SYMPOSIUM C

C: Ferroelectric Thin Films XII

November 30 - December 4, 2003

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TUTORIAL

FT C: Ferroelectric Thin Films
Sunday, November 30, 2003
10:00 AM - 4:00 PM
Room 203 (Hynes)

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

Instructors:
Paul Muralt, Swiss Federal Institute of Technology EPFL
Alexander Tagantsev, Swiss Federal Institute of Technology EPFL
Susanne Hoffmann-Eifert, Forschungszentrum Juelich
Stephen K. Streiffer, Argonne National Laboratory

SESSION C1: Fundamentals of Ferroelectric Films: Emphasis on Strain
Chairs: Angus Kingon and Alexander Tagantsev
Monday Morning, December 1, 2003
Room 203 (Hynes)

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

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

9:00 AM C1.2
Stress evolution in integrated $SrBi_2Ta_2O_9$ ferroelectric layers. Judit G. Lisoni, J. A. Johnson, L. Goux and D. J. Wouters; SPDT, IMEC, Leuven, Belgium.

The integration of ferroelectric materials with Si technology requires complex barrier layer schemes, whose combined stresses determine the mechanical stability of the system during subsequent processing steps. In this paper, we investigate the evolution of the stress of $Sr_{1-x}Bi_{2+y}Ta_2O_9$ (x, y $\langle$ 0.5) on a relevant electrode stack (TiAlN/Ir/IrO_2/Pt) and compare to that of SBT on SiO_2. SBT deposited by both metal organic vapor deposition (MOCVD) and solution spin-on techniques are evaluated. As deposited, the TiAlN/Ir/IrO_2/Pt stack is under a high compressive stress (-0.7 GPa). On the other hand, the stress of the crystallized SBT layer is always highly tensile and is dependent on the deposition technique used (+0.5 GPa for spin-on SBT and up to +1.0 GPa for MOCVD). The stress of the MOCVD film itself, is highly dependent on the orientation and microstructure of the film. Thermal cycling reveals a change from tensile to compressive around 390 °C. Further investigations will reveal whether this is correlated to the ferroelectric transition temperature of SBT or the initial stress state of the substrate. The thermal cycling curve will be qualitatively explained based on the thermal expansion behavior as reported for other ferroelectric thin films. When a Pt top electrode is deposited on the electrode/SBT stack, the stress is low compared to the Pt layer in the bottom electrode (+0.1 and +1.2 GPa respectively), reflecting the fact that the SBT ceramic dictates the mechanical behavior of the system. These results illustrate the need to understand the mechanical properties of the ferroelectric thin film for successful integration.

9:15 AM C1.3
The Contribution of Asymmetric Strain Fields in Epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ Nanoislands to Ferroelectric Size Effects. Ming-Wen Chu, Izabela Szafraniak, Roland Scholz, Dietrich Hesse, Marin Alexe and Ulrich Goesele; Experimental II, MPI of Microstructure Physics, Halle (Saale), Germany.

Paraelectric-ferroelectric phase transition of Pb(Zr$-{1-x}$Ti$-x$)O-3 exhibits a three-dimensional size effect: Ferroelectricity vanishes when the grain (particle) size is below a critical value. Phase transition is also accompanied by formation of 180$ô$ and ferroelastic 90$ô$ domains in order to minimize the electrostatic energy and residual internal stresses, respectively. In order to obtain a structural insight into the origin of size effects, it is therefore crucial to investigate single-domain nano-ferroelectrics. Using chemical solution deposition, PZT nanoislands were prepared at 800$ô$C on Nb-doped SrTiO-3(001) substrates. High-resolution transmission electron microscopy (HRTEM) investigations on a large number of samples indicated that these nanoislands appear as truncated pyramids with an average height of ∼9 nm and lateral size of ∼50 nm. HRTEM studies also suggested that the PZT nanoislands are single-crystalline and single-c-domain with an epitaxial relationship of (001)PZT[100]PZT——(001)STO[100]STO. The internal stress resulting from the phase transition and the lat-tice mismatch with the substrate is released by edge-type misfit dislocations observed at the inter-face, with Burgers vectors b = a <010>. Performing quantitative HRTEM measurements on the dis-placements of the atomic columns using the geometric phase method [1], it has been revealed that the strain field imposed by the dislocation cores is strongly localized and of triaxially asymmetric character, extending only into the PZT side, affecting a PZT region with an estimated height of ∼4 nm and width of ∼8 nm. The PZT lattice is strongly distorted within this region, deviating from the regular tetragonal structure, and should thus not possess ferroelectricity. It is therefore sensible to suggest that asymmetric strain fields in nanoislands have a potential influence on size effects of ferroelectric titanate perovskites. [1] M. J. Hÿtch et al., Nature 423, 270 (2003).

9:30 AM C1.4
Substrate-Suppressed Phase Transition in Nano-Crystalline Freestanding $BaTiO_3$ Thin Films. Igor Lubomirsky[1], Jaya P. Nair[1], Ilya Zon[1] and Alexander Roytburd[2]; [1]Materials & Interfaces, Weizmann Institute, Rehovot, Israel; [2]Materials and Nuclear Engineering, University of Maryland, College Park, Maryland.

Phase transitions accompanied by symmetry lowering are usually facilitated by an external mechanical stress. As a result, temperature of the cubic to tetragonal phase transition in $BaTiO_3$ shifts up if the material is subjected to uniaxial or by biaxial external stress. We have investigated the para- to ferroelectric phase transition in self-supported ferroelectric films. Randomly-oriented nano-crystalline $BaTiO_3$ films were prepared with moderate residual tensile stress by sol-gel processing or RF sputtering. Low dielectric constant (110±20) and X-ray diffraction spectrum identified the films as being cubic at room temperature. Despite the tensile stress in the substrate-supported films, the freestanding films became corrugated, indicating 0.3-0.5% lateral expansion. The fact that the cubic to tetragonal phase transition was responsible for the lateral expansion has been confirmed by a five-fold increase of the dielectric constant (620±10) and a detectable piezoelectric effect. Thus in nanocrystalline self-supported films biaxial mechanical strain may suppress rather than facilitate phase transition accompanied by symmetry lowering. This seeming contradiction can be explained if inter-grain strain and texture formation are taken into account for the calculation of free energy.

9:45 AM C1.5
In-Situ Studies of the Ferroelectric Phase Transition in $PbTiO_3$ Thin Films. D. D. Fong[1], G. B. Stephenson[1], Stephen Streiffer[1], J. A. Eastman[1], Carol Thompson[2], O. Auciello[1], P. H. Fuoss[1], D. S. Kim[3] and C. B. Eom[3]; [1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois; [2]Department of Physics, Northern Illinois University, De Kalb, Illinois; [3]Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Investigations of size-dependent behavior in ferroelectrics have been

greatly complicated by the materials processing variations used to achieve different system length scales, and by the common and uncontrolled occurrence of space-charge, which interacts directly with the order parameter, the polarization. Here we report synchrotron x-ray scattering studies of the ferroelectric phase transition in thin films of the prototypical perovskite $PbTiO_3$, as a function of film thickness ranging from tens of nanometers down to a single unit cell. Films were synthesized on $SrTiO_3$ substrates using a metalorganic chemical vapor deposition system situated on BESSRC-CAT Beamline 12-ID at the Advanced Photon Source, and x-ray scattering was performed in-situ under a controlled temperature, composition and strain environment. Even for growth on insulating $SrTiO_3$, where stripe domains must form to alleviate depolarizing electric fields, the ferroelectric phase transition is observed in ultrathin films. A Curie point of approximately 250°C is found for a 3 unit-cell-thick film coherently strained to the underlying $SrTiO_3$. Furthermore, the suppression of T_c determined from our in-situ measurements as a function of film thickness does not follow the simple power law predicted by mean-field theory. These results will be compared to those obtained for films grown on $SrRuO_3/SrTiO_3$, where the conductivity of the electrode layer modifies (but does not completely remove) the impact of depolarization on the phase transition. This work was supported by the US Department of Energy, BES-Materials Sciences, under Contract W-13-109-ENG-38, and by the State of Illinois under HECA.

10:30 AM *C1.6
Site-controlled nucleation of ferroelectric crystals. Paul Muralt and Simon Buehlmann; Materials, EPFL, Lausanne, Switzerland.

The continuous downscaling in microelectronic circuits will not only lead to the manifestation of size effects of physical properties, but also to new possibilities in processing. An new additive technique may simply be the application of suitable thermodynamic parameters such as temperature and supersaturation of a vapor to achieve a nucleation with the desired density, combined with a given growth time to obtain defined sizes before coagulation sets in. This approach is sometimes called "self assembly". In order to get a useful technique, one still has to add an essential element: the control of the nucleation site. In this work, this has been attempted using patterned seed layers for Pb(Zr,Ti)O3 (PZT) in-situ nucleation. The vapor is produced by reactive sputtering. An epitaxial Pt(111) film on a SrTiO3(111) single crystal has been used as substrate. 50 to 200 nm wide seed structures have been fabricated by e-beam lithography. It has been observed that the nucleation density on the seed islands is by far larger than on the bare Pt. A depletion zone around the seed areas can be clearly identified in case of PbTiO3 nucleation, proving that PbO adatoms are captured by the seeds. The nano crystals grew as triangular plates (PZT(111)) in case of PZT40/60 deposition, and as (100) oriented square plates when first a second seed layer of PbTiO3 was applied. Many of the observed features can be explained in a semi quantitative manner in the frame of a Volmer-Weber growth model including surface and interface energies. In addition, the variation of the PbO adatom density has been taken into account as a function of deposition flux, diffusion, desorption, and chemisorption rate. The piezoelectric response as well as the switching of ferroelectric elements has been verified by means of Atomic Force Microscopy.

11:00 AM C1.7
Relaxor Ferroelectricity in Epitaxial $SrTiO_3$ Thin Films on $DyScO_3$ Substrates. Michael David Biegalski[1], D. G. Schlom[1], S. Trolier-McKinstry[1], T. Heeg[2], J. Schubert[2], W. Chang[3] and S. W. Kirchoefer[3]; [1]Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania; [2]Forschungszentrum Julich GmbH, Julich, Germany; [3]Navy Research Labs, Washington, District of Columbia.

Epitaxial $SrTiO_3$ thin films were grown on $DyScO_3$ substrates by Molecular Beam Epitaxy or Pulsed Laser Deposition. These films exhibited good structural epitaxy with x-ray rocking curves of less than 0.35° in ω. The $SrTiO_3$ films show relaxor ferroelectric behavior with a transition temperature near 260 K. Relaxor behavior has not previously been seen in undoped $SrTiO_3$ thin films, and the peak permittivity is nearly 150 K above previously reported values. The dielectric data shows frequency relaxation that was well fit by a Vogel-Fulcher equation over six orders of magnitude. The Vogel-Fulcher fitting indicated a freezing temperature of 202 K, which agreed with measurements of coercive field as function of temperature. These films also exhibit clear hysteresis loops below the T_{max} with remenent polarizations up to 7 $\mu C/cm^2$.

11:15 AM C1.8
Preparation and basic properties of ferroelectric Bi_3TiNbO_9-$Bi_4Ti_3O_{12}$ thin films with different superlattice structures. Akira Shibuya, Minoru Noda and Masanori Okuyama; System Innovation, Osaka Univ., Toyonaka, Osaka, Japan.

Natural-superlattice-structured Bi_3TiNbO_9-$Bi_4Ti_3O_{12}$ (m=2-3) (BTN-BIT) thin films have been prepared. Lattice mismatch between the two psuedo-perovskite blocks and their different chemical characters are expected to induce large lattice distortion of Bi_2O_2 layer, leading to a quite distinct type of ionic displacement along a axis. BTN-BIT films have been grown on $Pt/TiO_2/SiO_2/Si$ and $SrTiO_3$ single crystal substrates at 400°C to 550°C by pulsed laser deposition (PLD) using BTN-BIT (1mol:1mol) target, and were post-annealed in O_2 for 45 minutes at 750°C. In the X-ray diffraction (XRD) patterns of BTN-BIT films on $Pt/TiO_2/SiO_2/Si$ substrates, all peaks below 16° are attributed to c lattice constant because these BLSFs have much longer c lattice constant (more than 2.516 nm of BTN) than a and b lattice constants (around 0.54 nm). BTN-BIT films prepared above 500°C has single phase whose c lattice constant is estimated to 8.300 nm in consideration of periodicity of lattice structures. This lattice constant is very close to the value (8.316 nm) of that of two unit cells of BTN and one unit cell of BIT, that is 2-1 superlattice structure of BTN-BIT. The lattice constant (2.905 nm) of post-annealed BTN-BIT films prepared at 400°C is very close to the value (2.900 nm) of that of one unit cell of BTN and one unit cell of BIT, that is 1-1 superlattice structure of BTN-BIT. The BTN-BIT bulk target is also 1-1superlattice structure. The BTN-BIT film with 2-1 superlattice structure prepared at 550°C has large remanent polarization ($2P_r = 50\mu C/cm^2$). In summary, two kinds of natural-superlattice-structured BTN-BIT thin films have been prepared and have very large remanent polarization.

11:30 AM C1.9
Strain-Induced Enhancement of Phase Transition Temperature in Epitaxial BaTiO3 Thin Films on (110) GdScO3 Substrates. K. J. Choi[1], Chang Beom Eom[1], J Schubert[2], M. Biegalski[3], Y.L. Li[3], L.-Q. Chen[3], D. G. Schlom[3], R. Uecker[4] and P. Reiche[4]; [1]Department of Materials Science and Engineering, Univ. of Wisconsin at Madison, Madison, Wisconsin; [2]Institut fur Schichten und Grenzflachen ISG1-IT, Julich, Germany; [3]Department of Materials Science and Engineering, Penn State University, University Park, Pennsylvania; [4]Institute of Crystal Growth, Berlin, Germany.

Epitaxial ferroelectric thin films often have quite different properties than bulk single crystals due to epitaxial and thermal strains arising from substrate constraints. This offers the opportunity to modify ferroelectric properties by heteroepitaxy and strain engineering. Using a variable temperature four-circle x-ray diffractometer, we have observed a significant enhancement of phase transition temperature in strained epitaxial (001) BaTiO3 thin films grown on by both (001) SrTiO3 and (110) GdScO3 substrates. The BaTiO3 films were grown by pulsed laser deposition (PLD) and molecular beam epitaxy (MBE). The BaTiO3 thin film on the GdScO3 substrate showed complete coherency below a thickness of 100 nm, due to the small lattice mismatch between BaTiO3 (a = 0.399 nm) and GdScO3 ($c/2 \sim$ (a2 + b2)0.5/2 = 0.397 nm). The x-ray diffraction data show the tetragonality of all of the BaTiO3 films to be maintained up to the highest measured temperature, 700oC, in contrast to 130 oC for bulk single crystals of BaTiO3. This is due to the clamping effect between BaTiO3 and the substrates. The correlation between transition temperature and ferroelectricity of BaTiO3 was confirmed by theoretical simulations, which calculate ferroelectricity using the Landau potential as a function of spontaneous polarization components. The calculations indicate that the ferroelectric transition temperature coincides with the location of the change in slope of the c lattice parameter of the strained BaTiO3 thin film as a function of temperature. The theory predicts that the polarization was not only increased to 0.305 C/m2 but also it maintained up to 407oC for the coherent BaTiO3 thin film on GdScO3. This result is consistent with the transition temperature obtained from variable temperature XRD measurements.

11:45 AM C1.10
Temperature-Strain Diagrams for Epitaxial Ferroelectric Thin Films: Theory and Experiment. Samrat Choudhury[1], Y.L. Li[1], J.H. Haeni[1], M.D. Biegalski[1], S. Trolier-McKinstry[1], D.G. Schlom[1], L.Q. Chen[1], J. Schubert[2], W. Chang[3], S. Kirchoefer[3], K.J. Choi[4], C.B. Eom[4], R. Uecker[5] and P. Reiche[5]; [1]Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; [2]Institut fuer Schichten und Grenzflaehen ISG1-IT, Forschungszentrum Juelich GmbH, D-52425 Juelich, Germany; [3]Naval Research Laboratory, Washington, District of Columbia; [4]Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; [5]Institute of Crystal Growth, Berlin, Germany.

The effect of an external mechanical constraint on the phase stability in epitaxial thin films of $SrTiO_3$, $BaTiO_3$, and $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) are studied using both 3D phase-field simulations and thermodynamic analysis. The temperature vs. misfit strain domain stability diagram for each case is constructed. It is shown that an external mechanical constraint can drastically change the ferroelectric

transition temperature in PZT and $BaTiO_3$ and both the ferroelectric and structural transition temperatures in $SrTiO_3$ films. Comparison with strained $SrTiO_3$ and $BaTiO_3$ epitaxial films grown by molecular beam epitaxy (MBE) will be made. The effect of elastic constants and gradient energy coefficients on the domain stability diagrams will be discussed. The validity of the single-domain assumption in the thermodynamic analysis in predicting the domain/phase stability is also investigated for the case of PZT thin films.

SESSION C2: Fundamentals of Ferroelctric Films:
Emphasis on Characterization and Domains
Chairs: Hiroyuki Odagawa and Stephen Streiffer
Monday Afternoon, December 1, 2003
Room 203 (Hynes)

1:30 PM *C2.1
Development of Ultra-high Vacuum Scanning Nonlinear Dielectric Microscope and Observation of Ferroelectric Polarization Distribution in Ferroelectric Thin Films and Single Crystals. Hiroyuki Odagawa and Yasuo Cho; Research Institute of Electrical Communication, Tohoku University, Sendai, Japan.

Recently, several researchers have studied and reported various techniques for determining ferroelectric polarization direction and observing domain structure with high spatial resolution. This research is important to clarify the relation between the material properties and the behavior of small ferroelectric domains, especially in polarization switching and domain wall movement. This is interesting not only from an academic standpoint, but also has the potential of improving the device characteristics. We have proposed and developed a purely electrical technique for imaging the state of ferroelectric polarization and local crystal anisotropy of dielectric materials called "scanning nonlinear dielectric microscopy" (SNDM) [1]. To date, the spatial resolution of SNDM has been improved down to 0.5 nm, exceeding piezoelectric scanning force microscopy resolution. [2] In this paper, we will describe a newly developed ultra-high vacuum type scanning nonlinear dielectric microscope and measurement results of ferroelectric domain structures in various ferroelectric thin films and single crystals with nanometer resolution. In this experiment, ultra-high vacuum chambers are used to remove an undesirable influence of an absorbed layer on the sample surface, and the samples are prepared by ion beam cleaning or by cleaving in the ultra-high vacuum atmosphere. Experimental results include a nano-scale observation of polarization distribution in PZT thin film and other ferroelectric thin films and single crystals, a domain movement in TGS single crystal after cleavage, and so on. [1] Y. Cho, A. Kirihara and T. Saeki: Rev. Sci. Instrum. Vol.6 (1996) 2297. [2] H. Odagawa and Y. Cho, Surface Science, Vol. 463, (2000) L621.

2:00 PM C2.2
Second Harmonic Piezoresponse Force Microscopy: a probe of high order ferroelectric processes. Rui Shao and Dawn A Bonnell; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

The characterization of local ferroelectric properties has been greatly facilitated by Piezoresponse Force Microscopy (PFM). The principle of PFM is the detection of the electromechanical response to an ac voltage applied at a tip/surface contact. It has proven useful in determining domain orientation, observing domain wall motion, and under some circumstances quantifying d33. There is a potential to examine fundamental processes involved in domain switching and ferroelectric relaxation if higher order response functions can be probed. To address this we have measured the second harmonic of the electromechanical response to the ac imaging voltage on various ferroelectric thin films as a function of both frequency and amplitude of the voltage. A theoretical model has been established that relates ferroelectric relaxation to the second harmonic response. The ferroelectric relaxation of several classes of materials will be compared, including BST, PDVF, PZT, and BaTiO3. Differences in dipole interaction in these compounds will be discussed. The approach is extended to imaging, Second Harmonic Piezoresponse Microscopy, that maps the distribution of relaxation times on surfaces by acquiring the spatial distribution of the second harmonic response.

2:15 PM C2.3
Probing Ferroelectric Domain Dynamics using Near-field Scanning Optical Microscopy and Transmission Electron Holography. Pradyumna Prabhumirashi, David Towner, Bruce Wessels and Vinayak Dravid; Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

Ferroelectrics have scientifically interesting and technologically useful properties related to their spontaneous electric polarization. Ferroelectric $BaTiO_3$ thin films are being studied using Near-field Scanning Optical Microscopy (NSOM) and Electron Holography to facilitate understanding of ferroelectric domain dynamics. NSOM makes it possible to locate, distinguish and characterize ferroelectric domains whose size and separation is smaller than the wavelength of light used and are otherwise invisible in conventional optical microscopy technique. Ferroelectric thin films consisting of epitaxial $BaTiO_3$ were deposited onto MgO (001) substrates using MOCVD. NSOM in reflection mode was used to directly observe the poly-domain structure. An Ar ion laser (λ= 514nm) was used as a light source. The laser beam was directed through a single mode optical fiber and $\lambda/2$ plate to produce the desired linear polarization direction. The images exhibited inhomogeneities in reflected intensity which was attributed to change in ferroelectric polarization over micrometer lengthscales and were largely uncorrelated with topographic features. Further, the films were patterned with interdigitated gold electrodes for in-situ biasing experiments. Application of an in-plane static electric field resulted in domain reorientation. These results demonstrate the capabilities of reflection mode NSOM for imaging domain structure in ferroelectric materials. Currently we are utilizing transmission electron holography to directly image ferroelectric nanodomains in $BaTiO_3$ thin films. Electron holography, a coherent interferometry technique based on interference of a reference wave with a scattered wave, is directly sensitive to the polarization change in solids. The presentation will highlight the correlation between domain structure obtain by NSOM and electron holography.

