS studies show that for the Ti-La terminated interface, excess electrons are found on the Ti sites, but not for the Sr-Al termination (where an extra ½ hole would be expected theoretically). Instead significant compensating oxygen vacancies are present and no free holes are found, probably explaining the electrical asymmetry. Controlling the interface termination lets us tune between insulator and conductor, trading chemical for electronic roughness.

8:30 AM T6.2

Terahertz radiation from multiferroic BiFeO₃ thin films as a new approach for ferroelectric memory readout and ferroelectric domain imaging microscopy. Kouhei Takahashi¹, Noriaki Kida² and Masayoshi Tonouchi¹; ¹Institute of Laser

Engineering, Osaka University, Suita, Osaka, Japan; ²ERATO-SSS, Tsukuba, Ibaraki, Japan.

Perovskite BiFeO₃ (BFO) is a promising material exhibiting simultaneous ferroelectricity and antiferromagnetism at room temperature. Ever since the discovery of an extremely large spontaneous polarization in BFO thin films, studies on this material have mainly been focused on its electronic functionality as a capacitor [1]. Consequently, much of the optical functionalities of BFO have not been revealed so far [2]. Of particular interest is the optical response of BFO to the illumination of ultrafast laser pulses with band gap energy. Here, we report the first discovery of terahertz (THz) electromagnetic pulse radiation from a ferroelectric-antiferromagnet BFO thin film triggered via photoconduction induced by the illumination of femtosecond blue laser pulses. Our results demonstrate a new approach for ferroelectric memory readout and also provide a new tool for visualizing the 180° ferroelectric domains. BFO photoconductive switch was prepared on a 200 nm thick BFO thin film grown on a (LaAlO₃)_{0.3}(Sr₂AlTaO₆)_{0.7} substrate. The second harmonic of a mode-locked Ti:Sapphire laser (wavelength of 800 nm, pulse duration of 100 fs, repetition rate of 82 MHz) was used for charge excitation. THz pulse generation from a voltage-biased photoconductive switch is a common phenomena observed in various materials, in which the applied electric field accelerates the photoexcited charge carriers to act as THz sources [3]. Thus, the radiated THz amplitude generally has a linear relationship with the applied bias voltage, and naturally, no THz radiation is observed at zero bias. However, on the contrary, we observed THz radiation from BFO thin films even under zero bias and the radiated THz pulse reversed its phase depending on the direction of the applied bias voltage, namely depending on the polarization state (memory effect). We assume that the spontaneous polarization of BFO acts as the bias voltage to accelerate the photoexcited charge carriers, which results in THz radiation. This feature enables us to visualize the 180° ferroelectric domain structures by measuring the two dimensional distribution of the THz radiation, in a spatial resolution limited by the diameter of the focused laser spot. [1] J. Wang *et al.*, Science **299**, 1719 (2003)., K. Y. Yun *et al.*, Jpn. J. Appl. Phys **43**, L647 (2004). [2] T. Kanai *et al.*, J. Phys. Chem. Sol. **64**, 391 (2003). [3] S. Gupta *et al.*, Appl. Phys. Lett. **59**, 3276 (1991)., N. Kida *et al.*, Opt. Lett. **29**, 2554 (2004).

8:45 AM T6.3

Nonlinear Optical Probing of Polarization Dynamics in Strained Ferroelectric SrTiO₃. Aravind Vasudeva Rao, Alok Sharan, Michael Biegalski, Yulan Li, Long-Qing Chen, Darrell Schlom and Venkatraman Gopalan; Materials Research Institute and Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

SrTiO₃ is a material that is not normally ferroelectric at any temperature. Recently, we have demonstrated room temperature ferroelectricity in strained SrTiO₃ films on (110) orthorhombic DyScO₃ substrate. Using optical second harmonic generation (SHG), we demonstrate that ferroelectric SrTiO₃ films are orthorhombic with point-group symmetry of mm2, a ferroelectric polarization in the film growth plane in the [110]_p pseudocubic direction of SrTiO₃, and a Curie temperature near room temperature (~300K). Using real-time SHG studies, we show domain reversal and hysteresis behavior in these films from 77-300K. Theoretical modeling of the SHG response is presented that yields quantitative measurements of nonlinear optical coefficients and birefringence as a function of temperature through the phase transition.

9:00 AM T6.4

Three-dimensional observation of nano-scale ferroelectric domain using scanning nonlinear dielectric microscopy. Yasuo Cho and Tomoyuki Sugihara; R.I.E.C. Tohoku Univ., Sendai, Japan.

Recently, we have developed the two types (needle-type and cantilever-type) of Scanning Nonlinear Dielectric Microscopy (SNDM) for measuring polarization distribution. In needle-type SNDM, a wide-scale polarization distribution can be measured with micrometer order resolution, whereas in cantilever type SNDM, we can measure the polarization distribution with sub-nanometer resolution. Originally, SNDM was developed to measure the polarization component perpendicular (out-plane) to the surface. However, today, the polarization component parallel (in-plane) to the surface can also be measured by applying an parallel electric field to the sample surface [1]. In this lateral measurement, to know the precise domain direction, it is quite important to apply the field exactly parallel to the surface without the normal component. Therefore, we reported a new system that makes more exact measurement of the in-plane polarization in needle-type SNDM by detecting displacement current distribution and canceling a normal component of the electric field to obtain the exactly parallel field. However, for the nano-scale three-dimensional

measurement using cantilever-type SNDM, a new technique has been required. In this paper, we have developed the cantilever-type SNDM for the in-plane measurement with the function of the electric field correction using Kelvin Force Microscopy. This newly developed SNDM has enough resolution to resolve the nano-scale lateral polarization. Using this new type of SNDM with high resolution, we measured the domain structure of a multi-domain (both congruent and stoichiometric) LiTaO₃ along the polarization direction. The in-plane measurement on the cross-sectional surface (x-cut plane) was carried out. It was confirmed that the domains do not penetrate along the z-axis contrary to a usual expectation. Moreover, it was found that there is a large response area at the charged domain boundary, which is expected to be an electric field distribution due to an electric charge in the charged boundary. Thus we succeeded to reveal the nano-scale complex charged domain structure of LiTaO₃ single crystal. [1]H. Odagawa and Y. Cho, Appl. Phys. Lett., **80** (2002)2159

9:15 AM T6.5

New method of ferroelectric thin film characterization using a polarization instability invoked by a voltage cycling. Yuki Yamada, Susumu Shuto and Iwao Kunishima; SoC Research & Development Center, Toshiba Corp. Semiconductor Company, Yokohama, Japan.

Reliability failures of Ferroelectric Random Access Memory (FeRAM) are closely related to the internal defects of a ferroelectric thin film. Therefore it is useful to characterize a quality of a ferroelectric thin film from a perspective of charge trap property. In this work, we focus on an instable polarization of a PZT thin film invoked by a voltage cycling and analyze the interaction between internal charge trap and polarization. A 220nm-thick PZT capacitor with Pt top and bottom electrodes was used for electrical characterizations. After a voltage cycling stress with 5V bipolar pulse was applied to the capacitor at temperatures ranging from 25°C to 100°C polarization was measured at around 1.5V. Then, the capacitor was baked at temperatures ranging from 150°C to 200°C. The polarization was measured at 25°C periodically during the bake. During the voltage cycling, we observed that polarization increased during the voltage cycling. The amount of the increase depended on the cycling number. In contrast, its temperature dependence was negligible. On the other hand, the polarization decreased with bake time and approached to the initial value. It indicates that the polarization gained by the voltage cycling is instable and decays during the bake. The decrease in the polarization was accelerated at higher bake temperature. The activation energy of the polarization decay is estimated to be 0.52eV. This value is close to the reported ionization energy of Ti4+ to Ti3+. Thus we consider that the electrochemical reaction that involves the valence change between Ti4+ and Ti3+ plays an important role in the instability of the polarization. The mechanism of the polarization instability is considered as follows. During the voltage cycling, holes are injected from the capacitor electrodes into an adjacent PZT by tunneling and captured by Ti3+ at the interface with changing their valence from 3 to 4. This process neutralizes a local fixed charge resulting in the release of pinned polarization and, therefore, causes the increase in the polarization. Since the hole injection is carried out by tunneling, the temperature dependence of the voltage cycling effect should be negligible. During the bake, the holes captured by Ti-related traps are released. This allows the local fixed charge to pin the polarization again. As a result, the polarization returns to the initial value. Since this process is dominated by a thermionic emission, the activation energy is correlated to the trap depth. In conclusion, we propose that the investigation of an instable polarization invoked by a voltage cycling is a good tool to evaluate a point defect density at the interface of a ferroelectric thin film capacitor.

9:30 AM T6.6

Nanoscale piezoelectric nonlinearity and domain wall depinning in ferroelectric thin films. Andrei L. Kholkin¹, V. V. Shvartsman⁴, J. M. Herrero², C. Zaldo² and N. A. Pertsev³; ¹Dept. of Ceramics and Glass Engineering / CICECO, University of Aveiro, Aveiro, Portugal; ²Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain; ³A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, St. Petersburg, Russian Federation; ⁴Dept. of Physics, Duisburg University, Duisburg, Germany.

Piezoelectric properties of ferroelectrics are strongly nonlinear reflecting nonlinear displacement of ferroelectric domain walls, phase boundaries, and electrically active defects under the application of external electric field. It is therefore fundamental to study the piezoelectric nonlinearity at the nanoscale, where the characteristics of individual domain or grain boundaries can be accessed. In this work, local piezoelectric deformation is measured in several ferroelectric thin films including (Pb,Lu)TiO₃ (PLT) and Pb(Zr,Ti)O₃ (PZT) as a function of the ac-voltage (V_{ac}) applied to the sharp tip of the atomic force microscope (AFM). The piezoelectric vibration is sensed by the same tip positioned in predetermined locations. Thus obtained voltage dependence of the effective piezoelectric coefficient (local piezoelectric

nonlinearity) is compared with the corresponding macroscopic piezoelectric behavior studied by laser interferometry. As can be expected, the local piezoresponse of PLT films measured inside uniformly polarizing areas remains almost linear with increasing V_{ac} until the driving voltage becomes comparable with the coercive one. The corresponding macroscopic response is substantially nonlinear, suggesting significant contribution from the motion of 90-degree domain walls. On the contrary, in PZT films the local piezoelectric behavior is strongly nonlinear, whereas the macroscopic piezoelectric coefficient is essentially field-independent. Moreover, the local piezocoefficient of PZT films is found to behave differently in domains of different orientation. The domains having polarization vector pointing at the film free surface are often unstable with increasing V_{ac} and switch into the opposite polarization state under an ac voltage several times smaller than that required for global polarization reversal. This effect is explained by the presence of charged domain boundaries below the surface and their local depinning induced by external field. The origin of pinning centers and depinning mechanism are discussed.

10:15 AM *T6.7

Role of Interface on Structure and Properties of Epitaxial Ferroelectric Thin Films. Xiaoping Pan¹, Haiping Sun¹, Yanbin

Chen¹, Jeffrey Haeni², Darrell G. Schlom², D. M. Kim³ and Chang-Beom Eom³; ¹University of Michigan, Ann Arbor, Michigan; ²Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; ³Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin.

This talk is given on the structure-property relationships of interfaces in epitaxial ferroelectric thin films. The effect of lattice mismatch (epitaxial strain), crystal defects, and chemistry at the film/substrate interfaces on the microstructure and properties of different systems (e.g., BaTiO₃, SrTiO₃, SrRuO₃, and Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT)) will be addressed. The interfacial atomic structure and defects of the films were investigated by high-resolution transmission electron microscopy (HRTEM). The structure and formation mechanisms of misfit dislocations and their significance for the relaxation of epitaxial strain were systematically investigated. Quantitative HRTEM analysis of strained BaTiO₃ predicts the enhancement of spontaneous polarization by 200%, which is consistent with the direct measurements of strained BaTiO₃ thin films using epitaxial SrRuO₃ electrodes. It will also be shown that epitaxial strain can be harnessed to elevate ferroelectric transition temperature (T_c) by hundreds of degrees in both BaTiO₃ and SrTiO₃ thin films and produce room-temperature ferroelectricity in SrTiO₃, a material that normally is not ferroelectric at any temperature. Furthermore, the effect of atomic steps on the substrate surface due to vicinal cutting on the epitaxial growth, microstructure and properties of perovskite oxide films will be described. It will be demonstrated that the existence of the atomic step flow on miscut substrate eliminates the formation of pyrochlore phases in epitaxial PMN-PT films. The PMN-PT films grown on 4 degree miscut (001) Si wafer with epitaxial (001) SrTiO₃ template layer and SrRuO₃ bottom electrode exhibit an exceptionally good piezoelectric properties, which is related to the high structural quality resulting from the step flows on the Si substrate.

10:45 AM T6.8

Domain Imaging in Ferroelectrics by Near-field Optical Microscopy. Stefan Grafstrom, Tobias Otto, Susanne Schneider and Lukas M. Eng; Institute of Applied Photophysics, Dresden University of Technology, D-01062 Dresden, Germany.

We report on two approaches to optical high-resolution imaging of ferroelectric domains, which compared to piezoresponse force microscopy (PFM) offer the advantage of being noncontact techniques and bear the potential of providing access to fast domain dynamics: 1. Electro-optical scanning near-field microscopy makes use of the symmetry breaking induced by the electro-optic effect [1]. The method is able to differentiate not only a from c domains, but also to distinguish antiparallel domains. The sample is illuminated through a glass fiber tip. An alternating electric field applied between the tip (made conductive by a thin chromium layer) and the sample back electrode modulates the refractive index via the electro-optic effect. This results in a modulation of the optical power transmitted through the sample, which is extracted by phase-sensitive detection. The complete ferroelectric domain distribution may be obtained from one single scan. The resolution achieved at domain boundaries of barium titanate (BaTiO₃) is ~250 nm for a tip having no additional aperture beside the fiber core. The resolution is not determined by the optical spot size but rather by the tip causing a strong localization of the electric field. Furthermore, we used the method to measure ferroelectric hysteresis. Hysteresis loops obtained for several tip-sample separations were compared with hysteresis monitored by PFM at the same surface spot. The results were analyzed on the basis

of the electric-field distribution underneath the tip as calculated by finite-element modeling [2]. 2. Scattering scanning near-field optical microscopy uses the scattering at the apex of a sharp tip to probe the near field. An image is obtained by monitoring the scattered light while the tip is scanned across the illuminated sample surface at a distance of a few nanometers. The interaction between the tip and the sample can be understood on the basis of a dipole model in which the incident light induces an electric dipole in the tip, giving rise to an image dipole in the sample that acts back on the tip dipole. In this way, the optical constants of the sample influence the scattering cross section, thereby producing image contrast. In the case of a ferroelectric sample, contrast is expected to arise from the optical anisotropy associated with the ferroelectric polarization. We analyze this effect, taking two contributions into account: (i) The anisotropy modifies the interaction between the probe and the sample according to the dipole model. (ii) The exciting field is a superposition of the incident wave and the field reflected at the surface of the anisotropic sample. We show that for BaTiO₃ in the visible range a domain contrast of several percent may be expected. [1] T. Otto, S. Grafstrom, H. Chaib, L.M. Eng, *Appl. Phys. Lett.* **84**, 1168 (2004). [2] T. Otto, S. Grafstrom, L.M. Eng, *Ferroelectrics* **303**, 149 (2004). [3] S.C. Schneider, S. Grafstrom, L.M. Eng, *Phys. Rev. B* **71**, 115418 (2005).

11:00 AM T6.9

Visualizing polarization switching in ferroelectrics with time-resolved x-ray microdiffraction. Alexei Grigoriev¹,

Dal-Hyun Do¹, Paul G. Evans¹, Dong Min Kim¹, Chang-Beom Eom¹, Bernhard Adams² and Eric Dufresne²; ¹Materials Science and Engineering, University of Wisconsin Madison, Madison, Wisconsin; ²Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

The intrinsic speed of the polarization switching process in ferroelectrics is generally unknown. Domain nucleation and growth are the key microscopic processes underpinning such macroscopic effects as the speed of the polarization switching and the magnitude of the coercive electric field. We present a direct visualization of polarization domains in motion in thin single-crystal ferroelectric Pb(Zr,Ti)O₃ film. The measurements are made with time-resolved x-ray microdiffraction, a method that combines the spatial resolution of better than 200 nm with time resolution provided by a synchrotron radiation source (<100 ps). The results allow us to find the domain wall velocity during polarization switching and its dependence on the sample characteristics applied electric field.

11:15 AM T6.10

Domain Dynamics and Coercive Field in BaTiO₃ Ultrathin Capacitors. Jiyoung Jo¹, D. J. Kim¹, Y. S. Kim¹, T. K. Song², J.-G.

Yoon³ and T. W. Noh¹; ¹Physics, Seoul National University, Seoul, South Korea; ²Ceramic Science and Engineering, Changwon National University, Changwon, South Korea; ³Physics, University of Suwon, Suwon, South Korea.

Under an electric field, a polarization of a ferroelectric material can be switched. Coercive field (E_C), which is an electric field enough to switch a polarization, has attracted technological interests as well as scientific issue. Especially, thickness-dependence of E_C has believed to provide physical understandings on polarization switching. At the same time, thickness-dependence of E_C can give a guideline for determining the device size to obtain a correct operating voltage of high density ferroelectric memory device. In this talk, we will show that, in ultrathin BaTiO₃ (BTO) capacitors, the initial domain nucleation stage governs the polarization switching process and thickness dependence of E_C . We fabricated fully-strained and passive-layer-free SrRuO₃/BTO/SrRuO₃ capacitors, whose BTO thicknesses (d) are between 5 and 30 nm, on SrTiO₃ (001) substrates using laser molecular beam epitaxy [1,2]. From hysteresis loops of the BTO capacitors, E_C values could be measured. As d decreases, E_C seems to increase initially but becomes almost independent of d . In order to explain this behavior, we used the theory on domain nucleation. Under the condition that half-prolate spheroidal nuclei are formed, we found that calculated E_C should be proportional to $d^{-2/3}$. With the literature values of the domain wall energy, 17 mJ/m², and $a(c)$ -axis dielectric constant, 220(80), we found that the domain nucleation theory can explain the experimental values quantitatively. Below 15 nm, the film thickness becomes so thin that cylindrical nuclei should be formed instead of the half-prolate nuclei. Under this condition, we could also explain the d -independent E_C values quantitatively using the same domain nucleation theory. This ferroelectric domain nucleation process should govern the polarization switching process of the ultrathin BTO films, whose domain wall velocity becomes extremely slow. In addition, this could provide an explanation for the strong polarization relaxation of the BTO capacitors, which was reported very recently [3]. [1] Y. S. Kim *et al.*, *Appl. Phys. Lett.* **86**, 102907 (2005). [2] Y. S. Kim *et al.*, *cond-mat/0506495*. [3] D. J. Kim *et al.*, *cond-mat/0506480*.

11:30 AM *T6.11

Nanoscopic Studies of Ferroelectric Domain Walls in Epitaxial Perovskite Thin Films. Patrycja Paruch, T. Giamarchi and J.-M. Triscone; DPMC, Physics, University of Geneva, Geneva, Switzerland.

We have applied the general framework of elastic systems in a pinning potential to the study of ferroelectric domain walls, elastic objects separating regions with opposite polarization states, embedded in a crystalline film with random defects. Understanding the behavior of ferroelectric domain walls is not only interesting from a fundamental point of view, but also important for many promising applications based on domain structures, such as non-volatile memories and sensors. Our previous studies have shown that radial domain wall motion in thin perovskite films is a disorder controlled creep process in which the velocity $v \propto \exp[-(R/k_B T) (E_c/E)^\mu]$, where R is a characteristic energy, T the temperature and E the applied electric field, with the dynamical exponent $\mu \sim 0.6$. We have also independently measured the static domain wall configuration, and extracted the roughness exponent $\zeta \sim 0.26$ from power law growth of the correlation function of relative displacements $B(L) \sim L(2\zeta)$. Combining the results of the two measurements, we obtain an effective domain wall dimensionality of 2.5, a value in very good agreement with theoretical calculations for a two-dimensional elastic interface in the presence of random-bond disorder and long-range dipolar interaction. One important additional aspect to be considered is the effect of heat on both the static and dynamic behavior of ferroelectric domain walls. Using AFM on epitaxial PZT thin films we have investigated the evolution of the static configuration of ferroelectric domain walls, and their subcritical dynamics, under the influence of progressively higher temperatures. We find very high domain stability at temperatures well beyond 500°C (the transition temperature of the bulk material), with identifiable nanoscale features clearly preserved between heating cycles up to 750°C. Measurements of domain wall roughness reveal an increase of the wandering exponent from ~ 0.26 in untreated samples, to ~ 0.5 as a result of heating. The results of heating on the creep motion of domain walls observed during the radial growth of individual nanoscale domains underneath the AFM tip will be presented, and the effects of thermal cycling on the samples, as compared to those of single heating events will be discussed. See: T. Tybell et al., PRL **89**, 097601 (2002) P. Paruch et al., PRL **94**, 197601 (2005)

SESSION T7: Characterization II

Chair: D. Muller

Wednesday Afternoon, November 30, 2005

Back Bay D (Sheraton)

1:30 PM *T7.1

In Situ Synchrotron X-ray Studies of Phase Transitions in PbTiO₃ Thin Films. S. K. Streiffer^{1,2}, G. B. Stephenson^{1,2}, R.-V. Wang^{1,2}, D. D. Fong^{1,2}, F. Jiang¹, P. H. Fuoss¹, J. A. Eastman¹, K. Latifi³ and Carol Thompson³; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; ³Department of Physics, Northern Illinois University, DeKalb, Illinois.

The nature of the phase transition in ferroelectric thin films is very sensitive to the manner in which any depolarizing fields are neutralized. However, in most experiments there is significant uncertainty in the degree to which divergences in polarization at interfaces are compensated by internal or external space charge (even for electroded thin films), or by the formation of domain structures that minimize depolarization energy. This in turn affects interpretation of size effects in thin films, as depolarization contributions are film thickness dependent. Here we will describe our work utilizing in-situ synchrotron x-ray scattering to study the phase transition and domain structure in epitaxial PbTiO₃ thin films deposited on SrTiO₃ substrates by metalorganic chemical vapor deposition. Our current understanding of thickness effects on the ferroelectric phase transition of PbTiO₃ will be outlined. We will show that we can control the degree of top interface compensation by controlling the gas environment in our deposition and analysis system, and monitor this via details of the 180° stripe domain pattern that forms for PbTiO₃ on insulating SrTiO₃. Implications of these results will be described for limits on ferroelectric behavior in nanostructures and for control of ferroelectric film surface reactivity.

2:00 PM T7.2

Extrinsic Contributions to Piezoresponse Force Microscopy. Frank Peter¹, Bernd Reichenberg², Andreas Ruediger¹, Rainer Waser¹ and Krzysztof Szot^{1,3}; ¹Center of Nanoelectronic Systems for Information Technology, Research Centre Juelich, Juelich, Germany; ²aixACCT Systems GmbH, Aachen, Germany; ³Institute of Physics, University of Silesia, Katowice, Poland.

Piezoresponse force microscopy (PFM) is the method of choice to investigate piezoactivity on a nanometer scale. A careful distinction between intrinsic and extrinsic effects are mandatory, especially when measuring ferroelectric nanostructures. We focus on two omnipresent extrinsic contributions with a substantial impact. Under ambient conditions Perovskite materials like BaTiO₃ or PbTiO₃ are covered by adsorbates. When a voltage is applied via the tip to the sample a considerable part of the potential drops across this adsorbate layer, thus reducing the potential actually applied to the piezoelectric. Analysing temperature-dependent X-Ray Photoelectron Spectroscopy data obtained from BaTiO₃ single crystals provides the parameters to partially remove the adsorbates by a thermal treatment under UHV conditions. After this desorption the piezoresponse increases on average by 250%. Measurements indicate that the shape of the sample also contributes to the piezoresponse. Starting from PFM simulations of nanograins with and without adsorbates, we show the calculated position-dependent out-of-plane and in-plane piezoresponse. The out-of-plane response on adsorbate-free surfaces is almost constant irrespective of the thickness of the material, however in the presence of adsorbates it decreases towards the perimeter of the grain. This is due to the steadily growing thickness-fraction of the adsorbates as we approach the perimeter, which results in a decreased potential applied to the piezoelectric. The in-plane response always shows a considerable increase near the perimeter of the grain. Measurements of this effect on Pulsed Laser Deposition fabricated BaTiO₃ grains (c-axis orientated) on a SrRuO₃ bottom electrode as well as an analytical explanation are presented. We conclude that for grains the out-of-plane piezoresponse is not only dependent on the piezoelectric coefficient d_{33} but also on d_{31} and d_{15} . Similar results hold true for the in-plane response. A thorough understanding of these extrinsic contributions is essential in order to avoid ambiguities in the analysis of PFM measurements.