2:30 PM *C2.4
Observation of Ferroelectric Domain Behavior in Bismuth Layer Structured Ferroelectrics with Raman Spectroscopy. Minoru Osada[1,2], Masato Kakihana[1], Yuji Noguchi[3,2] and Masaru Miyayama[2]; [1]Materials Structures Lab., Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; [2]PRESTO, JST, Kawaguchi, Saitama, Japan; [3]Institute of Industrial Science, University of Tokyo, Tokyo, Japan.

Recent studies of ferroelectric thin films have revived interest in properties of the ferroelectric domain structures. It became clear that some basic aspects of these properties remain unexplored, whereas they are of key importance for applications. In this study, we address some unique aspects of micro-Raman spectroscopy for characterization of bismuth layer structured ferroelectrics (BLSF), emphasizing the use of soft mode as a probe to elucidate domain behaviors of these materials. $Bi_4Ti_3O_{12}$(BIT) and $SrBi_2Ta_2O_9$ (SBT) single crystals were grown by a self-flux method, whereas La-doped BIT thin films were prepared by a sol-gel method. Polarization microscopy revealed clear 90-deg domain structures (with typical width $\sim$20 μm) in the $a-b$ plane for BIT and SBT. In BIT single crystal, the lowest frequency mode (soft mode) at $\sim$30 cm^{-1} appears exclusively for the aa polarization configuration (a // polar axis). We observe spike-like a and b domains well inside extended a and b-polarized areas, which were not conclusive with polarization microscopy. These characteristics are shared with other BLSF's such as SBT and doped BIT, which demonstrates the usefulness of the soft-mode spectroscopy for the study of domain structures in BLSF's. With Raman imaging of the soft-mode intensity, we also show the unambiguous identification of the domain distribution in the BIT thin film on the submicrometer scale. In addition, we will discuss some results on $in-situ$ observation of changes in the domain structure as a function of polarization field and temperature for La-doped BIT thin films.

3:30 PM C2.5
Dynamics of 90 Degree Domain Movement of Epitaxial Pb(Zr0.2Ti0.8)O3 Thin Film Grown on Si(100) Substrate Using SrTiO3 Template Layer. Z Ma[1], V Nagarajan[1], J Melngailis[2], R Ramesh[1] and D Schlom[3]; [1]Department of Materials Science and Engineering, University of Maryland at College Park, College Park, Maryland; [2]Department of Electrical and Computer Engineering, University of Maryland, College Park, Maryland; [3]Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

Dynamics of domain interfaces in a broad range of functional thin film materials is an area of great current interest. In ferroelectric thin films, a significantly enhanced piezoelectric response should be observed if non-180 degree domain walls were to switch under electric field excitation. However, in continuous, thin films they are clamped by the substrate, and therefore their contribution to the piezoelectric response is limited. In a recent paper we demonstrated 90 degree domain wall movement in discrete capacitors of epitaxial Pb(Zr0.2Ti0.8)O3 films grown on the STO substrate. The ferroelectric layer in these islands was milled free via focused ion beam milling, there by eliminating the clamping imposed by the substrate. Consequently the out-of-plane d33 for these islands was found to be 250 pm/V, $\sim$ 3 times the intrinsic value of 87 pm/V. In order to fully exploit the large piezoelectic coefficients shown by these discrete

islands we created these heterostructures on perovskite terminated Si substrate. The domain structure of the PZT layer grown on buffered Si was found to be different from the one observed on the STO substrate. By cross section TEM and piezoresponse microscopy we find that the density of 90 degree domains is larger and the domains are finer than the film grown on STO. Therefore the motivation of this presentation is to tune the 90 degreedomain structure using a variety of heteroepitxial tools and compare and contrast the dynamic behavior of the ferroelastic 90 degree domains as a function of the resulting microstructure . We also studied the polarization response of the nanostrctured island compared to a continuous film accompanying the ferroelastic domain movement. Our results show for both systems significant enhancement of piezoelectric response of the nanocapacitors associated with the movement of 90 degree ferroelastic domain in the absence of substrate clamping, compared to that of the continuous film, although the critical DC bias to cause the onset of ferroelastic domain wall motion are significantly different. This work is supported by the NSF-MRSEC under contract No. DMr-00-80008.

3:45 PM C2.6
Piezoresponse Force Microscopy: Fields below the Surface.
Sergei V. Kalinin[1], Junsoo Shin[1,2], Mark Kachanov[3], Edgar Karapetian[3] and Arthur P. Baddorf[1]; [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee; [3]Department of Mechanical Engineering, Tufts University, Medford, Massachusetts.

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

4:00 PM C2.7
TEM Analysis of Dislocation Structures in Epitaxial Barium Strontium Titanate Thin Films. Ibrahim Burc Misirlioglu[1], Alexandre Vasiliev[1], Neal Magdefrau[1], Mark Aindow[1], Ramamoorthy Ramesh[2] and Pamir Alpay[1]; [1]Metallurgy and Materials Engineering, University of Connecticut, Storrs, Connecticut; [2]Department of Materials and Nuclear Engineering, University of Maryland, College Park, Maryland.

Barium strontium titanate thin films are of considerable interest due to their desirable ferroelectric and dielectric properties. The characteristics of these materials differ significantly from their bulk forms especially due to the presence of internal stresses and dislocation type defects that are higher in density to accommodate the misfit between the substrate and the film. Considering that internal stresses are much higher in the vicinity of the dislocation core, one can expect a significant variation in the local electrical and electromechanical properties of ferroelectric thin films. Indeed, it has been shown experimentally that the relative dielectric constant of epitaxial BST films is strongly dependent on the defect structure as well as the epitaxial stresses [1,2]. In our current program, we are studying the effects of lattice misfit and deposition variables on the defect microstructure and electronic properties of epitaxial barium strontium titanate films. These data will be used to validate, and to guide the further development of microstructure-property models for such systems. In this paper we will present preliminary data obtained from Ba0.6Sr0.4TiO3 thin films of various thicknesses deposited on (001) LaAlO3 substrates by pulsed laser deposition The defect structure of the films have been characterized via transmission electron microscopy to reveal the character and distribution of the defects throughout the films. Plan view and cross-sectional observations showed that the character, density and morphology of the threading and the misfit dislocations in the films varied with both film thickness and substrate type. Moreover, electron diffraction revealed that there are small deviations from the nominal orientation relationship. The significance of these observations for both the mechanisms of misfit relaxation in this system and the viability of strategies for defect reduction will discussed.

4:15 PM C2.8
Surface Properties and Thermal Behavior of Epitaxial $SrRuO_3$ Thin Films. Junsoo Shin[1,2], Sergei V. Kalinin[1], Ho Nyung Lee[1], Hans M. Christen[1] and Arthur P. Baddorf[1]; [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee.

Metallic strontium ruthenium oxide $SrRuO_3$ has recently attracted significant attention as a prominent material for oxide electronics. To elucidate the qualities of this material, which make it a good electrode for ferroelectric capacitors, we have studied the surface properties of $SrRuO_3$ using a combination of electron spectroscopies, low energy electron diffraction (LEED) and scanning probe microscopy. Epitaxial $SrRuO_3$ thin films were grown by pulsed laser deposition using a stoichiometric target on (001) $SrTiO_3$ substrates. Atomic force microscopy (AFM) images taken in air confirm the high quality of grown films, showing uniformly spaced terraces with single steps on the film surface, which closely imitate those of the $SrTiO_3$ substrate. After reinsertion into vacuum, a (1x1) Low Energy Electron Diffraction (LEED) pattern has been observed from the as-inserted sample at room temperature without thermal treatment, revealing an excellent chemical stability in air. Corresponding vacuum scanning tunneling microscopy (STM) imaging and spectroscopy show some evidence of an inhomogeneous surface with insulating regions. The LEED pattern disappears after a brief anneal at 200 °C, indicating surface disordering. To quantitatively investigate this behavior, $SrRuO_3$ thin films have been annealed in high vacuum in steps of 100 °C up to 800 °C and studied after cooling by LEED, x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and STM. The evolution of the surface topography, atomic and electronic structure, and valence state of ruthenium was characterized and compared with results of thermodynamic calculations. The implications of these results for perovskite oxide electronic devices are discussed.

4:30 PM C2.9
Effect of thermal strain on the ferroelectric phase transition in polycrystalline $Ba_{0.5}Sr_{0.5}TiO_3$ thin films studied by Raman spectroscopy. Dmitri A Tenne[1], A Soukiassian[2], X X Xi[1,2,3], T R Taylor[4], P J Hansen[4], J S Speck[4] and R A York[5]; [1]Dept. of Physics, The Pennsylvania State University, University Park, Pennsylvania; [2]Dept. of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; [3]Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; [4]Materials Dept., University of California, Santa Barbara, California; [5]Dept. of Electrical and Computer Engineering, University of California, Santa Barbara, California.

We have applied Raman spectroscopy to study the influence of thermal strain on the vibrational properties of polycrystalline $Ba_{0.5}Sr_{0.5}TiO_3$ thin films. The films were grown by rf magnetron sputtering on Pt/SiO_2 surface using different host substrates: strontium titanate, sapphire, silicon, and vycor glass. These substrates provide a systematic change in the thermal strain while maintaining the same film microstructure. From the temperature dependence of the ferroelectric A_1 soft phonon frequency, the ferroelectric phase transition temperature, T_c, was determined. We found that T_c decreases with decreasing thermal expansion coefficient of the substrate, i.e. increasing tensile stress in the films. This dependence is different from the theoretical predictions for epitaxial ferroelectric films, demonstrating that the theory of strain effects in epitaxial ferroelectric films cannot be simply applied to polycrystalline films. The complex structural nature of the polycrystalline films has to be taken into account when studying the strain dependence of the ferroelectric phase transition in these films.

4:45 PM C2.10
^{18}O Tracer Studies in $Pb(Zr,Ti)O_3$ Thin Films. Ruey-Ven Wang and Paul C. McIntyre; Materials Science and Engineering, Stanford University, Stanford, California.

Ferroelectric thin films, such as $Pb(Zr,Ti)O_3$ (PZT), are currently used in low density non-volatile memories and are being considered for higher-density semiconductor memory applications. However, fundamental mechanisms controlling the reliable switching of PZT films remain uncertain. In particular, the role played by potentially mobile point defects, such as oxygen vacancies, in processes such as imprint and fatigue has not been clearer elucidated. Up to date, no quantitative measurements on the activation energy and mobility of oxygen vacancies in PZT thin films have been reported. As first step toward such quantitative understanding, we have recently conducted a

series of ^{18}O tracer in-diffusion experiments into state-of-the-art MOCVD-grown PZT films to monitor vacancy diffusion at different temperatures (400°C to 600°C) for various durations. Prior to ^{18}O incorporation, samples were pre-equilibrated in $^{16}O_{2(g)}$ at the same temperature and total pressure used for the following $^{18}O_{2(g)}$ annealing. The final ^{18}O profiles were obtained using secondary ion mass spectroscopy (SIMS), which provides a a high depth resolution of 3-5 $\AA$. The ^{18}O tracer results for annealing at relatively low temperatures and/or for shorter times show that the ^{18}O diffusion profiles in PZT thin films cannot simply be fitted by the solution of Fick's 2nd Law with constant (position-independent) diffusivity. Based on a previously developed model for point defect equilibrium in metal titanate thin films, an analysis of ^{18}O tracer diffusion into 100 nm PZT thin films will be presented.

SESSION C3: Poster Session: Ferroelectric Films: Fundamentals, Processing, and Epitaxy
Chairs: Vikram Joshi and Angus Kingon
Monday Evening, December 1, 2003
8:00 PM
Exhibition Hall D (Hynes)

C3.1
Size effects in ultra-thin epitaxial ferroelectric heterostructures. Nagarajan Valanoor[1,4], Tong Zhao[1], Jun Ouyang[1], Haimei Zheng[1], Ramamoorthy Ramesh[1], Wei Tian[2], Xiaoqing Pan[2], Dong-Min Kim[3], Chang-Beom Eom[3], Herman Kohlstedt[4] and Rainer Waser[4]; [1]Dept of Materials Science and Engineering, MRSEC, Univ of maryland, college park, Maryland; [2]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; [3]Dept of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; [4]Institute of Electroceramic Materials, Research Center-Juelich, Juelich, Germany.

Recent ab-initio calculations for a realistic $BaTiO_3/SrRuO_3$ ferroelectric electrode interface have shown that the critical thickness for ferroelectricity is of the order of 6 unit cells as a consequence of an electrostatic depolarizing field. While a theoretical understanding has been widely reported, there is a lack of direct experimental data for model ultrathin (<10 nm) films, because external factors from the materials processing overtly dominate the true size effect. Although ferroelectricity was detected in a 4nm thick epitaxial PZT film, no quantitative measurements of the ferroelectric order parameters was shown . In this talk we show a direct and systematic experimental study of the polarization, dielectric susceptibility and d_{33} of PZT films grown heteroepitaxially with $SrRuO_3$ electrodes in the thickness range of from 4 to 160 nm. Our results suggest that for such a model system, the scaling law obeys the depoling mechanism, with the critical exponent$\sim$1. This work was supported by NSF MRSEC Grant #00-8008. The work at University of Wisconsin is supported by NSF under contract No. DMR-9973801.

C3.2
Residual Stress Effects in Ferroelectric Thin Films. Thomas A Berfield[1], N. R. Sottos[1], R. Ong[2] and D. A. Payne[2]; [1]Theoretical and Applied Mechanics, University of Illinois Urbana/Champaign, Urbana, Illinois; [2]Material Science and Engineering, University of Illinois Urbana/Champaign, Urbana, Illinois.

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

C3.3
Anisotropic In-plane Strain in Pb(Sr,Ti)O3 Thin Film on NdGaO3 Substrate. Yuan Lin[1], Quanxi Jia[1], Xin Chen[2], Chonglin Chen[2] and A Bhalla[3]; [1]Material Science & Technology Division, Los Alamos National Lab, Los Alamos, New Mexico; [2]Texas Center for Superconductivity and Advanced Materials, and Department of Physics, University of Houston, Houston, Texas; [3]Materials Research Lab., Penn State University, University Park, Pennsylvania.

Anisotropic in-plane strain can be induced in Pb(Sr,Ti)O3 (PST) thin film by using an orthorhombic NdGaO3 (110) as a substrate which has in-plane lattice parameters of 7.7245 angstrom along [1-10] and 7.7016 angstrom along [001]. The PST film was deposited by laser ablation and was characterized using high-resolution X-ray diffraction. Rocking curve with a full-width at half maximum of less than 0.04 degree illustrated that the film had a nearly perfect crystallization quality. Reciprocal space maps around the (100), (103) and (013) reflections of PST film revealed an in-plane strain anisotropy along [100] and [010] orientations. Coplanar capacitance measurements also showed the systematic changes in dielectric constant and tunability due to the strain, which was another indicative of in-plane strain anisotropy.

C3.4
Spontaneous Buckling of Nanocrystalline Self-Supported Ferroelectrics Films. Isai Feldman[1], Ilya Zon[1], Vera Lyahovitskaya[1], Ellen Wachtel[3], Alexander Roytburd[2] and Igor Lubomirsky[1]; [1]Materials & Interfaces, Weizmann Institute, Rehovot, Israel; [2]Materials and Nuclear Engineering, University of Maryland,, College Park, Maryland; [3]Research Support, Weizmann Institute, Rehovot.

Thin ferroelectric films are very promising for a number of applications ranging from actuators to ferroelectric memories. In most of these applications the films are clamped. However, a number of applications, such as surface acoustic wave filters, piezoelectric actuators, pyroelectric sensors etc., employ the films that have some freedom to bend. We have investigated stability of nanocrystalline tethered ferroelectric membranes with respect to spontaneous buckling. It has been found that depending on the geometrical constraints the membranes may assume a single dome shape or buckle with a curvature radius, which is constant or varying within the membrane. Upon certain conditions one can observe coexistence of totally flat areas with areas that have a curvature radius as small as 0.045 mm. A theoretical description based on formation of a dynamic self-adjustable crystallographic texture was developed. This theory correctly relates the curvature radius with crystallographic parameters and film thickness. However, the symmetry and temperature dependence of the buckling patterns above the para- to ferroelectric transition temperature require further investigation. Buckling instability is observed only in nanocrystalline self-supported ferroelectric films and by its nature the buckling is similar to the buckling of lipid membranes. Since, the enthalpy associated with buckling can be comparable with that of the para- to ferroelectric transition, this phenomenon has to be taken into account during design and construction of the devices employing nanocrystalline ferroelectric films.

C3.5
Strain Effect in multiferroic $BiFeO_3$ Thin Films. Junling Wang[1], Haimei Zheng[1], Dwight Viehland[2], Valanoor Nagarajan[1], Venugopalan Vaithyanathan[3], Darrell G. Schlom[3], Manfred Wuttig[1] and Ramamoorthy Ramesh[4]; [1]Materials Science and Engineering, University of Maryland, College Park, College Park, Maryland; [2]Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia; [3]Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; [4]Physics, University of Maryland, College Park, College Park, Maryland.

In recent years the ferroelectromagnet $BiFeO_3$(BFO), which has both ferroelectric (T)C$\sim$1100k) and G-type antiferromagnetic (T)N$\sim$640K) orders, has attracted immense research interest. This unique system is responsive to a variety of stimuli (i.e electric field, magnetic field, stress etc) thereby creating pathways for novel and exciting applications. In this study, BFO thin films with different orientation were deposited using pulsed laser deposition (PLD). (001), (110) and (111) cut $SrTiO_3$(STO) single crystal substrates were chosen to systematically move the biaxial epitaxial strain from (001) plane to (111) plane. X-ray diffraction (XRD) and transmission electron microscopy (TEM) study show that the film structure changes from monoclinic to rhombohedral, corresponding to the strain direction. Effect of this change on the physical properties was studied by ferroelectric polarization and susceptibility (dielectric constant and piezoelectric coefficient) measurements. All the films show dramatically enhanced ferroelectric property compared with bulk. Origin of this enhancement will be discussed. We find that the spontaneous polarization systematically increases from 50μC/cm^2(001 oriented film) to 85μC/cm^2(111 oriented film) with a commensurate decrease in the piezoelectric coeffcient and dielectric susceptbility respectively. Thickness and crystallographic dependence of these properties demonstrates the important role of mismatch strain and

substrate induced changes to the crystal phase. This work is supported by the Office of Naval Research MURI N000140110761 and the National Science Foundation MRSEC DMR-00-80008.

C3.6

Suppression of low-temperature phases by strain in epitaxial $BaTiO_3$ thin films. Dmitri A Tenne[1], A Soukiassian[2], M H Zhu[1], A R James[1], X X Xi[1,2,3], Y L Li[2], L Q Chen[2], J Lettieri[2], D G Schlom[2,3], W Tian[4] and X Q Pan[4]; [1]Dept. of Physics, The Pennsylvania State University, University Park, Pennsylvania; [2]Dept. of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; [3]Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; [4]Dept. of Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan.

Lattice dynamics and phase transitions in $BaTiO_3$ thin films grown by pulsed laser deposition on $SrTiO_3$ and $LaAlO_3$ substrates with $SrRuO_3$ buffer layers were studied by Raman spectroscopy. Comparison of the Raman spectra over the temperature range 5-320 K for the films and single $BaTiO_3$ crystals shows that the phase transitions between different ferroelectric phases (tetragonal-orthorhombic-rhombohedral) characteristic for bulk barium titanate, are suppressed in the films. This behavior is explained by the presence of strain in $BaTiO_3$ films, caused by thermal mismatch with underlying $SrRuO_3$ layers. X-ray diffraction analysis shows that he films are under tensile strain, and the room temperature value for the strain with respect to the bulk $BaTiO_3$ is 0.45%. Our calculations of domain structures based on the thermodynamic phase-field approach predict an orthorhombic phase with in-plane polarization to be the stable phase for such value of biaxial strain. Theory predicts this phase to be stable for tensile-strained films over the entire temperature phase studied. Experimental Raman results provided a direct proof of the theoretical thermodynamic predictions of strain effects on phase diagram in ferroelectric thin films.

C3.7

Phase Transitions and Low Temperature Electrical Properties of BST/ZrO2 Multilayer Films. Dinesh Agrawal[1], Santosh K Sahoo[1], Subhasish B Majumder[2], Ram S Katiyar[2] and Y N Mohapatra[1]; [1]Materials Sc. Programme, IIT Kanpur, Kanpur, U.P., India; [2]Department of Physics, University of Puerto Rico, San Juan, Puerto Rico.

Thin films of Ba1-x SrxTiO3 (BST) are being actively investigated for applications in dynamic random access memories (DRAM) because of their properties such as high dielectric constant, low leakage current, and low fatigue. Several approaches have been used to improve the properties of thin films such as doping with aliovalent dopants, graded compositions, and layered structures. We have found that interposing layers of an electronic insulator such as ZrO2 in between BST layers results in a significant reduction in leakage current. In this paper the phase transition behavior and low temperature electrical properties of these multilayer structures is reported.. The structures consist of alternate layers of Ba0.8Sr0.2TiO3 and ZrO2 deposited by a sol-gel process on platinized Si substrates. The thickness and the number of layers are varied while keeping the total thickness of the film constant. The single layer BST film has a Curie temperature of 280 K at which the transition from a cubic phase to the ferroelectric tetragonal phase occurs. A further transition at about 160K occurs which may correspond to the cubic to rhombohedral transition . In the multilayered films these transitions become very broad and are spread over a large temperature range. A structure with several thin layers of ZrO2 interposed between the BST layers produces a less broad transition than a single layer of ZrO2 of same total thickness. This is attributed to more uniform distribution, as determined by XPS, of ZrO2 in the multilayer structure due to smaller diffusion distances. In the sample with single thick ZrO2 layer a very wide distribution of the Curie temperatures is obtained. This results in a considerable region with nearly a constant dielectric constant over a wide temperature range indicating that this approach may also be useful in applications requiring a low temperature coefficient of capacitance.

C3.8

Dipole Screening of Pyroelectric and Ferroelectric Grains in Semiconductor Matrix. Alexandre Dmitriev[1], Valentin Kachorovskii[1], Michael S. Shur[1] and Remis Gaska[2]; [1]RPI, Troy, New York; [2]Sensor Electronic technology, Inc., Columbia, South Carolina.

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

C3.9

Direct observation of domain-patterned ferroelectrics by Photo-Electron Emission Microscopy (PEEM). Woochul Yang[1], B.J. Rodriguez[1], A. Gruverman[2] and R.J. Nemanich[1]; [1]Physics, North Carolina State University, Raleigh, North Carolina; [2]Materials Science and Engineering, North Carolina State Univeristy, Raleigh, North Carolina.

Ferroelectric surfaces with polarity patterned domains of LiNbO3 (LNO) crystals and PbZrTiO3 (PZT) thin films were explored using in situ UV-photo-electron emission microscopy (PEEM). The photo-electrons were excited with UV-light from the tunable UV free electron laser (FEL) at Duke University. PEEM images were obtained with photon energies from 4.0 to 6.5eV, the surfaces were examined at room temperature and at elevated temperatures. The brightness contrast between different polar domains of the surfaces was observed through the difference of the photoelectric yields. The polarity of the domains was identified by piezoresponse force microscopy (PFM) and chemical etching. In both LNO and PZT, bright emission was detected from negative domain ends (negative domains), indicating that the emission threshold of the negative domain is lower than that of the positive domain. For LNO, the photo-threshold of the negative domains measured by PEEM was 4.6eV, while for PZT, the threshold of the negative domains was less than 4.3eV. A reduction in emission intensity was observed as the samples are annealed and can be understood in terms of a reduction in bound polarization charges. Moreover, the image contrast of the PZT surface disappeared at near the Curie temperature of $\sim$300C. The PEEM polarity contrast of the ferroelectric domains is discussed in terms of the built-in internal field and the surface band bending induced by the polarization bound surface charges. * Research supported by the ONR and the AFOSR through the MFEL programs

C3.10

Ferroelectric Domain Structure and Local Piezoelectric Properties of Sol-Gel Derived $Pb(Zr_{1-x}Ti_x)O_3$ Films. Igor Bdikin[1], Vladimir Shvartsman[1], Andrei Kholkin[1] and Seung-Hyun Kim[2]; [1]Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal; [2]Inostek Inc., Ansam Technopark 707, 1271-11, Sa-1 Dong, Snagrok, Ansan, Kyunggi 425-791, South Korea.

In the past several years, ferroelectric films have received significant attention in view of their applications in nonvolatile ferroelectric memories, pyroelectric detectors, electromechanical actuators, and field-effect transistors. Since the size of these devices is expected to approach sub-μm range, the local techniques to investigate dielectric, ferroelectric and piezoelectric properties of the films at such scale are becoming increasingly important. One of these techniques, Piezoresponse Force Microscopy (PFM), has been successfully used to investigate the physical properties of ferroelectrics at the scale limited by only the size of the PFM tip ($\sim$10 nm). However, the lack of the experimental data on films of different compositions and thicknesses (and their comparison with corresponding macroscopic results) limits the understanding of the contrast nature and its dependence on the microstructure and texture of the films. In this work, high-resolution PFM study has been performed on $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) films with Ti concentration x=0.30, 0.48 and 0.70. The chemical solution route has been used to prepare these polycrystalline films with the thickness 1 $_\mu$m and 4$_\mu$m. The films were spin-coated onto Pt/Ti//SiO_2/Si substrates and processed at 650 °C. The orientation of the films varied from purely (111) (related to the orientation of Pt bottom electrode) to a more random texture. Statistical processing of the obtained domain images has been used to analyze the relationship between the texture (or composition) of the films and their respective

piezoelectric properties. In general, the films with more random orientation demonstrated broader distribution of the piezoelectric signal, which thus can be used to evaluate preferred orientation by pure electrical means. We also observed a correlation between the grain size and the nanoscale piezoelectric response. Self-polarization (i.e., the difference between the number of oppositely oriented domains in as-grown films) has been investigated in detail. Self-polarization was found to depend on the composition, thickness and texture of the films being more pronounced for rhombohedral films. Finally, local piezoelectric hysteresis and macroscopic polarization hysteresis were compared and analyzed.

C3.11

Interface states of laser ablated BaTiO3 and Ba0.9Ca0.1TiO3 thin films in MFS structure determined by DLTS and CV technique. Victor Pushparaj[1], S B Krupanidhi[1] and Sangib Saha[2]; [1]Materials Research Center, Indian Institute of Science, Bangalore, Karnataka, India; [2]Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

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

C3.12

First-principles Study on Electronic Structure of PZTN Systems. Hiromu Miyazawa[1], Takamitsu Higuchi[1], Taku Aoyama[1], Takeshi Kijima[1], Eiji Natori[1], Tatsuya Shimoda[1] and Tamio Oguchi[2]; [1]Technology Platform Research Center, Seiko Epson corporation, Fujimi-machi, Nagano-ken, Japan; [2]ADSM, Hiroshima University, Higashi Hiroshima, Japan.

Kijima et. al. found that $Pb(ZrTiNb)O_3$ (PZTN) with 20% Nb at B site realizes high resistance in thin films. [1] In this study, from a viewpoint of the electronic structure we shall investigate what compositions enable such high resistance in PZTN. We adopt the density functional theory using the FLAPW method. We calculate the electronic structure of a super cell, $Pb_{1-\delta}(ZrTi)_{1-x}Nb_xO_{3-y}$ which contains 2x2x2 ABO_3 type structure. Here, Zr to Ti ratio is 1 to 2. In the case of x=0.25 the density of states (DOS) suggests that electrons which numbers correspond to the excess electrons carried in by Nb are introduced at the conduction band minimum (CBM) which mainly consists of Ti-3d orbitals. For this case, if Pb atoms of δ=x/2=0.125 are subtracted without the oxygen vacancy, holes appear at valence band maximum (VBM) which consists of oxygen-2p orbital and they cancel out the doped electrons at the CBM. Hence the system recovers insulator states. The calculation of heat of formation indicates that this insulator state is more stable than the conductive state of the case of no Pb deficit. The increase of equilibrium-lattice constants are within +0.18% comparing with the case of δ=x=y=0. This low lattice expansion in PZTN is because of the large Pb deficit, δ=x/2=0.125. The bandgap of PZTN of the above case is about 1.0 eV wider than that of PZT with Pb and oxygen deficit, δ'=0.125 and y=δ'/3. We found that in PZT the oxygen vacancy drastically reduces the bandgap. The oxygen vacancy lowers the orbital energy of the nearest-neighbor Ti-3d through the Mardelung potential. We suppose that in PZTN the Nb added at the B site suppress the oxygen vacancy and PZTN could have higher resistance rather than PZT which loses Pb atom accompanying oxygen vacancy. [1] MRS fall meeting (2003)

C3.13

Pressure as a Probe of the Physics of ^{18}O - Substituted $SrTiO_3$. George A Samara[1], E L Venturini[1] and M Itoh[2]; [1]Sandia National Laboratories, Albuquerque, New Mexico; [2]Tokyo Institute of Technology, Yokohama, Japan.

Studies of the dielectric properties and phase behavior of an ^{18}O-substituted $SrTiO_3$ (> 97% ^{18}O), or STO-18, crystal at 1 bar and as functions of hydrostatic pressure and applied *dc* biasing electric field, have shed much light on the mechanism of the ^{18}O-induced ferroelectric transition in this material. Dielectric measurements reveal an equilibrium phase transition ($T_c \simeq 24$ K at 1 bar) and an enhancement of the static dielectric constant, $\epsilon\prime$, over that of normal (i.e., ^{16}O) $SrTiO_3$, or STO-16 over a large temperature range above T_c. This enhancement is quantitatively shown to be attributed to additional softening of the ferroelectric soft mode frequency (ω_s) of STO-16, in agreement with lattice dynamic calculations. Thus, in STO-18 two effects due to the heavier mass of ^{18}O conspire to induce the transition: (i) this additional softening of ω_s and (ii) damping of quantum fluctuations. Pressure lowers T_c at the large initial rate of 20 K/kbar and completely suppresses the ferroelectric state leading to a quantum paraelectric state at $\geq$ 0.7 kbar, confirming earlier results. Very large effects of a biasing *dc* electric fields on the peak temperature and $\epsilon\prime$ are also observed in the quantum regime reflecting the small characteristic energies of the system. The results also reveal a dielectric relaxation process near 10 K with interesting properties. The implications of all the results on our understanding of the physics of STO-18 are discussed.

C3.14

Mechanism of Superfast Domain Kinetics in Ferroelectrics. Vladimir Ya. Shur, Ekaterina V. Nikolaeva, Eugene I. Shishkin and Alexander P. Chernykh; Institute of Physics&Applied Mathematics, Ural State University, Ekaterinburg, Russian Federation.

New mechanism of super-fast domain kinetics has been discovered recently by direct observation of the domain kinetics in congruent lithium tantalate. It was shown that the input of conventional growth of isolated domains is negligible. The wall motion is driven by domain merging and determined by concentration of nuclei/residual domains. The mechanism has been investigated in details by computer simulation. The experimental measurements were performed in commercial single crystalline CLT. Liquid electrolyte 1-mm-diameter electrodes allow us to TV record the domain evolution in the whole switching area visualized by polarizing microscope with subsequent image processing. The unique possibility to establish the correspondence between switching current data and domain kinetics was realized. Analysis of the instantaneous patterns allows us to distinguish mechanisms of domain evolution in CLT. Switching from the single domain state starts with appearance of small domains with the density up to 1000-per-mm-square and subsequent growth with velocity about one micron per second. The prevailing switching process is a fast anisotropic wall motion defined by step generation by merging of moving walls with isolated triangular domains and rapid growth of arisen steps along the wall. A super-mobile domain walls with the highest step concentration form after large domains merging. Detail computer simulation of the discovered mechanism of domain growth with step generation due to domain merging only has been done. The crucial dependence of the switching parameters on the nuclei concentration has been found. It is proposed that this mechanism allow to explain the super-fast domain switching in thin films. The research was made possible in part by RFBR (Grant 01-02-17443), by RFBR-DFG (Grant 02-02-04006), by Ministry of Education RF (Grant E02-3.4-395) and by program "Basic Research in Russian Universities" (Grant UR.06.01.031), and by Award No.REC-005 of CRDF.

C3.15

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

The properties of complex oxides are controlled by their defect structure, but a fundamental understanding of how electrical properties are determined by the underlying defects (vacancies, impurities, interfaces, etc.) has still not been achieved. Despite intensive investigation using macroscopic measurements, many unknowns remain regarding their defect chemistry and structure, and the relationship of these defects to the aggregate electrical behavior. We have used a customized electrical probe station to study the electronic transport and polarization behavior of complex oxide films and nanostructures, in order to gain a better understanding of the defect chemistry of complex oxide thin films. The system is designed to enable electrical transport measurements up to 1000 °C in controlled p_{O2} atmospheres, from 1 to 10^{-20} bar, at 1 to 10^{-8} bar total pressure. High sensitivity voltage and current measurements are possible through four fully triaxially shielded probes which are

repositionable *insitu* over an area of several mm^2. We present some of our initial results obtained using this system, including the establishment of a baseline using model systems such as $SrTiO_3$ and epitaxial (Ba,Sr)TiO_3 and Pb(Zr,Ti)O_3 films, as well as some results for polycrystalline structures. These studies are aided by e-beam patterning to isolate individual structures, and TEM diffuse scattering studies of defect structures in the same films.

C3.16

Effect of Interface Capacitance on Dielectric Dispersion of PMN-PT Relaxor Thin films. Apurba Laha[1] and Saluru Babu Krupanidhi[2]; [1]Materials Research Center, Indian Institute of Science, Bangaore, Karnataka, India; [2]Materials Research Center, Indian Institute of Science, Bangalore, Karnataka, India.

xPb(Mg1/3Nb2/3)O3-(1-x)PbTiO3 (x=0, 1, 0.8, 0.3) (PMN-PT) relaxor thin films were deposited on platinum coated silicon substrate using pulsed excimer laser ablation technique. The substrate temperature and oxygen partial pressure maintained during the deposition were in the range of 600 to 750 oC and 100 to 300 mTorr, respectively. The dielectric properties of as deposited films were studied as a function of frequency over a wide range of temperature. The films exhibited a diffused phase transition together with the frequency dispersion of dielectric constant in the temperature zone higher than the temperature of dielectric maxima (Tm). This dispersion in higher temperature (Tm) was attributed to the effect passive layers to the overall dielectric response of the heterostructure. These passive layers could be formed at interfaces between the film and electrodes and at the grain boundaries. The response from the grain boundaries was minimized by controlling the grain structure of the films. The interfaces between the electrodes and film, especially the top electrode which was deposited at room temperature, could be the main influential region to promote the passive layer formation. This problem was rectified by single step and multi step post deposition annealing of top electrodes at different atmosphere. The microstructure at both the interfaces was also investigated by the scanning electron microscopy. The films deposited at higher temperatures (>675 oC) showed diffused interface at bottom electrode. We have also analyzed the thickness dependence of different parameters of the ferroelectric hysteresis e.g. coercive field, remnant polarization etc. to identify the passive layers.

C3.17

Raman Spectra of Srm-3Bi4TimO3m+3 Thin Films. Jia Wang[1], Guangxu Cheng[2], Hongwei Cheng[3], Shantao Zhang[3] and Yanfeng Chen[3]; [1]Physics, Nanjing University, Nanjing, Jiangsu, China; [2]National Laboratory of Solid State Microstructures, Center of Materials Analysis, Nanjing, Jiangsu, China; [3]Science and Technology of Materials, Nanjing University, Nanjing, Jiangsu, China.

A series of Ionic-Type Phononic Crystal (ITPC), Srm-3Bi4TimO3m+3(m=3,4,5,and 6) thin films were made by PLD (Laser pulse deposition), SBTi /LNO/LAO. There is a sharp peak at 821-831 cm-1 in these Raman spectra of samples(only m=3,4 and 5), however, the spectrum of SBTi6 is obviously different from the other three samples. Raman spectra were studied within the temperature range of 80-823K. For reducing temperature process, the main peak at 821-831cm-1 were varied, including their Γ,ω, and I. It is shown interest in split up the low frequency peak (at 142 cm-1) into two peaks, at 138 cm-1 and 145 cm-1, respectively, for m=5,6. But there is no splitting of low frequency peak and the main peak has not varied, for m=4. In the reverse process, the situation of main peak is similar to above statement, but there is no peak split in low frequency range. The results can be interpreted by fundamental principles and properties of these materials.

C3.18

Microstructure and Ferroelectric Behavior of Nano-domains in Ultra-thin BaTiO3 Films. Yariv Drezner and Shlomo Berger; Material Engineering, Technion-Israel Institute of Technology, Haifa, Israel.

Microstructure studies of ultra-thin BaTiO3 thin films (2-7nm thick) show nano-domains having a width as small as one unit cell. Only 1800 nano-domains and 900 domain-boundaries are formed in multi-domains structures. The domain-boundaries are formed at {111} twin boundaries. Most of the domains are oriented in parallel to the film plane but out-of-plane domains are also observed. The films exhibit ferroelectric behavior characterized by a polarization hysteresis loop. A remanent polarization of 3nC/cm2, and coercive field of 0.7MV/cm were measured in vertical to the film plane. Temperature-dependent polarization measurements show two peaks of the dielectric constant at about 700C and 1100C. These peaks are attributed to two Curie temperatures associated with out-of plane and in-plane domain's orientation, respectively. The switching response of the nano-domains is relatively fast in the range of few nano seconds. The switching time decreases with increasing the applied electric field according to a power law dependence of -2.5. Fatigue tests show an initial degradation of the remanent polarization at about 107 cycles under a continuous 5Vac load at 1kHz. The Leakage current of the films, which is of about 10-8 A/cm2 under applied field of 0.1 MV/cm, increases with applied electric field according to a characteristic behavior of hopping mechanism. The thermodynamic criterions for the formation and stability of the BaTiO3 nano-domains are presented and discussed.

C3.19

Epitaxial BaTiO3 thin films deposited on different substrates. Changhui Lei[1], Gustaaf Van Tendeloo[2] and Juegen Schubert[3]; [1]Materials science and Engineering, U. of Illinois at Urbana, Urbana, Illinois; [2]EAMT-RUCA, University of Antwerp, Antwerp, Antwerp, Belgium; [3]Institute of Thin Films, Juelich Research Center, Juelich, Germany.

BaTiO3 thin films were epitaxially grown on SrTiO3, LaAlO3, MgAl2O4, MgO, and MgO-buffered R-Al2O3 substrates by means of pulsed laser ablation. The film microstructure was investigated by means of transmission electron microscopy. Dislocations, antiphase boundaries and stacking faults are main defects found in the films. These defects are characterized by means of high-resolution electron microscopy. It was found the microstructure of these BaTiO3 films is significantly different: the defects, defect densities and defect distributions are strongly substrate-dependent.

C3.20

Abstract Withdrawn

C3.21

Stability of Single-Stepped Epitaxial $SrRuO_3$ Thin Films Grown by Pulsed Laser Deposition. Ho Nyung Lee, Hans M. Christen, Christopher M. Rouleau, Junsoo Shin, Sergei V. Kalinin, Arthur P. Baddorf and Douglas H. Lowndes; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

$SrRuO_3$ is a widely studied conducting oxide for applications of ferroelectric, ferromagnetic, and superconducting materials. Due to its relatively small lattice misfit with most perovskite-type oxides, e.g., 0.6% with $SrTiO_3$, and to its relatively low resistivity, it is often used as bottom electrode in epitaxial ferroelectric capacitors. It is well-known that due to the volatility of RuO_x, $SrRuO_3$ is unstable at high temperatures in a low-oxygen pressure ambient, i.e., under the very conditions where most studies on the growth of nearly perfect oxide films and superlattices by molecular beam epitaxy (MBE) and laser-MBE are carried out. If not for the lack of systematic studies on the stability $SrRuO_3$ films in integrated device applications, the idea of having $SrRuO_3$ as a bottom electrode and synthesizing $nearly-perfect$ ferroelectric films thereon may seem mutually exclusive. In this contribution, we explore this idea by growing epitaxial $SrRuO_3$ thin films with single-terrace steps by pulsed laser deposited (PLD) at 700 °C in 100 mTorr O_2 on single-stepped $SrTiO_3$(001), and characterized the stability of the films as a function of temperature (25 $\sim$ 800 °C) and oxygen pressure ($10^{-7} \sim 10^{-2}$ Torr) by $ex-situ$ reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), atomic force microscopy (AFM), scanning tunneling microscopy (STM), and x-ray photoelectron spectroscopy (XPS). The combined $ex-situ$ analysis showed different features on the film surface, including islands and pits, that could destroy or deteriorate the quality of epitaxial films grown subsequently, and revealed a dramatic change of the structure and composition due mostly to high-temperature anneals under low oxygen background pressure. The present study allowed us to determine a stability phase-diagram (oxygen pressure and temperature) for $SrRuO_3$ films, which indicates conditions under which they can serve as bottom electrodes and transfer with high fidelity the crystallinity of single-crystal $SrTiO_3$ substrates to the subsequent oxide films. In addition, the preparation of single-stepped $SrTiO_3$ substrates and examples of high-quality oxide films and superlattices using such $SrRuO_3$ bottom electrodes will also be presented. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, as part of a BES NSET initiative on Nanoscale Cooperative Phenomena.