2:15 PM T7.3

Resolution and Image Reconstruction in Piezoresponse Force Microscopy. Sergei V. Kalinin, Stephen Jesse, Junsoo Shin, Arthur P. Baddorf, Albina Y. Borisevich and Ho Nyung Lee; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The ability of ferroelectric materials to form stable sub-10 nm domains makes them one of the most promising materials for information storage applications. However, despite the decade of experimental effort, relatively little is known about fundamental domain formation and imaging mechanism in PFM. Here we demonstrate the use of quantitative transfer function theory for the interpretation and reconstruction of PFM images. The applicability limits of the theory are established and unambiguous criteria for image resolution and minimal observable feature size are established. The contribution of surface layers and tip radius of curvature is analyzed. A set of calibration standards with both constant and variable mesh size grids for high-density ferroelectric storage is developed and implemented for domain writing. Using high quality single crystal PZT thin films grown by PLD, domains with diameters as small as 30 nm are reproducibly written. From an analysis of the thermodynamics of the switching process, we show that the minimal domain size for such films is only weakly dependent on the tip properties, and it should be possible to write domains as small as a few nanometers. From the fact that the minimum written domain size and resolution are virtually identical, we conclude that in this case the minimal observable domain size is limited by the resolution of the technique. Based on the linearity of PFM, methods for image deconvolution are demonstrated thereby increasing the effective resolution of the technique. Strategies to improve image resolution utilizing high frequency (~MHz) imaging and modified probes are discussed. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

3:30 PM *T7.4

Switching Behavior of FRAM Capacitors Studied by Piezoresponse Force Microscopy. Alexei Gruverman¹, Brian J. Rodriguez¹, Carsten Dehoff¹, John D. Waldrep¹, Dong Wu¹ and Jeff S. Cross²; ¹North Carolina State University, Raleigh, North Carolina; ²Fujitsu Laboratories Ltd, Atsugi, Japan.

In this paper, piezoresponse force microscopy (PFM) has been used to address several issues related to domain arrangement and polarization switching in FRAM capacitors. Three-dimensional reconstruction of the static domain patterns in the micrometer size PZT capacitors has been performed by mapping both the out-of-plane and in-plane components of polarization before and after switching pulse application. It has been found that the poled capacitors, which appear uniformly polarized in vertical PFM, are in fact in a polydomain state revealed by lateral PFM and contain both 90 and 180 domain walls. Implications of the presence of these domain walls for FRAM capacitor functionality have been discussed. A so-called step-by-step switching approach based on PFM imaging of instant domain

configurations has been used to study the domain switching dynamics in FRAM capacitors. By applying a sequence of such short pulses with incrementally increasing duration a consistent picture of domain dynamics has been obtained. Incorporation of the switching current measurement capability into piezoresponse force microscopy enables a detailed analysis of switching behavior in these ferroelectric capacitors. Analysis of the PFM data showed that the lateral wall velocity fluctuates during switching and is affected by the presence of the nearby domain walls. Consistency of the existing theoretical models with the observed switching dynamics has been discussed. The authors acknowledge support of the National Science Foundation (Grant No. DMR02-35632) and Fujitsu Laboratories Ltd.

4:00 PM *T7.5

Surface Photovoltage Spectroscopy for the Investigation of Perovskite Oxide Interfaces. Elke Beyreuther¹, Stefan Grafstrom¹, Christian Thiele², Kathrin Dorr² and Lukas Eng¹; ¹Institute of Applied Photophysics, Dresden University of Technology, 01062 Dresden, Germany; ²Institute of Metallic Materials, IFW Dresden, 01171 Dresden, Germany.

Surface photovoltage spectroscopy (SPS) has been shown to be an effective technique in determining the surface or interface electronic structure of semiconductors [1]. Especially for the study of high-bandgap materials, to which perovskite oxides such as the titanates can be assigned, SPS is superior to other spectroscopy methods [2]. SPS is based on the photostimulated population and depopulation of surface or interface trap states under subbandgap illumination. The implementation of SPS may be carried out in several ways such as the photoassisted Kelvin probe technique, photoelectron spectroscopy (PES) with additional optical excitation [3], and the capacitive detection of the displacement current in a MIS structure under chopped illumination [4]. We focus on interfaces formed by manganite (e.g. $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) films of 10-15 nm thickness on SrTiO_3 single crystals. The functional properties of perovskite oxide interfaces are assumed to be crucially influenced by the distribution of intrinsic and defect electronic interface states. Hence, applying a trap state sensitive technique such as SPS to investigate these structures seems to be obvious. The manganite films were grown epitaxially by pulsed laser deposition. At room temperature all manganite layers under investigation showed metallic conductivity. Hence, the films form a Schottky contact with the SrTiO_3 substrate with an estimated total band bending of 1-2 eV. Thus the precondition for observing a photovoltaic effect is fulfilled. Here, we present surface photovoltage spectra of manganite/ SrTiO_3 interfaces which have been acquired with the PES and the capacitive approach. All spectra were taken at constant photon flux with an illuminated area of $5 \times 10 \text{ mm}^2$. The excitation wavelength was swept between 280 and 780 nm. The dependence of the surface photovoltage (SPV) on the illumination intensity was shown to be logarithmic, as expected. The PES based measurements reflected the absorption characteristics of the substrate in the superbandgap range and showed a continuous distribution of interface states in the subbandgap range (spectral resolution: 10 nm under continuous illumination). Unfortunately photons from the X-ray source simultaneously contribute to SPV, which makes a quantitative interpretation of the results difficult. The capacitive approach does not suffer from this problem. That method was able to resolve distinct trap states at the interfaces with a spectral resolution of 1 nm. Comparative measurements on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films that were grown on conductive Nb-doped SrTiO_3 showed no SPV at all. This is in agreement with the fact that neither a space charge region nor a band bending is created in the conductive substrate. [1] L. Kronik et al., Surf. Sci. Rep. 37, 1 (1999), [2] H. Gatos et al., J. Vac. Sci. Technol. 10(1), 130 (1973), [3] S. Teich et al., Surf. Sci. 552, 77 (2004), [4] J. Lagowski et al., Semicond. Sci. Technol. 7, A182 (1993)

4:30 PM *T7.6

Study of Oxide Film Growth and Interface Processes Using Integrated Physical Vapor Deposition and *InSitu* Ion, Electron, and Photon-Based Spectroscopy Techniques.

Orlando Auciello, Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

We have developed unique combinations of *insitu* and *exsitu* analytical techniques capable of providing information about thin film growth and interface processes at the atomic scale. These techniques are not only powerful for understanding fundamental thin film science, but are also useful for establishing composition-microstructure-property relationships critical for the development of film-based micro and nanodevices. We will discuss examples of application to understanding ferroelectric and high-k dielectric film growth and interface processes and using this knowledge for developing integration of ferroelectric capacitors with silicon microcircuits for non-volatile ferroelectric random access memories (FERAMs) and high-frequency devices among many other advanced micro and nanodevices. Our recent work has been focused on developing diffusion barrier layers and heterostructured bottom

electrodes that play a critical role in high-density FeRAM integration and high-frequency devices. We demonstrated that Ti-Al layers can be used as a material with a double diffusion barrier / bottom electrode functionality for integration of ferroelectric capacitors with complimentary metal oxide semiconductor (CMOS) devices for fabrication of FeRAMs. We discuss here results from systematic studies designed to understand Ti-Al film growth and oxidation processes using sputter-deposition in conjunction with complementary *insitu* atomic layer-resolution mass spectroscopy of recoil ion (MSRI) and surface sensitive X-ray photoelectron spectroscopy (XPS) and *exsitu* transmission electron microscopy and electrical characterization. We will also discuss the applications of these techniques to understand critical interfacial problems related to high-k dielectric thin films for high-frequency devices and the new generation of high-k CMOS gates. * This work was supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38.

SESSION T8: Size Effects and Nanoscale Phenomena

Chair: S. Streiffer

Thursday Morning, December 1, 2005

Back Bay D (Sheraton)

8:00 AM *T8.1

First-principles calculations on size effects in epitaxial ferroelectric heterostructures. Javier Junquera^{1,3}, Philippe Ghosez² and Karin M. Rabe³; ¹CITIMAC, Universidad de Cantabria, Santander, Spain; ²Departement de Physique, Universite de Liege, Sart-Tilman, Belgium; ³Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey.

The recent realization that ferroelectricity in perovskite oxide thin films persists well below the long-accepted critical thickness of 10 nm has led to a high level of excitement and research activity focused on understanding the nature of ferroelectricity in ultrathin films. Mechanical and electrical boundary conditions imposed by the substrate and/or metallic electrodes are the key points for the scaling of ferroelectric properties. The delicate competition between the compressive strain typically imposed by the substrate, which tends to enhance the ferroelectricity, and the depolarization field that tends to suppress the later result in a wealth of different phases: from uniformly polarized films with a reduced polarization in the ultrathin limit, to the breaking of the film into 180 degree stripe domains.

First-principles calculations are an invaluable tool to understand the origin of these phase transitions. We will compare the results of state-of-the-art simulations with experimental observations on high-quality thin films.

8:30 AM *T8.2

Ultra-thin epitaxial ferroelectric heterostructures.

Nagarajan Valanoor^{1,3}, Javier Junquera^{2,4}, Chun Lin Jia³, Kilho Lee⁵, Yong Kwan Kim⁵, Jiaqing He³, Hermann Kohlstedt³, Burc Misirliglu⁶, Philippe Ghosez⁷, Pamir Alpay⁶, Karin Rabe², Rainer Waser³ and Sunggi Baik⁵; ¹School of Materials Science and Engineering, University of New South Wales, Sydney, New South Wales, Australia; ²Department of Physics and Astronomy, Rutgers, New Brunswick, New Jersey; ³Centre of Nanoelectronic Systems for Information Technology and IFF, Forschungszentrum Juelich, Juelich, Germany; ⁴CITIMAC, Universidad de Cantabria, Santander, Spain; ⁵Ferroelectric Nano Materials Lab, Pohang University of Science and Technology, Pohang, South Korea; ⁶Institute for Materials Science, University of Connecticut, Storrs, Connecticut; ⁷Institut de Physique, Universite de Liege, Liege, Belgium.

Scaling of structural and ferroelectric properties will be presented in model epitaxial ferroelectric heterostructures as a function of reduced thickness. Two model compositions have been investigated in detail— $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT 20/80) and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT 52/48). The PZT (20/80) system is closely lattice matched with top and bottom SrRuO_3 oxide electrodes and therefore facilitates the investigation of highly coherent interfaces without the extrinsic effect of dislocations. The structure has been investigated by direct lattice high resolution electron microscopy as well as synchrotron radiation. Our studies show that a high tetragonality ($c/a \sim 1.06$) is maintained down to 40 Å thick films, suggesting indirectly that ferroelectricity is fully preserved at such small thicknesses. However, measurement of the switchable polarization (ΔP) using a novel pulsed probe setup revealed a systematic drop from $\sim 140 \mu\text{C}/\text{cm}^2$ for a 150 Å thick film to $11 \mu\text{C}/\text{cm}^2$ for the thinnest film. This apparent contradiction between the structural measurements and the measured switchable polarization can be explained by the increasing of the depolarizing field with decreasing thickness. Below a critical thickness the system breaks down into a pinned 180 polydomain state to produce a further screening of this field, even in the presence of metallic electrodes. These results suggest that the limit for a practical ferroelectric

memory device would be much larger than the fundamental limit for ferroelectricity. For the PZT (52/48) system high resolution Transmission Electron Microscopy reveals that even the thinnest films (~ 8 nm) are fully relaxed with a dislocation density close to 10^{12} cm^{-2} and a spacing of approximately 12 nm. Quantitative piezoelectric and ferroelectric measurements show a drastic degradation in the out-of-plane piezoelectric constant (d_{33}) and the switched polarization as a function of decreasing thickness. Supporting theoretical calculations show that the variations in the strain field around the core of the dislocation leads to highly localized polarization gradients and hence strong depolarizing fields, which results in suppression of ferroelectricity in the vicinity of a dislocation. Support by NSF-MRSEC, Alexander von Humboldt foundation, the Volkswagen Stiftung and a joint DFG-NSF program is acknowledged.

9:00 AM *T8.3

Studying Ferroelectric Nano Structures with Synchrotron Radiation. Sunggi Baik, Hee Han and Kilho Lee; Materials Science & Engineering, POSTECH, Pohang, Kyungbuk, South Korea.

A number of synchrotron radiation facilities and their users have been growing rapidly world wide and have feasted new important discoveries and excitement in various scientific and technological areas including materials science, biological science, electronics, environmental engineering, etc. Drastic improvements in time, spatial, energy, and spectroscopic resolutions have been realized in comparison to the conventional light sources and provided strong motivations to revisit many unresolved scientific issues. Ferroelectrics have been one of such issues that have been explored extensively using this new light source in recent years. In this presentation, some of recent attempts and discoveries in studying various issues related to ferroelectric nano structures including ultra thin films and nano-islands are summarized to demonstrate the unique features and opportunities of synchrotron radiation. In addition, as an example, our recent study on domain structures in the epitaxial PZT thin films and nano-islands will be described in detail. Evolution of unique domain structures were characterized as a function of film compositions, substrate selection, film thickness, and 2D planar size employed in film fabrication. The c-domain abundance and crystalline quality of the films are studied and quantified by two-dimensional reciprocal space mapping technique in the PLS 3C2 and 10C1 X-ray Scattering Beamlines equipped with in-situ high temperature stages and 2C1 X-ray microscopy. Domain switching dynamics are studied by AFM. Attempts have been also made theoretically to establish the correlation with various electrical and thermomechanical factors involved in nano structure processing.

9:30 AM T8.4

Energy levels of Pb and O vacancies in PbTiO₃, and fatigue. John Robertson and Ka Xiong; Engineering, University of Cambridge, Cambridge, United Kingdom.

Pb(Ti,Zr)O₃ is an important ferroelectric material for memory applications. The mechanisms of fatigue and imprint are often associated with the behaviour of O and Pb vacancies in these materials. We have calculated the energy levels of O vacancies, Pb vacancies and Pb-O divacancies in PbTiO₃ using ab-initio local density formalism based (LDA) methods. LDA and generalised gradient approximation (GGA) generally give a good description of the ground state properties of compounds but tend to under-estimate the band gap of semiconductors and insulators. This is a severe problem when discussing defect levels as it is not possible to correct these errors. Here we use more advanced methods, the screened exchange (sX) method and the weighted density approximation (WDA) which give the correct band gap [1]. We use them to calculate the band structures and defect levels. Full lattice relaxation was carried out. We find that both the O and Pb vacancy to give shallow levels. This contrasts with the previous calculations of Poyko and Chadi [2,3]. However, we believe that their results may have been affected by their band gap correction. Ferroelectric distortions tend to make the levels deeper. The Pb-O divacancy does give deep levels. 1. J Robertson, K Xiong, S J Clark, MRS (Fall 2004); IEEE Trans Device Mats Reliability 5 84 (2005) 2. S Poyko, D J Chadi, App Phys Lett 76 499 (2000) 3. C H Park, D J Chadi, Phys Rev B 57 13961 (1998)

10:00 AM *T8.5

Recent Developments in Thermodynamic Theory of Ferroelectric Thin Films. Nikolay A. Pertsev,¹ A. F. Ioffe Physico-Technical Institute, St. Petersburg, Russian Federation; ²Institut fuer Festkoerperforschung, Forschungszentrum Juelich, Juelich, Germany.

The nonlinear thermodynamic theory of epitaxial ferroelectric films has predicted several important strain-induced phenomena, which have been already confirmed experimentally. This justifies further development of this theory aiming at the better understanding of the structure/property relationships in thin-film ferroelectrics. To that end, a number of new theoretical studies have been performed

recently. The results of these studies will be discussed in the talk. For Pb(Zr_{1-x}Ti_x)O₃ (PZT) films epitaxially grown on dissimilar cubic substrates, the stability ranges of laminar polydomain states in the "misfit strain-temperature" plane have been determined for the set of compositions $x = 0.9, 0.8, 0.7, 0.6, 0.5, 0.4$. The phase diagrams of PZT films with $x \geq 0.7$ were found to be similar to the diagram of PbTiO₃ films. They involve stability ranges of only four different polarization states. In contrast, at $x = 0.4, 0.5,$ and 0.6 , the diagram displays a rich variety of stable polarization states, including at least one monoclinic state. Using the developed diagrams, the mean out-of-plane polarization of a poled PZT film is calculated as a function of the misfit strain and composition. The results are compared with the measured remanent polarizations of PZT films grown on SrTiO₃. Dependences of the dielectric and piezoelectric constants on the misfit strain are also reported. The thermodynamic formalism has been further extended to epitaxial films grown on orthorhombic substrates. In this case, three-dimensional phase diagrams must be developed to describe the stability ranges of equilibrium polarization states, because two different misfit strains appear in the epitaxial system. The calculations performed for single-domain PbTiO₃ and Pb_{0.35}Sr_{0.65}TiO₃ films showed that the substrate-induced strain anisotropy may lead to the appearance of new phases which do not form in the films grown on cubic substrates. Besides, this in-plane strain anisotropy modifies the dielectric properties of ferroelectric films. The strain-induced dielectric anisotropy in the film plane has been calculated and compared with the anisotropy observed in Pb_{0.35}Sr_{0.65}TiO₃ films deposited on NdGaO₃. When the polarization charges on the film surfaces are not completely compensated by free charge carriers, the depolarizing-field effect superimposes on the strain one. The influence of depolarizing field has been described for poled films sandwiched between continuous electrodes. It was shown that the depolarizing field may change the thickness dependence of the film permittivity qualitatively. Owing to the thickness-dependent shift of the transition temperature, the permittivity may increase with decreasing thickness, in agreement with some experimental data.

10:30 AM *T8.6

Epitaxial strain effects from first principles. Claude Ederer and Nicola A. Spaldin; Materials Research Laboratory, University of California, Santa Barbara, California.

Epitaxial strain can substantially enhance the spontaneous polarizations and Curie temperatures of ferroelectric thin films compared to the corresponding bulk systems. It can even induce ferroelectricity in otherwise paraelectric systems like SrTiO₃. In this work we use first principles calculations to investigate the influence of epitaxial strain on the spontaneous polarization of several ferroelectrics, including BaTiO₃, LiNbO₃, and the multiferroic material BiFeO₃. We show that while BaTiO₃ shows a large strain-induced increase in the polarization, the corresponding effect in LiNbO₃ is weak, and nearly negligible in BiFeO₃. The reasons for this different strain dependence are discussed and it is shown that the effect of epitaxial strain can easily be understood in terms of the piezoelectric constants of the unstrained materials.

11:00 AM T8.7

Answering Fundamental Questions of Ferroelectric Behaviour at Nanoscale Dimensions through Focused Ion Beam Milling of Single Crystal Materials. Alina Schilling¹, T. Adams¹, R. M.

Bowman¹, J. M. Gregg¹, F. D. Morrison² and J. F. Scott²; ¹Department of Physics and Astronomy, Queen's University, Belfast, United Kingdom; ²Earth Sciences Department, University of Cambridge, Cambridge, United Kingdom.

Developing an understanding of the behaviour of ferroelectrics, which have been size-constrained into the nanoscale regime, has become a topic of intense research [1]. However, experimentally, the fundamental influence of reduced dimensionality is frequently difficult to disentangle from various extrinsic influences that can alter both the state and dynamic properties of ferroelectrics. Therefore there has been a pressing need for clean, incisive experiments, where confusing extrinsic factors have been minimized. Ideally, the behaviour of free-standing nanoscale single crystal ferroelectric materials, that have already been heavily characterized in bulk, should act as a model system; this has been demonstrated in recent literature [2]. In this talk we will present progress in the understanding of the effects of reduced size on domain structures in free-standing single crystal BaTiO₃, where size constraint has been introduced through the use of Focused Ion Beam milling (FIB); 1D and 3D nanostructures have been prepared and their properties investigated. Such studies have become particularly important, as the possibilities of completely new toroidal domain behaviours have again been theoretically identified [3]. First, BaTiO₃ lamellae were fabricated and lifted free from their host bulk single crystals. Their typical dimensions were around $15 \times 10 \mu\text{m}^2$ with thicknesses varying from 300 nm (edges) down to 50 nm (middle) along the length of the lamella. Second, *ring* or *toroidal*

structures have been milled in the middle of the lamellae allowing behavioural observations in highly constrained 3D structures to be made. Scanning Transmission Electron Microscopy (STEM) was used for imaging domain configurations within these size-constrained ferroelectrics. Single crystal lamellae were found to contain areas of parallel domain walls with 90° boundaries between sets of domains. Ferroelectric domain wall density varied systematically with the lamellar thickness. Decreasing the thickness increased the domain wall density, and interesting domain bifurcations on reduction of lamellar thickness were frequently seen. In the ring or toroidal shapes, domain behaviour was such that *herringbone* domain patterns were frequently observed - presumably an energy minimizing configuration. Horizontal *ladder*-like domains are also present indicating a possible relaxed state and reproducing the orientation of the lamella domain walls. Although, the experiments are still under investigation, it is clear that the domain pattern present in the ring-shape 3D structures is radically different from less spatially constrained geometries. Combining FIB and STEM techniques proves to be a way forward in mapping and understanding domain configurations in novel 3D geometries. [1] S.K. Streiffer *et al.*, *Phys.Rev.Lett.* **89**, 067601 (2002); [2] M.M. Saad *et al.*, *J.Phys : Condens.Matter* **16**, L451 (2004); [3] I.I. Naumov *et al.*, *Nature* **432**, 737 (2004)

11:15 AM T8.8

Preparation and characterization of mesostructured thin films of perovskites and ternary oxides by using novel block copolymer templates. Bernd Smarsly¹, David Grosso², Heinz Amenitsch³, Clement Sanchez² and Cedric Boissiere²; ¹ Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany; ²Chimie de la Matière Condensée, UMR UPMC-CNRS, Paris, France; ³Austrian Academy of Sciences, Graz, Austria.

Mesostructured thin films with a crystalline framework have attracted significant attention to their potential use in sensing and other applications. Oxides like TiO₂ and CeO₂ can be obtained by using evaporation-induced self-assembly by a suitable block copolymer templates, [1] but so far mesostructured perovskites and other complex ternary oxides have not been available. Here we report for the first time the successful preparation of thin films of several perovskites (SrTiO₃, Li₂TiO₃, LiTaO₃, MgTa₂O₆) and ternary oxides such as Indium-Tin-Oxides (ITO) with well-defined mesostructural order. [2] These oxides possess interesting physical properties (dielectric SrTiO₃, ferroelectric LiTaO₃). Starting from metal chlorides or alkoxides, thin mesostructured films are obtained by dip-coating, the mesostructured being established through a novel type of block copolymer template as structure-directing agent (KLE). Afterwards, a suitable temperature treatment is applied generating mesopores of ca. 10 nm and perovskite nanoparticles in the pore walls without disrupting the mesostructure. KLE was synthesized in our institute and has a hydrophilic PEO block and a poly(ethylene-co-butylene) hydrophobic block, thereby possessing advanced templating properties in terms of the thermal stability and hydrophilic-hydrophobic contrast [1]. The temperature-induced changes were studied by combined Small- and wide-angle scattering experiments at the Synchrotron facility at Elettra (Italy). These studies revealed that the main benefit of this type of polymer is the higher temperature stability compared to recently used polymers such as Pluronic F127: KLE (or its fragments) is able to mechanically stabilize the still highly ordered mesopore structure of an amorphous and almost water-free metal oxide at ca. 400 deg C, which is then converted into its crystalline counterpart in a solid-solid transition, contrary to previous assumptions. Also, the block lengths were designed to be long enough to allow for sufficiently thick walls, i.e. nanocrystals in the pore walls of at least 5 nm, being compatible with the nucleation. Based on the x-ray studies, the temperature could be adjusted to obtain thin films with perovskite nanocrystals in the mesopore walls whilst maintaining the mesostructural order, was confirmed by High-Resolution Transmission Electron Microscopy (HRTEM) [2]. The present strategy to obtain mesostructural multi-metal-oxide nanocrystalline films creates for the first time the bridge between conventional mesoporous materials and the remarkable properties of crystalline ternary or quaternary metallic oxides that contribute to the richness of solid state chemistry. The mesoporosity introduced into such oxides allows for the infiltration with other oxides or metals with interesting functionality, for instance to obtain new magnetic or dielectric properties. [1] Smarsly *et al.* *Chem. Mater.* 2004, 16, 2948. [2] Grosso, Smarsly *et al.* *Nature Materials*, 2004.