C3.22

In-plane orientation control of $SrTiO_3$(111) epitaxy on sapphire(0001). Isao Ohkubo, Hans M. Christen and Matthew F. Chisholm; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Perovskite titanate thin films are important as ferro- and/or dielectric materials both for device application and in basic research, but most previous efforts have focused on (001)-oriented layers. From the viewpoint of oxide heteroepitaxy and heterointerface issues, growth of

(111)-oriented $SrTiO_3$ on sapphire (0001) is very attractive with a lattice mismatch of less than 0.5 %. The oxygen sublattice in $SrTiO_3$ has a fcc closed packed structure (ABCABC···) along the [111] direction, whereas that in sapphire exhibits a hcp closed packed structure (ABABAB···). Here we have grown $SrTiO_3$(111) thin films on sapphire(0001) substrates by pulsed laser deposition (PLD) under various growth conditions. Using growth rates typical for PLD, $SrTiO_3$ was found to crystallize with two in-plane orientations, $SrTiO_3$[2-1-1] // sapphire[11-20] and $SrTiO_3$[2-1-1] // sapphire[10-10]. However, films grown at much lower growth rates showed only $SrTiO_3$[2-1-1] // sapphire[11-20]. This orientation change is discussed in terms of thermodynamic stability and growth kinetics. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, and in part by the Laboratory Directed Research and Development Program.

C3.23

High Pressure Deposition of Epitaxial PZT Films on Sr(Nb)TiO_3. Jesus L. Heiras[2], O. Blanco[1], J. M. Siqueiros[2], E. Martinez[1] and E. Andrade[3]; [1]Fisica de Materiales, CICESE, Ensenada, B.C., Mexico; [2]Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, B.C., Mexico; [3]Instituto de Fisica, UNAM, Mexico, D.F., Mexico.

Thin ferroelectric films of $Pb(Zr_{0.53},Ti_{0.47})O_3$ (PZT) were successfully grown on Sr(Nb)TiO_3(SNTO) single crystal substrates by rf high pressure sputtering. Pure O_2 was used as working gas at pressures above 1 Torr. Deposition temperature was varied from 550 °C to 600 °C. Under these conditions we were able to deposit films at a rate of 2.7 Å/min. Film crystallinity, evaluated by θ-2θ, ϕ and ω scans, show c-axis orientation. FWHM of 0.36 ±0.02 was measured in the rocking curves. In plane and out of plane orientation was also determined with the crystallographic relationship [001]PZT——[001]SNTO and [010]PZT——[010]SNTO. Film composition and film-substrate interface characteristics were studied by RBS. A good fit to the experimental RBS spectra was obtained assuming composition ratios of 0.97 ±0.03 for Pb/(Zr+Ti), 0.32 ±0.02 for Pb/O, and 1.2 ±0.1 for Zr/Ti; also a very thin diffusion layer of Pb at the film-substrate interface was introduced. Pb deficiency, which is correlated to the presence of oxygen vacancies, resulted lower in films produced by high O_2pressure technique than that reported for films grown by sputtering at lower pressures. The hysteresis loops for the Pt/PZT/SNTO heterostructure show good ferroelectric behavior with remanent polarizations of 12 μCcm^{-2} and coercive field of $50kVcm^{-1}$ at 5V. The high-pressure technique turned out to be a simple and useful method to grow in situ epitaxial PZT ferroelectric thin films with high structural quality and good compositional and dielectric properties, without post-deposition heat treatment. Work supported by DGAPA-UNAM Proj. IN110800 and IN104000, CONACyT Proj. 40604-F and 33586-E. O. Blanco thanks the support of PROMEP-CONACYT.

C3.24

Compositionally Asymmetric Tri-Color Superlattices Grown by High-Pressure Pulsed Laser Deposition. Ho Nyung Lee[1], Hans M. Christen[1], Christopher M. Rouleau[1], Douglas H. Lowndes[1], Sung Kyun Lee[2], Stephan Senz[2] and Dietrich Hesse[2]; [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Max Planck Institute of Microstructure Physics, Halle (Saale), Germany.

Advances in modern epitaxial growth techniques have enabled the growth of nearly perfect thin films, superlattices, etc. by the atomic-scale control of surfaces and interfaces. For instance, oxide heterostructures with atomically-flat interfaces and single unit-cell steps on the surface can be grown onto well-prepared single-stepped substrates. Moreover, artificial superlattices, i.e. materials that do not exist in bulk forms, can be grown with great control on such substrates and can result in unprecedented physical properties. Using pulsed laser deposition (PLD) at ~700 °C in 10 mTorr O_2 on $SrRuO_3$-covered $SrTiO_3$(001) substrates, we have grown asymmetric tri-color superlattices (TCS) with a combination of $BaTiO_3/SrTiO_3/CaTiO_3$, in which the inversion symmetry can be broken by a composition gradient. $SrRuO_3$ thin films with single-terrace steps that closely mimic those of the $SrTiO_3$ substrate were also grown by PLD. Due to the layer-then-island growth mechanism of $BaTiO_3$ on $SrTiO_3$ that involves a lattice misfit of about 2%, growing $BaTiO_3$ on $SrTiO_3$ usually destroys the sharpness of subsequent interfaces if the $BaTiO_3$ thickness exceeds two unit cells. The deterioration of the interface sharpness has been confirmed by reflection high-energy electron diffraction (RHEED) and transmission electron microscopy (TEM). Therefore, a *recoveryprocess* is required in order to keep the overall superlattices flat and perfect on the atomic scale. This can be achieved by depositing $CaTiO_3$ followed by $SrTiO_3$ with a well-controlled number of laser pulses for growing single or multiple unit cells. Pronounced regular oscillations of the RHEED specular spot were recorded over the entire growth of TCS structures – even when grown to a total thickness of more than 1000 nm. We present the growth of superlattices and their structural and electrical properties as well as the stability of $SrRuO_3$ bottom electrodes as function of background pressure and temperature. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, as part of a BES NSET initiative on Nanoscale Cooperative Phenomena.

C3.25

Perovskite PZN-PT Thin Films Grown by MOCVD. Phillip Allan Friddle[1] and Haydn Chen[2,1]; [1]MatSE, University of Illinois, Champaign, Illinois; [2]Physcics and Materials Science, City University of Hong Knog, Hong Kong, Kowloon, China.

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

C3.26

MOCVD Growth of $Pb_xBa_{1-x}TiO_3$ Films on MgO. David A. Boyd, Mohamed Y. El-Naggar and David G. Goodwin; Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California.

We have prepared well-oriented $Pb_xBa_{1-x}TiO_3$ (PBT) films of varied compositions, $0.2 \leq x \leq 0.9$, and thicknesses ranging from several hundred nanometers to approximately one micron on MgO substrates by Metal Organic Chemical Vapor Deposition (MOCVD). Ultraviolet Absorption Spectroscopy (UVAS) of the gas phase Pb, Ba, and Ti precursors is used to regulate precursor flow rates and control film composition. The films have been characterized by X-ray Diffraction (XRD), micro Raman spectroscopy, Fourier Transform Infrared Reflection Absorption Spectroscopy (FTIRRAS), Electron Microprobe Analysis (EMPA), and Electron Dispersive Spectroscopy (EDS). The a and c axes of the grains are oriented perpendicular or parallel to the surface normal, only. The Raman modes have been identified and compared with published results of bulk crystals of similar compositions. SEM images show rough a surface structure with grains of several hundred nanometers. However, there appear to be no cracks or columnar structures visible in the cross sectional images. In an effort to reduce the growth temperature and control the crystalline orientation of the film, UV assisted deposition has been explored and has been found to significantly enhance the growth rate.

C3.27

Low Temperature Crystallization of Bi-Layered Perovskite Thin Films using $PbTiO_3$ Nuclei and Their Electrical Properties. Junichi Karasawa, Eiji Natori, Takeshi Kijima and Tatsuya Shimoda; Technology Platform Research Center, Seiko Epson Corporation, Fujimi-machi, Nagano-ken, Japan.

Bi-layered structure ferroelectric (BLSF) thin films such as $SrBi_2Ta_2O_9$ (SBT) and $(Bi,La)_4Ti_3O_{12}$ (BLT) are one of the most promising ferroelectric materials for use in high-density ferroelectric random access memory (FeRAM) because of their excellent reliability. However, some fundamental problems originating from BLSF nature such as low remnant polarization (Pr), high porosity and difficulty of crystallizing at low temperature, have been pointed out. On the other hand, Pb-containing ferroelectric thin film having pervskite structure such as $PbTiO_3$ (PT) can easily crystallize at low temperature ranging from 400°C to 450°C. If a $PbTiO_3$ perovskite unit cell is substituted or inserted into a Bi-layered perovskite unit cell, extreme low temperature crystallization of Bi-layered perovskite is significantly expected due to the role of nuclei during the crystallization process. In this work, three type of $PbTiO_3$-added Bi-layered perovskite thin films, which include (1-x)$SrBi_2Ta_2O_9$ - x$PbTiO_3$ (SBT-PT), (1-x)$Bi_4Ti_3O_{12}$ - x$PbTiO_3$ (BiT-PT) and (1-x)$(Bi,La)_4Ti_3O_{12}$ - x$PbTiO_3$ (BLT-PT), were systematically investigated as a function of the composition and the crystallization temperature. In case of BiT-PT system, as the amount of $PbTiO_3$ is increased, the crystallization temperature is dramatically decreased down to 550°C. Furthermore, 2Pr of $19\mu C/m^2$ was successfully obtained in 668°C-crystallized 0.96BLT-0.04PT thin film. The detailed results, which include crystallographic phase diagram and electrical properties of SBT-PT, BiT-PT and BLT-PT solid solutions, will be presented.

C3.28

Novel chlorine based chemistry for growth of ferroelectric

materials by molecular beam epitaxy. Alexander Gilman Carver, Walter Henderson and W Alan Doolittle; ECE, Georgia Institute of Technology, Atlanta, Georgia.

Recent interest in crystalline ferroelectric materials by the semiconductor industry has nurtured a drive towards improved material quality and the need for the precise compositional control afforded by molecular beam epitaxy (MBE). Current MBE growth of ferroelectric materials, especially those composed of refractory metals such as niobium, tantalum and vanadium normally requires extremely high temperature sources, such as electron beam evaporators, to produce the required fluxes for some components of the films. This article discusses a novel use of chlorine based chemistry in an MBE environment to grow lithium niobate ($LiNbO_3$) without the need for costly high temperature sources while still providing precise control over flux rates. The proposed niobium source can achieve deposition rates as high as several microns/hour and is operated near room temperature. Difficulties in handling the chlorine chemistry in a stainless steel chamber are eliminated through the use of special gettering processes. SIMS analysis on several samples confirms a large incorporation of niobium and lithium in the grown films with chlorine levels remaining below the detection limit of the SIMS system. X-ray diffraction analysis shows the formation of crystalline films having a FWHM of approximately 670-770 arcseconds for a 2θ-ω scan. Preliminary SIMS analysis shows a niobium rich deviation from the stoichiometry found in bulk $LiNbO_3$ substrates.

C3.29
Effect of Cationic Substitution on Raman Spectra of SrBi2Ta2O9 Ceramics and Thin Films. William Perez, Rasmi R Das, Yuri I Yuzyuk, Pijush Bhattacharya and Ram S Katiyar; Physics, University of Puerto Rico, San Juan, Puerto Rico.

Bismuth layered ferroelectrics, in particular $SrBi_2Ta_2O_9$ (SBT), have been widely investigated for non-volatile memory applications. SBT has orthorhombic crystal structure at room temperature and has tetragonal symmetry above the transition temperature. We have previously reported the enhancement of ferroelectric properties of SBT thin films with the cationic substitution at Sr and Ta-sites. In the present work micro-Raman spectroscopy has been used to understand the lattice dynamics of doped SBT thin films. Different concentrations of Ca and V were introduced into SBT lattices. Incorporation of Ca ion at Sr-site was confirmed by decrease in the lattice parameters calculated from x-ray diffraction data. The lowest Raman modes at 27 cm^{-1} and 58cm^{-1} showed upward shift with increasing Ca concentration and was attributed to the lower mass and lower ionic radii of Ca. The temperature dependant Raman studies revealed the increase of the phase transition temperature with increased Ca content. The increase in the transition temperature with concentration of Ca in SBT compound could be due to decrease in tolerance factor. Substitution of smaller cation at Sr site in SBT compound has increased lattice mismatch between SrO and TaO_2 planes inside the stable perovskite unit of $SrTa_2O_7$ which has pronounced influence on ferroelectric properties of SBT. Substitution of vanadium at Ta-site of SBT did not influence the low frequency Raman modes of SBT. However, it showed a pronounced influence on the O-Ta-O stretching modes. Detailed results of the lattice vibrational modes with the substitution of various cations in SBT will be presented.

C3.30
A Novel Iridium Precursor for MOCVD. Kazuhisa Kawano[1], Mayumi Takamori[1], Ken-ichi Tada[1], Tetsu Yamakawa[1], Souichi Watari[2], Hirokuni Fujisawa[2], Masaru Shimizu[2], Hirohiko Niu[2] and Noriaki Oshima[3]; [1]Catalysis Group, Sagami Chemical Research Center, Ayase, Kanagawa, Japan; [2]Electrical Engineering and Computer Sciences, Himeji Institute of Technology, Himeji, Hyogo, Japan; [3]Tokyo Research Center, Tosoh, Ayase, Kanagawa, Japan.

Iridium (Ir), ruthenium (Ru), platinum (Pt), other noble metals and their oxides are investigated as the capacitor electrodes of next generation memory devices including FeRAMs. Among them Ir and IrO2 have heatproof character and are effective for the improvement of fatigue loss of PZT capacitors so it is the most attractive material for the electrodes of FeRAMs. (Ethylcyclopentadienyl)(cyclooctadiene) iridium (Ir(EtCp)(COD)) is intensively investigated as the liquid Ir precursor for MOCVD. Ir(EtCp)(COD) which has rigid structure is very stable under the MOCVD conditions and has enough vapor pressure. However, films that shows good step coverage or conformal films could be deposited under limited conditions. And it is difficult to deposit iridium oxide thin film with Ir(EtCp)(COD) by MOCVD so far. In previous MRS fall meeting (2002), we had reported the characteristics of the ruthenium precursors for MOCVD. In those studies the relationship between decomposition temperature of the precursors and characteristics of deposited film was revealed. Lower decomposition temperature of the precursors make step coverage and nucleation density better. We synthesized a novel iridium precursor (Ethylcyclopentadienyl)(cyclohexadiene) iridium(Ir(EtCp)(CHD)) for MOCVD. The structure of the novel precursor was identified by proton NMR, carbon NMR, IR and mass spectrometry. The melting point of Ir(EtCp)(CHD) is 15°C, therefore it is liquid at room temperature. The thermal characteristics of the novel iridium precursor were measured by thermal gravimetry analysis (TG) and differential scanning calorimeter (DSC). TG was carried out in inert atmosphere (Ar) and it could be found out that Ir(EtCp)(CHD) vaporized stably and is more volatile than Ir(EtCp)(COD). DSC was measured under N2 atmosphere and thermal decomposition temperature (300°C) of Ir(EtCp)(CHD) is lower than that (380°C) of Ir(EtCp)(COD). Using this novel precursor, Ir and IrO2 thin film were tried to deposit by MOCVD. Some same phenomena was observed as the case of the Ru precursor. Higher nucleation density was observed in early period of deposition than Ir(EtCp)(COD). The novel precursor have shorter incubation time than Ir(EtCp)(COD). Furthermore IrO2 thin film could be deposited with Ir(EtCp)(CHD).

C3.31
Time-domain terahertz spectroscopy of strontium bismuth tantalate thin films. Kenta Kotani, Mukul Misra, Iwao Kawayama and Masayoshi Tonouchi; Research Center for Superconductor Photonics, Osaka University, Suita, Osaka, Japan.

Strontium bismuth tantalate (SBT) has received a considerable amount of attention as an important candidate for nonvolatile ferroelectric random access memories due to its good fatigue properties and low switching voltage. In recent years, research for its fundamental properties show interesting behavior, *e.g.* relaxer-like dielectric peak shift and enhancement of its polarization due to the cation substitution. Here, we report the measurement of the dielectric properties, stoichiometric and Sr-deficient Bi-excess SBT thin films, in terahertz (THz) frequency region by time-domain THz spectroscopy (TDTS) method. The purpose of the study is to get the details of dielectric function around soft phonon mode which play an important role in ferroelectric phase transition. TDTS has become a powerful method for studying optical and dielectric properties of the materials in sub-THz and THz regions that are not easily accessible with other methods. In this technique, an electromagnetic wave passing through sample under investigation is directly detected in the time domain by using a photoconducting sampling technique. Through Fourier transformation of the waveform, both amplitude and phase of the frequency spectrum can be obtained at the same time. Therefore, real and imaginary parts of optical parameters in the THz region are directly accessible without Kramers-Kronig analysis. In this work, we measured the electromagnetic waveforms through SBT thin films of various compositions and calculated the reflective index and the dielectric constant in the frequency range between 0.3 and 2 THz. The samples are all *c*-axis oriented epitaxial SBT thin films prepared on MgO (100) substrates by pulsed laser deposition techniques. The stoichiometric and off-stoichiometric SBT thin films were grown under same condition, and dielectric properties were compared. The imaginary part of the dielectric constant (ϵ_2) of stoichiometric SBT has two broad peaks around 0.8 THz and 1.8 THz. The behavior of ϵ_2 is consistent with Raman scattering data, and the peaks in ϵ_2 correspond to the soft mode and rigid layer mode which are commonly observed in the series of bismuth layer-structured oxides. The real part of the dielectric constant is below 100 in the observed frequency range and is much smaller than the static dielectric constant, reported to be about 200. The reason for this behavior is unclear, however, we consider that the polarization components may exist in a lower frequency range. In a similar way, we measured dielectric properties of off-stoichiometric SBT, and will discuss the effects of variation in Sr/Bi ratio on dielectric properties in THz region.

C3.32
Low-Temperature Synthesis and Dielectric Properties of Single-Phase Lead Zirconate Titanate Thin Film with a nm-Seeding Technique. Tomokazu Tanase[1], Takao Miwa[3], Yoshio kobayashi[2] and Mikio Konno[2]; [1]Tohoku Technoarch CO.,LTD., Sendai, Japan; [2]Tohoku university, Sendai, Japan; [3]Hitachi,Ltd, Hitachi, Japan.

Reduction in size of high performance electrical devices has lead to downsizing and integration of constituent parts such as dynamic random access memory, non-volatile memory and micro-actuators. For the case of memory capacitors, stacking of the films to obtain large capacitance areas is usually applied to increase charge capacity. On the other hand, high dielectric constant films are required to achieve large capacitance, because the complexities of the integrated circuit have reached a practical limitation in terms of current lithotechnology. Lead zirconate titanate (PZT) and barium strontium titanate (BST) films with dielectric constants greater than 1000 are future promising candidates for high dielectric capacitors as opposed to silicon nitride (Si_3N_4) or tantalum oxide (Ta_2O_5). In general, dielectric films have to be promote formation of crystal structures that have high dielectric constants. Since the films are deposited on the surface of the electrode

with the underlying circuit, the following high temperature treatment often damages the films/electrode interfaces seriously by the diffusion of the constituent elements. To avoid annealing damage, it is desirable to prepare films having high dielectric constants at low temperature. In our study, PZT thin films containing nano-crystalline seeds of BST particles were prepared by the complex alkoxide precursor method with a low annealing temperature. The BST nanocrystallines with ca. 20 nm in diameter were prepared by hydrolysis and condensation of the Ba-Ti complex alkoxides. The BST suspension was mixed with the PZT precursor solution to obtain spin-coating solution containing 0-25.1 mol% BST nanoparticles, which were dispersed homogeneously in the precursor solution. The BST mixed precursor solutions were spin-coated onto the $Pt/Ti/SiO_2/Si$ substrate and the films were annealed at 200 °C on a hotplate to form gel films. This deposition process was repeated 5 times to obtain ca. 500-800 nm-thickness PZT film containing the BST nanoparticles. The measurements of XRD analysis revealed that seeding of the BST particles prevented the formation of pyrochlore phases, which appeared at temperatures above 400 °C in unseeded PZT films, and induced crystallization of the PZT into perovskite structures at 420 °C that was more than 100 °C below the crystallization temperature of the unseeded PZT film. Measurements of dielectric properties at 1 kHz showed that the 25.1 mol% BST-seeded PZT films annealed at 450 °C attained a dielectric constant as high as 298 with a dissipation factor of 0.048. Leakage current density of the film was less than 10^{-6} A/cm^2 at applied voltages from 0 to 5V. Thus, the present work could achieve preparation of dielectric films having high dielectric constants, low leakage current densities and small dissipation factors by the application of a low temperature synthetic method.

SESSION C4: Processing: Emphasis on CVD and Pattern Formation
Chairs: Hiroshi Funakubo and Masaru Shimizu
Tuesday Morning, December 2, 2003
Room 203 (Hynes)

8:30 AM *C4.1
Liquid Injection MOCVD of SBTN Using an All Alkoxide Precursor System. Paul Andrew Williams[1], Anthony C Jones[1,2], Hywel O Davies[1], Neil L Tobin[2], Paul R Chalker[3], Paul A Marshall[3], John L Roberts[2] and Lesley M Smith[1]; [1]Epichem Limited, Bromborough, Wirral, United Kingdom; [2]Chemistry, University of Liverpool, Liverpool, Merseyside, United Kingdom; [3]Materials Science and Engineering, University of Liverpool, Liverpool, Merseyside, United Kingdom.