11:30 AM *T8.9

Growth of Ferroelectric BaTiO₃/SrTiO₃ Superlattices by MBE. Darrell G. Schlom¹, A. Soukiasian¹, W. Tian¹, Y. L. Li¹, L. Q. Chen¹, N. D. Lanzillotti Kimura², A. Bruchhausen², A. Fainstein², D. A. Tenne³, X. X. Xi³, H. P. Sun⁴, X. Q. Pan⁴, K. J. Choi⁵, C. B. Eom⁵, K. Johnston⁶, K. M. Rabe⁶, A. Cross⁷, A. Cantarero⁷ and R. S. Katiyar⁸; ¹Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; ²Centro Atomico Bariloche & Instituto Balseiro, C.N.E.A., S. C. de Bariloche, Argentina;

³Department of Physics, Pennsylvania State University, University Park, Pennsylvania; ⁴Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ⁵Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; ⁶Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey; ⁷Materials Science Institute, University of Valencia, Valencia, Spain; ⁸Physics Department, University of Puerto Rico, San Juan, Puerto Rico.

Molecular beam epitaxy (MBE) has achieved unparalleled control in the integration of semiconductors at the nanometer level; its use for the integration of oxides with similar nanoscale customization appears promising. This talk will describe the use of reactive MBE to synthesize metastable ferroelectric perovskite superlattices, whose structures are engineered using epitaxy. In particular, we will discuss BaTiO₃/SrTiO₃ superlattices grown on TiO₂-terminated SrTiO₃ substrates by reactive molecular beam epitaxy (MBE). With the aid of reflection high-energy electron diffraction (RHEED), precise single-monolayer doses of BaO, SrO, and TiO₂ were deposited sequentially to create fully strained or partially relaxed BaTiO₃/SrTiO₃ superlattices with a variety of periodicities. Structural characterization by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (TEM) revealed that the samples studied are of high quality with nearly atomically abrupt interfaces. UV Raman results (the first ever reported for thin ferroelectric films) show that BaTiO₃ is tetragonal and SrTiO₃ is polar due to strain in these BaTiO₃/SrTiO₃ superlattices. Temperature-dependent UV Raman and XRD reveal the paraelectric-to-ferroelectric transition temperature. BaTiO₃/SrTiO₃ superlattices containing as few as two strained BaTiO₃ layers exhibit ferroelectricity. Comparisons to *ab initio* and phase-field modeling of the properties of these ferroelectric superlattices will be made and the importance of strain demonstrated. In addition to probing finite size effects and the importance of mechanical boundary conditions, these heterostructures may be relevant for novel phonon devices, including mirrors, filters, and cavities for coherent phonon generation and control.

SESSION T9: Size Effects II

Chair: V. Nagarajan

Thursday Afternoon, December 1, 2005

Back Bay D (Sheraton)

1:30 PM *T9.1

Ferroelectricity in Ultrathin Perovskite Films. C. Lichtensteiger¹, L. Despont², P. Abei², E. Bousquet³, P. Ghosez³ and Jean-Marc Triscone¹; ¹DFMC, University of Geneva, Geneva, Switzerland; ²Institut de Physique, Université de Neuchâtel, Neuchâtel, Switzerland; ³Departement de Physique, Université de Liege, Sart-Tilman, Belgium.

Ferroelectricity in ultrathin films was investigated in epitaxial PbTiO₃ films prepared by off-axis magnetron sputtering onto (001) Nb-SrTiO₃ metallic substrates. Finite size effects were first probed by measuring the evolution of tetragonality with thickness in a series of c-axis oriented PbTiO₃ perovskite films, with thicknesses ranging from 500 Å down to 24 Å. High resolution x-ray diffraction showed a systematic decrease of the c-axis lattice parameter with decreasing film thickness below 200 Å and down to 24 Å. Using a first-principles model Hamiltonian approach, this decrease in tetragonality is related to the reduction of the polarization. Our analyses demonstrate that films well below 100 Å are ferroelectric and that the progressive reduction of the polarization in thin films is related to the depolarizing field resulting from imperfect screening. In a second experiment, ferroelectricity in ultrathin films was probed by x-ray photoelectron diffraction allowing us to measure tetragonality down to the unit cell level and to directly probe the non-central symmetric ferroelectric structure in thin films. The data, combined with *ab-initio* calculations of surface relaxation/rumpling, demonstrate ferroelectricity in films down to 12 Å and suggest, for even thinner films, a non central symmetric non switchable structure.

2:00 PM T9.2

Ultraviolet Raman Spectroscopy of Ferroelectric BaTiO₃/SrTiO₃ Superlattices. Dmitri A. Tenne¹, Xiaoxing Xi^{1,2,3}, Arsen Soukiasian^{2,3}, Venugopalan Vaithyanathan³, Wei Tian³, Darrell G. Schlom^{2,3}, Axel Bruchhausen⁴, Alejandro Fainstein⁴, Yulan Li², Long-Qing Chen², Xiaoping Pan⁵, Andres Cantarero⁶ and Ram S. Katiyar⁷; ¹Physics, The Pennsylvania State University, University Park, Pennsylvania; ²Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; ³Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; ⁴Centro Atomico Bariloche & Instituto Balseiro, San Carlos de Bariloche, Argentina; ⁵Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan; ⁶Materials Science Institute, The University of Valencia,

Valencia, Spain; ⁷Department of Physics, The University of Puerto Rico, San Juan, Puerto Rico.

Fundamental properties of ferroelectric nanostructures can be dramatically different from those of homogeneous bulk ferroelectrics. Experimental investigation of the lattice dynamics in nanoscale ferroelectrics is a very difficult task, hardly feasible with conventional visible or infrared spectroscopies. Here we present the first experimental study of ferroelectric short-period SrTiO₃/BaTiO₃ superlattices (SLs) by ultraviolet (UV) Raman spectroscopy. The high quality (BaTiO₃)_m/(SrTiO₃)_n SLs (m, n are between 2 and 13 unit cells) with atomically smooth interfaces were grown by molecular beam epitaxy on SrTiO₃ substrates. X-ray diffraction data show nearly perfect superlattice diffraction patterns with all superlattice peaks present in the θ - 2θ scans and very small full width at half maximum values of the rocking curves and ϕ scans. Excellent epitaxial quality and atomically abrupt interfaces between BaTiO₃ and SrTiO₃ layers are also evidenced by the high resolution transmission electron microscopy. Raman spectroscopy using ultraviolet excitation allowed to overcome the problem of overwhelming substrate contribution in the spectra and made possible the observation of phonons in superlattices having the ferroelectric BaTiO₃ layers as thin as 2 unit cells. The ferroelectric-paraelectric phase transitions have been observed. The phase transition temperature varies from \sim 140 K to over 500 K depending on thickness of BaTiO₃ layers and strain. The observed behavior is interpreted taking into account two competing mechanisms. Strain in BaTiO₃ layers increases T_c , while small thickness suppresses ferroelectricity, reducing the phase transition temperature. Below the T_c , the superlattices likely remain in the same (tetragonal) phase down to 7 K, i.e. the low-temperature phases (orthorhombic and rhombohedral) characteristic for bulk BaTiO₃, are suppressed by compressive strain. The soft phonon modes, which are heavily overdamped in bulk BaTiO₃, have been observed in the superlattices with ultrathin BaTiO₃ layers. Signature features of superlattice phonon spectra - doublets of folded acoustic phonons - have been observed; their positions agree well with the elastic continuum model calculations. Our results have demonstrated the capability of UV Raman spectroscopy and shed light to the phase transitions of nanoscale ferroelectrics. This work was partially supported by the US Department of Energy and the National Science Foundation.

2:15 PM T9.3

Strain, symmetry, and polarization in artificial ferroelectric superlattices. Ho Nyung Lee, Hans M. Christen, Matthew F. Chisholm, Christopher M. Rouleau and Douglas H. Lowndes; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

We recently demonstrated that oxide heterostructures with hundreds of individual building blocks (single unit-cell thick) of dielectric and ferroelectric titanates, including BaTiO₃, SrTiO₃, and CaTiO₃, can be artificially grown, yielding superlattices with atomically abrupt interfaces and highly-enhanced ferroelectric properties. The superlattices provide a new materials challenge by opening up opportunities to investigate a previously-unavailable phase space region. The key elements of our approach include the deliberate control of the amount of material deposited per laser pulse and the integration of continuous in-situ monitoring by reflection high-energy electron diffraction. Artificial oxide "superlattice crystals" are grown with properties surpassing those of the individual building blocks by epitaxial engineering of the superlattices' architecture and strain. Particular examples include two-component [e.g., (BaTiO₃)_x/(SrTiO₃)_y, (BaTiO₃)_x/(CaTiO₃)_y, and (CaTiO₃)_x/(SrTiO₃)_y] and three-component superlattices [e.g., (BaTiO₃)_x/(SrTiO₃)_y/(CaTiO₃)_z]. In this presentation, we will address the role of strain in polarization enhancement within strained superlattices. In addition, partial or complete strain relaxation in superlattices is seen to change the properties of such heterostructures. We therefore relax intentionally the structures' strain by changing the thickness ratios of the constituent components while keeping the superlattice period constant. Results will also be shown for structures with architectures beyond a simple stacking of constituent layers - those including more complex local structures and compositions, for example. Various designer superlattices of complex perovskite oxides with tuned physical properties will be presented, indicative of the wealth of opportunities afforded by artificial superlattice crystals. 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.

2:30 PM T9.4

First-principles modeling of ferroelectric nanowires. Philippe Ghosez¹, Gregory Geneste¹, Eric Bousquet¹ and Javier Junquera²; ¹Physique, Universite de Liege, Liege, Belgium; ²CITIMAC, Univesidad de Cantabria, Santander, Spain.

First-principles simulations constitute a fundamental tool to understand finite size effects in ferroelectric nanostructures. While various theoretical studies provided recently valuable insight into the physics of ferroelectric thin films and multilayers, basically nothing is known concerning the evolution of the ferroelectric properties in nanowires with respect to their size and shape. Here, we study the size dependence of the ferroelectric properties of stoichiometric BaTiO₃ nanowires within density functional theory. We show that the ferroelectric distortion along the wire axis disappears below a critical diameter of about 1.2 nm, although it can be recovered under appropriate tensile strain conditions. The ferroelectric behavior of the nanowires is shown to be monitored by the strong sensitivity of ferroelectricity on the unit cell volume, itself influenced by low coordination effects at free surfaces.

3:15 PM T9.5

Growth-structure-property Relations in Epitaxial Ferroelectric Pb(Zr₂₀Ti₈₀)O₃/SrRuO₃/SrTiO₃(001) Heterostructures: The Role of Threading Dislocations. Ionela Vrejoiu, Gwenael Le Rhun, Lucian Pintilie, Nikolai D. Zakharov, Dietrich Hesse and Marin Alexe; Max-Planck-Institute of Microstructure Physics, Halle, Germany.

Threading dislocations are well known to significantly influence the physical properties of semiconductor thin films and heterostructures. Although their possible presence in (multi)functional ternary-oxide thin films and heterostructures is well known, details on their origin, role, and particularly avoidance, are not sufficiently understood. We have grown epitaxial Pb(Zr₂₀Ti₈₀)O₃/SrRuO₃/SrTiO₃ heterostructures by pulsed laser deposition onto SrTiO₃(001) substrates. The macroscopic properties (P-E and C-V hysteresis curves, dielectric constant, and leakage current), the ferroelectric domain structure and local microscopic switching behavior determined by piezoresponse force microscopy (PFM), and the density and structure of threading dislocations determined by cross-sectional and plan-view (high-resolution) transmission electron microscopy (TEM), were studied on identical samples. The number density of threading dislocations could be varied using targets of different composition and quality. Corresponding changes of the ferroelectric properties were observed. Many threading dislocations were shown to be dissociated into dipoles spanning a stacking fault. Most probably these dislocations are able to pin 180 deg domain walls, as indicated by a comparison of TEM and PFM images obtained on identical samples. Local PFM backswitching was observed at such 180 deg boundaries. Work is in progress to analyse the influence of these microstructural details onto the macroscopic properties of the heterostructures.

3:30 PM T9.6

Real-time X-ray Diffraction Studies of Pulsed Laser Deposition: Collision Dynamics and Relaxation Kinetics. Aaron Fleet^{1,4}, Darren Dale^{2,4}, Yuri Suzuki^{3,4} and Joel D. Brock^{1,4}; ¹Applied & Engineering Physics, Cornell University, Ithaca, New York; ²Materials Science & Engineering, Cornell University, Ithaca, New York; ³Materials Science, UC Berkeley, Berkeley, California; ⁴Cornell Center for Materials Science, Cornell University, Ithaca, New York.

We grew SrTiO₃ on SrTiO₃ [001] by pulsed laser deposition, while observing x-ray diffraction at the (0 0 0.5) position. The drop ΔI in the x-ray intensity following a laser pulse contains information about plume-surface interactions. Kinematic scattering theory predicts $\Delta I/I = -4\sigma(1-\sigma)$, so that $\Delta I/I$ depends only on the amount of deposited material σ . In contrast, we observed experimentally that $-\Delta I/I < 4\sigma(1-\sigma)$, and that $\Delta I/I$ depends on the phase of x-ray growth oscillations.¹ This result is strong evidence for the smoothing role collisions near steps play in the PLD process. We have modelled the time dependence of the anti-Bragg x-ray intensity in the period between laser pulses using basic diffusion theory. We show that observed multi-exponential relaxation of the "anti-Bragg" intensity is consistent with the surface relaxing by simple two-dimensional surface diffusion.² 1. Fleet, A., D. Dale, Y. Suzuki, and J.D. Brock, Observed Effects of a Changing Step-Edge Density on Thin-Film Growth Dynamics. Physical Review Letters, 2005. 94: p. 036102.1-4. 2. Fleet, A., D. Dale, A.R. Woll, Y. Suzuki, and J.D. Brock, Multiple Time Scales in Diffraction Measurements of Diffusive Surface Relaxation. Submitted to Physical Review Letters, 2005(cond-mat/0504264).

3:45 PM T9.7

Ion-beam probing of He⁺ and H⁺ ion-sliced LiNbO₃ and SrTiO₃. Ryan M. Roth¹, Djordje Djukic¹, Richard M. Osgood¹, Sasha Bakhru² and Hassaram Bakhru³; ¹Department of Electrical Engineering, Columbia University, New York, New York; ²Department of Material Sciences and Engineering, Johns Hopkins University, Baltimore, Maryland; ³College of Nanoscale Science and Engineering, SUNY, Albany, New York.

Crystal Ion Slicing (CIS) is a technique that uses ion implantation

and subsequent thermal treatment and etching to exfoliate thin, single-crystalline films from the surface of a bulk metal-oxide crystal, such as lithium niobate. CIS has been used to create new optical devices, such as integrated optical filters, low-voltage scanners and polarization converters, etc. The performance of these devices was enhanced relative to their bulk crystal counterparts through the use of CIS single-crystal thin films. In addition, it has been shown that the CIS process can produce high-quality films of variable thickness for a wide variety of other oxide optical materials, including LiNbO₃, LiTaO₃, KTaO₃, YIG, BaTiO₃, and SrTiO₃. Despite its great utility, there has been a relatively small effort to characterize the materials physics of the process, including the distribution and mobility of the ion-implanted species in the presence of low-temperature annealing/processing. Such a heat treatment is needed to enhance the exfoliation process and after exfoliation to eliminate any stress within the film. Precise control of crystalline stress is crucial to developing large films without fractures, particularly for the case of very thin films (<1 μ m), and to achieving high-quality electrical and optical properties. In this paper, we present an investigation of the implanted ion-distribution, ion-induced defects, and any chemical changes induced by shallow He⁺ or H⁺ ion implantation in LiNbO₃ and SrTiO₃. The change in these quantities as a result of annealing was also investigated. This study was conducted using ion beam analysis techniques, including Rutherford Backscattering (RBS) and Nuclear Reaction Analysis (NRA), conducted at the Ion Beam Laboratory at SUNY. In particular, NRA is extremely useful in providing a detailed profile of specific atomic concentrations within implanted samples and can be used to directly observe the composition of the implanted ion layer. Transmission electron microscopy and atomic force microscopy have also been used to examine local stress and surface morphology after implantation. After being analyzed, heat treatment and etching techniques were used to exfoliate the thin films; once sliced, these films were examined with optical techniques, AFM, SEM, TEM, and additional ion beam analysis to determine the film quality and residual ion concentration. *Work supported by NSF Grant #DMR-0405145.

4:00 PM T9.8

Ferroelectric domain switching and piezoelectric response in BaTiO₃ nanowire. Zhaoyu Wang and Min-Feng Yu; Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

One-dimensional ferroelectric nanostructures are optimal samples for the study of size and dimensionality effect in ferroelectricity and piezoelectricity. Here we report the study of chemically synthesized single crystalline BaTiO₃ nanowires with piezoresponse force microscopy (PFM) for the first time. Measurements of hysteresis P-E loop, piezoelectric response and dynamic polarization switching all indicate that in BaTiO₃ nanowire a preferred ferroelectric polarization exists along its length direction, and the piezoelectric response is highly anisotropic. Each BaTiO₃ nanowire is thus a one-dimensional single domain ferroelectric. Dynamic polarization switching studies further reveal that the existing polarization is very stable: the reversed polarization created by a short DC pulse switches back spontaneously to its original polarization state upon the cancellation of the bias, and can be stabilized only by a long duration DC pulse (as long as 3 minute). We will report also the effect of mechanical stress on the domain formation and the piezoelectric response of BaTiO₃ nanowire, and discuss the implications.

4:15 PM T9.9

Polarization Quenching in Ultrathin Ferroelectric Films. Chun-gang Duan^{1,2}, Renat F. Sabirianov², Sitaram S. Jaswal², Wai-Ning Mei¹ and Evgeny Y. Tsybmal²; ¹Department of Physics, University of Nebraska-Omaha, Omaha, Nebraska; ²Department of Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, Nebraska.

We investigate the role of the electrostatic screening and interatomic bonding at the metal/ferroelectric interfaces in controlling the critical thickness for ferroelectricity in ultrathin perovskite films sandwiched between two metals. Using the projector augmented plane wave method within density functional theory we calculate electronic and ferroelectric properties of SrRuO₃/KNbO₃/SrRuO₃ and Pt/KNbO₃/Pt junctions. For the SrRuO₃/KNbO₃/SrRuO₃ junctions we find that the dominant mechanism responsible for the quenching of ferroelectricity at 2.4nm thickness of KNbO₃ is the depolarizing electrostatic field caused by the incomplete screening of the surface polarization charges [1]. For the Pt/KNbO₃/Pt junctions we predict, however, a larger critical thickness of more than 3nm which is contrary to what is expected purely from the screening argument based on the fact that the screening length of Pt is shorter than that of SrRuO₃. We demonstrate that the interatomic bonding at the Pt/KNbO₃ interface is the origin of the polarization quenching in these junctions. Our results are important for the understanding of the interplay between different mechanisms controlling ferroelectricity

at nanoscale and may lead to designing devices with new functional properties. [1] J. Junquera and P. Ghosez, Nature 422, 506 (2003).

4:30 PM *T9.10

A fundamental thickness limitation of ultrathin ferroelectric SrRuO₃/BaTiO₃/SrRuO₃ capacitors. Dong Jik Kim¹, Ji Young Jo¹, Yong Su Kim¹, Tae Kwon Song², Jong-gul Yoon³ and Tae Won Noh¹; ¹Seoul National University, Seoul, South Korea; ²Changwon National University, Changwon, South Korea; ³University of Suwon, Suwon, South Korea.

As electronic devices become smaller and smaller, it is highly desirable to understand phenomena occurring in nanoscale and their fundamental limitations set by the miniaturization. In nanosized ferromagnetic particles, the super-paramagnetism will pose a fundamental size limit. In a field effect transistor, the quantum mechanical tunneling between gate electrode and channel will pose a fundamental limit. Does such a fundamental limit exist for capacitor-type ferroelectric (FE) devices? In this talk, we will address the intriguing issues related to the fundamental limit of FE capacitors using fully-strained SrRuO₃/BaTiO₃/SrRuO₃ capacitors, whose BaTiO₃ thicknesses are between 5 and 30 nm [1,2]. Note that the polarization charge at the interface will be screened by free carriers at the electrode, but that its screening will be imperfect due to the Thomas-Fermi screening length and result in depolarization field E_d inside the FE capacitor. First, we will show that the critical thickness and the scaling of thickness-dependent polarization of our capacitors follow the predictions of the recent first principles calculation, which takes into account of E_d [1,3]. Second, our capacitors show a very strong time-dependent polarization relaxation, caused by E_d [4]. Finally, we will show that their coercive fields remain almost independent of the BaTiO₃ thickness, and explain this behaviour based on the FE domain dynamics. The dominant stage of polarization reversal turns out to be the domain nucleation process, which has been known to be thermodynamically impossible for bulk FEs (called the Landauer's paradox). We will demonstrate that the 50-year-old paradox should not become an issue in our high quality ultrathin BaTiO₃ films. In addition, the thermodynamic limit should pose a much stricter limitation than the critical thickness: namely, the FE domain nucleation due to E_d should work as the fundamental limit. For our BaTiO₃ capacitors to have stable FE polarization over several years, they should be thicker than 50 nm. We will also discuss this fundamental limitation for other FE capacitors, which are currently used for FeRAM applications. [1] Y. S. Kim *et al.*, Appl. Phys. Lett. **86**, 102907 (2005). [2] Y. S. Kim *et al.*, cond-mat/0506495. [3] J. Junquera and P. Ghosez, Nature **422**, 506 (2003). [4] D. J. Kim *et al.*, cond-mat/0506480.

SESSION T10: Poster Session II

Chairs: M. Alexe, V. Joshi, J.-P. Maria and R. Ramesh
Thursday Evening, December 1, 2005
8:00 PM
Exhibition Hall D (Hynes)

T10.1

Fabrication of Ba_{0.48}Sr_{0.52}TiO₃ /LaNiO₃ Artificial Superlattice Structure by rf Sputtering. Hsin-Yi Lee¹, Heng-Jui Liu¹, Kun-Fu Wu² and Chih-Hao Lee²; ¹Research Division, National Synchrotron Radiation Research Center, Hsinchu, Taiwan; ²Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan.

Artificial superlattices structure consisting of ferroelectric Ba_{0.48}Sr_{0.52}TiO₃ (BST) and conductive LaNiO₃ (LNO) sublayers have been successfully grown on a SrTiO₃ (001) substrate with rf magnetron sputtering. X-ray reflectivity and high-resolution diffraction measurements were employed to characterize the microstructure of these films. Formation of a superlattice structure was confirmed from the appearance of Bragg peaks separated by Kiessig fringes in x-ray reflectivity curves and a diffraction pattern. The fitted result from x-ray reflectivity curves shows that the densities of the BST and LNO sublayers are slightly less than their bulk values. The appearance of discernible satellite peaks beside the main peak of the crystal truncation rod observed for deposited films clearly demonstrates that a well defined superlattice structure can be formed with rf sputtering. The largest dielectric constant value 706, obtained for a film having a stacking periodicity 4 nm, is three times as large as that of BST single-phase films, with dielectric constant $\epsilon \sim 190$, prepared under the same conditions. The artificial BST/LNO superlattices exhibit a large dielectric constant and a small dielectric loss.

T10.2

Strain Relaxation and Dislocation Confinement in Epitaxial SrTiO₃ by Two-Step Growth Technique and the Resulting

Dielectric Response. Tomoaki Yamada, Vladimir O. Sherman, Alexander K. Tagantsev, Dong Su, Paul Muralt and Nava Setter; Laboratoire de Ceramique, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

A two-step growth technique using pulsed-laser deposition was applied to epitaxial SrTiO₃ (STO) thin films on LaAlO₃ substrates providing a way to obtain an effective strain relaxation in these films, otherwise strained due to lattice mismatch between film and substrate. In a first step, a very thin STO layer of less than 10 nm was deposited at low temperature. The main part of the film was deposited in a second step at high temperature, as commonly used for epitaxial growth. By varying the thickness of the first layer, different strain relaxation states of the films were systematically realized even when keeping the substrate, the total thickness of the film and the deposition condition unchanged. In-situ reflection high-energy electron diffraction of the film with 10-nm thick first layer showed that almost full strain relaxation was realized before the deposition of the second layer, whereas the normally grown film was not fully relaxed even when the film thickness exceeded 300 nm. The relaxation process of the two-step grown film took place through the crystallization of the first, thin and quasi-amorphous layer with substantial misfit dislocation's formation. Since the normally grown film possesses compressive strain due to less strain relaxation from the lattice mismatch, the two-step grown film showed larger permittivity and larger tunability compared to the normally grown film, which is basically compatible with the trend of theoretical prediction. Nevertheless, a difference between the observed and predicted permittivities was observed. The analysis of the extrinsic loss contribution at microwave frequency implied that the two-step growth technique could suppress the extrinsic loss, which might be due to the redistribution of defects in the film. The first layer leads to two effects: (i) strain relaxation and (ii) lower loss of the film. Through a systematic study by using two-step growth technique, we survey the effect of mechanical strain on the dielectric response (permittivity, tunability and loss) of incipient ferroelectric films.

T10.3

Embedded High Dielectric Thin Film Capacitors for New Generation Printed Wiring Boards. Seung-Hyun Kim, Chang Young Koo, Jung-Hoon Yeom, Jong-Hyeon Cheon, Hyun-Jung Woo and Jowoong Ha; R&D Center, INOSTEK Inc., Ansan, Gyeonggi, South Korea.

Recently, the embedding high-permittivity dielectric materials using BaTiO₃ and PZT based thin films into high density printed circuit boards have been utilized to develop device reliability, manufacturing cost down and make small size products for passive devices. However, many parts of those passive devices include somewhat expensive materials and complicate processing steps. Especially, the electrodes of capacitors, which use an expensive noble metal, have an effect on the product cost rising in typical passive devices. An additional difficulty in developing high k embedded capacitors is high process temperature. In general, polymer packages are unable to withstand the high temperatures for inducing the required properties in bulk ceramics or paste derived thick films. To solve these drawbacks, we prepared thin film capacitors using chemical solution deposition techniques at low process temperature onto very thin Ni-based metal foils instead of noble metal substrates before the embedding process. By incorporating these embedded high k thin film capacitors into the printed wiring boards, we achieved high capacitance density in the range of ~ 800 nF/cm² and the low loss tangent below 1 %. These results represent a remarkable improvement of several orders of magnitude over typical current embedded capacitors in passive devices. In this experiment, Ni-plated Cu foils are used as substrates to achieve less-expensive process and LNO buffer layers are inserted underlying BaTiO₃ and PZT based thin films to prevent the oxidation of Ni foil substrate and the subsequent degradation of dielectric properties. BaTiO₃, PZT based films and LNO thin films are prepared using modified chemical solution deposition method. In an effort to develop robust capacitors on cost competitive Ni-plated Cu foil, several parameters including annealing conditions, dopants, composition, and thickness are systematically investigated. The dielectric properties are evaluated to investigate the role of interfacial state. The dielectric breakdown strength, an important parameter for passive devices is also investigated 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. *This work was supported by National Research Laboratory Program (NRL)

T10.4

Abstract Withdrawn

T10.5

Development of interfacial layers in barium titanate films on Ni coated silicon. Tanawadee Dechakupt, Hajime Nagata and Susan Trolier-McKinstry; Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

Growth of barium titanate films on Ni coated (100) silicon substrate was investigated using spectroscopic ellipsometry (SE). In this study, barium titanate films were prepared by two method: i) rf-sputtering and ii) chemical solution deposition. Modeling of SE data revealed the presence of nickel oxide interfacial layer in both films. The film structures were in good agreement to depth profiles obtained from x-ray photoelectron spectroscopy. An approximately 50 angstrom thick nickel oxide layer was formed at the interface when barium titanate film was sputtered on Ni coated silicon at 700°C for 1 hour. The rate of nickel oxide growth decreased as a function of sputtering time. For chemical solution deposition, the nickel oxide layer grows linearly as a function of barium titanate thickness. The influence of the interfacial layers on the electrical properties of barium titanate films on Ni coated silicon will be described.

T10.6

Low-Voltage Ferroelectric Phase Shifters Operated at the Microwave Regime. Zhiyong Zhao¹, Xiaoyan Wang¹, Dave McStay¹, J. Stevenson Kenney² and Andrew T. Hunt¹; ¹nGimat Co., Atlanta, Georgia; ²School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Phase shifters are an essential component in electronically scanned phased-array antennas for communication and radar applications, and typically represent a significant amount of the cost of an antenna array. Jamming and interferers of mobile communication devices can be eliminated via phase shifters while still receiving the desired signal even with the interferer being at the same frequency. Technology of choice for phase shifters includes ferrite, MMIC, MEMS, and ferroelectrics. Ferrite phase shifter technology has been very successfully employed in military systems despite high cost, size and complex current switching circuitry. GaAs switched-line phase shifters have demonstrated good phase and amplitude error control. However, they involve a relatively large loss and have low power handling capability. As for MEMS, they provide low insertion loss, high isolation, negligible power consumption, and low intermodulation distortion (IMD); on the other hand, they require high driving voltage (e.g., 40 V or higher), have low switching speed (> 10 μs), and suffer from packaging and lifetime problems. Ferroelectric barium strontium titanate (BST) materials, due to their fast tuning speed, low loss, high power handling, and inherently analog tunability from the voltage-controlled dielectric constant, have attracted much attention for microwave applications. Nevertheless, the progress made on BST tunable devices has been elusive. The problem has been multi-faceted: (i) the loss is still high compared to its counterparts, attributed to the poor crystalline quality, (ii) a process of making high-quality, large-area BST films at low cost does not exist, and/or (iii) the required DC bias voltage is too high (~100 V). nGimat has developed a process of making highly epitaxial BST thin films on inexpensive large-size substrates, which demonstrated low loss and high tunability. A proprietary low-voltage (<20 V) capacitor structure was designed and fabricated, which displayed improved IMD performance. In this paper, we will present a novel phase shifter utilizing the low-voltage capacitor structure and epi-BST materials. The phase shifters exhibit phase shifts greater than 100 degrees spanning from L- to C-band (0.7 to 7 GHz) with a DC bias of 0-20 V, insertion loss of 2.0 dB or less, and VSWR of 2:1 or better. The die size is 2 x 2 mm or smaller, and IIP3 is higher than 30 dBm for high power handling. Phase shifters can be designed and built that can perform from 100s of MHz to >50 GHz. *The project was supported by the National Science Foundation SBIR/STTR program.

T10.7

The effects of PBB on the dielectric properties of BST film. Jin Cheol Kim and Jun Rok Oh; PCB, ACI division, Suwon, South Korea.

The mixture of PbO-Bi₂O₃-B₂O₃(PBB) phase was formed in the Ba_{0.5}Sr_{0.5}TiO₃(BST) film and the effects of PBB on the dielectric properties of the BST film was investigated. The amorphous PBB layer was deposited on the BST film using rf magnetron sputtering and diffused into the film by heat treatment. The PBB phase in BST film was identified by energy dispersive spectrometer(EDS). Dielectric properties of BST film were significantly improved after the diffusion of PBB. The leakage current densities of BST film decreased from 3.24*10⁽⁻⁵⁾A/cm² to 9.45*10⁽⁻⁸⁾A/cm² at 1.5V and the dielectric constant increased from 238 to 533. These results show that the formation of insulating metal oxide in the thin film can improve the dielectric properties of the film

T10.8

Application of net-shape processing for ferroelectric capacitor preparation. Vladimir Petrovsky and Harlan U. Anderson; EMARC, University Missouri-Rolla, Rolla, Missouri.

It is important for many practical applications to bring multiple

capacitors or distributed capacitor layers into electronic circuit board. Different technological approaches can be used to address this problem and net-shape processing is one of them. Net-shape processing combines two types of the metal oxide sources (powder and metal organic polymer) together to form oxide coatings. It allows preparation of the dense coating at low temperature without shrinkage so depositing layer will not crack during the deposition or at the consequent heat treatments. Barium-strontium titanate (BST) was used in this investigation to demonstrate applicability of the net-shape processing to ferroelectric materials. Platinized sapphire and alumina ceramic plates were used as substrates as well as platinum foil. BST layers were deposited on the substrates by net-shape processing in the thickness range from 2 to 25 μm at low temperature (less than 500°C). The samples were annealed at elevated temperatures up to 1000°C. It was shown by SEM investigation that coatings are dense (or nearly dense) and do not crack during the annealing. Top platinum electrodes of different size and shape were deposited by sputtering and screen printing to form capacitors. No shorts were found on the capacitors with surface area up to 10 cm² which characterizes quality of the coatings. Capacitance and dielectric losses were measured by HP Impedance analyzer 4192A in the frequency range 1 to 1000 kHz. Temperature and bias dependences of the capacitance and dielectric losses were also investigated using this equipment. Keithley Electrometer 6517A was used for I-V measurements and break down strength estimation. Electrical characterization showed steady increase of dielectric constant with the increase of annealing temperature (from 500 after 700°C annealing to 1000 after 1000°C annealing). Dielectric losses were relatively low (on the level of 1%) as well as leakage current (on the level of 10 to 50 nA/cm² at 10V). Break down strength was from 200 to 500 kV/cm depending on annealing temperature which looks acceptable for BST capacitors. Overall behavior of the net-shape processed BST capacitors shows that this technology can be successfully used in different applications which require multiple microfarad size capacitors inside circuit board or distributed capacitors with specific capacitance of several hundred nanofarad per square centimeter.

T10.9

MOCVD of CaCu₃Ti₄O₁₂ Thin Films: Synthesis, Characterization and Dielectric Properties. Raffaella Lo Nigro¹, Graziella Malandrino², Roberta G. Toro² and Ignazio L. Fragala^{1,2}, ¹IMM-CNR, Catania, Italy; ²Dipartimento di Scienze Chimiche, Università di Catania, Catania, Italy.

In capacitors devices both improvements of performances and miniaturization are strictly related to insulator dielectric constant values. To date, ferroelectric materials have been used although their phase transitions and the consequent dielectric constant temperature dependence represent problems for microelectronics applications. Recently, the calcium copper-titanate, CaCu₃Ti₄O₁₂ (CCTO), has been shown to possess one of the largest dielectric constants ever measured (100000 at micro frequencies), which remains stable in a wide temperature range, in accordance with its structural stability. Nevertheless, major efforts have been focused on the understanding of powder and single crystal properties. Microelectronics applications, however, require CCTO in the form of thin films. To date, CCTO films have been grown only by pulsed laser deposition and few studies have been reported on the CCTO thin film properties. We report on a novel, "simple" and unique MOCVD approach as an interesting alternative to the fabrication of CCTO films. A molten multi-element source, which represents a great finding in the perspective of industrial production, has been used. The adopted molten source consist of Ti(tmhd)₂(i-Op)₂, Ca(hfa)₂tetraglyme and Cu(tmhd)₂ precursor mixture. The synthesis of this mixed oxide phase has required considerable efforts to define the appropriate deposition conditions for the fabrication of high quality CCTO thin films on LaAlO₃(001) substrates and on technological important substrates. The growth of the oxide layer by a two step in-situ process, namely deposition of an amorphous matrix and the consequent in-situ annealing, has resulted in epitaxial (001) CCTO thin films. The structural, morphological and dielectric characterization of CCTO films are reported. In particular, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis have been performed to characterize, structural, morphological and compositional features of CCTO thin films. Dielectric properties have been found to be strictly related to structural characteristics.

T10.10

Defect and Contact Properties – Their Influence on Shape and Magnitude of I(V)-Leakage Current Curves in High-Permittivity Thin Film Capacitors. Herbert Schroeder, IEM am IFF and cni, Forschungszentrum Juelich GmbH, Juelich, Germany.

High-permittivity thin insulating films of the perovskite-type mixed-oxides such as BST are candidates for replacing the traditional

low-k materials in CMOS integrated circuits, silicon-oxide and -nitride, as capacitor dielectric in advanced DRAM cells and as new gate materials in FETs. One of the most important issues for these applications are sufficiently low leakage currents to avoid malfunction of the devices. Although a large number of experimental data on leakage through metal-insulator-metal (MIM) thin film capacitor structures is published for perovskite-type mixed oxides, the mechanistic interpretation is still rather unsatisfactory because of two main reasons: First, in most cases just one experimental parameter has been varied only, which is not sufficient to identify a working mechanism with high probability, and second, there are too many unknown numbers (band properties of insulator, interface offsets, defect properties, electronic vs. ionic compensation, etc.) for a quantitative description. In such cases simulation studies can help to show trends and dependencies on these unknown parameters. Simulation studies will be presented for an advanced leakage current model combining the electronic carrier injection/ejection at the electrode interfaces (described by thermionic emission) with the film conduction properties of the thin dielectric film (modelled as wide band gap semiconductor). This model was successfully used to explain the field, temperature and thickness dependence of experimental leakage currents through paraelectric BST thin films between platinum electrodes [APL 83, 4381 (2003)]. This contribution reports additional results of I(V)-leakage curves dependent on contact and defect properties. The band-offsets at the interface (i.e. different electrodes), defect concentration as well as defect energy level in the gap of shallow and deep donor and acceptor states, respectively, have been systematically studied for their influence on the I(V)-curve. The main result is a very strong dependence of the shape and magnitude of the I(V)-curves on these parameters, e.g. straight line for shallow donors and S-shape-like for shallow acceptors in a Schottky-plot; and six orders of magnitude difference in the absolute value of the leakage current between these cases. An additional variation is introduced by unsymmetrical contacts and different ratios of electronic and ionic compensation in the film, respectively. Examples for experimental data with similar shape and magnitude in leakage current density will also be presented.

T10.11

Structural and Electrical Properties of Ba_xSr_{1-x}TiO₃ Bi-layer Thin Films by Pulsed Laser Deposition. Kumaravinathan Sarma, Peter K. Petrov, Bin Zou, Hsin-I Chien, Rayon A. Walters and Neil McN. Alford; Physical Electronics and Materials Centre, London South Bank University, London, United Kingdom.

Thin film Ba_xSr_{1-x}TiO₃BSTO) has gained considerable research attention as a potential material for electrically tuned microwave devices. The wider use of these films in devices is inhibited by the high temperature dependence of the dielectric properties. Work done elsewhere has suggested a multilayer structure with different BSTO ratios as a possible solution to the problem. In this paper bi-layer structures of Ba_{0.25}Sr_{0.75}TiO₃/ Ba_{0.75}Sr_{0.25}TiO₃ (structure 1) and Ba_{0.75}Sr_{0.25}TiO₃ / Ba_{0.25}Sr_{0.75}TiO₃ (structure 2) were deposited in-situ on MgO substrates using pulsed laser deposition (PLD). Conventional X-ray diffraction (C-XRD) was used to study the structural properties of the film. Simple co-planar capacitor structures were patterned on the film using a liftoff process, these were then used to measure the capacitance and tunability of the films at room temperature in the frequency range of 1 to 3 GHz. XRD patterns indicate films of both structures to be epitaxial. The capacitance value fell with increasing frequency, where as tunability remained constant. When the electrical properties of both structures are compared, we find structure 2 exhibited higher capacitance and tunability. This was attributed to the tensile strain arising from the lattice mismatch between the film and substrate. Reference 1. S. Gervorgian , P.K. Petrov , Z. Ivanov and E Wilkborg, App Phys Lett., 79, pp 1861, 2001

T10.12

Dielectric and optical properties of highly oriented pulsed laser deposited BaTiO₃ thin films. Jussi Antero Hiltunen^{1,2}, Dilan Seneviratne¹, Yong Woo Choi¹, Michael Stolfi¹, Jyrki Lappalainen³, Vilho Lantto³ and Harry L. Tuller¹; ¹MIT, Cambridge, Massachusetts; ²VTT Electronics, Technical Research Centre of Finland, Oulu, Finland; ³Electrical Engineering, University of Oulu, Oulu, Finland.

BaTiO₃ is a widely studied perovskite ferroelectric material possessing excellent functional properties that offers a wide variety of applications in microelectronics, mechanics and optics. Key physical properties of perovskite thin films (dielectric, piezoelectric, electrooptic) are, however, often lower in magnitude as compared to bulk values due to substrate constraints. In this paper we examine the substrate-induced effects on the optical and dielectric properties of the BaTiO₃. Pulsed laser deposition (PLD) is utilized to grow highly oriented BaTiO₃ thin films on single crystal MgO substrates from a stoichiometric target. By controlling the background oxygen pressure during deposition the lattice parameter of the films can be tuned to

be within 1% of the bulk value. Dielectric properties are characterized with inter-digitized-electrodes (IDE) as a function of temperature to study the influence of the substrate induced stresses on the ferroelectric film properties. The dielectric measurements indicate that the paraelectric-ferroelectric transition temperature is shifted to higher temperatures compared to the single crystal phase transition temperature. Refractive indices along horizontal and vertical directions evolve correspondingly to the changes in the lattice parameter. The amount of birefringence can be varied from -0.03 to 0.03. Finally, the tunability of the index with external electric field is examined.

T10.13
Pb_{0.6}Ba_{0.4}ZrO₃ Thin Films for Tunable Microwave Applications. Lin-Jung Wu and Jenn-Ming Wu; National Tsing Hua University, Hsinchu, Taiwan.

In the past few years, ferroelectric materials have been studied for microwave frequency-agile devices due to their electrically tunable properties. The most important material issues for this kind of application are tunability and dielectric loss. In the present study, Pb_{0.6}Ba_{0.4}ZrO₃ (PBZ) thin films were grown on Pt/Ti/SiO₂/Si substrates by rf-magnetron sputtering. The growth conditions were optimized for best dielectric properties. In addition, the effect of excess Pb content and post annealing on electrical properties was investigated. The electrical properties of PBZ thin films were measured by parallel-plate capacitor structure in both low frequency (<1MHz) and high frequency (50MHz-5GHz) regions. At higher frequency, the top electrodes of Ag shaped by a circular-patch capacitor structure with one outer diameter (150 μm) but two inner diameters (50- and 80-μm) were patterned by photolithography and wet etching. Relatively high dielectric constant (~350), low dielectric loss tangent (<0.02) and high tunability (50% under 200kV/cm) can be achieved at 1MHz. Furthermore, capacitance extracted by reflective S-parameter showed no evidence of onset of dielectric relaxation in the measured frequency range (50MHz-5GHz).

T10.14
Electrical Properties of (Ba,Sr)TiO₃ Thin Films Revisited: The Case of MOCVD Grown Films on Pt Electrodes. Peter Ehrhart and Reji Thomas; IFF, FZ-Juelich, Juelich, Germany.

Due to the dependence on both bulk and interface properties neither the effective dielectric constant, k , nor the leakage current, J , can be scaled in a straightforward manner with film thickness for high- k thin film capacitors. Based on detailed investigations of different thickness series of (Ba,Sr)TiO₃ films on platinized substrates the bulk and interfacial properties are separated: e.g. for (100)-textured (Ba_{0.7}Sr_{0.3})TiO₃ films the interfacial capacitance is higher for Group-II rich films than for Ti rich films and it is higher for SrTiO₃ than for (Ba,Sr)TiO₃. The nature of the interfacial layer is discussed. The behavior of the leakage current is revisited: for low applied fields, E , the leakage currents at room temperature are very low, $\sim 10E^{-10}$ A/(cm²cm), and dominated by the relaxation currents (Curie-von Schweidler behavior) even after holding times of 100s. At higher applied fields a change to a very strong power law increase is observed, $J \sim E \exp 16$. The thickness dependence is removed by scaling with the internal field or polarization of the film, $D = kE$. Hence, a direct connection between the decrease in k and the decrease in leakage with decreasing film thickness is revealed and scaling rules for the electrical properties can be derived. This behavior is accompanied by a larger scatter of the data and seems to be controlled by a more inhomogeneous conduction, e.g. by the formation of filaments. Further details on the conduction mechanism are deduced from the temperature dependence. For measuring temperatures up to 100 degree C there is no change of the dominating leakage mechanisms. At temperatures up to 200 degree C increased currents are observed in the low field region. This increase can be attributed to the overrun of the relaxation currents by a temperature dependent mechanism, which shows the characteristics of a Schottky injection. At very high fields the currents merge again into the power law behavior. Influences of different film modifications are discussed: stoichiometry, microstructure, and interfacial properties. Implications for the application are discussed in terms of a figure of merit plot for capacitor applications, e.g. for applied voltages <1.5V films with thickness <60nm remain within the relaxation regime and the leakage does not significantly change with thickness (or corresponding effective capacitance density). At higher voltages the leakage runs into the power law regime and a fast increase of the leakage is observed with decrease in thickness.

T10.15
Polarization switching in epitaxial BiFeO₃ films. Florin Zavaliche^{1,2}, M. P. Cruz³, T. Zhao^{1,2}, P. Shafer², S. Y. Yang², R. R. Das⁴, D. M. Kim⁴, C. B. Eom⁴ and R. Ramesh^{1,2};
¹Department of Materials Science and Engineering, University of California, Berkeley, California; ²Department of Physics, University of

California, Berkeley, California; ³Centro de Ciencias de la Materia Condensada (CCMC) - UNAM, Ensenada, B.C., Mexico; ⁴Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin.

Polarization switching in 600 nm thick epitaxial BiFeO₃ films grown on miscut SrTiO₃(001) substrates were studied by piezoelectric force microscopy (PFM). To determine the polarization direction in each domain, both out-of-plane and in-plane piezoelectric response signals were simultaneously recorded. PFM amplitude and phase images were acquired with the cantilever pointing along the principal crystallographic directions to confirm the in-phase PFM data. Electrical poling was performed by applying different biases on the scanning conducting probe. By combining the out-of plane and in-plane piezoelectric data we found that polarization rotates by 71° and 109°, but 180° switching is observed as well. This work has been supported in part by the U. of Maryland NSF-MRSEC under grant #DMR 00-80008, by ONR under a MURI program, and NSF-FRG under awards #DMR-0313764, ECS-0210449, DMR-0103354. We acknowledge the support of David & Lucile Packard Fellowship (C.B.E.).

T10.16
W doping effects on Ba_{0.5}Sr_{0.5}TiO₃ thin films for radio-frequency applications. JeaHo Oh, Christophe Durand, Sebastien Delprat and Mohamed Chaker; INRS-EMT, Varennes, Quebec, Canada.

The Ba_xSr_{1-x}TiO₃ (BST-x) ferroelectric is certainly the most promising material for radio-frequency (RF) applications because of its high permittivity and its high tunability. Nevertheless, significant loss tangent of this material at GHz frequencies (tan δ 0.05) remains the main quandary, which strongly limits the integration of BST material in actual devices. Nowadays, the key challenge is to reduce loss tangent value without degrading the other dielectric properties, especially the tunability. In the literature, elaboration of acceptor doped BST material has shown a significant loss tangent reduction. In particular, 1 mol% W (tungsten) doping has clearly shown a significant improvement of loss tangent (tan δ 0.005) with an adequate tunability (10% at 67 kV.cm⁻¹). However, the exact role of W dopant on the microstructure, which involves an improvement of electrical properties, is presently not well understood. This work proposes to study the effect of W doping concentration on BST microstructure and RF electrical characteristics. In particular, the strain induced by the dopant is carefully studied, since this parameter is known to be critical for electrical properties. This work is focused on W-doped Ba_{0.5}Sr_{0.5}TiO₃ (BST-0.5) thin films, which are elaborated by pulsed laser ablation of 0.5wt, 2%wt and 10%wt WO₃ doped BST-0.5 targets. Films are deposited at 400 °C at various oxygen pressure on polycrystalline alumina substrate, a very low-loss and low-cost material. A post-annealing treatment is carried out at 750 °C under oxygen flux for 3 hours to crystallize the films. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are combined to accurately analyze the microstructure. RF electrical measurements are done by two complementary diagnostics: interdigital capacitors (IDC) and coplanar waveguide (CPW) transmission line. Appropriate analytical and numerical models are used to determine the BST dielectric constant and loss tangent from 2 to 10 GHz. The IDC design also permits the capacitance measurement at various applied electric fields, in order to extract the BST tunability. It is shown that the presence of W in BST films, detected by XPS, does not form any new compound or new phase, since XRD patterns do not show any new peak with increasing the W concentration (especially the BaWO₄ phase is not observed). XRD analysis shows that the W atoms, which are included in the crystalline cubic structure of BST, modify the lattice parameter of the films. It is observed that the lattice parameter directly increases with both the W content and the oxygen pressure. A correlation between this lattice parameter modification and the RF electrical properties is discussed and the real effectiveness of W doping on BST-0.5 polycrystalline thin films is pointed out.