Thin films of $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ (SBTN) have applications in non-volatile ferroelectric memories. MOCVD is an attractive technique for the deposition of these materials, but progress has been restricted due to lack of suitable precursors. Conventional precursors include $Sr(thd)_2$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate), $Bi(thd)_3$, $BiMe_3$ and $Ta(OEt)_5$ or $Ta(OPr^i)_4(thd)$, but these are generally incompatible, having very different physical properties and deposition characteristics. To alleviate the mis-match between the Sr and Ta or Nb sources, we have developed the "single-source" precursors $Sr[Ta(OEt)_5(dmae)]_2$ and $Sr[Nb(OEt)_5(dmae)]_2$ $Sr[Ta_{0.5}Nb_{0.5}(OEt)_5(dmae)]_2$ (dmae = $OCH_2CH_2NMe_2$) in which the presence of the donor functionalised alkoxide ligand [dmae] inhibits gas-phase dissociation. Bi-alkoxides, $Bi(OR)_3$, are likely to be suitable co-precursors, with similar decomposition behaviour to the Sr-Ta and Sr-Nb heterometal alkoxides, but the majority are involatile polymers. The sterically hindered ligand mmp ($OCMe_2CH_2OMe$) inhibits polymerisation and can be used to form a volatile monomeric complex, $Bi(mmp)_3$. In this paper we describe the liquid injection MOCVD of SBTN using the all-alkoxide precursor combination, $Sr[Ta(OEt)_5(dmae)]_2$ and $Sr[Nb(OEt)_5(dmae)]_2$ and $Bi(mmp)_3$.

9:00 AM C4.2
Orientation Control of $Bi_4Ti_3O_{12}$-Based Thin Films Deposited on Silicon Substrate by MOCVD. Takayuki Watanabe[1], Syoji Okamoto[1], Hiroshi Funakubo[1] and Keisuke Saito[2]; [1]Innovative and Engineered Materials, Tokyo Tech., Yokohama, Japan; [2]Analytical Dept., PANalytical Japan, Tokyo, Japan.

We have demonstrated various kinds of epitaxial growths of lanthanide-substituted $Bi_4Ti_3O_{12}$ (BIT) films on single crystal substrates to characterize their spontaneous polarization values (P_s) along the a-axis. P_s of neodymium-substituted BIT (BNT) was estimated to be the largest value of 58 μC/cm^2 among the investigated BLSFs. To utilize the large polarization on silicon substrates, orientation control of both of epitaxial and one-axis-oriented BNT films on (100)Si substrates was tried by MOCVD, which is the most important preparation method for mass-production. As an approach for epitaxial application, heteroepitaxial stacking structure, $(110)SrRuO_3//(100)YSZ//(100)Si$, was used as a substrate. BNT films deposited at around 750°C showed a preferred a-/b-axis orientation in contrast to (118) single orientation of films prepared at lower deposition temperature. These results show that the one-axis-preferred orientation of BNT film was achieved by the selection of kinds of substrates and optimization of MOCVD conditions.

9:15 AM C4.3
Property improvement of MOCVD-PZT films deposited below 400 °C. Hiroshi Funakubo[1], Gouji Asano[1], Atsushi Nagai[1], Hitoshi Morioka[1], Shintaro Yokoyama[1], Tetsuo Shibutami[2] and Noriaki Oshima[2]; [1]Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; [2]Tokyo Research Center, Tosoh Corporation, Ayase, Kanagawa, Japan.

RuO_2/(200-nm-thick PZT)/RuO_2 capacitor was deposited by MOCVD. RuO_2 and PZT films were prepared at 350, and 395 and 445 °C from DER - O_2 and $Pb(C_{11}H_{19}O_2)_2$ - $Zr(O{\cdot}t\text{-}C_4H_9)_4$ - $Ti(O{\cdot}i\text{-}C_3H_7)_4$ - O_2 systems, respectively. Clear hysteresis originated to ferroelectricity was observed for the PZT films deposited at 445 °C but was not at 395 °C. However, by the addition of 10-nm-thick Pt layer on the RuO_2 bottom electrode, ferroelectricity above 30 μC/cm^2 in remanent polarization (P_r) was obtained by the increase of the crystallinity of the PZT films for the films deposited at 395 °C. This shows that Pt layer improved the crystallinity of PZT phase. This capacitor show hardly fatigue by the 1×10^{10} switching cycles. However, it occurred by using Pt-top electrode instead of RuO_2-top electrode. This result suggests that the top electrode plays a dominant role for the fatigue phenomena of the capacitor as already pointed out. In conclusion, fatigue-free $RuO_2/PZT/RuO_2$ capacitor was deposited by MOCVD below 395 °C. In addition, in order to decreasing the operating voltage of FeRAM, films thickness of PZT films deposited at 395 °C was decreased down to 100 nm. P_r value decreased with decreasing film thickness, but large P_r value above 25 μC/cm^2 was obtained and the ferroelectricity saturation up to 3 V was ascertained. These results suggest that the good ferroelectricity was obtained for the films deposited below 400 °C by MOCVD.

9:30 AM C4.4
$Ba(Ti_{1-y}Zr_y)O_3$ Thin Films grown by MOCVD for high-K Dielectrics Applications. Susanne Hoffmann-Eifert, Ralf Ganster, Jochen Puchalla and Rainer Waser; IFF / EKM, Forschungszentrum Juelich, Juelich, Germany.

High-k ceramic thin films are being investigated as dielectric materials for integrated capacitors where the permittivity has to be increased with respect to common SiO2 layers in order to further decrease the devices' dimensions. Applications are future GBit DRAM integration circuits and tuneable microwave devices, the most prominent material is $Ba_{0.7}Sr_{0.3}TiO_3$, and the most favoured deposition process for industrial use is metal organic chemical vapour deposition (MOCVD). Due to the industrial forced restriction to only a few materials systems a large potential of other interesting candidates has not been made use of so far. One of these systems which is already used in the large area of ceramic passive components is the solid solution $Ba(Ti_{1-y}Zr_y)O_3$ (BTZ). BTZ thin films deposited by means of chemical solution deposition (CSD) or sputtering showed interesting electrical properties, which puts the material into a competitive position to comply with the necessities for integrated capacitor structures. In our work we now apply the industrial relevant MOCVD method for the deposition of $Ba(Ti_{1-y}Zr_y)O_3$ films. CVD provides compatibility to state-of-the-art integration scales, and is even more an excellent choice for conformal 3D growth. Using an AIX-200 horizontal reactor connected to a TriJetTM vaporizer module we deposited BTZ films on Pt/Si substrates. The three liquid sources contained a $Ba(thd)_2$, a $Ti(OPr)_2(thd)_2$, and a $Zr(OPr)_2(thd)_2$ precursor, respectively. The focus of our investigations lies on the correlation between processing conditions (evaporation resp. substrate temperature, growth rate) and film properties, namely stoichiometry, texture effects, and surface morphology. Further studies are attributed to the relationship between physico-chemical properties and the electrical response of the films. We studied the dielectric response with respect to frequency and voltage dependence as well as the effect of the Zr-substitution on the leakage characteristics of the capacitor structures.

9:45 AM C4.5
EXAFS Study Of PZT Thin Films. Barbara Malic[1], Iztok Arcon[1,2], Marija Kosec[1] and Alojz Kodre[1,3]; [1]Electronic Ceramics, Jozef Stefan Institute, Ljubljana, Slovenia; [2]Nova Gorica Polytechnic, Nova Gorica, Slovenia; [3]Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia.

Ferroelectric thin films have been widely studied for a range of applications such as memories, capacitors, sensors or microelectromechanical devices. In chemical solution deposition

(CSD) of thin films the main processing steps include the synthesis of a heterometallic precursor, typically in a nonaqueous medium, the deposition of the film, and the processes occurring upon thermal treatment: drying, consolidation and crystallization of the target ferroelectric phase. Understanding the structural transitions in the process of film formation from the sol would allow a better tailoring of the properties of the final product. The sols for Pb(Zr0.53Ti0.47)O3 (PZT) thin films were prepared by 2-methoxyethanol-route from lead acetate, titanium n-propoxide and zirconium n-propoxide, the latter either unmodified or modified with acetic acid, and deposited on sapphire (0001) or platinized silicon substrates. The addition of the modifier evokes the crystallization of the perovskite phase in the films at a lower temperature as determined by XRD. In this work the persistence of Zr-O-Zr bonding formed in the sol is traced through the process of film synthesis. We examined the local environment of zirconium atoms in sols and in amorphous films on sapphire. Zr K-edge EXAFS spectra of sols were measured in transmission mode while spectra of the as-pyrolyzed films on sapphire were detected in fluorescence mode in synchrotron radiation laboratory HASYLAB at DESY, Hamburg. To our knowledge this is the first EXAFS study of amorphous PZT thin films. The results show that a decreased number of Zr-O-Zr links in the acetic acid modified PZT sol, compared to unmodified sol, is retained also in the amorphous film, implying a more homogeneous constituent metal distribution. The improved chemical homogeneity is reflected in the improved functional response of the acetic-acid modified PZT films.

10:30 AM *C4.6
Self-Assembled PbZrxTi1-xO3 Nano-Islands Prepared on SrTiO3 and MgO by MOCVD. Hajime Nonomura[1], Hironori Fujisawa[1], Masaru Shimizu[1], Hirohiko Niu[1] and Koichiro Honda[2]; [1]Department of Electrical Engineering and Computer Sciences, Himeji Institute of Technology, Himeji, Japan; [2]Fujitsu Laboratry Ltd., Atsugi, Japan.

Ferroelectric properties of ferroelectric nano-structures are very interesting not only from the point of view of applications for FeRAMs but also from that of three dimensional size-effects of ferroelectricity. Ferroelectric nano-structures have been prepared by electron beam (EB) lithography, focused ion beam (FIB) milling and self-assembled crystal growth processes. Among these methods, self-assembled crystal growth process is one of the most promising methods for fabricating ferroelectric nano-structures with lateral dimensions under 50nm. We have already reported that PbZrxTi1-xO3 nano-islands with ferroelectricity were successfully fabricated on Pt(111)/SiO2/Si(100) by MOCVD. However, islands grown on Pt/SiO2/Si showed different sizes and directions. In this paper, in order to control the size, shape and direction of self-assembly prepared nano-structures, PbZrxTi1-xO3 nano-islands were grown on Pt/SrTiO3 (STO) and Pt/MgO substrates by MOCVD. From AFM observations, triangular shaped PbTiO3 islands with the same direction and size were observed both on Pt(111)/STO(111) and Pt(111)/MgO(111) substrates. Piezoresponse force microscopy (PFM) measurements revealed that these PbTiO3 nano-islands (with: 37-73nm, height: 6.6-19.3nm) had ferroelectricity. When Pt(110)/STO(110) and Pt(110)/MgO(110) were used as substrates, triangular prism shaped PbTiO3 islands, which preferentially grew along the <10-1> direction, were obtained. These nano-islands (width: 49-200nm, length: 72-636nm, height: 3.8-59nm) also showed ferroelectricity. These results showed that size, shape and direction of self-assembled ferroelectric nano-islands by MOCVD were fairly controllable using epitaxial relation. Micro structures and crystalline properties observed by TEM and XRD will also be discussed.

11:00 AM C4.7
Site- and Shape Specific Nanopatterning of Ferroelectrics. Vinayak P Dravid[1], Aroop B Chatterjee[1], Orlando Auciello[2], Ming Su[1], D J Kim[2] and Sanjib Saha[2]; [1]Mat Sci & Engg, Northwestern University, Evanston, Illinois; [2]Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Most of the approaches for patterning functional inorganics, e.g., ferroelectrics, magnetics, rely on the "top-down" approach. In this traditional scheme, thin films are grown on appropriate substrates, followed by etching and patterning to create arrays of structures (e.g., capacitors for ferroelectric memories) for high-density devices. For high-density ferroelectric memories (FeRAMs) capacitors with nanodimensions will be required. We have undertaken a novel approach for patterning ferroelectrics, which is based on the "bottom-up" approach wherein it is possible to directly deposit, site- and shape-specifically, nanoscale ferroelectric (and other inorganic) structures on arbitrary substrates. The approach is based on dip-pen nanolithography (DPN), originally developed for nanopatterning of molecular structures. Instead of using molecular "inks", sol-based precursors are employed as "inks" and the as-patterned soft structures are converted into functional inorganics with subsequent thermal treatment. Based on the earlier success of nanopatterning simple oxides (e.g., SnO2, ZnO etc.), we have now extended the approach to complex structures such as hard magnets (e.g., Fe-hexaferrites) and ferroelectrics such as BaTiO3 and PZT. By its very nature, DPN allows for both site- and shape specificity, down to nanoscale, controlled by AFM-based patterning software. With this approach, it is readily possible to pattern ferroelectric nanodots down to 150 nm, with the prospects for even smaller dimensions with improved properties of substrate surface and precursor inks. The patterned ferroelectric nanodots exhibit ferroelectric behavior as probed by the piezo-response technique. The presentation will cover the strategy for further enhancement of nanoscale patterning of ferroelectrics, possibility for epitaxial templating, and their extensive structural, chemical and functional characterization.

11:15 AM C4.8
Self-Patterning of Ferroelectric Nanocrystals. Izabela Szafraniak, Ming-Wen Chu, Roland Scholz and Marin Alexe; Max Planck Institute of Microstructure Physics, Halle (Saale), Germany.

Multifunctional ferroelectric materials offer a wide range of useful properties from switchable polarisation that can be applied in memory devices, to piezoelectric and pyroelectric properties used in actuators, transducers and thermal sensors. At the nanometer scale, unique material properties and effects are expected. The method of self-patterning offers an appealing alternative to lithography for the fabrication of nano-sized ferroelectric crystals. We have applied the method based on the instability of ultra-thin films to produce PZT nanocrystals. Ultra-thin layers obtained by chemical solution deposition break up into islands with a narrow size distribution after high-temperature annealing. The formation of nanostructures was investigated by scanning and transmission electron microscopy, atomic force microscopy and X-ray diffraction as a function of the initial film thickness and crystallisation temperature. The relatively thicker layers give discontinuous films with faceted holes. Below a critical layer thickness, the film breaks up into separate non-regular islands. Using a highly diluted precursor results in films that pattern themselves into small separated nanostructures. Different Zr/Ti compositions of PZT and different substrates have been chosen to determine the role of mismatch stress on the nanoislands growth and their properties. The lateral size and the height of the nanocrystals can be tuned within a small range by adjusting the initial thickness of the deposited layer and the post-deposition thermal treatment. PZT nanostructures with average lateral sizes down to about 50 nm and heights as small as ~9 nm show an epitaxial relationship to the substrate. Structure-property relations were investigated by HRTEM and atomic force microscopy in piezoresponse mode. Part of this work has been supported by Volkswagen Stiftung Project "Nano-sized Ferroelectric Hybrids" (No. 5/77737).

11:30 AM C4.9
Biaxial Texture Development In $Ba_xPb_{1-x}TiO_3$ Through Heteroepitaxy On Biaxially Textured MgO. Rhett T. Brewer[1], Youngbae Park[1], David A. Boyd[2], Stacey W. Boland[3], Mohamed El-Naggar[2], Sossina M. Haile[3], David G. Goodwin[2] and Harry A. Atwater[1]; [1]Applied Physics, California Institute of Technology, Pasadena, California; [2]Mechanical Engineering, California Institute of Technology, Pasadena, California; [3]Materials Science, California Institute of Technology, Pasadena, California.

We have grown biaxially-textured $Ba_xPb_{1-x}TiO_3$ (PBT) thin films (x = 0.03-0.55) using three growth methods: sol-gel synthesis, metal organic chemical vapor deposition (MOCVD), and molecular beam epitaxy (MBE) with narrow in-plane and out-of-plane grain orientation distributions (biaxial texture) on biaxially-textured IBAD MgO templates. The biaxial texture observed in the PBT layers was strongly correlated with the biaxial texture of the MgO template. The in-plane orientation decreased from 11.5° and 11.2° FWHM for the MgO template to 6.2° and 6.1° FWHM in the heteroepitaxial PBT, for sol-gel and MOCVD films respectively. MBE grown films exhibited a closer correlation between the MgO template and heteroepitaxial PBT in-plane orientation distributions (10.3° and 8.9° FWHM respectively). In cross section transmission electron microscopy (TEM) the MgO biaxially textured template layer appeared to be comprised of a significant fraction of amorphous or disordered material in templates for the MOCVD and sol-gel PBT films. By contrast, the MgO biaxially textured layer in the MBE films was crystalline throughout the entire sample. We suggest that the narrowing of the in-plane orientation distribution from the MgO template observed in the MOCVD and sol-gel PBT growth processes results from selective PBT nucleation on well-aligned grains in the MgO templates which contain fewer ion induced defects and are less susceptible to disordering via hydroxylation during atmospheric exposure. The nucleated PBT grains then laterally overgrow neighboring disordered MgO regions, resulting in a more highly in-plane aligned PBT film with larger grain size than in the MgO template. The MBE PBT was grown without breaking vacuum after

the MgO growth, which inhibits hydroxylation of even highly damaged MgO grains, resulting in PBT grain nucleation on all MgO grains, regardless of grain orientation. Piezoresponse force microscopy was performed to map ferroelectric domain structure and PFM hysteresis loops revealed no ferroelectrically inactive areas.

11:45 AM C4.10
Abstract Withdrawn

SESSION C5: Dielectric Applications: Low Frequency to Microwave
Chairs: Angus Kingon and Ivo Koutsaroff
Tuesday Afternoon, December 2, 2003
Room 203 (Hynes)

1:30 PM *C5.1
Leakage Currents in High Permittivity Perovskite Thin Films. Herbert Schroeder, IFF-EKM, Forschungszentrum Juelich GmbH, Juelich, Germany.

This paper will review the present understanding of steady state leakage currents through high permittivity thin films such as strontiumtitanate (STO) or barium-strontiumtitanate (BST). The first part consist of a discussion of the experimental conditions to measure the true leakage current and from that necessary conditions will be extracted to create reliable leakage current data for mechanistic studies. In the second part the most common leakage current mechanisms will be introduced with special emphasis on the characteristic parameters for experimental verification. The third part will give some selected examples of experimental data and possible difficulties in identifying the controlling mechanism. In a fourth part a model is offered combining carrier injection by thermionic emission and tunnelling at the electrode interface with the transport properties of the film bulk, which can be described by drift and diffusion with an effective mobility/diffusivity such as band or large-polaron conduction.

2:00 PM C5.2
Understanding Leakage in "Thick" (Ba,Sr)TiO_3 Films. S. K. Streiffer[1], S. Saha[1] and D. Y. Kaufman[2]; [1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois; [2]Energy Technology Division, Argonne National Laboratory, Argonne, Illinois.

Despite significant progress over the last ten years, one of the outstanding issues in ferroelectric film science and technology is the lack of understanding of size and interface effects. While much of the effort in this area has concentrated on what happens as film thickness is reduced below 100nm, many applications require significant power-handling capability and thus film thicknesses approaching or even exceeding 1 μm. The required thicknesses are still below those that are easily produced by traditional ceramic thick film processing routes, so vapor-phase and chemical solution deposition methods still have a role in enabling technologies based on these thicker films. One example of this is the use of (Ba,Sr)TiO_3 (BST) thin films for tunable dielectric applications. However, one open issue for BST is fully reconciling dielectric and leakage behavior as film thickness is increased above twice the depletion length. Changes in band bending give rise to very different electric field distributions within the film as thickness is increased, and this has generally not been incorporated into discussions of size effects in this system. With this framework in mind, we have investigated the leakage and dielectric properties of a thickness series (90-480 nm) of {100} fiber-textured MOCVD $(Ba_{0.75},Sr_{0.25})Ti_{1+y}O_{3+z}$ thin films with well-controlled microstructure. A positive temperature coefficient of resistance (PTCR) was observed in the leakage current behavior as film thickness was increased. The observed PTCR effect in our thicker films? leakage behavior will be discussed in the light of the Schottky-Heywang model most widely used to explain PTCR behavior in bulk $BaTiO_3$ ceramics, with attention to how our films depart from that model. Simulations of leakage current that incorporate nonlinear effects and variations in internal field distribution as a function of film thickness will be presented, that incorporate different interface effects (low permittivity dead layers, electrode-induced depolarization, etc.) as boundary conditions for the simulations. The implications of our results for the understanding of BST properties will be described.
This work was supported by the US Department of Energy, BES-Materials Sciences and FreedomCAR and Vehicle Technologies Program, under Contract W-13-109-ENG-38.

2:15 PM C5.3
TEM and Electrical Analysis of Sputtered Barium Strontium Titanate Films on Copper Substrates. Brian Laughlin, Jon Ihlefeld and Jon-Paul Maria; Materials Science, North Carolina State Univ., Raleigh, North Carolina.

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) films were deposited on electroplated copper foils (18 μm thickness) by radio frequency magnetron sputtering. These films will be an integral part of flexible capacitor sheets intended for space borne re-configurable antenna arrays. By the use of controlled pO_2 high temperature anneals, the films were fully crystallized and of high quality. X-ray diffraction data showed no existence of copper oxidation (i.e. Cu_2O or CuO phases). The deposited BST films demonstrated a high permittivity ($\sim$1000) and a low tan δ ($\sim$0.015) at zero bias. A pronounced electrical tunability ratio of 3:1 was observed on these devices. Devices showed loss tangents as low as 0.002 in fields as high as 30 kV/cm. Electrical field calculations were based on cross-sectional atomic force microscopy (AFM) images that revealed a film thickness of $\sim$1 μm. Temperature dependent measurements show a $T_c\sim$250K with a diffuse dielectric anomaly. High-resolution transmission electron microscopy (TEM) analysis of the Cu / BST interface will be presented along with conventional TEM analyses showing the film's grain morphology.