T10.17
Dielectric properties of SrTiO₃ thin films under external electrical fields in THz frequency range. Kenta Kotani, Mukul Misra, Iwao Kawayama, Hironaru Murakami and Masayoshi Tonouchi; Institute of Laser Engineering, Osaka University, Suita, Osaka, Japan.

Paraelectric / Ferroelectric thin films such as SrTiO₃ (STO), BaTiO₃ (BTO) and Ba_xSr_{1-x}TiO₃ (BSTO) offer a promising technology for electrically tunable frequency-agile THz devices, as they have been extensively studied and successfully employed for various microwave tunable devices and high-density dynamic random access memories. From the physical point of view, the lowest transverse optic (TO) soft phonon modes of these displacive ferroelectric materials lie in the THz frequency range, which are supposed to have a strong influence on the dielectric properties of these ferroelectric materials. On the other hand, it is well-known that dielectric properties of STO are sensitive

to the induced electrical field at low temperatures. Therefore, it is considered very interesting to examine the behavior of the TO₁ soft mode in applied external electrical field. The STO thin film was prepared by pulsed laser deposition technique. We have performed the THz-TDS of virgin STO thin film by conventional THz time domain spectroscopy (THz-TDS) in the temperature range from 20 K to 290 K. THz-TDS is a very powerful technique as it simultaneously and accurately measures both the phase and amplitude of waveforms from which complex material properties such as complex refractive index and dielectric constant can be obtained without complicated Kramers-Kronig analysis or fitting to the spectroscopic data. After the measurement, Au/Cr interdigital electrodes were fabricated on the surface of the film by sputtering and conventional lift off photolithographic technique, and we measured the dielectric properties of field-induced STO thin films. Without electrical fields, the frequency dispersions of both the real and imaginary parts of the measured dielectric constant of STO thin film show a clear Lorentzian oscillator behavior below 180 K. We have fitted both the real and imaginary parts of dielectric constant using the classical damped oscillator dispersion model, and we observed a peak in the eigen frequency and the damping of the soft mode just before the phase transition at 105 K. In the meeting, we will also present the properties of electrical-field-biased STO thin films.

T10.18

Stress-influence on the Properties of Mg doped SrTiO₃ Thin Films. Paula Maria Vilarinho, Olena Okhay and Aiying Wu; Department of Ceramics and Glass Engineering, University of Aveiro, Aveiro, Portugal.

Dielectric permittivity of SrTiO₃ (ST) increases continuously during cooling until almost 0K, reaching considerable high polarization values. However no ferroelectric phase transition is observed. Besides the high dielectric permittivity, ST possess low dielectric losses and a non linear electric field effect at low temperatures, making ST and ST based functional materials important candidates for high dielectric permittivity applications, such as Dynamic Random Access Memories, and field dependent applications, such as tunable microwave devices. Properties optimization for specified applications has been done by atomic substitutions in ST lattice. These studies have been mainly conducted in single crystals and ceramics, not systematically in films. Recent results reported by the authors revealed that the solid solubility of Mg in ST lattice is higher in thin films than in ceramics. The higher degree of homogeneity at the molecular level attained in the sol-gel precursor and the tensile strains induced in the film by the underlayer Si platinised substrate might be responsible for the higher atomic substitution tolerated in film's lattice. In this work the dependence of the solid solubility of Mg on ST lattice on the stresses induced by the substrate and its effect on the dielectric response is studied. Sr_{1-x}Mg_xTiO₃ (x = 0.01-0.40) (SMT) thin films were prepared by sol-gel on different substrates (Si/SiO₂/TiO₂/Pt and SrTiO₂/Pt and Al₂O₃/Pt) and annealed in different conditions (T_{ann.} = 750 °C and 900 °C). The chosen substrates provide a systematic change in the thermal strain while maintaining the identical film microstructure. The phase purity, lattice parameters and film stress were evaluated by X-ray diffraction (XRD) analysis. Using a high resolution X-ray diffractometer, the residual stresses were determined by measuring, for each sample, the (211) ST Bragg diffraction peak for Ψ values ranging from -60 ° to 60 °, and applying the sin² Ψ method. Special attention was paid on deviations from linear dependence of d Ψ with sin² Ψ along with asymmetry of XRD line profiles that results from stress-depth profiles as well as lateral stress distributions in the stressed films. Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to inspect the microstructure of the deposited films. The interfaces were analysed by TEM and Rutherford Backscattering (RBS). The solid solubility of Mg evaluated by XRD analysis, is limited to x <= 0.30 for SMT films at T_{ann.} = 750 °C. Ilmenite type grains were found by TEM in SMT films on Si/SiO₂/TiO₂/Pt with x >= 0.20 and annealed at 900 °C. The dielectric properties of some of the films were evaluated at RF frequencies. The relationship between stresses - doping - electric response in SMT films is established.

T10.19

Dielectric and Ferroelectric Properties KNN-LT-LS Thin Films. William Kurt Simon, Kian Kerman, E. K. Akdogan and A. Safari; Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Lead-free piezoelectric thin films, in the newly discovered KNN-LT-LS system (Saito et al.), have been grown by Pulsed Laser Deposition on platinum coated Si wafers. Phase pure films are demonstrated through a systematic process optimization, and the conditions of best quality film growth are exemplified. The polycrystalline films are examined for elemental and phase composition, film thickness, texture, and strain using X-ray diffraction and Rutherford Backscatter

Spectroscopy. The dielectric and ferroelectric properties of selected compositions in the vicinity of morphotropic phase boundary are reported, and the properties are discussed in the context of texturing, strain effects, and grain size.

T10.20

Characteristics of thin ion-sliced bonded SrTiO₃ thin films. Yoo Seung Lee¹, Djordje Djukic¹, Ryan M. Roth², Richard M. Osgood^{1,2}, Sasha Bakhru³ and Hassaram Bakhru³; ¹Electrical Engineering, Columbia University, New York, New York; ²Applied Physics and Applied Mathematics, Columbia University, New York, New York; ³Ion Beam Laboratory, SUNY, Albany, New York.

Strontium titanate, SrTiO₃, is a ferroelectric material whose outstanding electrical properties make it an important material for numerous applications such as electrically tunable low-loss microwave components. Thin film forms are important both as substrates and for high-frequency applications requiring thin-film devices. One recently developed approach to fabricating thin films relies on exfoliation from the bulk using deeply implanted H⁺-ions. However, such ion-slicing also requires a durable wafer bonding step to enable the realization of thin, i.e. <1 μ m, large-area films. In this paper, we report on ion-slicing of thin SrTiO₃ thin films using a variety of H⁺ implantation and thermal annealing conditions, which is enabled by the bonding of the implanted wafer onto a handle wafer of SiO₂. The film quality is characterized by measurement of its surface roughness, dielectric properties and crystal structure. We have determined the optimum process conditions of ion implantation and anodic bonding to bond SrTiO₃ thin films on Pyrex glass and show that it is determined by a careful matching of thermal expansion conditions as well as by the stress and deformity of implanted wafer. SrTiO₃ bulk crystals implanted with different hydrogen implanted concentrations were used; the best results were obtained from 8x10¹⁶ cm⁻² dose. Since SrTiO₃ and Pyrex glass have very different thermal expansion coefficients, it is crucial to find the optimum anodic bonding temperature otherwise sample fracture occurs. The optimum temperature and applied voltage were 220 °C and 2000-3000 V, respectively. Bonded SrTiO₃ thin films of ~1 μ m thickness could then be separated from a bulk crystal by rapidly increasing the temperature (260 °C). We have also examined the properties of the SrTiO₃ thin films after bonding. Atomic force microscopy (AFM) was used to investigate the surface morphology of the top surface after the thin film bonding. The dielectric properties of the thin film are measured using near field microwave microscopy and capacitive techniques to determine both the room-temperature dielectric response and loss tangent of these films. Uniformities of permittivity and loss tangent of the thin film were examined by that measurement. Finally, the crystal structure of the thin film was investigated by X-Ray diffraction measurements. * Work supported by NSF Grant #DMR-0405145 and ONR Grant #N00014-03-1-0984

T10.21

Comparative Study of Effects of Annealing on Barium Strontium Titanate Thin Films with Different Deposition Methods. Venkataramanan Gurumurthy^{1,3}, Sathyaharish

Jeedigunta^{1,3}, Ashok Kumar^{2,3} and John W. Bumgarner⁴; ¹Electrical Engineering, University of South Florida, Tampa, Florida; ²Department of Mechanical Engineering, University of South Florida, Tampa, Florida; ³Nanomaterials and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; ⁴Center for Ocean Technology, University of South Florida, Tampa, Florida.

Barium Strontium Titanate (BST) thin films with a large dependence of permittivity on electric field, low losses, and high electrical breakdown fields are required for successful integration into tunable high frequency devices. The deposition methods employed and the post-deposition annealing have profound effect on the electrical properties of Barium Strontium Titanate thin films. This paper reports a comparative study of annealing effects on BST films by different deposition methods like Pulsed Laser Deposition (PLD), RF Magnetron Sputtering and sol-gel. The films were deposited on platinum-coated silicon substrates and as deposited samples are annealed at different parameters. It was found that the crystallinity of the films improved with the increase in annealing temperatures but the degree of crystallinity differed with each deposition technique. Based on the results obtained an analysis was made on the combined effect of different deposition techniques and annealing on the electrical properties of BST thin films.

T10.22

Effects of Chemical Mechanical Polishing on Barium Strontium Titanate Thin Films for Tunable Microwave Applications. Venkataramanan Gurumurthy^{1,3}, Subrahmanya

Mudhivarthi^{2,3} and Ashok Kumar^{2,3}; ¹Electrical Engineering, University of South Florida, Tampa, Florida; ²Department of Mechanical Engineering, University of South Florida, Tampa, Florida;

³Nanomaterials and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida.

Dielectric nonlinearity and low losses of Barium Strontium Titanate ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$) thin films with perovskite structure have made them prospective candidates for electric field tunable microwave devices. The performance of the Barium Strontium Titanate (BST) based devices is strongly dependant on the surface morphology and the dielectric properties of the thin film. In the present research, BST films were deposited on Pt/TiO₂/SiO₂/Si substrates using sol-gel process. Deposited BST films were characterized for their crystallinity, surface roughness and dielectric properties using x-ray diffraction (XRD) technique, Atomic Force Microscope (AFM) and Impedance analyzer respectively. Chemical Mechanical Polishing (CMP) was carried out on BST films in an effort to reduce the surface roughness. The film morphology before and after CMP was then investigated using AFM. The roughness of the BST films reduced from 5.4 nm to 1.5 nm. After fabricating a Metal-Insulator-Metal (MIM) capacitor using polished BST films, the dielectric properties were measured, and tunability of the device was compared with the capacitor structure using as-deposited (unpolished BST films). The main goal of this research work is to investigate the effects of CMP on the device performance in terms of tunability and Quality factor.

T10.23

Integrating Barium Titanate Based Optical Devices with Silicon and Amorphous Substrates. Matthew J. Dicken, Young-Bae Park, Jennifer L. Ruglovsky and Harry A. Atwater; Applied Physics, California Institute of Technology, Pasadena, California.

The deposition of thin film electro-optic materials such as barium titanate is an active area of research today. Thin film electro-optic devices have been studied in depth for films grown on bulk substrates such as magnesium oxide. Recently, attempts have been made to integrate thin film barium titanate with silicon compatible materials. Optical quality thin films of barium titanate integrated with CMOS processing techniques would allow for the design of smaller optoelectronic components. We have grown thin films of biaxially oriented barium titanate on silicon, silicon nitride, and various conductive substrates using ion beam assisted deposition (IBAD) of a template layer of magnesium oxide. The barium titanate films were deposited by molecular beam epitaxy using a shuttered growth technique. X-ray diffraction and transmission electron microscopy have been used to quantify the crystal orientation in the thin films. Piezoforce microscopy has been used to analyze the domain structure of the films grown on conductive substrates. The optical properties of these thin films will be measured using variable angle spectroscopic ellipsometry.

T10.24

Thermionic Emission Current in Metal-SrTiO₃ Contacts – An Approach Based on Ab-initio Band Structure Calculations. Herbert Schroeder and Phivos Mavropoulos; IEM am IFF and cni, Forschungszentrum Juelich GmbH, Juelich, Germany.

Leakage currents through metal/insulator/metal (MIM) thin film capacitor structures with high-permittivity or ferroelectric thin insulating films of perovskite-type mixed-oxides such as SrTiO₃ or (Ba,Sr)TiO₃ are an important issue because such materials are candidates for replacing the traditional low-k materials in CMOS integrated circuits, siliconoxide and siliconnitride, as capacitor dielectrics in advanced DRAM cells and as new gate materials in FETs, or may be used in switchable resistive memories (RRAM). One of the favoured mechanisms to interpret experimental leakage current curves (current vs. applied voltage) is the thermionic emission over a Schottky barrier at the cathode interface into the conduction band of the insulator. Assuming this interface limited mechanism, the so-called Richardson current equation for electron emission from the metal is used for the fitting of experimental data, including the Schottky barrier lowering by the image potential (Schottky-effect). Plotting $\log(\text{current})$ vs. $\sqrt{\text{applied voltage}}$, i.e. the so-called Schottky-plot, one can extract the optical dielectric constant of the insulator from the slope and, knowing the Richardson constant $A^*(m^*)$ ($=120 A/cm^2/K^2$ for free electrons, the asterisk indicates the use of an effective electron mass m^*), the zero-voltage barrier height can be found from the extrapolated absolute value at $V=0$. Many of the fits deliver an unphysical value for the optical dielectric constant (<1 !) and the determination of the barrier height depends on the knowledge of the respective effective mass. We have taken the band structure of the model material SrTiO₃, calculated from first principles, for which the conduction band minimum is formed by three bands with light and heavy electrons, so that the dispersion is highly anisotropic and the surfaces of constant energy are three-dimensional crosses (instead of ellipsoids). Using the usual approximation of an anisotropic, parabolic energy dispersion results in an effective mass of $m^*=1.98$. If we take this value for the calculation of the Richardson constant, and

neglect the anisotropic nature of the group velocity, the calculated current and thus the effective Richardson constant is reduced by more than a factor of four compared to the current when the full anisotropy of the band structure and of the group velocity are accounted for. These numbers are used as an input for model simulations of the leakage current [see Appl. Phys. Lett. 83, 4381 (2003)] and compared to results of calculations with literature data. Also the implications on the determination of the zero-voltage barrier height are discussed.

T10.25

Epitaxial Growth by Pulsed Laser Deposition of Dielectric $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ Thin Film on MgO, Intended for a Microwave Phase Shifter. Y. Y. Tse¹, P. M. Suherman², T. J. Jackson² and I. P. Jones¹; ¹Metallurgy and Materials, The University of Birmingham, Birmingham, United Kingdom; ²Electronic, Electrical and Computer Engineering, The University of Birmingham, Birmingham, United Kingdom.

Perovskite dielectric $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BSTO) thin films were grown on (001) MgO using a pulsed-laser deposition. The microstructure of in-situ and ex-situ annealed BSTO films were studied by X-ray diffraction and transmission electron microscopy (TEM). The films showed a cube on cube epitaxial relationship with $\langle 100 \rangle$ BSTO // $\langle 100 \rangle$ MgO. Cross-sectional TEM showed that the BSTO films were single crystals with a columnar structure and possessing smooth surfaces. All BSTO films were stoichiometric and no compositional difference between the different columns was found. Using high resolution TEM, the interfaces were seen to be atomically sharp, with misfit dislocations. Better crystallinity and fully strain relaxed ex-situ annealed BSTO films showed a 30% increase in tuneability compared with that of the in-situ annealed films fabricated at 10^{-1} mbar oxygen pressure. However, a similar trend was not observed in films deposited at 10^{-4} mbar oxygen pressure. The correlation between the deposition parameters, microstructure and the microwave properties of the BSTO thin film phase shifter is discussed.

T10.26

Strontium Oxide Template Monolayers by Surface Reactions of Metal-Organic Precursors with Si(100). Amalia Cuadra and Brian G. Willis; Chemical Engineering, University of Delaware, Newark, Delaware.

The crystalline structure of strontium titanate (SrTiO_3) consists of alternating sublayers of SrO and TiO₂. This talk presents an experimental approach for monolayer growth of a SrO template on a Si(100) 2x1 surface using strontium dipivaloylmethanate [$\text{Sr}(\text{dpm})_2$] and water precursors as the sources of Sr and oxygen, respectively. Metal organic chemical vapor deposition techniques have been investigated for nucleating SrO on Si(100) in the absence of an oxide interface layer by tuning the surface chemistry of the substrate to direct surface reactions of the strontium metal-organic precursor. Following the desorption of a protective chemical oxide layer, dissociative chemisorption of H₂O is carried out in UHV to hydroxyl terminate Si(100). Previous work has shown that metal oxide growth can be correlated to the concentration of hydroxyl groups on the silicon surface due to the facilitation of ligand exchange from the surface.¹ Furthermore, hydroxyl terminated surfaces initiate two-dimensional nucleation of the metal oxide while avoiding incubation periods common to the atomic layer deposition (ALD) of metal oxides. A novel solid source vaporizer has been developed to control the vaporization of the metal-organic precursor, $\text{Sr}(\text{dpm})_2$. Vapor delivery to the growth surface is carried out under steady vapor pressures while preventing thermal decomposition of the solid source. A monolayer growth scheme for SrO on Si(100) is made possible because of the successful integration of the solid source vaporizer with the reaction chamber. This talk focuses on the initial SrO nucleation layer. In-situ auger electron spectroscopy (AES), low energy electron diffraction (LEED), and reflection high energy electron diffraction (RHEED) are used to investigate the crystalline quality of the nucleation monolayers and the epitaxial orientation of SrO films on Si(100) 2x1 surfaces.¹ R.L. Puurunen, Applied Surface Science, 245, 6-10 (2005).

T10.27

Transient-Current Measurement of the Trap Charge Density at Interfaces of a Thin-Film Metal/Ferroelectric/Metal Structure. Lyuba A. Delimova¹, Igor V. Grekhov¹, Dmitri V. Mashovets¹, Sangmin Shin², June-Mo Koo³, Suk-Pil Kim³ and Youngsoo Park³; ¹Solid State Electronics Division, Ioffe Physicotechnical Institute Russian Academy of Sciences, St.Petersburg, Russian Federation; ²Materials and Devices Laboratory, Samsung Advanced Institute of Technology, Suwon, South Korea; ³Process Engineering Laboratory, Samsung Advanced Institute of Technology, Suwon, South Korea.

Traps localized at metal/ferroelectric (M/F) interfaces strongly affect the performance of metal/ferroelectric/metal (M/F/M) memory

elements with a thin ferroelectric film in the modern FeRAM. An interface charge connected with charging or recharging of these traps compensates or masks the real value of the ferroelectric polarization. Therefore, an ability to estimate the trap density at the M/F interfaces is of great importance since can yield valuable information on the basic memory property in the M/F/M structure. We have developed a method providing estimation of the trap density at interfaces of a depleted ferroelectric film (FF) with back-to-back Schottky barriers. The method is based on the recharge of interface traps under external bias pulse applied to M/F/M structure. The bias shifts the FF surface potential in respect to the Fermi level. Some portion of traps is shifted below the Fermi level, so holes from these traps are emitted to the valence band and swept out of the depletion region by the electric field, thus producing a transient current in the external circuit. We found the conditions where the transient current can be controlled by the trap recharge on the reverse-biased interface and have found the relation between the interface trap density and the measured transient current. The external bias applied to M/F/M structure shifts the potential of one Schottky barrier in the reverse, and the other one in the forward direction. So, changing the polarity of external bias, we can measure the trap density either at the top or bottom interface. Using the developed method, we have studied the trap charge density at interfaces of Pt/PZT/Ir(Ti/SiO₂/Si) and Ir/PZT/Ir(Ti/SiO₂/Si) capacitors. The bottom 100 nm-thick Ir electrode was produced by DC magnetron sputtering onto Ti(10nm)/SiO₂(200nm)/Si substrate at 200°C. PZT films of 80-100 nm in thickness were MOCVD-deposited onto this electrode. Post-growth annealing at 650°C for 3 min under oxygen atmosphere was done. The PZT parameters were: saturation polarization $P_S \sim 38 \mu\text{C}/\text{cm}^2$, remnant polarization $P_R \sim 23 \mu\text{C}/\text{cm}^2$, coercive field $E_C = 6 \times 10^4 \text{ V}/\text{cm}$. The trap density was found to be an order of magnitude less than the polarization of PZT film. Most of the samples show a close value of the trap charge at the top and bottom interfaces and symmetrical hysteresis loops. For some samples, however, a difference in the trap charge on the top and bottom interfaces is observed, that should result in an internal built-in electric field in the structure. Indeed, the hysteresis loop of these structures demonstrates a shift relative to zero along the voltage axis. The value of the shift agrees well with the observed trap charge asymmetry. The correlation between the symmetries of the interface trap charge and hysteresis loop indicates that the developed method provides a reasonable estimation of the interface trap density.

T10.28

Giant Electroresistance Effect in Ferroelectric Tunnel Junctions. Mikhail Ye Zhuravlev¹, Renat F. Sabirianov², Sitaram S. Jaswal¹ and Evgeny Y. Tsymbal¹; ¹Department of Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, Nebraska; ²Department of Physics, University of Nebraska-Omaha, Omaha, Nebraska.

We investigate electronic transport in ferroelectric tunnel junctions which represent two metal electrodes separated by an ultrathin ferroelectric barrier. Using a model which takes into account screening of polarization charges in metallic electrodes and direct quantum tunneling across a ferroelectric barrier we calculate the change in the tunneling conductance associated with the polarization switching. We find the conductance change of a few orders of magnitude for metallic electrodes with significantly different screening lengths [1]. This giant electroresistance effect is the consequence of a different potential profile seen by transport electrons for the two opposite polarization orientations. Our results are encouraging in view of potential applications of ferroelectric tunnel junctions as binary data storage media in nonvolatile random access memories. We hope that our theoretical predictions will stimulate experimental studies of the giant electroresistance effect in ferroelectric tunnel junctions. [1] M. Ye. Zhuravlev, R. F. Sabirianov, S. S. Jaswal, and E. Y. Tsymbal, cond-mat/0502109, to be published in Physical Review Letters.

T10.29

Device Parameter Dependence of Electrical Properties of Ferroelectric-Gate BLT/ITO TFTs. Yue Shen, Masaru Senoo and Eisuke Tokumitsu; Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

We previously reported a (Bi,La)₄Ti₃O₁₂(BLT)/ITO structure TFT which controls the accumulation and depletion of the ITO channel by the ferroelectric polarization. [1] We have used a ferroelectric BLT film as a novel gate insulator by which much larger charge density can be induced than the conventional gate insulators such as SiO₂. We also demonstrated that indium tin oxide (ITO) can be used as a channel, although it has a high carrier concentration (10^{18} - 10^{21} cm^{-3}), because the polarization of the ferroelectric films is as large as 10 - $30 \mu\text{C}/\text{cm}^2$. In addition, the BLT/ITO structure TFT has nonvolatile memory effect due to the ferroelectric gate insulator. Hence, the proposed device is promising for display applications, e-papers, and so on. In this paper, we report the details of device

parameter dependence of electrical properties of BLT/ITO TFTs. We discuss the dependence of the channel length, ITO film thickness, and the overlap length between the drain-source and the gate, on the electrical properties of the device. Ferroelectric thin film Bi_{3.35}La_{0.75}Ti₃O₁₂(BLT) was used as a gate insulators in this work, which was crystallized at 750°C for 30min. ITO channel was deposited by RF sputtering. To discuss the channel length dependence on the on-current of the device, we varied the channel length from 5 to 120 μm . Moreover, we have fabricated BLT/ITO TFTs which have the ITO channel thickness of 5, 10, and 35 nm to discuss the ITO channel thickness dependence. We have also examined the overlap length dependence. We have fabricated 9 kinds of devices which have the different channel length (L), channel width (W) and the overlap length (d). The overlap length between the source, drain and the gate is varied from -10 to 10 μm . At first, we have confirmed that the on-current of the device increases linearly as the channel length is decreased. A on-current of about 2.5 mA can be obtained for the device with L=5 μm and W=25 μm when $V_G=8\text{V}$, which corresponds to 0.1 mA/ μm . It is interesting to note that the trend of the on-current vs. channel length of the BLT/ITO TFTs is similar to that of Si-MOSFETs. When the ITO thickness is as thin as 10 nm, excellent transistor operation with large on/off current ratio is obtained. On the other hand, when the channel thickness is 35 nm, the observed on/off current ratio is as small as 1.1, which is probably because the maximum depletion width of the ITO channel with high carrier concentration is less than 35 nm. Finally, we demonstrate that the on-current of the device is independent on the overlap length. This means a matrix structure will be fabricated easily. [1] T. Miyasako, M. Senoo and E. Tokumitsu, Appl. Phys. Lett., 86, 162902 (2005)

T10.30

SBT/SSBT (Sm-Substituted SBT) Stacked Capacitor by Sol-Gel Technique for Ferroelectric-Gate Transistors. Hirokazu Saiki, Syahhibul Azwar and Eisuke Tokumitsu; Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

We previously reported that sol-gel derived Sm-substituted SBT (Sr_{0.5}Sm_{0.27}Bi_{2.2}Ta₂O₉, SSBT) has smaller remanent polarization (P_r , $\sim 2 \mu\text{C}/\text{cm}^2$) and spontaneous polarization (P_s , $\sim 4 \mu\text{C}/\text{cm}^2$) than conventional SBT (SrBi₂Ta₂O₉)^[1]. These characteristics are favorable for ferroelectric-gate transistors. However, the saturation characteristics of the P-E hysteresis loops of sol-gel derived SSBT films are inferior to those of SBT films. This causes a problem that the memory window of the metal-ferroelectric-insulator-semiconductor (MFIS) diode or FET using SSBT becomes small at small gate voltage. In this work, we have fabricated the SBT/SSBT stacked capacitors to solve this problem. The objective of this work is to obtain the ferroelectric film which has P-E hysteresis loops with good saturation characteristics as in the conventional SBT, and small remanent and spontaneous polarizations as in the SSBT. The stacked SBT/SSBT capacitors were fabricated on Pt/Ti/SiO₂/Si substrates by following procedure: (1) sol-gel solution (SBT or SSBT) was spin-coated on Pt bottom electrodes (BE), (2) samples were dried at 240°C for 10 minutes, and then (3) crystallized at 750°C for 30 minutes in oxygen ambient. (4) These steps were repeated for 3 times. (5) Next, Pt top electrodes (TE) were deposited. (6) Finally, the capacitors were annealed at 750°C for 10 minutes in oxygen ambient again. We fabricated two kinds of samples by changing the order of the SBT or SSBT layers; TE/SSBT(40nm)/SBT(80nm)/BE and TE/SBT(80nm)/SSBT(40nm)/BE capacitors. Pt/SBT/Pt and Pt/SSBT/Pt capacitors were also fabricated for comparison. We have found that X-ray diffraction peaks from c-axis oriented crystallites of TE/SSBT(40nm)/SBT(80nm)/BE capacitor is weak and (115) diffraction peak is dominant, which is similar to the Pt/SBT/Pt capacitor. On the other hand, TE/SBT(80nm)/SSBT(40nm)/BE capacitor has strong c-axis diffraction peaks, similar to the Pt/SSBT/Pt capacitor. We have also found that the P_r value of TE/SBT(80nm)/SSBT(40nm)/BE capacitors ($\sim 2 \mu\text{C}/\text{cm}^2$) is smaller than that of TE/SSBT(40nm)/SBT(80nm)/BE capacitor ($\sim 5 \mu\text{C}/\text{cm}^2$). These results indicate that the control of orientation and electrical characteristics is possible by selecting the bottom layer of SBT-based ferroelectric materials. This work was supported by a Grant-in-Aid for Scientific Research (No.15360157), from the Ministry of Education, Science, Sports, and Culture. [1] H. Saiki and E. Tokumitsu, Mat. Res. Soc. Proc. 784, C9.8/E9.8 (2004).

T10.31

Electrical Properties of (Pb_{1-x}Ba_x)ZrO₃ Ferroelectric Films with Metal/Ferroelectric/Metal (MFM) and Metal/Ferroelectric/Insulator/Semiconductor (MFIS) Structures. Hung-Yao Chen and Jenn-Ming Wu; Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan.

The metal/ferroelectric/insulator/semiconductor field effect transistor (MFIS-FET) has attracted much attention due to the advantages of

possessing a nondestructive read-out (NDRO) process and its capability of integration with Si-based memory technology. For the proper operation of MFIS structure, both structural and electrical properties of the ferroelectric films and the insulator layer should be optimized. In this work, $(\text{Pb}_{1-x}\text{Ba}_x)\text{ZrO}_3$ ($0.2 \leq x \leq 0.4$) (PBZ) ferroelectric films were deposited on Pt/Ti/SiO₂/Si and SrTiO₃/Si stacks (or other insulator/Si stacks) by sol-gel and spin-coating process. After heat treatment at 600-750 degree C in O₂ atmosphere, PBZ films showed good crystallinity and ferroelectric properties. The electrical properties of PBZ films were derived from MFIS capacitor structures for the capacitance-voltage (C-V) measurement, and from metal/ferroelectric/metal (MFM) capacitor structure for the polarization-electric field (P-E) measurement. The Pt/(Pb_{0.75}Ba_{0.25})ZrO₃/Pt capacitor had a hysteresis loop with remnant polarization of 5 $\mu\text{C}/\text{cm}^2$ and coercive field of 153 kV/cm at an applied field of 667 kV/cm, when the PBZ films was annealed at 650 degree C. This large coercive field is helpful to obtain a larger memory window in the MFIS structure. However, the memory window of Pt/(Pb_{0.75}Ba_{0.25})ZrO₃/SrTiO₃/Si structure was only 0.4 V at the operation voltage of 2 V. As the operation voltage increased above 2 V, the C-V characterization showed strong trapping behavior. It implied that the insulator/Si interface should be improved. The electrical and structural properties of capacitors on different insulator stacks and the effect of Pb/Ba ratio on PBZ films will be reported.

T10.32

Ferroelectric Monolayer Newly Developed by Vacuum Evaporation. Shuichiro Kuwajima¹, Kenji Ishida², Toshihisa

Horiuchi², Hirofumi Yamada² and Kazumi Matsushige²;
¹Nanotechnology Support Project, Kyoto University, Kyoto, Japan;
²Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan.

Regarding representative organic ferroelectric material such as polyvinylidene fluoride (PVDF) having the electric dipole moment which is perpendicular to the molecular chain, it is important for appearance of the ferroelectric property to control their molecular conformation, orientation and crystal structure. It is also expected eventually to develop novel molecular devices by accessing the dipoles per molecule and/or per monomer unit in the future. However, uncertainties have remained about the ferroelectricity with low dimensional arrangement of the dipoles. Though two-dimensional ferroelectricity about the Langmuir-Blodgett bilayer film of the copolymer with trifluoroethylene P(VDF/TrFE) was already reported, the elements taking the discussion complicated include two points; 1) the perpendicular direction of the dipole moment to substrate is disadvantageous for polarization reversal because of an interaction with substrate, 2) the contamination by the wet process is unavoidable. In this research, therefore, we try to fabricate the self-assembled monolayer of vinylidene fluoride (VDF) oligomer having finite molecular chain length by the new dry process, and to develop two-dimensional ferroelectric film with the dipoles parallel to substrate. The monolayer of VDF oligomer, CF₃-(CH₂CF₂)_n-I (n=12), was fabricated on a silicon wafer substrate by vacuum evaporation with well controlling of the substrate temperature and the deposition rate. In the X-ray reflectivity measurement for detail estimation of the layer structure, the homogeneous single molecular film with three layers structure, $I[0.31\text{nm}]/\text{CF}_3\text{-(CH}_2\text{CF}_2\text{)}[2.87\text{nm}]/\text{silicon}$, was observed, which indicates that the VDF oligomer molecules align perpendicular to the substrate and the iodine atoms at the end of molecule are arranged to the film surface. It is, furthermore, found that the crystal structure in the molecular packing direction corresponds to the ferroelectric phase (Form I) of PVDF by the in-plane X-ray diffraction. These results show the newly developed two-dimensional-sheet-like dipole arrangement, in which appearance of the novel ferroelectricity depending on lateral electric field is expected.

T10.33

Modulating the depletion layer of Si semiconductor by organic ferroelectric dipole. Kenji Ishida¹, Hiroshi Uemura¹,

Shuichiro Kuwajima², Toshihisa Horiuchi¹, Hirofumi Yamada¹ and Kazumi Matsushige¹;
¹Electronic Science and Engineering, Kyoto University, Kyoto, Japan;
²Nanotech Support Program, Kyoto university, Kyoto, Japan.

Ferroelectric films on Si have been widely studied to develop metal-ferroelectric silicon field effect transistors (MFS-FETs) as next generation non-volatile memory with 1T type. However, the fabrications of ideal MFS structure using typical inorganic ferroelectrics, such as Pb(Zrx, Ti1-x)O₃ and SrBi₂Ta₂O₉(SBT), are difficult, because the film fabrication on Si at high temperature of 400-600°C by metal oxide chemical vapor deposition(MOCVD) process causes a formation of needless SiO₂ layer and intermixing of inorganic elements to Si surface. However, the clear interface between ferroelectrics and semiconductors have been strongly desired to

directly modulate depletion and inversion layers of Si semiconductor by ferroelectric dipoles. Here, we demonstrate a novel approach to overcome these problems by using ferroelectric organic molecules, vinylidene fluoride oligomers; CF₃-(CH₂CF₂)_n-I (n=10-29), which can be deposited on Si at low temperature in high vacuum. The VDF oligomer films of 5-200nm were fabricated on heavy- and low-doped Si substrates by vacuum deposition. Then, Al upper electrode was deposited on VDF/Si. A polarization hysteresis loop of Al/VDF/Si was clearly observed with similarly to that of Al/VDF/Al device. Furthermore, the high frequency (1MHz) C-V curve indicates the change of capacitance depending on sweep direction of applied DC voltage. The poled VDF oligomer can be modulate the depletion layer of low-doped Si by two stable polarization states(up and down), and the ON/OFF ratio of the capacitance is 2:1. The organic/inorganic hybrid MFS structure will open a new way for developing the MFS-FETs.

T10.34

Nonlinear Electrical Dipolar Switching at Single Molecular Scale. Jaewu Choi, G. S. Khara and Youngsik Song; Electrical and Computer Engineering, Wayne State University, Detroit, Michigan.

At the single molecular scale (less than 0.2 nm x 0.2 nm x 0.98 nm), the nonlinear electrical dipolar switching behavior from crystalline two-monolayer polyvinylidene fluoride films was measured using a scanning tunneling microscope (STM). The atomic structure of the polymer chain was clearly imaged by the STM. The nonlinear switching behavior at the single molecular scale appears as the hysteresis in the tunneling current-voltage relationship with switching onset voltage of 0.19 V/monomer. The nonlinear dipolar switching behavior at the single molecular scale has many potential applications including single molecular scale switching devices and re-writable nonvolatile memories.

T10.35

Phase-Field Simulation of Ferroelectric Domain Switching in Polycrystalline Bulk and Thin Films. Samrat Choudhury, Yulan Li and Long Qing Chen; Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

Roles of grain orientation, grain boundary and grain size on domain structures and polarization switching in polycrystalline ferroelectric materials are studied using phase-field simulations. Hysteresis loops are obtained for PZT single crystal, bi-crystal and polycrystal bulk and thin films, and the differences in their coercive fields are examined. It was found that the grain boundary provides a primary site for nucleation of new domains during domain switching in bulk polycrystals. The effect of the grain boundaries on the polarization distribution, domain structure and switching is studied by varying the ferroelectric transition temperature across the boundaries. The effect of PZT composition, substrate constraint and texture on the domain switching mechanism in PZT thin film are also investigated. The results will be compared with experimental measurements of single crystals and polycrystals.

T10.36

Field induced morphology transition of 90° domain structure of PbZr_{0.2}Ti_{0.8}O₃ film on Si substrate. Zhengkun Ma¹, J.

Slutsker³, J. Ouyang¹, F. Zavaliche², T. Zhao², R. Ramesh², J. Melngailis¹ and A. Roytburd¹;
¹Materials Research Science and Engineering Center, Department of Materials Science and Engineering, University of Maryland at College Park, College Park, Maryland;
²Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, California;
³Materials Science and Engineering Laboratory, Metallurgy Division,, National Institute of Standards and Technology, Gaithersburg, Maryland.

90° in ferroelectric thin films have cellular or hierarchical structures depending on a film substrate misfit. A cellular structure is usually formed in PZT films on a Si substrate. In this presentation we show that by locally applying an electric field through AFM tip, the domain morphology can be transformed from cellular architecture to hierarchical one in a high quality epitaxial PbZr_{0.2}Ti_{0.8}O₃ film grown on Si substrate. The Phase field modeling of dependence of 90° domain architectures on electric field gives an adequate explanation of the result observed. Electro-optical and piezoelectric applications of the morphology transition are discussed.

T10.37

Probing the piezoelectric effect in PZT thin films using time-resolved synchrotron x-ray microdiffraction.

Dal-Hyun Do¹, Alexei Grigoriev¹, Dong Min Kim¹, Chang-Beom Eom¹, Paul G. Evans¹ and Eric Dufresne²;
¹Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin;
²Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

Pb(Zr,Ti)O₃ (PZT) thin films are of great interest for applications including electronic and micromechanical devices. The domain evolution that occurs during polarization switching in ferroelectric materials is fundamentally interesting and also has an important role in determining the electromechanical properties of these materials. Synchrotron microdiffraction is a structural probe that allows us to observe the local piezoelectric response and polarization switching in PZT thin film capacitors directly by measuring the change in the PZT lattice constant in an applied electric field. The 400 nm-thick PZT (001) films were grown epitaxially on (001) SrTiO₃ substrate with SrRuO₃ bottom and top electrodes. The piezoelectric coefficients measured with bipolar electric field pulses were different for two opposite electric field directions. The difference in piezoelectric response can be explained with a model based on the existence of polarization domains that do not switch ferroelectric polarization. This effect leads to a reduction in the piezoelectric response and a broadening of the x-ray reflections of PZT. With electric field pulses of a single sign the non-switching domains were eventually poled and the piezoelectric coefficients were the same for both electric field polarities.

T10.38

Structural and Ferroelectric Properties of Pr doped SrTiO₃ thin films Prepared by Pulsed Laser Deposition. M. P. Cruz^{1,2}, Y. H. Chu², A. C. Duran¹ and J. M. Siqueiros¹; ¹Centro de Ciencias de la Materia Condensada (CCMC)-UNAM, Ensenada, B.C., Mexico; ²Department of Materials Science and Department of Physics, University of California, Berkeley, California.

SrTiO₃ is a material with a perovskite structure extensively used as substrate for the epitaxial growth of thin films with compatible lattice parameters. This material presents a structural instability at low temperatures associated to a ferroelectric transition that has not been observed due to quantum fluctuations. Nevertheless, when SrTiO₃ ceramics are doped with Pr, ferroelectric behavior is observed at room temperature. In this work, ceramics of this material were used to grow thin films by pulsed laser ablation, using the 248 nm wavelength radiation of a KrF excimer laser, on Pt(111)/Ti/SiO₂/Si and SrRuO₃(111)/SrTiO₃ substrates. The films were deposited at different oxygen pressures (0-600mTorr) and temperatures (room-600°C) and heat treated in an air at a 750°C to improve their structural properties. XRD, TEM and PFM techniques were used for the microstructural and piezoelectric characterization. Hysteresis loops were obtained demonstrating ferroelectricity after SrRuO₃ top electrodes were deposited on the films. The microstructural results and ferroelectric properties of the Sr_{1-x}Pr_xTiO₃-electrode system were correlated to optimize the system performance. Preliminary results show that the ferroelectric behavior of the ceramic is enhanced in the films. Ferroelectricity may be explained by a distortion of the oxygen octahedron provoked by the substitution of Pr in the ceramics, and enhanced by stress in the film form. These are preliminary but encouraging results that may lead to interesting theoretical and applied research in this material. This work was partially supported by grants of DGAPA-UNAM, Proj. IN100903 and CoNaCyT Proj. No. 47714-F

T10.39

Ferroelectric Domain Structure in Epitaxial BiFeO₃. M. P. Cruz^{1,2}, F. Zavaliche¹, P. Shafer¹, Y. H. Chu¹, T. Zhao¹, S. Y. Yang¹, R. R. Das³, D. M. Kim³, C. B. Eom³ and R. Ramesh¹; ¹Department of Materials Science and Department of Physics, University of California, Berkeley, California; ²Centro de Ciencias de la Materia Condensada (CCMC)-UNAM, Ensenada, B.C., Mexico; ³Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin.

A comparison of the ferroelectric domain structure in BiFeO₃ films grown by 90° off-magnetron sputtering, pulsed laser deposition (PLD) and metal-organic chemical vapor deposition (MOCVD), is presented. For this study, both out-of-plane and in-plane piezoelectric force microscopy (PFM) data were used as well as the phase, amplitude and images. Scans were taken along the principal crystallographic directions to determine the polarization direction. The domain pattern in epitaxial films grown by sputtering on miscut SrTiO₃(001) substrates evolves from a mosaic to a stripe-like pattern as the substrate miscut angle is increased. In addition, the number of dominant polarization variants decreases from 4 to 2. In the case of epitaxial films grown by PLD and MOCVD, mainly 4 polarization variants were observed as well, but the characteristic domain size is smaller and different morphologies were observed. This work has been supported in part by ONR under a MURI program, and NSF-FRG under awards #DMR-0313764, ECS-0210449, DMR-0103354. We acknowledge the support of David & Lucile Packard Fellowship (C.B.E.).

T10.40

Electrical Characterization of Ferroelectric Barium Strontium

Titanate Thin-Films Fabricated by Pulsed Laser Deposition Using Contact-Mode AFM, Surface Potential Imaging and Piezoresponse AFM. Angela L. Campbell¹, Rand R. Biggers¹, Guru Subramanyam² and Bonnie D. Riehl¹; ¹Air Force Research Laboratory/Materials Directorate, USAF Wright-Patterson AFB, WPAFB, Ohio; ²Department of ECE, University of Dayton, Dayton, Ohio.

A series of nanostructured ferroelectric thin-films of barium strontium titanate were fabricated on La(AlO₃), Pt/La(AlO₃) and Pt/TiO₂/Ti/SiO₂/Si substrates by a pulsed laser deposition system with real-time in-situ process control. Pulsed laser deposition parameters were controlled during nanostructured thin-films for use in the development of high frequency tunable microwave devices and other applications. Thin-films were grown at the same substrate temperature and energy density as the oxygen ambient partial pressures were varied in steps from 19 mT through 1 T. Structural and electrical characterization were performed using contact-mode AFM, surface potential imaging and piezo-response AFM. Contact-mode AFM showed that grain size and morphology varied as a function of oxygen ambient partial pressure, substrate type and buffer layer. Surface potential imaging demonstrated that X-patterns written by applying a voltage to thin-films with an AFM tip in contact mode are electrically switchable. Piezo-response measurements were performed to observe domain structure as a function of oxygen partial pressure, grain size and grain morphology.

T10.41

Real Information Recording in Ferroelectric Data Storage Medium with Memory Density of 1 Tbit/inch². Tanaka Kenkou, Hiranaga Yoshiomi and Cho Yasuo; Research Institute of Electrical Communication, Tohoku University, Sendai, Japan.

We have developed ultra high-density ferroelectric data storage system that is expected to be next generation memory device with large capacity. Writing is performed by applying relatively large voltage pulses to a ferroelectric medium and by switching the local polarization direction as an information bit using conductive cantilever (typical tip radius is not more than 30 nm). Scanning Nonlinear Dielectric Microscope (SNDM), which is the purely electrical method for observing polarization distribution of ferroelectric material, was used for detecting the recorded bit [1]. UP to now, the simple closed pack inverted domain dot array with the density of 1.5 Tbit/inch² was successfully formed on Congruent Single-Crystal LiTaO₃ (CLT) thin plate [2]. However actual stored information is randomly distributed. Therefore, real data storage with the density of 1 Tbit/inch² has not been performed yet. In this study, we propose new method to achieve the real information recording with the density of 1 Tbit/inch². At first we fabricated the thin CLT medium (thickness is ≈ 40 nm) with good homogeneity. This is the most basic step needed to form nano size dots with 25.6 nm bit spacing and to achieve 982 Gbit/inch² recording density with low bit error. Next, we investigated optimum value of pulse voltage. Because, the dot size varies according to the environmental polarization direction. Therefore, to keep the bit size constant (25.6 nm), we individually determined the pulse height for each dot as a function of the combination of the surrounding data bits polarities. Then, the actual information storage at the density of 1 Tbit/inch² was successfully achieved with small bit error rate of 1.8 * 10⁻². [1] Y. Cho, A. Kirihiro and T. Saeki : Rev. Sci. Instrum. 67, 2997 (1996.6) [2] Y. Cho, K. Fujimoto, Y. Hiranaga, Y. Wagatsuma, A. Onoe, K. Terabe and K. Kitamura : Appl. Phys. Lett. 81, 4401(2002)

T10.42

10Tbit/inch² Ferroelectric Data Storage with Offset Voltage Application Method. Sunao Hashimoto and Yasuo Cho; Research Institute of Electrical Communication, Tohoku University, Sendai, Japan.

Ferroelectrics are expected as one of the next generation ultra-high density data storage media. Already, we had succeeded in forming ferroelectric domain dot arrays with 1.5 Tera-bit/inch² areal density in congruent LiTaO₃ (CLT) thin single crystal film using scanning nonlinear dielectric microscopy (SNDM) domain engineering system. [1] This SNDM is the purely electrical method for observing polarization distribution of ferroelectric materials with the resolution of sub-nanometer range. And ferroelectric domain was inverted by applied voltage pulse between probe tip of SNDM and bottom electrode of the specimen. This time, using new domain stabilizing method, we made the great progress on the memory density of ferroelectric data storage, that is 10.1 Tera-bit/inch² areal density has been successfully achieved. Details are described as follows. Keeping the inverted ferroelectric domain stably requires stabilizing time, which is voltage-keeping time until inverted domain is stabilized. At the thick specimen, stabilizing time is about 1 sec. [2] As the thickness of specimen gets thinner, the required stabilizing time also becomes shorter. [3] For the very thin specimen, very short stabilizing

time is also needed not to switch the polarization back. Normally, inverted domain was stabilized with the surface voltage generated by the injection charges or accumulated charges supplied from the tip. To emphasize this effect positively by artificial way, the DC bias voltage was applied following the pulse voltage. Using this offset voltage application method, required pulse amplitude and duration to switch the domain were both decreased extremely. Additionally, using this method, it became possible to invert smaller domain with diameter less than 10 nm. Finally, by applying this new method, we have succeeded to form domain dot arrays with 10.1 Tera-bit/inch² areal density, representing the highest memory density for rewritable data storage reported to date. [1] Y. Cho et al., Appl. Phys. Lett. **81**, 4401 (2002) [2] S. Kim et al., J. Appl. Phys. **90**, 2949 (2001) [3] K. Fujimoto et al., Appl. Phys. Lett. **83**, 5265 (2003)

T10.43

Analysis of imprint mechanism in ferroelectric memory using molecular-dynamics simulation. Hiromu Miyazawa¹, Yasuaki

Hamada¹, Takamitsu Higuchi¹, Takeshi Kijima¹, Eiji Natori¹, Tatsuya Shimoda¹, Masato Yoshiya² and Tamio Oguchi³; ¹TPRC, EPSON, Fujimi-machi, Nagano-ken, Japan; ²JFCC, Nagoya, Aichi-ken, Japan; ³ADSM, Hiroshima University, Higashi Hiroshima, Hiroshima-ken, Japan.

We studied imprint mechanism of ferroelectric memory based on oxygen-vacancy screening (OVS) model. According to this model, oxygen vacancies in ferroelectric-oxide thin film are accumulated at electrode interfaces to screen electric polarization and induces offset-bias field to the system. This model is not the same as the conventional defect dipole alignment (DDA) model, because in our model oxygen vacancy itself, which acts as positively-charged particle, moves toward negatively-polarized side of ferroelectric film. We estimated this offset-bias field has comparable strength to coercive field, 100kV/cm, of conventional lead zirconate titanate (PZT) films with the following condition: (i) charge imbalance caused by oxygen vacancy (2 minus ion) at electrode interfaces is around 1%, (ii) the thickness of that imbalance region is around 1nm, and (iii) relative dielectric constant of ferroelectrics is around 1000. We also suggested that this accumulation of oxygen vacancies induces diode like behavior. Oxygen-vacancy, i.e., oxygen-ion dynamics and its diffusion constant was calculated using molecular dynamics (MD) simulations for PZT and our imprint model was examined. For 2mol% oxygen vacancies we obtained reasonable oxygen diffusion length of 0.4pm/sec at 150 centi degree. This diffusion length corresponds to 1.0nm/1000hour, which can well explain our imprint mechanism model. These analysis indicate that material design and development of deposition process which intend to suppress the oxygen vacancy at electrode interfaces enable us to improve the imprint properties.