2:30 PM *C5.4
Base-metal Integration and Enhanced Dielectric Properties of <100> Oriented $SrTiO_3$ and (Ba,Sr)TiO_3 Thin Films. Jeff Dawley[1], Ryan Ong[2], Jacob Richardson[1] and Paul Clem[1]; [1]Microsystem Materials, Tribology and Technologies, Sandia National Laboratories, Albuquerque, New Mexico; [2]Materials Science & Engineering, University of Illinois, Urbana-Champaign, Illinois.

Base metal integration of high K' dielectrics is of interest for microelectronic packaging and low cost passive component production. Processing and properties are presented for random and enhanced <100> orientation $SrTiO_3$ and $Ba_xSr_{1-x}TiO_3$ (x = 0.33, 0.50, and 0.67) films fabricated on base-metal <100> Ni tapes using a chemical solution deposition (CSD) approach. Permittivity values over 1000 were obtained for several BST film compositions on Ni substrates. Films were crystallized in a reducing atmosphere, which prevented Ni oxidation, but permitted growth of oxygenated $SrTiO_3$ and $Ba_xSr_{1-x}TiO_3$ films with dielectric loss tan d = 0.003 - 0.015. For randomly oriented $Ba_xSr_{1-x}TiO_3$ (x = 0, 0.33, 0.5, 0.67) films processed at 900 °C, zero-field 100kHz dielectric constants ranged from 250 to 420. Films with enhanced <100> orientation exhibited zero-field dielectric constants of 980 to 1500, three times higher than random films. The impact of microstructure of the films on the measured dielectric properties will also be discussed.
Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the U.S. Department of Energy, under contract No. DE-ACO4-94AL85000.

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

The development of tuneable microwave devices based on ferroelectric films calls for determination of the microwave properties of these films. At present there is no apparatus capable of measuring directly the relative dielectric constant and dielectric loss (tan δ) at microwave frequencies. The usual way [of their microwave properties evaluation] is patterning a simple device, (like a coplanar wave guide, microstrip line, planar capacitor etc.), measuring its response at microwave frequencies and evaluating its properties using a suitable device model. This algorithm however, requires a careful selection of measurement techniques and device design, taking into account the associated error and limitations. This paper is devoted to the problem of evaluating the microwave properties of thin ferroelectric films patterned as planar capacitors. Two types of microwave measurements of ferroelectric thin films are considered: reflection and resonance types measurements. Algorithms are presented for evaluation of capacitance-permittivity and dielectric loss. Using sensitivity analysis, the error and limitations associated with these measurements (evaluations) are estimated. The end result is a series of formulae that use the network analyser measurement data to calculate the capacitance-permittivity, the dielectric loss, and the associated error. The comparison between the measurement techniques shows that the use of reflection type measurement provides information on the microwave properties over a wide frequency range while the resonance type provides more accurate measurements but at a single frequency.

3:45 PM C5.6
Enhanced Dielectric o Compositionally Modified BST Based Thin Films for Voltage Tunable Microwave Devices. Melanie Will Cole[1], William D. Nothwang[1], Richard Geyer[2], Clifford Hubbard[1], Eric Ngo[1] and Matt Ervin[1]; [1]WMRD, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland; [2]RF technology Division, National Institute of Standards and Technology, Boulder, Colorado.

Low dielectric loss in conjunction with high tunability are simultaneous requirements for tunable device applications, which have proved problematic to achieve. In this work, material compositional

design and optimized film processing methods, were employed to simultaneously lower the dielectric loss and enhance the dielectric tunability of Ba0.6Sr0.4TiO3 (BST) based thin films without compromising the device impedance matching (er<500) and control voltage (<10 V) requirements. The films compositional design was achieved by acceptor doping BST from 1 to 10 mol %. The films were fabricated on MgO and Pt-Si substrates via the metalorganic solution deposition technique using carboxylate-alkoxide precursors and postdeposition annealed at 900 oC (film/MgO substrates) and 750 oC (film/Pt-Si substrates). Dielectric properties were measured at 10 GHz using unpatterned films via a coupled/split dielectric resonator system and at 100 kHz using metal-insulator-metal capacitors. The films dielectric loss measured at 100 kHz was identical, tand ~0.007, for all doping levels. In contrast, the films permittivity (423 to 220), leakage current density (2.55x10-8 to 2.43x10-9 A/cm2), tunability (23.0 to 5.7 %), and grain size (75.2 to 61.55 nm) were observed to decrease with increasing dopant concentration levels from 1 to 10 mol%, respectively. The dielectric properties measured at 10 GHz exhibited improved dielectric loss [tand decreased from 0.0248 to 0.01] and lower permittivity [(er decreased from 411 to 223] with increasing acceptor dopant concentration from 1 to 10 mol%. Device quality values of tunability, 40 and 32 %, for the 3 and 7 mol% doped BST films, respectively, were achieved by elevating the applied bias from 237 to 474 kV/cm. This device quality tuning is compatible with voltage requirements of current semiconductor based systems. The enhanced dielectric and insulating properties of the 3 to 7 mol% Mg doped BST thin films make them excellent candidates for integration into tunable devices.

4:00 PM C5.7
Silicon Substrate Integrated High Q-Factor Parallel-Plate Ferroelectric Varactors for Microwave/Millimeterwave Applications. Andrei Vorobiev, Dan Kuylenstierna, Par Rundqvist, Khaled Khamchane and Spartak Gevorgian; Department of Microtechnology and Nanoscience, Chalmers University of Technology, Gothenburg, Sweden.

Parallel-plate $Ba_{0.25}Sr_{0.75}TiO_3$ (BST) varactors with record high Q-factor are fabricated on Si substrate. At 45 GHz the Q-factor is about 40, and the tuneability at 25 V is more than 40 % in the measured frequency range 0.045-45 GHz. These parameters are far better than corresponding parameters of best Si and GaAs analogues. The improvement in Q-factor is achieved by using thick bottom electrode consisting of Pt(50 nm)/Au(0.5 μm) allowing to reduce the microwave losses associated with metal layers. The BST films exhibit relatively high permittivity (150) at zero bias and high resistivity (10^{10} Ωcm) at fields up to 700 kV/cm. Tuneable one-dimensional electromagnetic band gap structures, based on coplanar waveguides periodically loaded by the high-Q-factor BST varactors, have been prepared and measured in the frequency range 1-50 GHz. The superior performance of ferroelectric varactors (in comparison with semiconductors) shows that they can be used in practical designs of tuneable microwave devices.

4:15 PM C5.8
Microwave Properties of Parallel Plate Capacitors Based on (Ba,Sr)TiO_3 Films Grown on SiO_2/Al_2O_3 Substrates. Ivo Koutsaroff, Thomas Bernacki, Marina Zelner, Paul Woo, Lisa Woodward, Arif Kassam, Jake Obeng, Andrew Cervin Lawry and Atin Patel; Technology R&D, Gennum Corporation, Burlington, Ontario, Canada.

(Ba,Sr)TiO_3 (BST) is a promising ferroelectric material for tunable microwave device applications. Lumped element planar capacitors effectively utilize the tunability of the material. This paper presents the results of the characterization of such capacitors, in the context of their applicability to decoupling applications [1], as well as recently demonstrated applications such as tunable filters and phase-shifters [2]. Various BST films were utilized to fabricate planar capacitor structures with Pt electrodes on glazed polycrystalline alumina (Al2O3) substrates. Thin films of $(Ba_{0.7}Sr_{0.3})TiO_3$ and $(Ba_{0.5}Sr_{0.5})TiO_3$ were grown by two methods, metal-organic decomposition (MOD) and RF magnetron reactive sputtering, at 650-750 °C. For BST film thicknesses of 100-150 nm the capacitance densities typically ranged from 16 to 38 fF/μm2, and were strongly influenced by the film compositions and the growth and post-annealing processing conditions. BST film morphologies were characterized by Field Emission Scanning Electron Microscopy (FE-SEM) and Powder X-ray Diffraction (PXRD) spectroscopy. Parallel plate capacitors with an effective area of 100 μm2 were fabricated using standard photolithographic patterning and ion milling techniques, and were used for electrical characterization. Capacitance, tan δ (Re(Y)/Im(Y)) and equivalent series resistance (ESR) were extracted from two port scattering parameters over the frequency range 100 MHz - 20 GHz using a vector network analyzer (VNA). De-embedding structures were used to remove the parasitic effects of the test fixture. Capacitance and tan d were measured at low frequencies (1-100 KHz) using an LCR meter. C-V and I-V characteristics were also obtained up to 600 kV/cm. The correlation for a given composition between low frequency and high frequency tunability, as well as the calculated figure of merit, was investigated. Combinations of BST processing conditions for both compositions and deposition techniques, suitable for high-yield large-scale manufacturing of such capacitors, were established. [1] I.P. Koutsaroff, et al, "Dielectric Properties of (Ba,Sr)TiO_3 Thin Film Capacitors Fabricated on Alumina Substrates", Vol. 748, U6.1.1 (2002). [2] J. Serraiocco, et al, "Tunable Passive Integrated Circuits Using BST Thin Films", Integrated Ferroelectrics, Vol. 49, pp. 161-170 (2002).

4:30 PM C5.9
Thickness and Strain Effects on RF/MW Properties of BST Thin Films on $NdGaO_3$ Substrates. William Kurt Simon, Koray Akdogan and Ahmad Safari; Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey.

$Ba_{0.60}Sr_{0.40}TiO_3$ thin films were deposited on <100> oriented $NdGaO_3$ substrates by pulsed-laser deposition. Film thickness ranged from 20 nm to 1 μm. Microstructural features, as evaluated with AFM and FESEM, have exhibited high quality thickness- dependent film topography. XRD has shown consistently <110> textured films of high crystallinity. Permittivity, loss and tunability are investigated in the range 100 MHz-20 GHz (X-band) on interdigitated capacitors, which were then correlated with the thickness-dependent in-plane biaxial strain as determined by X-ray diffractometry. The X-band dielectric response of such films will be discussed in the context of interface quality, i.e. strain relaxation and dislocation density, thickness size effects, and lattice misfit strain.

4:45 PM C5.10
Fabrication and Microwave Characterization of Ba0.60 Sr0.40TiO3 Based Thin Films. Eric Ngo[1], William Nothwang[1], Melanie W Cole[1], Clifford Hubbard[1], Wontae Chang[2], Steven Kirchoefer[2] and Jeff Pond[2]; [1]Weapons and Materials Directorate, Army Research Laboratory, Aberdeen, Maryland; [2]Navy Research Laboratory, Washington DC, District of Columbia.

Ferroelectric thin films have been recognized for their unique dielectric properties and, appear to be desirable for tunable microwave device applications. Among the most promising candidates for such applications are Ba(x)Sr(1-x)TiO3 [BST] and BST-based thin films. In this work pure BST and acceptor doped BST-based thin films were fabricated on (100) MgO substrate via pulsed laser deposition [PLD]. X-ray diffraction (XRD) in conjunction with the atomic force microscope (AFM) was used to analyze the optimized post-deposition annealing temperature. The dielectric properties were characterized at both 100 kHz and 10 GHz. The MIM capacitor configuration was used to attain the dielectric properties at 100 kHz and the microwave measurements, S11 reflection parameters, were achieved via interdigitated capacitor design with Au/Ag top electrodes. The parallel resistor-capacitor models were used to determine the microwave capacitance and Q factors of the films and the permittivity was calculated using a modified conformal-mapping partial-capacitance method using the dimension of the capacitors. The low frequency and microwave frequency dielectric properties were strongly influenced by the film composition. Specifically, the Mg doping served to lower the dissipation factor, permittivity, and tunability of the BST based films at both frequencies. Results of this work demonstrate that the acceptor doped thin films possessed excellent microstructural, structural, and dielectric properties. The structure-process-property correlations of the pulsed laser deposited BST and acceptor doped BST-based thin films will be presented and discussed in detail.

SESSION C6: Ferroelectric Films for Memories: Materials and Domains
Chairs: Jeffrey Cross and Paul McIntyre
Wednesday Morning, December 3, 2003
Room 203 (Hynes)

8:30 AM *C6.1
Defect-Engineered $SrBi_2Ta_2O_9$ Single Crystals with Enhanced Polarization Properties. Yuji Noguchi[1,2], Koichiro Murata[1], Masatake Takahashi[1] and Masaru Miyayama[1]; [1]Institute of Industrial Science, The University of Tokyo, Tokyo, Japan; [2]PRESTO, Japan Science and Technology Corporation, Saitama, Japan.

Since thin films of ferroelectric $SrBi_2Ta_2O_9$ (SBT) have been reported to show a fatigue-free polarization property with Pt electrodes, SBT has attracted considerable interest from the technological and fundamental points of view. Recently, Noguchi et al. have reported that rare-earth elements (RE) such as La, praseodymium (Pr), and Nd as well as Bi occupy the Sr site, and that a drastic change in

polarization properties is induced by the defect-related modification, i.e., "*defectengineering*". The charge neutrality is satisfied through the formation of Sr vacancies to compensate the charge difference between Sr^{2+} and trivalent cations (Bi^{3+}, Pr^{3+} and so on). Polarization measurements using dense ceramics revealed that Bi substitution increased a remanent polarization (Pr) from 7 μC/cm^2 (SBT) to 13 μC/cm^2. For Pr-modified SBT (Pr-SBT), the low-electric-field polarization properties were markedly improved (a larger Pr of 10 μC/cm^2 and lower coercive field (Ec) of 30 kV/cm). In this study, single crystals of defect-engineered SBT were grown by flux method and the polarization properties along the a(b) axis were investigated. Single crystals were grown in air by flux method similar to the way reported by Sih et al. The mixed powder with the composition (Bi_2O_3: B_2O_3: SBT=65:5:30 wt%) was put into a Pt crucible, and heated at 1100 deg for 5 h. After soaking at 1375 deg for 10 h, the material was slowly cooled to 1300 deg at a rate of 1 deg/h. This growth procedure resulted in single crystals with 5*5*0.1 mm^3 at the maximum size. The composition of the crystals was determined by inductively coupled plasma spectrometry. SBT single crystals showed an excellent squareness of loop, and the Pr value was 18 μC/cm^2, which was over twice as large as that of the ceramics. Furthermore, Ec of SBT crystals was 20 kV/cm, and this value was much lower than those of other reported values reported for thin films and ceramics. Crystals of Bi-SBT ($Sr_{0.8}Bi_{2.12}Ta_2O_9$) showed a significantly larger Pr of 28 μC/cm^2 and the same Ec as SBT. It was concluded that defect engineering leads to a larger spontaneous polarization (Ps) for Bi-SBT. Neutron diffraction study confirmed that the Bi substitution with Sr vacancies enhances the shift of perovskite blocks with respect to Bi_2O_2 layers along the a axis as well as results in a higher angle of TaO_6 octahedral rotation in the a-b plane. These are the origin of the larger Ps for Bi-SBT. The polarization properties of La-, Pr-, and Nd-SBT single crystals will be also reported.

9:00 AM C6.2
Growth of epitaxial tetragonal Pb(Zr,Ti)O_3 thin films with 100% polar-axis-orientation and their electrical properties.
Hitoshi Morioka[1], Shintaro Yokoyama[1], Takahiro Oikawa[1], Hiroshi Funakubo[1] and Keisuke Saito[2]; [1]Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; [2]Analytical Department, PANalytical Japan, Minato-ku, Tokyo, Japan.

We have reported the relationship between the electrical properties and the domain structure of a- and c-axes mixture-oriented epitaxially grown tetragonal Pb($Zr_{0.35}Ti_{0.65}$)O_3 thin films on (100)$_c$$SrRuO_3$//(100)$SrTiO_3$ substrates by metalorganic chemical vapor deposition and estimated the spontaneous polarization (P_s) value along the polar-axis (c-axis) to be about 90 μC/cm^2.[1)] In the present study, we succeeded in growing the perfectly c-axis-oriented epitaxial Pb($Zr_{0.35}Ti_{0.65}$)O_3 thin films when the deposition temperature increased to 540 °C together with a decrease in the film thickness down to 50 nm. We also succeeded in direct measuring the P_s value. The perfectly c-axis-oriented epitaxial Pb($Zr_{0.35}Ti_{0.65}$)O_3 thin films showed large P_s value over 90 μC/cm^2 together with good square-shape in hysteresis loops.[2)] In addition, we were successful in growing 50 nm-thick PZT films with 100% c-axis-orientation for the Zr/(Zr+Ti) ratio ranging from 0.0 to 0.56. The saturation polarization (P_{sat}) values of these films were unchanged over 90 90 μC/cm^2 for the Zr/(Zr+Ti) ratio was ranged from 0.15 to 0.40, but monotonously decreased down to about 60 μC/cm^2 for 0.56. Furthermore, the ratio of remanent polarization (P_r) to P_{sat}, *i.e.*, P_r/P_{sat} ratio of these films were, also, unchanged over 0.90 for the Zr/(Zr+Ti) ratio ranging from 0.15 to 0.40, but monotonously decreased down to about 0.70 for 0.56. These results show that Ti rich tetragonal PZT thin films have large P_s values with good square-shape hysteresis loops applicable for the high-density capacitor-type ferroelectric random access memory.
Refs. [1)] K. Saito *etal.*, J. Appl. Phys. **93**, 545 (2003). [2)] H. Morioka *etal.*, Appl. Phys. Lett., in press.

9:15 AM C6.3
Origin of thickness-dependence-free characteristics of c-axis-oriented bismuth layer-structured oxide thin films.
Takahiro Oikawa[1], Yukio Sakashita[1], Takashi Kojima[2], Takayuki Watanabe[2] and Hiroshi Funakubo[2]; [1]Materials Research Center, TDK Corporation, Chiba, Japan; [2]Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Japan.

We have already reported that c-axis-oriented bismuth layer-structured oxide films were a novel candidate for high dielectric capacitor due to the low capacitance change against the applied voltage, the smooth surface, and the low leakage current regardless of the film thickness down to 20 nm. These superior characters were considered to be strongly related to the stack structure, bismuth oxide and pseudo-perovskite layers along c-axis. In the present study, epitaxial $SrBi_4Ti_4O_{15}$ (SBTi) films having various orientations were grown by selection of the substrates and investigated the electrical properties. On the basis of these data, we discuss the origin of "thickness-dependence-free" characteristics of c-axis-oriented films. Epitaxial SBTi films with various thickness were grown on $(100)_c$, $(110)_c$, $(111)_c$$SrRuO_3$//$SrTiO_3$ and (101)RuO_2//(012)Al_2O_3 substrates by metalorganic chemical vapor deposition. (001)-, (11$\underline{10}$)-, (105)-, and (100)- and/or (010)-oriented SBTi films were ascertained to be grown on these substrates by x-ray diffraction and the pole figure measurement. Tilting angles of c-axis of the films from surface normal were 0, 45, 55, 90 degree for (001)-, (11$\underline{10}$)-, (105)-, and (100)- and/or (010)-oriented films. Relative dielectric constant (ϵ_{itr}) were 200, 225, 250, and 300 for (001)-, (11$\underline{10}$)-, (105)-, and (100)- and/or (010)-oriented films with 160 nm in thickness, respectively. When the film thickness decreased, these values started decreasing around 115, 85, and 50 nm for (100)- and/or (010)-, (105)-, and (11$\underline{10}$)-oriented films. These results suggest that ϵ_{itr}-degradation started at thicker film when the tilting angle increased. On the other hand, the leakage current increased with increase of the tilting angle, while (001)-oriented films had the lowest regardless of the film thickness. The stack structure along c-axis perpendicular to the applied voltage contributes to thickness-dependence-free character of ϵ_{itr} and leakage current.

9:30 AM C6.4
Imaging Polarization Switching and Fatigue in PZT Devices with Submicron Resolution Using Hard X-ray Microdiffraction.
Dal-Hyun Do[1], Dong Min Kim[1], Chang-Beom Eom[1], Eric Dufresne[3], Eric Isaacs[2] and Paul Evans[1]; [1]Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; [2]Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey; [3]Physics, University of Michigan, Ann Arbor, Michigan.

The development of optical, electronic, and acoustic devices based on the physical phenomena exhibited by ferroelectric materials depends critically on the visualization and manipulation of polarization domains. Ferroelectricity is a structural effect for which x-ray diffraction techniques are a natural probe. We have used synchrotron x-ray microdiffraction to image polarization reversal and the development of fatigue in epitaxial Pb(Zr,Ti)O_3 (PZT) thin film devices with submicron resolution. These devices were formed from (001)-oriented PZT thin films fabricated on conducting $SrRuO_3$ bottom electrodes epitaxially grown on $SrTiO_3$ substrates. Because ferroelectric materials lack a center of inversion symmetry, the intensity of x-ray reflections from regions of opposite ferroelectric polarization (i.e. separated by 180 ° domain walls) differs in intensity. With 10 keV x-rays, regions of opposite polarization differed in intensity by 20 to 30% in our thin film PZT samples. The extent of the switched area was directly related to the remenant polarization stored in the device deduced from electrical measurements. After a number electric field cycles, the development of polarization fatigue in devices with Pt top electrodes was accompanied by the lateral spread of regions in which the PZT (002) x-ray reflection was shifted in lattice constant and greatly reduced in intensity. At lower electric fields we observed an earlier, partially reversible onset of polarization fatigue that was not accompanied by this structural change.