T10.44

Dynamics of polycrystalline macro-domains in ferroelectric films. Yahin Ivry¹, Vera Lyahovitsky¹, Ilya Zon¹, Ellen Wachtel², Igor Lubomirsky¹ and Alexander Roytburd³; ¹Materials & Interfaces, Weizmann Institute, Rehovot, Israel; ²Chemical Research Support, Weizmann Institute, Rehovot, Israel; ³Materials Science and Engineering, University of Maryland, College Park, Maryland.

It was recently demonstrated (Adv. Mater. in press) that 40-80 nm ferroelectric grains in 200-1000 nm thick self-supported films of BaTiO₃ may undergo self-organization into polycrystalline macro-domains, i.e., regions in which the grains closely align their c-axes in one direction. These regions may, in turn, form macroscopic (hundreds of microns), periodic structures with a multilevel hierarchy that combines two differently shaped regions: linear and wedge-ordered. The current research concentrated on studying the dependence of the macro-domain hierarchy on temperature and on applied electric field. It was found that with increasing temperature, wedge-ordered regions grow at the expense of the linear regions, until the latter disappear completely. This process is fully reversible and can be easily tracked by monitoring birefringence, which is a characteristic feature of the wedge-ordered regions. The characteristic time associated with these changes in the polycrystalline macro-domains is on the order of a few seconds, which indicates that they are capable of rapid adaptation to external conditions. Changes in the macro-domains can explain a set of highly unusual properties of the self-supported ferroelectric films. a) Upon heating, the shape of the films undergoes reversible changes, first at the temperature at which the linear regions disappear completely (T_l) and then above the cubic-to tetragonal phase transition (T_c), which may be as high as 160 oC. b) Despite the relatively small grain size, the films possess a dielectric constant of more than 2500. No maximum in the temperature dependence of the dielectric constant versus temperature was observed. Instead, the first derivative of the dielectric constant versus temperature is linear between T_l and T_c c) As measured by the Chynoweth method, some of the films exhibit a pyroelectric coefficient which may exceed 100 times that of a single BaTiO₃ crystal. This enhanced pyroelectric current reaches a maximum at T_l and quickly

decreases below and above this temperature, which indicates that this effect is directly linked to the dynamic rearrangement of the macro-domains. Analysis of the time dependence of the pyroelectric current confirmed that there are two contributions to the pyroelectric effect with different time constants. A theory explaining this feature is presented. Our experimental data and their theoretical description strongly suggest that the behavior of polycrystalline films containing ordered macro-domains can be controlled. Unconventional electrical properties, such as an enhanced pyroelectric effect, make these materials very promising for a large variety of devices ranging from infrared detectors to microwave resonators.

T10.45

Subtle morphological change of step-flow grown SrRuO₃ thin films. Ho Nyung Lee¹, Mina Yoon¹, Zhenyu Zhang¹, Wei Hong², Zhigang Suo², Matthew F. Chisholm¹, Sergei Kalinin¹, Hans M. Christen¹ and Douglas H. Lowndes¹; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Atomically-flat conducting buffer layers grown on chemically uniform single-stepped substrates could provide an ideal starting point for the growth of atomically-flat oxide heterostructures, including thin films, multilayers, and superlattices. Recently, we found that the surface of SrRuO₃ is thermally unstable under reducing conditions; therefore, the SrRuO₃ should be kept in relatively high oxygen background pressure when it is subjected to high temperatures. Here we report a combined experimental and theoretical study of heteroepitaxial growth of strained SrRuO₃ films on vicinal substrates, emphasizing the subtle morphological change of SrRuO₃ grown under various growth conditions. In order to study the step-flow instability of SrRuO₃, we have grown SrRuO₃ thin films by pulsed laser deposition on (001) SrTiO₃ substrates while systematically varying the miscut angle of the substrate, deposition flux, thickness, and temperature and investigated the resulting topography by atomic force microscopy (AFM) and the interface with other oxide films by Z-contrast scanning transmission electron microscopy. In combination with a theoretical model of persistent step flow, we finally construct a morphological phase diagram, delineating the regime of step flow from regimes of step bunching and island formation. In particular, we show that the deposition flux, temperature, and substrate miscut value yielding persistent step flow are strongly cross-correlated and cannot be chosen independently. In addition, we also find that there is a critical thickness at which step bunching occurs, depending primarily on the substrate miscut angle and deposition flux. Based on this systematic investigation, we have further investigated oxide heterostructures grown on atomically-flat SrRuO₃ electrodes. As an example, our work on piezo-response AFM for high-quality ferroelectric PbZr_{0.2}Ti_{0.2}O₃ thin films grown on SrRuO₃ indicates that it is even possible to write ferroelectric domains with sizes below 40 nm, the smallest ferroelectric domain size reported to date. This study on step-flow instability thus provides not only the basic information on the growth behavior of SrRuO₃, but also yields the information needed for the fabrication of functional materials with unprecedented quality. 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.

T10.46

First-Principles Studies of Phase Stability and the Neutral Atomic Vacancies in LiNbO₃, NaNbO₃ and KNbO₃.

Akio Shigemi and Takahiro Wada; Materials Chemistry, Ryukoku University, Otsu, Japan.

Recently, lead-free piezoelectric ceramic materials have come under the spotlight from the viewpoint of environmental protection. ANbO₃ (A = Li, Na and K) has been studied as a candidate for a lead-free piezoelectric material that can replace Pb(Zr,Ti)O₃ (PZT). It is known that LiNbO₃ and KNbO₃ show piezoelectricity and NaNbO₃ show antiferroelectricity at room temperature. In addition, LiNbO₃ have the distorted Perovskite (P)-type structure called LiNbO₃(LN)-type which is similar to Ilmenite(I)-type structure. LiNbO₃ does not change crystal system under atmosphere pressure, but NaNbO₃ and KNbO₃ show a number of structural phase transitions between a paraelectric cubic phase and a ferroelectric rhombohedral phase. In this research, we overall evaluated the formation enthalpies and the formation energies of neutral vacancies in LiNbO₃[1], NaNbO₃[2] and KNbO₃[3] using a plane-wave pseudopotential method[4] within a density functional formalism. In obtaining the formation enthalpies of all ANbO₃ phases, the model structures of these phases were constructed based on experimental crystal structural data (LiNbO₃: P, LN, and I, NaNbO₃: *Pm3m*, *P4/mbm*, *Ccmm*, *Pnmm*, *Pbma*, and *R3c*, and KNbO₃: *Pm3m*, *P4mm*, *Bmm2*, and *R3m*), in order to evaluate phase stability for all the ANbO₃ crystal phases appeared under atmospheric pressure. The LiNbO₃ phase with the LN-type structure was confirmed to have the

lowest enthalpy of formation. The NaNbO_3 and KNbO_3 phases with the lowest symmetry were found to have the lowest enthalpy of formation. The calculation of the formation energies of A, Nb or O vacancies in ANbO_3 including the effects of the surrounding chemical potentials was carried out to determine which type of neutral atomic vacancy was most likely to form when ceramic ANbO_3 was sintered under various atmospheres. Calculations for atomic vacancies were performed using supercells with 120 atoms for LiNbO_3 and with 40 atoms for NaNbO_3 and KNbO_3 . The formation energy of a A vacancy was found to be the lowest under an oxidizing atmosphere and that of an O vacancy was found to be the lowest under a reducing atmosphere. The formation energy of a Nb vacancy was the highest under both oxygen-rich and -poor conditions. These results are in agreement with the empirical rule that B site defects in perovskite-type oxide do not exist. Additionally, these results are discussed on the basis of the band structure of ANbO_3 . This work was partially supported by a grant based on the High-Tech Research Center Program for private universities from the Japan Ministry of Education, Culture, Sports, Science and Technology. [1] A. Shigemi and T. Wada, *Jpn. J. Appl. Phys.*, to be submitted. [2] A. Shigemi and T. Wada, *Jpn. J. Appl. Phys.* **43** (2004) 6793. [3] A. Shigemi and T. Wada, *Jpn. J. Appl. Phys.*, submitted. [4] V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatkaya and R. H. Nobes, *Int. J. Quantum Chem.* **77** (2000) 895.

T10.47

Piezoelectric Boron Nitride Nanotube. Jie Hu, Zhaoyu Wang and Min-Feng Yu; Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Boron Nitride (BN) nanotube, besides possessing unique structures and excellent mechanical properties, was also found to be potentially piezoelectric according to recent theoretical studies. We report here, for the first time, the experimental study of the piezoelectric properties of BN nanotube with Piezoresponse Force Microscopy (PFM). The piezoelectric response from individual BN nanotube under various conditions, for example, under different electric bias and different mechanical stress, was systematically investigated. It was found that the effective piezoelectric constant of BN nanotube along the radial direction is in the order of 1 pm/V, and increases with the application of positive DC bias. The piezoelectric constant, however, decreases with the increase of contact forces between PFM tip and BN nanotube, and decreases even faster when the BN nanotube is under a positive DC bias. The hysteresis loop of PFM phase acquired from BN nanotube shows a typical response from a pure piezoelectric. Our results, thus, not only verify the theoretical prediction on the existence of piezoelectricity in BN nanotube, but also imply its potential applications as novel nanotube devices, such as high sensitivity strain sensor and high work density actuators.

T10.48

Characterization of Lead Zirconate Titanate Nanocrystal Powders Prepared by a Hydrothermal Method. Lingjuan Che, Jinrong Cheng, Chao Chen and Zhongyan Meng; Shanghai University, Shanghai, China.

In this paper, lead zirconate titanate (PZT) nanocrystalline particles were synthesized from $\text{Pb}(\text{CH}_3\text{COOH})_2 \cdot 3\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ at temperatures in the range of 120-220°C for 2-50 hours. The KOH or NaOH solution was utilized as mineralizer. The influences of hydrothermal conditions (including starting materials, reaction temperature and time) on the crystal structure and the morphology of PZT particles were investigated systematically. The X-ray diffraction (XRD) results revealed that a typical perovskite PZT was obtained, and both tetragonal and rhomboedral phases coexist in the powder. The transition electron microscopy (TEM) observed that the morphology of PZT nanoparticles was depended on starting materials, and the particle size was about 100 nm. The nucleation of PZT initiated in (101) surface, resulting in faceted platelet morphology. The growth of particles proceeded with further dissolution and precipitations on existing (101) surface, and large cuboidal particles were formed subsequently. The synthesis temperature of 220°C and reaction time of 5 hours combining a mineralizer concentration of 5M have been identified as the optimized hydrothermal conditions.

T10.49

Synthesis and Controlling Shapes of BST Nanoparticles via Polymer Template Method. Shinji Shibamoto^{1,2}, Tooru Kinoshita² and Kikuo Okuyama³; ¹Japan Chemical Innovation Institute, Higashi-Hiroshima, Hiroshima, Japan; ²New Technology Research Lab., Sumitomo Osaka Cement Co., Ltd., Funabashi, Chiba, Japan; ³Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima, Japan.

Barium Strontium Titanate (BST; $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$) nanoparticles are suitable for microelectronic device component such as multilayer

ceramic capacitors and dielectric layer in dynamic random access memories (DRAM) due to a high dielectric constant and thermal stability. To achieve the designed properties of BST films, the particles need to be controllable of stoichiometry and nanostructure. We have studied the synthesizing of nanoparticles using polymer templates for the purpose of size and shape controlling of nanoparticles in addition to a controlling of the stoichiometry. Recently, we have succeed in the synthesis of monodisperse BST ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$) nanoparticles by using this technique. We also applied to synthesize BST films to use this technique. The properties of the particles and films will be presented. This work was supported by the New Energy and Industrial Technology Development Organization (NEDO)'s Nanotechnology Materials Program - Nanotechnology Particle Project based on fund provided by the Ministry of Economy, Trade, and Industry (METI), Japan.

T10.50

Surface Potential Investigation on Nano Domain Formation in Lithium Tantalate Single Crystal. Mirai Katoh and Yasuo Cho; Research Institute of Electrical Communication, Tohoku University, Sendai, Miyagi, Japan.

Unexpected phenomena observed in the course of the study on the nano domain formation under the tip, such as anti-parallel polarization reversal and the generation of ring shaped domain patterns, were reported[1,2,3]. Our previous report suggested that these phenomena was related to the density of lattice defect[3]. In this work, observation of surface potential distribution after applying pulse voltage was made by Kelvin probe Force Microscopy(KFM)[4] to obtain information how electric field exists after polarization reversal to lead to clarify the mechanism of polarization reversal. As specimens, congruent lithium tantalate (CLT) with many lithium vacancy defect, and stoichiometric lithium tantalate (SLT) with few defects were used. To apply electric field and to measure surface potential, gold-coated SPM cantilever tip was used. The tip radius was not more than 30nm. Pulse voltage applies to a bottom electrode; the tip is grounded. First, observation of the surface potential distribution after polarization reversal was carried in CLT. Obtained surface potential of reversed polarization area unexpectedly became lower than that before polarization reversal. This effect originates from the cancellation of the polarization charge and the injected charge into the specimen from the tip, because the sign of the injected charge was opposite to that of polarization charge. Second, the same measurement in SLT was carried out. The surface potential after polarization reversal had same polarity with the polarization, differing from the case of CLT. This means, there is no or few injected charge in SLT. Therefore, it is strongly supported that lattice defects in CLT become charge-trapping sites, which cause phenomena, such as anti-parallel polarization reversal and ring shaped domain patterns. Finally, the measurement in CLT thickness under controlled humidity environment was carried out. The relative humidity (RH) was controlled at 20, 40, 60 and 80%. Relatively long pulse duration (ex. 40V, 100 μ sec) caused polarization reversal under low RH 20, 40 and 60%, But did not occur at RH 80%. However, in the case of short pulse duration (ex. 40V, 10msec), the reversed polarization area increased in accordance with the RH increment. When pulse duration is shorter than polarization stabilization time[5], injected charge generates the electric field to stabilize the polarization. But in higher RH, polarization reversal never occur, because injected charge is rapidly compensated by the existence of surface water molecular with high conductivity. When pulse is longer, polarization reversal is caused by only applying pulse. [1] M. Abplanalp et al. *Phys. Rev. Lett.* **86**, 5799 (2001) [2] T. Morita and Y. Cho: *Appl. Phys. Lett.* **84**-2, 257-259 (2004) [3] M. Katoh, T. Morita and Y. Cho: *Integr. Ferroelectr.* **68**, 207-219, (2004) [4] M. Nonnenmacher et al.: *Appl. Phys. Lett.* **58** (25), 2921-2923 (1991) [5] S. Kim et al.: *J. Appl. Phys.* **90** (6), 2949-2963 (2001)

T10.51

Phase Transition Temperature of Ferroelectric Thin Film Evaluated by Four-State Potts Model. Wing Yee Winnie Chung and Veng Cheong Lo; Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China.

An epitaxial ferroelectric thin film can be modeled by a two-dimensional array of dipoles. The orientation of each of these dipoles is assigned to one of the four possible states which are mutually perpendicular to each other. Consequently, the whole film is divided into ferroelectric domains with the dominance of 90° domain walls. The polarization switching is implemented by the 90° rotation of individual dipoles. Two switching mechanisms have been considered. For the first one (model A), only the dipoles at the domain walls are allowed to rotate. For the second (model B), every dipole inside the film is allowed to rotate, provided that it is thermally activated. The phase transition temperatures have been evaluated under these two models. Furthermore, the effects of sample size and boundary condition have also been taken into account.

T10.52

Effect of PLT Buffer Layers on the PZT Thin Films in Study of Scaling-Down Ferroelectric Materials. Li Dong Hua, Lee Eun Sun, Chung Hyun Woo, Ahn Byung Du and Sang Yeol Lee; Electrical and Electronic Engineering, Yonsei University, Seoul, South Korea.

The Hysteresis characteristics of below 400 nm- thick Pb(Zr_{0.52}Ti_{0.48})O₃(PZT) thin films grown on Pt(111)/Ti/SiO₂/Si substrates have showed very poor with remanent polarization of 1~3 uC/cm² in our previous research. To study the further scaling-down, we introduced the method of our previous research by Eun Sun Lee et al[1] who suggested that the (Pb_{0.72}La_{0.28})Ti_{0.94}O₃(PLT) buffer layers play an important role in enhancing the ferroelectric properties of the PZT thin films. As a result, the remanent polarization of 300 nm-thick PZT thin films with the 10 nm- thick PLT buffer layers has showed 32 uC/cm² at applied voltage of 8 V and 24 uC/cm² at applied voltage of 5 V. Inserted the PLT seed layers between the PZT thin films and Substrate, the hysteresis characteristics of PZT thin films were improved a lot. The leakage current and dielectric properties of PZT thin films also were investigated.

T10.53

Electronic properties of SrTiO₃ / wide-gap insulator oxide heterointerfaces. Keisuke Shibuya¹, Tsuyoshi Ohnishi¹, Takayuki Uozumi¹, Taisuke Sato¹, Hideomi Koinuma² and Mikk Lippmaa¹; ¹University of Tokyo, Kashiwa, Chiba, Japan; ²National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

A field-effect transistor is a sensitive probe for the investigation of interfacial electronic properties. The behavior of carriers accumulated by electric field effect is very sensitive to the structure of the interface between a gate insulator and a channel layer. We have demonstrated the importance of an epitaxial interface, using SrTiO₃ (100) single crystal field-effect transistors with amorphous and epitaxial CaHfO₃ layers as gate insulators. The devices with amorphous insulator layers showed n-type transistor operation with a field-effect mobility of 0.4 to 0.5 cm² / V s and an on-to-off channel current ratio of ~ 10⁵ at room temperature. A large threshold voltage shift was observed at low temperatures and the transistor performance was temperature independent when that shift was taken into account. The device properties were greatly affected by the interface between amorphous insulator and SrTiO₃. To improve the quality of the channel layer-insulator interface, an ultra-thin epitaxial CaHfO₃ layer was grown on the SrTiO₃ substrate surface at high temperature, followed by room-temperature deposition of an amorphous insulator layer. The aim was to suppress the interface state density. The devices with epitaxial interfaces exhibited a large improvement over the amorphous transistors. A field-effect mobility of 1.8 cm² / V s and an on-to-off channel current ratio of ~ 10⁵ were attained at room temperature. The field-effect mobility was found to increase at low temperature, reaching 25 cm² / V s at 50 K. This result means that the carriers induced by the field effect behaved as would be expected for electron-doped SrTiO₃.

T10.54

Transparent Ferroelectric-Gate Thin Film Transistors with Nonvolatile Memory Operation using BLT/ITO Structures. Eisuke Tokumitsu, Masaru Senoo and Etsu Shin; Precision and Intelligence Lab., Tokyo Institute of Technology, Yokohama, Japan.

We demonstrate transparent thin film transistors (TFTs) with nonvolatile memory operation using Bi_{4-x}La_xTi₃O₁₂ (BLT) as a gate insulator and indium tin oxide (ITO) as a channel. We previously reported that BLT/ITO ferroelectric-gate thin film transistors fabricated on SiO₂/Si substrates exhibit excellent transistor characteristics with nonvolatile memory operation, where Pt is used as source, drain, and gate electrodes[1]. In this work, we have fabricated the ferroelectric-gate TFTs on quartz substrates using ITO electrodes to realize transparent devices. Bottom-gate structure TFTs have been fabricated. First, ITO bottom gates were formed by RF sputtering and patterned. Then, ferroelectric BLT layer (230 nm) was formed by the sol-gel technique. The BLT film was crystallized at 750°C in O₂ ambient. Next, 10-nm-thick ITO channel was deposited by RF sputtering. Then, ITO source and drain electrodes were deposited, and finally the device was isolated by dry etching. The channel length (L) and width (W) of the fabricated devices are 5 and 50 um, respectively. Drain current-drain voltage (I_D-V_D) characteristics of transparent BLT/ITO ferroelectric-gate TFTs exhibit typical n-channel transistor operations. The on-current of more than 0.5 mA was obtained when the gate and drain voltages are 6 V. On the other hand, the off-current of the device is as low as 10⁻¹⁰ A, which indicates that the ITO channel is sufficiently depleted by the ferroelectric polarization. The polarization used in the device is estimated about 10 uC/cm². In addition, drain current-gate voltage (I_D-V_G) characteristics demonstrate clear counterclockwise hysteresis loop due to the ferroelectric gate insulator. We have confirmed nonvolatile memory

operation up to 1 day. Optical transmittance of the fabricated device is greater than 60% including the quartz substrate. [1] T. Miyasako, M. Senoo and E. Tokumitsu, Appl. Phys. Lett., **86**, 162902 (2005).

T10.55

Out-of-phase Boundary (OPB) Nucleation in Epitaxial Complex Oxides. Mark A. Zurbuchen^{1,2,3}, James Lettieri³, Yunfa Jia³, Juergen Schubert^{4,3}, David J. Comstock³, Wei Tian^{3,5}, Goh Asayama³, Stacy B. Knapp³, Marilyn E. Hawley⁶, Altaf H. Carim^{7,3}, Xiaoping Pan⁵, Stephen K. Streiffer^{2,8} and Darrell G. Schlom³; ¹Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ³Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Maryland; ⁴Institut fuer Schichten und Grenzflaechen, Forschungszentrum Juelich, Juelich, Germany; ⁵Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ⁶Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico; ⁷Scientific User Facilities Division, U.S. Department of Energy, Washington, District of Columbia; ⁸Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

Out-of-phase boundaries (OPBs), planar faults between regions of a crystal that are misaligned by a fraction of a unit-cell dimension, occur frequently in materials of high structural anisotropy. Although rarely observed in the bulk, OPBs are frequently observed in epitaxial films of layered complex oxides, such as YBCO-type, Aurivillius, and Ruddlesden-Popper phases. OPBs have previously been demonstrated to have a significant impact upon properties, so it is important to understand their generation. These faults arise through the same few mechanisms in the various layered complex oxides. They typically nucleate at the film-substrate interface, and frequently propagate through the entire thickness of a film, due to their large offset and the improbability of opposite-sign OPB annihilation. The mechanisms of OPB formation both during nucleation and post-growth will be described and presented with experimental examples characterized by high-resolution transmission electron microscopy (HRTEM) and diffraction techniques. The implications of these mechanisms for material selection will be discussed. The results stress the importance of microstructural characterization and its complementarity with characterization by diffraction. Parallel study by both methods yields predictive correlations. An example of the limitations of diffraction analysis will be demonstrated using the recent example of the *n* = 8 Aurivillius composition, Bi₉(Ti₃Mn₅)O₂₇.

T10.56

Characterization of Domain Walls in Ferroelectrics using Atomic Force (AFM) and Piezo Response Force Microscopy (PFM). Christian Franck, Guruswami Ravichandran and Kaushik Bhattacharya; Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California.

Ferroelectrics are spontaneously polarized in their natural state and the regions of uniform polarization known as domains are separated by boundaries known as domain walls. The structure of domain walls and their interaction with defects has important implications for the behavior of ferroelectrics and hence their applications in MEMS and non-volatile memories. Large strain actuation and 90 degree domain switching is achieved by domain wall motion. In order to describe domain wall kinetics, characterization of both the physical and electrical domain walls is necessary. Experimental techniques for determining the twin wall thickness of both the physical and electrical domains with nanometer resolution are described. The surface topography and the displacement field due to the piezo-response of the material are measured using atomic force (AFM) and piezo response force microscopy (PFM). The experimental techniques are illustrated through the measurements on single crystals of barium titanate. The measurements of the surface topography are then analyzed by comparison to their respective atomistic displacement fields and thus the domain wall thickness is determined. Similarly, the electrical domain wall thickness is determined by comparison of the piezo response force data with its respective polarization field. Surprisingly, these are found to differ by orders of magnitude. The structure and role of defects on domain wall thickness are also discussed.

T10.57

Local ferroelectric switching properties in BiFeO₃ films and structures. Catalin Harnagea, Cristian Cojocaru and Alain Pignolet; University of Quebec, INRS-EMT, Varennes, Quebec, Canada.

The attention recently attracted by the multiferroic material Bismuth Ferrite BiFeO₃ (BFO) is due to its ferroelectric properties which are very much enhanced in the thin film form. For example, epitaxial films a few hundreds nm thick (therefore strained by the substrate) exhibit a spontaneous polarization of the order of 100 uC/cm², more than one order of magnitude higher than that of BFO bulk single

crystal. This enhanced ferroelectricity, together with the multiferroic character of BFO (it is also antiferromagnetic, with a canted weak ferromagnetism at room temperature), have opened perspectives for novel applications. For real device fabrication, however, a very good understanding of the basic ferroelectric - electromechanical properties, both in continuous film and structured forms, is necessary. We have grown BFO films with thickness ranging from 50 nm to 500 nm. Using adequate deposition and crystallization conditions, we also obtained distinct BFO structures with lateral sizes ranging from 300 nm to 3000 nm and an aspect ratio (lateral size/thickness) of $\sim 1:10$. We have used the well-known piezoresponse force microscopy (both vertical and lateral) technique to study the domain structure and local switching in these BFO films and structures. Despite the difficulties in interpreting the experimental data, due to the rhombohedral crystal symmetry of BiFeO₃ (therefore the piezoelectric response is not simply related to the components of spontaneous polarization), we found a strong piezoresponse of both films and structures, comparable to that of lead-containing PZT films. We did not find any size effects for the distinct structures. However, in contrast to local switching in PZT films, a careful analysis of the local piezoresponse hysteresis curves revealed that non-180 degree switching takes place much more often than 180 degrees switching of polarization. Our finding is important for applications where ferroelectric switching in BFO is crucial.

T10.58

Compositional Symmetry Breaking in Ferroelectric Bilayers. Shan Zhong¹, Pamir Alpay¹ and Joseph Mantese²; ¹Materials Science and Engineering, University of Connecticut, Storrs, Connecticut; ²Materials, Components and Packaging, Delphi Research Laboratories, Shelby Township, Michigan.

Compositional variations across ferroelectric bilayers result in broken spatial inversion symmetry that can lead to asymmetric thermodynamic potentials. For the case of insulating materials, ferroelectric multilayers will self-pole due to the electrostatic coupling between the layers. Polarization-graded ferroelectrics with smooth composition, temperature, or stress gradients are viewed as bilayer structures in the limit of ever increasing number of bilayer couples, thus permitting us to conclude that the unconventional hysteresis associated with "up" and "down" polarization graded structures are real phenomena, and not artifacts associated with free charge or asymmetric leakage current.

T10.59

Nano-Tubes-Patterned Ferroelectric Thin Films of Barium-Strontium Titanate (BST) Hydrothermally-Synthesized at 200 C. Nitin P. Padture¹, Xuezheng Wei², Rosalia Poyato² and Bryan Huey²; ¹Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio; ²Department of Materials Science and Engineering, University of Connecticut, Storrs, Connecticut.

A novel, low-temperature synthesis method for producing BaxSr(1-x)TiOx (BST) thin films patterned in the form of nano-tubes ("honeycomb") on Ti substrates is reported. In this two-step method, the Ti substrate is first anodized to produce a surface layer (about 300 nm thickness) of amorphous titanium oxide nano-tube (about 100 nm diameter) arrays. In the second step, the anodized substrate is subjected to hydrothermal treatment in aqueous Ba(OH)₂ Sr(OH)₂ at 200 C, where the nano-tube arrays serve as templates for their topotactic (shape-preserving) hydrothermal conversion to polycrystalline BST nano-tubes. A simple geometrical model is proposed to elucidate the mechanism of the hydrothermal growth of BST nano-tubes. Piezoresponse atomic-force microscopy (P-AFM) has been used to characterize local piezoelectric and ferroelectric properties of these nano-tubes patterned thin films. P-AFM images show ring-shaped piezoelectric regions that resemble the "honeycomb" pattern of the nano-tubes. These regions are found to be piezoelectric prior to the application of DC field, indicating the existence of a built-in field. The as-prepared thin films are found to be ferroelectric, as confirmed by non-linear, hysteretic piezoelectric response. This opens the possibility of tailoring the titanium oxide nano-tube arrays, and of using various precursor solutions and their combinations in the hydrothermal bath, to produce ordered, patterned thin-film structures of various Ti-containing ferroelectric ceramics. These thin films and their variations may find use not only in a variety of electronic, opto-electronic, and sensor device applications but also in biomedical and catalysis applications, where patterned thin films are desirable.

T10.60

Tailoring Nanoscale Domain Size in Epitaxial Ferroelectric Multilayers. Ting Zhu^{1,2} and Zhigang Suo¹; ¹Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; ²George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Epitaxial multilayers of dielectric, ferroelectric and conducting oxides can now be fabricated with a control to a single layer of unit cells. This paper investigates a possible way to tailor the size of ferroelectric domains over a large range. When a ferroelectric layer is subject to a compressive epitaxial strain, the constraint may force the spontaneous polarization vector to be normal to the layer. If this ferroelectric layer is sandwiched between two dielectric layers, the discontinuity in the polarization vector at the interfaces causes an electrostatic field. To reduce the electrostatic energy, the ferroelectric layer forms domains with anti-parallel polarizations. We determine the equilibrium domain size that minimizes the combined electrostatic and domain wall energies. Our calculations show that the equilibrium domain size can be tailored over a large range by changing the thicknesses of the ferroelectric and dielectric layers.

T10.61

Asymmetric Properties of Strained SrTiO₃ Films on DyScO₃ Substrates. Michael D. Biegalski¹, D. D. Fong², J. H. Haeni¹, Y. L. Li¹, A. Sharan¹, W. Tien¹, V. Gopalan¹, L. Q. Chen¹, P. H. Fuoss², J. A. Eastman², X. Q. Pan³, M. E. Hawley⁴, W. Chang⁵, S. W. Kirchoefer⁵, A. K. Tagantsev⁶, R. Uecker⁷, P. Reiche⁷, Stephen K. Streiffer², Darrell G. Schlom¹ and Susan Trolier-McKinstry¹; ¹Material Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ³Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan; ⁴Materials Science & Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico; ⁵Naval Research Laboratory, Washington, District of Columbia; ⁶Laboratoire de Ceramique, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland; ⁷Institute for Crystal Growth, Berlin, Germany.

Using reactive MBE, strained epitaxial SrTiO₃ films were grown on DyScO₃ substrates. Films with thicknesses ranging from 50 Å to 1000 Å were prepared to examine the films above and below the critical thickness. The strain state and structural perfection of these films were examined using synchrotron x-ray scattering at the Advanced Photon Source. These films have excellent crystalline quality with the narrowest rocking curve (full width at half maxima) reported for a perovskite film (0.002-0.005°). These films also retain excellent crystallinity above the critical thickness, with only a modest amount of relaxation even after high temperature annealing. One consequence of the strain is that the films experience a ferroelectric transition near room temperature, even though unstrained SrTiO₃ is an incipient ferroelectric. These films also exhibit peak dielectric constants near 20,000. The dielectric data shows frequency relaxation that was well fit by a Vogel-Fulcher equation over six orders of magnitude in frequency. The Vogel-Fulcher fitting indicated a freezing temperature of 204 K. These films also exhibit clear hysteresis loops below the T_{max} with an in-plane remanent polarization up to 10 μC/cm² at 77 K. Interestingly, the in-plane electrical properties are anisotropic. The orientation dependence of the dielectric properties will be explained in view of the crystallography of the DyScO₃ substrate and its relation to the strain state of the SrTiO₃ film.

T10.62

The Microwave Frequency Dielectric Response of (Ba,Sr)TiO₃ Thin Films With Anisotropic Epitaxy. William Kurt Simon¹, E. K. Akdogan¹, Jeffery Bellotti² and A. Safari¹; ¹Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey; ²Electronic Sciences and Technology Division, Naval Research Laboratory, Washington D.C., District of Columbia.

Thin films of Ba_{0.6}Sr_{0.4}TiO₃ have been grown via pulsed laser deposition on (110) orthorhombic NdGaO₃ substrates. High quality films, with rocking curve widths of approximately (0.03°) are seen. The radio/microwave frequency dielectric response of these films is intentionally modified through the application of anisotropic epitaxial stress. The orthorhombic unit cell of the substrate strains the (100) oriented films unequally along the in-plane principal directions. The anisotropic residual strains modify the symmetry of the permittivity tensor according to the Curie Principle. A two dimensional cross-section of the permittivity ellipsoid measured in the (100) oriented films. The modified symmetry of the permittivity tensor is probed by measuring the in-plane dielectric response with interdigitated electrodes, systematically aligned along crystallographic directions. A novel x-ray diffraction technique is used to quantify the anisotropic residual strain and their directions over a wide range of film thicknesses (25 to 1200 nm). The anisotropic epitaxial strain is shown to vary with film thickness, as does dislocation density. In this system, misfit dislocations and Burgers vectors are independent along the two principal directions, and as such strain relief along those directions is also independent. The influence of the anisotropic residual strains, as well as the different dislocation densities on the rf/microwave dielectric properties and its symmetry are investigated. Modification of the permittivity tensor by engineered anisotropic epitaxy creates a new degree of freedom for tailoring the dielectric

T10.63

(001) Epitaxial Silver Tantalate Niobate, Ag(TaxNb1-x)O3, Thin Films on (001)SrRuO3 / (001)LaAlO3 Substrates by Chemical Solution Deposition. Mustafa Burak Telli, Srowthi S. N. Bharadwaja, Michael Biegalski, Jian-Gong Cheng and Susan Trolier-McKinstry; Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

(001) epitaxial silver tantalate, AgTaO3 (ATO), silver tantalate niobate, Ag(Ta0.5Nb0.5)O3 (ATN), and silver niobate, AgNbO3 (ANO), thin films were deposited on (001)SrRuO3 / (001)LaAlO3 substrates using chemical solution deposition. The ATN films that were crystallized from 500 °C to 800 °C in O2 ambient demonstrated cube-on-cube epitaxy with a limited reaction between the ATN thin films and the SrRuO3. With an increase in the crystallization temperatures from 500 °C to 800 °C, dielectric constants of the epitaxial ATN films increased from 260±25 to 360±35 at 100 kHz at room temperature and crystallinity of the films were improved. The DC field tunability of ATN film that was deposited at 750 °C was not hysteretic but small, 4.8 % at 100 kHz and 150 kV/cm. While ATO film that was crystallized at 750 °C had a slightly lower dielectric constant of 110±10 than the bulk ceramic value of 150, the ANO film that was crystallized at 750 °C had high room temperature permittivities of 550±55 than the bulk ceramic value of 120 at 100 kHz and at room temperature. Although the DC field tunability of the ATO film was not hysteretic but limited to 1.6 % at 100 kHz and at 230 kV/cm field, the DC field tunability of the ANO film was higher, with a 12.8 % at a negative bias of -140 kV/cm and 21.4 % at 190 kV/cm.

T10.64

High Tunability of Ba0.6Sr0.4TiO3 Film in an In-Plane Interdigital Capacitor Geometry. Jong Hoon Cho, Jung Ho Kim, Tesu Kim and Kookrin Char; Center for Strongly Correlated Materials Research, School of Physics, Seoul National University, Seoul, South Korea.

We deposited epitaxial Ba0.6Sr0.4TiO3 (BST) films via laser ablation on r-plane sapphire substrate with MgO buffer layer. For epitaxial MgO buffer layer, we used reactive pulsed laser deposition technique by ablating a Mg target in a moderate oxygen pressure and oxidizing it during the deposition. We achieved a very smooth MgO surface: 0.6 nm RMS roughness in a 20 nm thick MgO film. With a MgO buffer layer on the sapphire substrate, we have successfully reduced the loss tangent of BST interdigital capacitor to as small as 0.005 in a surface electric field 60 V/μm, while keeping the 78 % tunability at room temperature for 150 nm thick BST film. To pattern the interdigital capacitor on BST film, we used e-beam direct writing technique and a 250 nm gap was used for the interdigital capacitor. We attribute the high tunability and the low loss to the in-plane tensile stress existing in the BST film grown epitaxially on sapphire substrate.

T10.65

Molecular Volume and Polarizabilities for Zr-Sn-Ti Oxide Dielectrics. S. C. Barron and R. B. van Dover; Materials Science and Engineering, Cornell University, Ithaca, New York.

Novel semiconductors such as carbon nanotubes may demonstrate exotic properties once injected to a high charge density. The required areal charge density, however, can not be realized by standard dielectrics such as SiO2 whose areal charge density at its breakdown field is ~3.5 μC/cm². The thin film amorphous oxide Zr0.2Sn0.2Ti0.6O2 has demonstrated both a high dielectric constant ε ~ 62 and a high breakdown field Ebr ~ 4 MV/cm. With these two values, an areal charge of 25 μC/cm² can be injected into a semiconductor, allowing for the investigation of properties at higher charge densities than previously attainable. The thin film dielectric is prepared by an on axis rf sputter deposition of the oxide from a Zr0.2Sn0.2Ti0.6 alloy target in a 40% O2 in Ar atmosphere. The dielectric constant is shown to be a strong function of the deposition temperatures, as it decreases from the highest ε ~ 62 at 200 C at both higher and lower temperatures. Ellipsometric measurements of the refractive index are used to determine the molecular volume of samples prepared at different temperatures. The Clausius Mossotti relationship is used to evaluate the strong nonlinear dependence of dielectric constant on molecular volume and polarizability. The additivity of polarizabilities for the ions of this composition is shown to deviate from that of 'well-behaved' oxide dielectrics [1]. The proposed mechanism for that deviation is that the Ti⁴⁺ ion is too small to fill the surrounding oxygen octahedron. To further elucidate the effect of the titanium ion environment on dielectric constant, an off-axis co-sputtering technique with three elemental targets is used to prepare samples covering ~80% of the ZrO2-SnO2-TiO2 phase diagram. The molecular volume and additivity of polarizabilities are discussed as a function of composition. [1] R. D. Shannon. J. Appl.

T10.66

Ferroelectric Characterization of Vanadium Doped Strontium Bismuth Niobates for Memory Devices. Kanhaiya Lal Yadav and Anjan Sil; Physics, Indian Institute of Technology, Roorkee, Roorkee, Uttaranchal, India.

Ferroelectrics are excellent candidates for the applications in data storage in digital memory systems. Among them bismuth oxide layered perovskite materials, such as SrBi2Nb2O9 (SBN) and SrBi2Ta2O9 (SBT) have attracted an increasing attention for FeRAM applications, because they are fatigue-free and lead free and possess ferroelectric properties independent of film thickness. Recently, efforts have been made to enhance their properties by the addition or substitution of alternative cations. In particular, partial substitution of niobium by pentavalent vanadium cations in SBN (SBNV) has been reported to enhance the ferroelectric properties. In this paper, we will present a systematic study on the influence of V doping on the dielectric properties of SBN systems. The polycrystalline samples of V-modified SBN were prepared by solid-state reaction at 900-1100 degree Celsius in air, using SrCO3, Bi2O3, V2O5 and Nb2O5. X-ray diffraction analysis indicated the formation of a pure single-phase material within the composition range studied. Further, it was found that the addition of V lowered the sintering temperature, which may be due partly to the low melting point of vanadium oxide. Temperature dependence of dielectric constant study shows an increase in peak dielectric constant along with increase in ferro-paraelectric phase transition temperature. This observation may be explained by the increasing rattling space due to the incorporation of smaller cation (i.e. V) in the present system. The P-E hysteresis measurements performed at various temperatures are in agreement with the dielectric measurements. The dc conductivity measurement ranging from 40 to 600 degree Celsius show two predominant conduction mechanisms at different temperature ranges. The experimental results observed in this study suggest that the effects of V doping on the dc conduction is complex, which will be discussed in details at the time of presentation. In summary, the partial substitution of Nb by V (up to 9 at.%), the single-phase layered perovskite structure was preserved, and the sintering temperature of the system was found to decrease along with shift of Curie point to higher temperature. The above results can also be explained from microstructure study.

T10.67

Correlation between domain structures and dynamics in highly (001)-oriented epitaxial PZT thin films. Yong Kwan Kim, Hitoshi Morioka and Hiroshi Funakubo; Department of Innovative and Engineered Materials, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan.

The twin-domain structure of tetragonal ferroelectric materials which usually consists of contributions from both 180° domains and 90°-type domains and their switching dynamics are coupled together and their interplay is of great importance in various practical applications such as nano-storage devices, actuators and sensors for MEMS.¹ Recently, for the first time, we reported the systematically controlled domain structures with various volume fractions of c-domains in tetragonal epitaxial (100)/(001)-oriented Pb(Zr0.35,Ti0.65)O3 [PZT] films on the same substrates.² In the PZT films with large volume fraction of a-domains, we found that experimentally measured values of polarization properties larger than that of predicted by the assuming that only the c-domains contributed to polarization. It showed that this film has the possibility of attaining large piezoelectric coefficient, d33, values due to switching dynamics. In this work, we re-visited the issue experimentally using in epitaxial PZT thin films grown on (100)cSrRuO3/(100)SrTiO3 substrates by metalorganic chemical vapor deposition. Here, ferroelectric twin-domain structures in epitaxial PZT thin films with various c-domain volume fractions were investigated using synchrotron x-ray diffraction and transmission electron microscopy (TEM), and attempted to rationalize the piezoelectric properties of epitaxial ferroelectric films in terms of domain dynamics associated with the domain structure. The domain structure was distinguished three region such as a-domain dominant, mixed, and c-domain dominant regions. Each region showed a characteristic domain structure. The a-domain dominant region showed a1-a2 domain structure with a small amount of c domains embedded in matrix a domains. The c-domain dominant region showed highly c-axis oriented domain structures consisting of a periodic array of twin domains (a-c domain structure). The mixed region showed co-existed both structures. The bottom layer is the a1-a2 domain structure and top layer is the a-c domain structure. The tetragonal PZT films with large a-domain have the unique domain structure and thereby enhance the piezoelectric coefficient. 1 Y. Xu, Ferroelectric Materials and Their Applications (Elsevier Science, Amsterdam, 1991). 2 Y. K. Kim, H. Morioka, R. Ueno, S. Yokoyama and H. Funakubo, Appl.

T10.68

Influence of Spatially Varying Local Strain on Piezoelectric Hysteresis Characterized Experimentally and Theoretically. Ramesh Nath¹, Edwin R. Garcia², John E. Blendell² and Bryan D. Huey¹; ¹Materials Science and Engineering, University of Connecticut, Storrs, Connecticut; ²Materials Engineering, Purdue University, West Lafayette, Indiana.

The influence of strain on ferroelectric properties is of growing importance for ferroelectric thin films, multilayer structures, and multiferroics. In this investigation, piezoelectric hysteresis has been quantitatively characterized as a function of position in polycrystalline PZT thin films using piezoelectric force microscopy (PFM). These results are compared to two dimensional finite element calculations incorporating electromechanical fields that result from the actual grain structure and orientations determined ex situ via electron backscattering diffraction. The precision of individual PFM measurements are first proven based on multiple measurements performed over two days. The hysteresis loops are shown to vary with orientation in amplitude and width as predicted. Most important, the hysteresis loops are also found to vary with position, particularly approaching and at grain boundaries. These locations correspond to regions of extreme strain according to the finite element calculations.

T10.69

Effective Electromechanical Response of Porous Piezoelectric Materials. Ronit Kar-Gupta and T. A. Venkatesh; Mechanical Engineering, Tulane University, New Orleans, Louisiana.

Piezoelectric materials, with their unique coupled properties, in the thin film and bulk forms, have been widely researched for their use in a number of applications as sensors and actuators. Porous piezoelectric materials with their enhanced hydrostatic figures of merit and reduced impedances have been targeted for particular applications such as in hydrophones and in biological imaging. In the present study, a finite element based numerical approach that utilizes a representative volume (or unit-cell), is developed to study the effects of distributed porosity in a monolithic piezoelectric material, on the electro-mechanical response of piezoelectric materials. The present study systematically characterizes the effects of pore- shape, size, and volume fraction, and poling characteristics, on the effective coupled properties of the porous piezoelectric systems. The impact of porosity on the spatial distribution of electric potentials and mechanical stresses is also examined with a view to identifying locations that could be most susceptible to failure due to electrical or mechanical breakdown, respectively. The numerical model developed in the present work is validated with analytical models for select pore configurations and compared to experiments on porous piezoelectric materials. Furthermore, unique bi-directional properties that can be realized from multi-layered porous piezoelectric thin films are identified as well.

T10.70

Heterostructures of functional oxide thin films: Relationships between the properties of the ferroelectric layer and the oxide electrode properties. Olivier Gautreau¹, Riad Nechache¹, Catalin Harnagea¹, Francois Normandin², Teodor Veres² and Alain Pignolet¹; ¹INRS EMT, INRS / Universite du Quebec, Varennes, Quebec, Canada; ²Industrial Material Institute, National Research Council Canada, Boucherville, Quebec, Canada.

Integration of functional materials is nowadays a key field of investigation in industrial and academic research. More precisely, there is a high demand for high-quality epitaxial thin films and heterostructures of perovskite oxides (exhibiting a wide range of useful properties, such as electric, magnetic, and optical properties) for applications such as information storage and sensors. As those devices require bottom and top electrode, investigations have been done on several conducting perovskite candidates such as Ru-based perovskites (SrRuO₃ or CaRuO₃¹). SrRuO₃(SRO) appears to be one of the most appropriate conductive oxides as bottom electrode for a variety of ferroelectric and multiferroic thin films heterostructures (BLTⁱⁱ, BFO, SBT, PZT) and recently for multiferroic BTO and CFO nanostructuresⁱⁱⁱ. SRO also displays a host of different properties already investigated and reported (conductivity, ferroelectricity, extraordinary Hall Effect). It is one of the most conductive metallic oxides, is a good diffusion barrier to prevent interdiffusion for ferroelectric materials, have very good thermal conductivity and stability, as well as a high resistance to thermal corrosion. We report here the use of SRO high-quality films as electrodes and template for the heteroepitaxial growth of ferroelectric functional materials such as BFO (BiFeO₃), BLT (La-doped Bi₄Ti₃O₁₂) and BTO (BaTiO₃) by Pulsed Laser Deposition. Investigation of the structural and microstructural properties by XRD and AFM, as well as detailed transport properties will be presented and discussed. The global and

local ferroelectric properties were investigated using a ferroelectric tester and by Voltage-modulated Scanning Force Microscopy (also called Piezoresponse Force Microscopy or PFM). Relationships between the ferroelectric properties of the films and the microstructure and transport properties of the SRO layers, as well as the nature of the substrate (silicon and strontium titanate) have been investigated in details and a complete review of the different effects will be presented. ⁱ C. B. Eom, R. J. Cava, R. M. Fleming, Julia M. Phillips, R. B. van Dover, J. H. Marshall, J. W. P. Hsu, J. J. Krajewski and W. F. Peck, Science 258, 1766, (1992) ⁱⁱ B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee and W. Jo, Nature 401, 682, (1999) H. N. Lee, D. Hesse, N. Zakharov and U. Gösele, Science 296, 2006 (2002) ⁱⁱⁱ H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wutting, A. Roytburd and R. Ramesh, Science 303, 661, (2004)

T10.71

A real 3D PZT capacitor for high density ferroelectric random access memory and its electrical properties. Sangmin Shin¹, June-Mo Koo¹, Suk-Pil Kim¹, Bum-Seok Seo², Jung-Hyun Lee², Hionsuck Baik³, Jang-Ho Lee³, Mino Yang³, Hee Han^{4,5}, Sunggi Baik^{4,5}, Jae-Young Choi⁵, Yong Jun Park⁵ and Youngsoo Park¹; ¹Devices Lab., Samsung Advanced Institute of Technology, Suwon, South Korea; ²Nano Fabrication Center, Samsung Advanced Institute of Technology, Suwon, South Korea; ³AE Center, Samsung Advanced Institute of Technology, Suwon, South Korea; ⁴Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, South Korea; ⁵Beamline Division, Pohang Accelerator Laboratory, Pohang, South Korea.

We have made a trench structure of PbZr_xTi_{1-x}O₃ (PZT) capacitor and evaluated its electrical properties. A tri-layers, bottom Ir(20nm), PZT(60nm), top Ir(20nm) were packed in the SiO₂ trench hole by atomic layer deposition (ALD) for top and bottom Ir electrodes, and by metal organic chemical vapor deposition (MOCVD) for PZT layer. In this article, we mainly report the fabrication process and the Ir and PZT film quality on both horizontal and vertical part of the trench cup structure. And we discuss on the increased charge value from the trench capacitor, to make it related with PZT grain structure on the side wall. Also, we clarify the additional SrRuO₃ layer between top Ir and PZT will improve the retention property.