9:45 AM C6.5
3-Dimensional Reconstruction of Polarization in Ferroelectric Capacitors by Piezoresponse Force Microscopy.
Brian Rodriguez[1], Alexei Gruverman[2], Angus Kingon[2], Robert Nemanich[1] and Jeff Cross[3]; [1]Physics, NCSU, Raleigh, North Carolina; [2]Materials Science and Engineering, NCSU, Raleigh, North Carolina; [3]Fujitsu Laboratories, Ltd., Atsugi, Japan.

Piezoresponse force microscopy (PFM) was used to evaluate nanoscale spatial variations of domain orientation and switching behavior of (111)-oriented Pb(Zr,Ti)O_3- capacitors on Pt electrodes. A combination of vertical and lateral piezoresponse force microscopy (VPFM and LPFM, respectively) has been used to map the out-of-plane and in-plane polarization distribution, respectively, of ferroelectric capacitors. While VPFM and LPFM have previously been used to determine the orientation of the polarization vector in ferroelectric crystals, this is the first time the technique has been applied to thin-film ferroelectric capacitors, and as such, is of importance to the implementation of nonvolatile ferroelectric random access memory. Sequential VPFM and LPFM imaging of poled 1x1.5 μm^2 capacitors when combined with LPFM of the same capacitors after a 90-degree rotation of the sample allows the visualization of the polarization distribution in the poled capacitors and the subsequent 3-dimensional reconstruction of the polarization vector of the underlying (111)-oriented PZT tetragonal thin film. Regions larger than the average PZT grain size are found to have the same polarization orientation. The obtained results are discussed in terms of electrical and/or mechanical coupling between neighboring grains. This technique has potential for clarifying the capacitor size effect on imprint and switching in ferroelectric capacitors.

10:30 AM *C6.6
Stress Effects on Phase Stability and Ferroelectric Properties of Polycrystalline $Pb(Zr,Ti)O_3$ Thin Films for Nonvolatile Memories. Maxim Kelman[1], Alexei Gruverman[2], Jeffrey Roeder[3], Steven Bilodeau[3], Bryan Hendrix[3] and Paul Cameron McIntyre[1]; [1]Materials Science and Engineering, Stanford University, Stanford, California; [2]Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; [3]ATM, Inc., Danbury, Connecticut.

Mechanical strains arise in thin film capacitor dielectrics during many stages of the fabrication process for semiconductor memory devices. In the case of nonvolatile memories based on ferroelectric materials such as $Pb(Zr,Ti)O_3$ (PZT), the consequences of these strains and their resulting stresses can be very significant. In addition to the typical effect of electrostriction, in which stress alters the dielectric constant of ferroelectrics and other materials, stresses can drive the motion of 90° domain boundaries, thus modifying the out-of-plane polarization of PZT films. Furthermore, the $PbZrO_3$-$PbTiO_3$ binary system contains many related crystal structures which are distortions of the high temperature (paraelectric) cubic perovskite solid solution. Externally-imposed or residual stresses in thin film PZT can promote transitions among these structures which change the observed ferroelectric properties of the films. In this presentation, previous reported results on the effects of stress on the behavior of ferroelectric thin films are briefly reviewed. We also present the results of a recent systematic study of the stress-driven stabilization of a rhombohedral phase in (001)-textured polycrystalline $Pb(Zr_{0.35}Ti_{0.65})O_3$ thin films. Finally, the effects of well-controlled, externally-imposed biaxial tensile strains on the dielectric and polarization properties of these PZT thin films are presented.

11:00 AM C6.7
Polarization Reversal Model and Prediction of Temperature-Dependent Switching of Ferroelectric Capacitors. Igor Stolichnov[1], Alexander Tagantsev[1], Nava Setter[1] and Jeffrey S Cross[2]; [1]IMX, EPFL, Ecublens, Switzerland; [2]Fujitsu Laboratories, Atsugi, Japan.

Temperature dependent performance of ferroelectric non-volatile memories is an important issue, which impacts device reliability and ferroelectric memory applications. In general, the device temperature strongly influences the speed of polarization reversal in ferroelectric capacitors. In particular, the switching speed decreases with the decreasing temperature, which may give rise to incomplete switching. On the other hand, at elevated temperatures the phenomenon of polarization retention impacts the long-term stability. In the present work, the recently proposed Nucleation-Limited Switching model for ferroelectric thin films is extended for description of the temperature dependence of the polarization reversal. The model is shown to be valid for the temperature range important for memory applications. This model enables quantitative prediction of the switching performance of ferroelectric capacitors and retention losses at different temperatures based upon results obtained at room temperature.

11:15 AM C6.8
Wake-up, Fatigue and Rejuvenation Effects in Sol-gel PZT and PLZT Thin Films Analyzed by New Approach. Vladimir Ya. Shur[1], Evgenii L. Rumyantsev[1], Ivan S. Baturin[1], Dmitrii K. Kuznetsov[1], Rainer Waser[2] and Theodor Schneller[2]; [1]Ferroelectric Laboratory, Ural State University, Ekaterinburg, Russian Federation; [2]IWE, Rhein.-Westf. Technichen Hochschule Aachen, Aachen, Germany.

We have investigated experimentally the wake-up, fatigue and rejuvenation phenomena during cyclic switching in PZT and PLZT thin films of different compositions. New kinetic approach has been used for analysis of the experimental data. The films have been deposited by sol-gel method on Pt bottom electrode. The cycling in rectangular and triangular pulses in frequency range from 10 to 100 Hz with voltage amplitude ranged from 5 to 10 V has been used. The hysteresis loops and switching current on voltage dependences have been measured in triangular pulses. Three different stages of switching charge change has been revealed and investigated. Wake-up stage. Increase of the switching charge has been observed at the beginning of cycling. We have shown recently that the current pulse shape for switching at low frequency is determined by spatial distribution of bias field. Thus we have extracted the evolution of the bias field distribution function during cycling. The switching current contains two inputs corresponding to switching of the regions with opposite sign of bias field. During wake-up these peaks merged in one. Fatigue stage. The observed increasing of switching time and changing of the switching current shape induced by fatigue have been attributed to growth of the bias field dispersion. Rejuvenation stage can be realized for switching in triangular pulses with increased amplitude. Kinetic of the process and evolution of the current shape has been studied in details. It was shown that the switching current maximum is the most sensitive parameter for characterization of all stages. The obtained results are in accordance with our recent model of self-organized frozen domain evolution during cyclic switching [1,2]. The proposed fatigue mechanism is related to spatially inhomogeneous imprint effect. Important role of the spatial nonuniformity of the applied field due to the variation of the film thickness measured by atomic force microscope has been revealed and confirmed by computer simulation. The research was made possible in part by RFBR (Grant 01-02-17443), by RFBR-DFG (Grant 02-02-04006), by Ministry of Education RF (Grant E02-3.4-395) and by program "Basic Research in Russian Universities" (Grant UR.06.01.031), and by Award No.REC-005 of CRDF. 1. V.Ya. Shur, E.L. Rumyantsev, E.V. Nikolaeva, E.I. Shishkin, I.S. Baturin, M. Ozgul, C.A. Randall, Integrated Ferroelectrics, 2001, 33, 117. 2. V.Ya. Shur, E.L. Rumyantsev, E.V. Nikolaeva, E.I. Shishkin, I.S. Baturin, J. Appl. Phys., 2001, 90, 6312.

11:30 AM C6.9
Polarization Reversal Anti-parallel to the Applied Electric Field Observed Using a Scanning Nonlinear Dielectric Microscopy. Takeshi Morita and Yasuo Cho; Research Institute of Electrical Communication, Tohoku University, Sendai, Miyagi, Japan.

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

11:45 AM C6.10
lateral size effects in the retention properties of Pb(Zr,Ti)O3 capacitors. Dong-Jik Kim[1], B S Kang[1], T W Noh[1], J -G Yoon[2], T K Song[3], J K Lee[4] and Y K Lee[4]; [1]School of Physics, Seoul National University, Seoul, South Korea; [2]Department of Physics, University of Suwon, Suwon, South Korea; [3]Department of Ceramic Science and Engineering, Changwon National University, Changwon, South Korea; [4]Samsung Advanced Institute of Technology, Yongin, South Korea.

There has been lots of interest in ferroelectric thin films due to their potential applications to ferroelectric random access memory (FeRAM). However, the commercialization of FeRAM has been hindered by reliability problems. Currently, the retention problem is the most serious reliability issues as the capacitor size is reduced. Retention properties should be categorized into the same-state and the opposite-state failures, where the opposite-state retention failure is much more serious [1]. However, there have been only a few studies on the opposite-state retention characteristics We investigated the same-state and the opposite-state retention characteristics of

$Pt/Pb(Zr,Ti)O_3/Pt/Ti/SiO_2/Si$ and $Ir/IrO_2/Pb(Zr,Ti)O_3/Pt/IrO_2/Ti/SiO_2/Si$ thin film capacitors with various lateral sizes from 10x10 μm^2 to 0.5x0.9 μm^2. In case of the capacitors with Pt electrode, smaller capacitors were more susceptible to external factors such as etching and annealing process, and showed rapid retention failures. On the other hand, the capacitors with oxide electrodes showed relatively stable retention characteristics. However, decrease in lateral size of capacitors deteriorated the opposite-state retention. We suggest that the retention failure occurs by the increase of the leakage current and/or by the increase of the internal field and polarization backswitching. The effects of test pulse, amplitude and ratio of perimeter to area were taken into account to explain the experimental results. [1] B. S. Kang, J.-G. Yoon, D. J. Kim, T. W. Noh, T. K. Song,
Y. K. Lee, J. K. Lee, and Y. S. Park, Appl. Phys. Lett. **82**, 2124 (2003).

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

1:30 PM *C7.1
Evaluation of PZT based metal oxide electrode FRAM capacitors and reliability. Jeffrey S. Cross[1] and Yoshimasa Horii[2]; [1]Inorganic Materials and Polymers Lab, Fujitsu Laboratories Ltd., Atsugi, Japan; [2]FRAM Division, Fujitsu Limited, Atsugi, Japan.

Understanding FRAM capacitor reliability issues and polarization loss mechanisms are extremely important topics for the industrial ferroelectric film community in order to develop higher density memories. Conducting metal oxide electrodes when combined with ferroelectric films containing $Pb(Zr,Ti)O_3$ [PZT] to form a capacitor have improved reliability, particularly relating to resistance to polarization loss due to bi-polar fatigue, imprint and hydrogen degradation. These types of metal oxide electrodes have been combined both in a symmetrical structure, where the top and bottom electrodes are the same material, as well as in asymmetrical structure, where the bottom electrode is metal such as Pt and top is an oxide electrode, such as iridium oxide or $SrRuO_3$. At Fujitsu, top metal oxide electrodes consisting of IrO_2 and IrO_x (where, 1 $\langle x \leq 2$) were combined with sputtered deposited PZT films on a Pt bottom electrode to form an asymmetrical capacitor, which have been shown to exhibit high reliability and high endurance with 5 and 3 V operation. The interaction of the top electrodes and ferroelectric film, contribute greatly to the ferroelectric properties, but it is difficult to distinguish the impact of the electrode and interface on the ferroelectric capacitor because of limitations in quantitative analysis of Ir in PZT. Furthermore, it has been reported by several different groups that capacitor areal size effects have been observed for sub-micron size capacitors which show higher polarization than larger capacitors. As a result, we have been working to understand ferroelectric capacitor reliability and switching issues from a quantitative analysis point of view by combining materials characterization, diffusion studies of isotopes, ion implantation, sub-micron capacitor measurements, and applied stress as well as collaborating with university researchers to develop comprehensive models of FRAM capacitors. In this presentation, recent results will be presented focusing on metal oxide electrode interaction with PZT in order to explain polarization losses and their related mechanisms.

2:00 PM C7.2
Polarization switching of sub-micron ferroelectric capacitors using an atomic force microscope. Sanwarit Prasertchoung[1], Valanoor Nagarajan[1], Zhengkun Ma[1], Ramamoorthy Ramesh[1], Jeffrey S. Cross[2] and Mineharu Tsukada[2]; [1]Materials Research Science and Engineering Center, University of Maryland, College Park, Maryland; [2]Fujitsu Laboratories, Ltd., Atsugi, Japan.

We report on the measurement of switchable pulse polarization of micron and sub-micron ferroelectric capacitors contacted using an atomic force microscope. Fast square pulses with rise-times on the order of 10 nanoseconds are used to obtain the switchable polarization (ΔP) of discrete polycrystalline PbZr0.4Ti0.6O3 capacitors of 21.5μm2, 0.69μm2, and 0.19μm2 prepared by sputtering and reactive ion etching. Our studies show that the switching characteristics of these capacitors are well behaved indicating that high speed and high density ferroelectric memory capacitors are not limited by scaling down the capacitor area. Based on this experiment setup, we further investigated the properties of the discrete sub-micron capacitors as a function of: 1) film's structure: comparison between polycrystalline and epitaxial films and various compositions 2) film thickness down to $<$10nm. We will report results of these studies in this presentation. This work was supported by the Fujitsu visiting researcher scholarship program, and the NSF-MRSEC under contract No. DMR-00-80008.

2:15 PM C7.3
Prevention Of Hydrogen-Induced Degradation In Three Dimensional Structured MIM Capacitor With MOCVD Ta_2O_5 Dielectric and Ru Electrode. HanJin Lim, SukJin Chung, Wan-Don Kim, Kwanghee Lee, Jinil Lee, ChaYoung Yoo, SungTae Kim, Uin Chung and JooTae Moon; Process Development Team, Memory Division, Samsung Electronics, Yongin-City, 449-711, South Korea.

The leakage current degradation by hydrogen post-annealing after the formation of MIM capacitor in sub-100nm DRAM device was examined. The effect of hydrogen on capacitor degradation was evaluated with various annealing and capping processes by measuring the capacitance-voltage bias and leakage current-voltage bias. Hydrogen annealing at 450°C incurred the grain growth of Ru electrode and increased the leakage current while nitrogen annealing up to 600°C did not affect the I-V characteristics in spite of Ru grain growth. This degradation might be induced by hydrogen attack such as the formation of oxygen-depleted layer within a Ta_2O_5 dielectric beneath a catalytic Ru electrode rather than the deformation like micro-voids by Ru grain growth. To prevent it, various capping layers as hydrogen barriers were applied in 3 dimensional capacitor structure. The conformal Al_2O_3 or TiO_2 layer was deposited in the stack-type capacitor structure by using the ALD method. In order to protect against capacitor degradation in COB (capacitor on bit-line) structured DRAM, while facilitating hydrogen curing effect into Si substrate to improve DRAM refresh property as well, a novel scheme for capping only the capacitor cell area by Al_2O_3 was applied, where the top Ru was covered with Al_2O_3 and its spacer was formed on the side wall simultaneously. The thickness and post-treatment of Al_2O_3 capping layer were varied to optimize the protection conditions. The minimum thickness of Al_2O_3 was about 10nm. In the case of O_2 plasma treated spacer, the degradation of the leakage current of MIM capacitor was completely prevented after H_2 annealing at 450°C. Etch-damaged spacer seemed to be cured by oxygen supplement through the post-treatment. By doing this, such electrical properties as the equivalent oxide thickness (EOT) having 1.3nm, the leakage current value less than 1fA/cell at $\pm$1.5V bias voltage were obtained without variations before and after H_2 annealing.

2:30 PM *C7.4
Ferroelectric Thin Film Sputtering Technology for Mass Production. Koukou Suu, Institute for Semiconductor Technologies, ULVAC, Incorporated, Susono, Shizuoka, Japan.

Mass-productive sputtering technologies of ferroelectric and dielectric materials such as PZT($PbZrTiO_3$), BST($BaSrTiO_3$), Al_2O_3 and so on are developed in aiming at applications of the ferroelectric and dielectric thin films to next-generation semiconductor memories such as FRAM (Ferroelectric Memory), giga-bit DRAM (Dynamic Random Access Memory) and other embedded memories as well as MEMS (Micro-electro-mechanical system) and OMEMS (Optical Micro-electro-mechanical system). Requirements to mass-productive ferroelectric/dielectric material sputtering technology come with three aspects which are (1) production tool, (2) production sputtering technique and (3) thin film or device (ex. ferroelectric capacitor) performance. All of these three aspects must satisfy the production requirements such as good and sufficient reliability and reproducibility of sputtering process and tool, good and sufficient thickness and compositional uniformity over large size substrates, good and sufficient particle control and maintenance capability ensuring good and sufficient production throughput as well as good and sufficient properties for ferroelectric films and their device integration. We have been working on and overcome the challenges from the above-mentioned aspects including arcing on the targets and shields, target cracking, variations of sputtering rate, film composition, uniformity and the properties over process running as well as defects and throughput issues related to particle control during sputtering. A production solution was achieved by developing and implementing an original sputtering chamber, high-quality sputtering targets and advanced sputtering techniques/processes. In this paper, we will report our R&D results of ferroelectric/dielectric material sputtering as well as the data from FRAM production.

3:30 PM *C7.5
Effective Orientation Control of $Pb(Zr_{0.4}Ti_{0.6})O_3$ Thin Film Capacitors Using $Ti/Pb(Zr_{0.4}Ti_{0.6})O_3$ Seeding Method. Bum-Ki Moon[1], Oasmu Arisumi[2], Karl Hornik[1], Rainer Bruchhaus[1], Hiroshi Itokawa[2], Andreas Hilliger[1], Haoren Zhuang[1], Ulrich Egger[1], Soichi Yamazaki[2], Toru Ozaki[2], Nicolas Nagel[1], Iwao Kunishima[2], Koji Yamakawa[2] and Gerhard Beitel[1]; [1]FDA, Infineon Technologies Corp., Yokohama, Japan; [2]FDA, Toshiba Corp. Semiconductor Company, Yokohama, Japan.

The most promising material for future FeRAM devices is $Pb(Zr,Ti)O_3$ (PZT). For this material, control of crystallographic

orientation is essential for achieving excellent electrical performance. In previous studies, the orientation was controlled by inserting TiO_2 or $PbTiO_3$ based seed layers, or by proper crystallization steps. In this paper, the effect of thin Ti/$PbZr_{0.4}Ti_{0.6}O_3$ seed layers on the properties of $PbZr_{0.4}Ti_{0.6}O_3$ capacitors has been investigated. The seed layer is based on a bi-layer of thin Ti and thin PZT with a total thickness ranging from 10 to 25nm, which were deposited by sputtering on Pt(111)/Ir(111) bottom electrodes at room temperature. After crystallization of the seed layers at 650°C for 30 sec using RTO, the main 130nm-PZT film was deposited and crystallized. As a result, a highly preferred (111)-orientation of the PZT was obtained on a 10nm thick seed layer, where the peak intensity ratios of (111)/{100} and (111)/{110} are about 100 and 20, respectively. However, PZT on a 25nm thick seed film showed much lower (111)-intensity. Careful XRD and TEM investigations revealed that the 10nm thick seed forms a pyrochlore phase with very smooth surface, while the 25nm thick seed layer is a mixed phase of pyrochlore and {110}-oriented perovskite. The formation of the pyrochlore phase is attributed to Pb diffusion into the bottom electrode, resulting in a Pb deficient stoichiometry. The seed layer transformed to the perovskite phase during the main PZT crystallization. Capacitors with $SrRuO_3$/Pt top electrodes and 10nm thick seed layer showed a Q_{sw} of typically 34.9 $\mu C/cm^2$, however, a lower Q_{sw} of 18.9 $\mu C/cm^2$ was obtained in case of a thicker seed layer. The 10nm seed capacitors exhibited a fatigue-free behavior up to 10^{10} switching cycles. In conclusion, inserting a thin Ti/$PbZr_{0.4}Ti_{0.6}O_3$ seed layer is a very effective method for fabricating PZT capacitors with excellent ferroelectric properties.

4:00 PM C7.6
Low Voltage Operation of The PZT Ferroelectric Thin Film Prepared by Liquid-Source MOCVD. Yutaka Nishioka, Takeshi Masuda, Masahiko kajinuma, Takakazu Yamada, Masaki Uematsu and Koukou Suu; Institute for Semiconductor Technologies, ULVAC, Inc., Shizuoka, Japan.

Ferroelectric random access memories (FeRAM) are compared very favorably with other non-volatile memories, such as electrically erasable programmable read-only memories (EEPROM) and flash memories, since high speed and low voltage operation. So the preparation of Pb,(Zr,Ti)O_3(PZT) ferroelectric thin film has been widely developed for application of portable electronic devices such as mobile phones. In this work, we succeeded a low saturated voltage (V90), high switching charge (Qsw) and low leakage current density (JL) of the PZT thin film. 100nm PZT were grown on 8inch-Ir(111)/SiO_2/Si substrate at 620°C and O_2 ambient by metal organic chemical vapor deposition (MOCVD). $Pb(thd)_2$, $Zr(dmhd)_4$ and $Ti(iPrO)_2(thd)_2$ were used as precursors. After preparing PZT films, 100-nm-thick Pt top electrodes were formed by DC magnetron sputtering through a shadow mask with 0.3mm diameters dots. After forming top electrode, post-annealing was performed at 580°C for 60min in oxygen ambient at 1atm. Normalized oxygen/precursors ratio was varied at the PZT growth. Composition, Phase and thickness of the PZT films were made adjustment to $Pb_{1.15}(Zr_{0.45}, Ti_{0.55})Ox$, PZT single phase and 100nm respectively for all sample. V90, Qsw(@2V) and JL(@1.5V) were 2.2V, 36.9uC/cm^2 and 2.5E-6A/cm^2 respectively at the normalized oxygen/precursors ratio = 1. Increasing the normalized oxygen/precursors ratio from 1 to 3, the electrical properties were improved. Their values are 1.7V, 47.4uC/cm^2 and 7.5E-8A/cm^2 respectively. Acknowledgments: We thank Mitsubishi Materials Corporation for supporting precursors and solvents.

4:15 PM C7.7
Fabrication of Ru/$Bi_{4-x}La_xTi_3O_{12}$/Ru Ferroelectric Capacitor Structure Using a Ru Film Deposited by Metalorganic Chemical Vapor Deposition. Taisuke Furukawa[1], Takeharu Kuroiwa[1], Yoshihisa Fujisaki[1,2], Takehiko Sato[1] and Hiroshi Ishiwara[2]; [1]R&D Association for Future Electron Devices, Yokohama, Japan; [2]Tokyo Institute of Technology, Yokohama, Japan.

Ruthenium has been paid much attention as a promising candidate for the electrode material of semiconductor devices. There have been many researches on the Ru film deposited by RF sputtering or metalorganic chemical vapor deposition (MOCVD). For the Ru film deposited by MOCVD, some advantages are expected such as good step coverage, low damage to the underlying structures and so on, which might be an important properties for the fabrication of future ferroelectric random access memories (FeRAM). Therefore, we believe that realization of metal-ferroelectrics-metal capacitor using MOCVD-deposited Ru films will give important contribution to the future FeRAM. A Ru film was deposited by a MOCVD system. The wafer was heated with infrared lamps and the temperature was measured and controlled with a pyrometer. A liquid type source, $Ru[EtCp]_2$, was injected into the vaporizer through an injector composed of a normally closed valve that worked in a pulse regime. Then source was vaporized and introduced into the growth chamber with nitrogen. No oxidant to enhance the decomposition of $Ru[EtCp]_2$ such as O_2 gas was mixed. The deposition temperature was 350°C and deposition pressure was 9 torr. Without forming a seed layer deposited by another deposition system, smooth and flat Ru film was successfully deposited on SiO_2/Si substrate. After the deposition, post annealing at a temperature of 400°C was performed, which was effective for the suppression of leakage current of the capacitor fabricated on the Ru film. Next, a $Bi_{4-x}La_xTi_3O_{12}$ (BLT) film was formed on the CVD-deposited Ru film by spin-coating a sol-gel solution. After drying, the sample was baked in O_2 ambient at 400°C. This process was repeated twice to obtain a 150-nm-thick BLT film. Then, annealing for crystallization was performed at 650°C. The thermal process was tuned so that oxidation of Ru was suppressed. Finally, Ru film was deposited on BLT/Ru structure by the same MOCVD system. Then, Ru film was patterned through a dry etching process. As a result, Ru/BLT/Ru capacitor structure was successfully fabricated. This work was performed under the auspices of the R&D Projects in Cooperation with Academic Institutions (Next-Generation Ferroelectric Memories), supported by NEDO (New Energy and Industrial Technology Development Organization in Japan) and managed by FED (R&D Association for Future Electron Devices).

4:30 PM C7.8
Rf Magnetron Sputtering Process for BST Thin Films with Higher Dielectric Constant. Takehito Jimbo, Isao Kimura, Yutaka Nishioka and Koukou Suu; Institute for Semiconductor Technologies, ULVAC, Incorporated, Susono, Shizuoka, Japan.

(Ba, Sr)TiO_3 (BST) is of interest for use in electronic element such as bypass capacitor because of its high dielectric constant. In this talk, rf magnetron sputtering process for BST film with higher dielectric constant is described. Dielectric constant is strongly affected by sputtering condition such as substrate temperature, sputtering power, pressure and so on. These condition is thought to be affect crystallinity, composition, stress of BST films. Actually, major change of dielectric constant and crystallinity of BST thin films by changing the sputtering condition was also confirmed in our experiment. In addition, though post-annealing aiming at recovery of crystallinity and damage between top electrode and BST film was conducted after top electrode deposition, dielectric constant was not approved. For this reason, sputtering conditions of BST deposition have to be carefully selected for higher dielectric constant. At this moment, 30-nm-thick BST film with dielectric constant of 300 and uniform columnar structure is obtained on Pt electrode at deposition temperature of 650°C.

SESSION C8: Poster Session: Dielectric Films and Applications
Chairs: Angus Kingon and Ivo Koutsaroff
Wednesday Evening, December 3, 2003
8:00 PM
Exhibition Hall D (Hynes)

C8.1
Measuring Residual Stress Effects In Tunable Microwave Dielectric Thin Films. William D Nothwang, M. W. Cole, C. Hubbard and E. Ngo; WMRD-Emerging Materials Research Group, U.S. Army Research Laboratory, APG, Maryland.

There has been a recent shift towards a tunable phase shifter for microwave antenna design. Barium strontium titanate (BaxSr(1-x)TiO3) thin films are the principal materials of interest in these applications, primarily because of their low loss, high dielectric constant and large tunability. Both magnesium doped and undoped films were made, and they were deposited on MgO or Pt-Si substrates using metal organic solution deposition and pulsed laser deposition. Residual stress within these materials is known to have a drastic effect on the material, electrical, and dielectric properties. This becomes of particular importance in thin film materials, where the residual stress can be several orders of magnitude higher than in bulk materials. The residual stress in the films was measured in three ways. A Tencor stress analysis system was employed to measure the change in the substrate curvature due to the film stress, and a nano-indentation method was used to calculate the residual stress in a system by measuring the maximum penetration, the force at maximum penetration, and the slope of the initial unloading curve. These methods were validated using XRD lattice calculations. The results indicate that an 80% drop in dielectric constant is observed in undoped films with a residual stress as low as 200 MPa. Stresses as high as 2 GPa were observed under certain conditions. The tunability also decreased by a factor of 80% for the same residual stress. Atomic force microscopy results indicate that different nucleation behavior was observed at different doping levels, and this was confirmed with the nano-indentation results. The results also show that the surface region of the films is not stress free at these thicknesses (~200 nm) as was mathematically suggested.

C8.2

The Effect of Strain Variation on the Dielectric Properties of (Ba,Sr)TiO3 Thin Films. Jang-Sik Lee, Y Lin, Y Li and Q.X. Jia; Materials Science and Technology Division, Los Alamos National Lab., Los Alamos, New Mexico.

It has been reported that the strain state of the (Ba,Sr)TiO3 (BST) thin films can be changed according to the substrates, film thickness, oxygen partial pressure during deposition, strain variation of the thin buffer layers, and so on. In this work, we grew epitaxial BST thin films either directly on (001) LaAlO3 (LAO), (001) SrTiO3 (STO), and (001) MgO or SrRuO3 (SRO)-coated LAO, STO, and MgO by pulsed laser deposition. Coplanar capacitors and metal-insulator-metal (MIM) capacitors were fabricated thereafter using gold as the electrode. All BST films were (001) oriented. The good alignment in the plane of the BST and SRO with respect to the major axes of the substrates was also confirmed by XRD ϕ-scans of the (303) BST, (303) SRO, and (303) substrates reflections. The dielectric properties of the BST films on different substrates and capacitor architectures were characterized by the capacitance-voltage and capacitance-frequency measurement. The effects of epitaxial strain on the properties of BST thin films with coplanar capacitor and MIM capacitor structures will also be discussed in detail.

C8.3

Temperature dependent Raman scattering and dielectric permittivity measurements of Pb_{1-x} Sr_x TiO_3 films grown by metalorganic decomposition. Vaman M Naik[1], Mackenzie J Smith[1], Houbei Dai[2], Ratna Naik[2], Gregory W Auner[3] and Joseph Mantese[4]; [1]Natural Sciences, U Michigan-Dearborn, Dearborn, Michigan; [2]Department of Physics, Wayne State University, Detroit, Michigan; [3]Department of Electrical and Computer Engineering, Wayne State University, Detroit, Michigan; [4]Delphi Automotive Systems, Shelby Township, Michigan.

Pb_{1-x} Sr_x TiO_3 (x = 0 to 1.0) films of thickness $\sim$ 4 μ m have been prepared on sapphire and Pt substrates by the metalorganic decomposition (MOD) technique. X-ray diffraction results show that the films are polycrystalline with a perovskite tetragonal phase at room temperature for x $<$ 0.5 and a cubic phase for x $>$ 0.5. Room temperature Raman spectra show a systematic variation of lattice vibrational modes with composition. The most notable changes in the Raman spectra with x are the coalescence of A_1(3TO) and E(3TO) modes into one at approximately x = 0.6, and a considerable softening of A_1 (2TO) mode. Although the x-ray diffraction peaks for x = 0.6 show a cubic phase at room temperature, the Raman spectrum shows the characteristic phonon modes of a tetragonal phase. The dielectric permittivity versus temperature measurements for films with x $\leq$ 0.6 show a dielectric anomaly, although broad, corresponding to a ferroelectric to paraelectric phase transition. However, the phase transition temperatures (Tc) are lower than the corresponding values of bulk ceramic alloys. Furthermore, the temperature dependent Raman measurements of these films show that the tetragonal modes persist much beyond T_c + 100 ^oC. This is consistent with the observation of a rather diffuse phase transition in the mixed perovskites caused by distribution of phases in the film perhaps due to a variation in Pb content along the film thickness and /or near grain boundary regions

C8.4

An Investigation of the Importance of Interface and Bulk Transport Mechanisms on the Leakage Current of High Dielectric Constant Thin Film Capacitors. John David Baniecki, Takeshi Shioga and Kazuaki Kurihara; Microelectronics Lab, Fujitsu Laboratories, Atsugi, Kanagawa, Japan.

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

C8.5

Influence of Relaxation on Leakage Current for BST Films. Ping Sun and Harry E. Ruda; Center for Advanced Nanotechnology, University of Toronto, Toronto, Ontario, Canada.

We report on current-voltage (I-V) and current-time (I-t) characteristics of 500 nm thick Ba0.7Sr0.3TiO3 (BST) films deposited on Pt/TiO2/SiO2/Si substrate by sol-gel processing. The relaxation current influences the leakage current and introduces a positive error, especially for small bias fields and at low temperatures. The leakage current originates from the Frenkel-Poole effect. The deep electron trap barrier height was 0.54 + - 0.03 eV, estimated from fitting of the conductivity-field dependence in the range of high bias field (i.e., from 400 to 800 kV/cm), and corrected to 1.1 + - 0.2 eV after removing the contribution from the relaxation current using a nonlinear least squared fitting of the I-t curve.

C8.6

Simulation Of Conduction In High Permittivity Thin Films With Thermionic And Tunneling Injection At The Schottky Barrier. Herbert Schroeder, IFF-EKM, Forschungszentrum Juelich GmbH, Juelich, Germany.

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

C8.7

Conduction and Microwave Loss Mechanisms in $Ba_{0.25}Sr_{0.75}TiO_3$ Films. Andrei Vorobiev, Khaled Khamchane, Par Rundqvist and Spartak Gevorgian; Department of Microtechnology and Nanoscience, Chalmers University of Technology, Gothenburg, Sweden.

The silicon integrated parallel-plate $Ba_{0.25}Sr_{0.75}TiO_3$ (BST) varactors with record low loss tangent, due to application of the bottom Au electrode, have been prepared and characterized by microwave impedance and DC current-voltage measurements. In the frequency range 0.045-45 GHz the loss tangent is less than 0.025. However, this is still 10 times higher than losses in single crystal indicating that along with fundamental losses the additional loss mechanisms exist. The low field DC current through varactor is controlled by Pool-Frenkel mechanism associated with hopping charge carriers by internal traps formed by positively charged oxygen vacancies. The presence of internal traps in the bulk of BST film allows to explain the additional microwave losses by hopping charge carrier polarization. The domination of this polarization mechanism is confirmed by linear frequency dependence of loss coefficient and decreasing the losses by applied voltage observed in our experiments. The knowledge of the dominant loss mechanism allows optimizing the varactor preparation and further improving the Q-factor.

C8.8

Reliability Of Tunable Capacitors For Microwave Applications. Barry W. Treadway, Guang Lin, Luna Chiu and Xubai Zhang; Paratek Microwave, Inc., Columbia, Maryland.

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

Parascan® family of materials. These materials exhibit excellent tunability and loss characteristics at RF frequencies. Variable capacitors suitable for microwave applications have been fabricated from these materials using both thick and thin film processes. In addition to capacitance, tunability, and loss measurements, the reliability of these variable capacitors has been determined using Highly Accelerated Lifetime Testing and Mean Time Between Failure techniques. We have shown that the capacitance drift is less than 1% at 70° C under an electric field of 37.5 volts/micron for thin film capacitors, and less than 10% at 70° C under an electric field of 15 volts/micron for thick film capacitors. In addition, the failure rates for both thin and thick film capacitors have been determined as a function of electric field strength.

C8.9

Ferroelectric Films and Multilayers with Ultrahigh Dielectric Constant. Kewen Li, Kevin Zou, Yanyun Wang and Hua Jiang; Boston Applied Technologies, Woburn, Massachusetts.

Ferroelectric materials have shown great potential for microwave, energy storage and integrated circuit applications. However, two major issues related to the ferroelectric materials hampered the further advancement of the technology; i.e. the dielectric constant drops significantly (almost an order of magnitude) in a ferroelectric thin film from the value of its counterpart bulk crystal. Another drawback of ferroelectric films is their large temperature dependency of dielectric constant, especially near the Curie temperature of the material. A solution to these two serious issues becomes very urgent and strategically important. This work presents a systematic study of ferroelectric films and multilayer interface nanostructures made by a Metal-Organic Chemical Liquid Deposition method. La-modified Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT), Pb(Zn1/3Nb2/3)O3-PbTiO3 (PZN-PT), and BaxSr1-xTiO3 (BST) films, as well as multilayer interface nanostructures incorporated with these materials have been grown at different conditions. Ultrahigh dielectric constant (~8000) has been achieved in the PMN/PZT-PT material system when the sublayer thicknesses approaching to nanometer scale, where interfaces become dominant. When the sublayer materials with desired Curie temperatures are properly chosen, the temperature dependent dielectric constant of the multilayer structure can be greatly reduced. These multilayer interface nanostructures may find very important applications where temperature variation is a key concern. We also studied the effects of various dopants (Pb, Mg in BST, and rare earths in Pb-based compositions) on the properties of these films/multilayers; some very important microwave and optical properties will be presented.

C8.10

Abstract Withdrawn

C8.11

The Dielectric Characteristics of PZT/LNO Films Deposited on Base-metal Sheets For Power Electronic Systems. Jung-Hoon Yeom[1], Seung-Hyun kim[1], Chang Young Koo[1], Jong-Hyeon Cheon[1], Dong-Joo Kim[2], David Y Kaufman[3], Stephen K Streiffer[2] and Jowoong Ha[1]; [1]R&D Center, Inostek Inc., Ansan-si, Gyeonggi-do, South Korea; [2]Material Science Division, Argonne National Laboratory, Argonne, Illinois; [3]Energy Technology Division, Argonne National Laboratory, Argonne, Illinois.

Recently, the embedding high-permittivity (high K) dielectric materials using PZT and La-doped PZT thin film have been utilized to develop device reliability, manufacturing cost down and make small size products for power electronic systems. However, many parts of those electronic systems include somewhat expensive materials and complicate processing steps. Especially, the electrodes of capacitors, which use an expense noble metal, have an effect on the product cost rising in electronic system. The capacitor cost reduction is capable of changing the expensive noble metal electrode to base-metal and alloys. In this experiment, Ni-based sheet is used as a substrate to achieve less-expensive process and LNO buffer layer is inserted underlying PZT films to prevent the oxidation of Ni sheet substrate. PZT and LNO thin films are prepared using modified chemical solution deposition method. In an effort to develop robust capacitors on cost competitive Ni sheet, several parameters including annealing conditions, dopants, Zr/Ti ratios, 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 power electronic system 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.

C8.12

Tailoring of Dielectric Properties of Ferroelectric Films with Low Loss Dielectric Material by Sol-Gel Technique. M. Jain[1], S. B. Majumder[1], R. S. Katiyar[1], A. S. Bhalla[2], F. A. Miranda[3] and F. W. VanKeuls[3]; [1]Physics, University of Puerto Rico, San Juan, PR, Puerto Rico; [2]Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania; [3]Communications Technology Division, NASA, GRC, Cleveland, Ohio.

$Ba_{1-x}Sr_xTiO_3$ (BST) is a suitable material for several frequency agile microwave electronic devices, such as phase shifters, filters, varactors, delay lines etc. due to its high response of the dielectric constant to an applied electric field. However large dielectric constants and dielectric losses found in this system limits its usefulness at microwave frequencies. In an effort to bring down the insertion loss, we have deposited composite films of BST with low loss dielectrics like MgO and $MgTiO_3$ by sol-gel technique. The structural and microstructural studies of these films have been carried out in detail. The pure and composite BST thin films were characterized by X-ray diffraction and were found to be highly (100) oriented. The dielectric properties, including tunability, loss tangents, and phase transition behavior, are measured in the frequency range of 1kHz-1MHz on the films. For the BST:$MgTiO_3$ and BST:MgO composite films, considerable reduction in the dielectric constant and loss values at low frequency (upto 1MHz) was observed, which translates to a moderate or high K factor (tunability/loss tangent) depending upon the layer sequence or thickness. The synthesized films were used to make eight element coupled micro-strip phase shifters and characterized in terms of their degree of phase shift and insertion loss characteristics in a frequency range of 13-15 GHz. The high frequency figure of merit (defined as the ratio of degree of phase shift and insertion loss) was found to be markedly improved (62 and 74°/dB for type I an II respectively) for the BST50:MgO composite films as compared to 30°/dB for the pure BST50 films under the same preparation and measurement conditions. The dielectric properties of one of the potential and isomorphous compound, (Pb,Sr)TiO_3, and its composite films with the low loss dielectrics prepared by sol-gel technique will also be presented.

C8.13

Structural and Electrical characterization of laser ablated Ca doped Barium Titanate thin films on different substrates. Victor Pushparaj[1], S B krupanidhi[1] and Sangib Saha[2]; [1]Materials Research Center, Indian Institute of Science, Bangalore, Karnataka, India; [2]Materials Science division, Argonne National Laboratory, Argonne, Illinois.

The doping of Ca in the BaTiO3 ceramics showed a remarkable improvement in the electromechanical behavior, increase in the temperature range of the stability of the tetragonal phase and inhibited the formation of the unwanted hexagonal phase of BaTiO3. Photo refractive barium titanate crystals are used for self pumped phase conjugation in advanced laser systems for laser beam cleanup via two wave mixing and for optical interconnects. BCT is a promising photorefractive materials with larger electro optic coefficients(r13 and r33) compared to other conventional materials. Ba1-xCaxTiO3 (at. % Ca x = 0.05, 0.1, 0.13 and 0.18 at%) and La0.5Sr0.5CoO3 targets were prepared by solid state reaction technique and the BCT and LSCO thin films were deposited on Pt coated Si substrates and Si(100) substrates by pulsed excimer laser ablation technique. The dielectric constant and the phase transition temperature in both the bulk and the thin films were found to decrease with the increase of Calcium content in Barium titanate matrix. The dielectric phase transition was studied for the BCT thin films deposited on the Pt coated Si, LSCO/PT and Si substrates. Calcium doped BaTiO3 properties are highly dependent on the processing parameters. There is a strong anomaly observed in the decrease of phase transition and could be tailored accordingly to the processing parameters. The decrease in the phase transition was analysed in terms of the size dependence of ferroelectric domains, intergranular stresses and strain existing at the film/substrate interface. XRD, XPS, SIMS and Micro Raman analysis on these thin films, were carried out for the structural characterization. SIMS analysis carried on the BCT thin films on Si showed a sharp interface existing at the substrate/thin films without any interdiffusion of the elements. The possibility of the Ca occupancy in the Ba or Ti site has been extensively investigated through this structural characterization and their extensive correlation with the electrical properties are also dealt.

C8.14

Single- and Multi-Target Pulsed Laser Deposition of Thin $Ba_xSr_{1-x}TiO_3$ Films: Preparation, Microstructure and Electrical Properties. Peter Petrov, Kumaravinothan Sarma and Neil Alford; Centre for PEM, F.E.S.T., South Bank University, London, United Kingdom.

This paper presents the results of a comparative study of microstructure and electrical properties of $Ba_xSr_{1-x}TiO_3$(BSTO) films made by single- and multi-target pulsed laser deposition. A set of thin $Ba_{0.50}Sr_{0.50}TiO_3$, $Ba_{0.60}Sr_{0.40}TiO_3$ and $Ba_{0.75}Sr_{0.25}TiO_3$ films were deposited on $LaAlO_3$ substrates using a single target with corresponding stoichiometry. Another set of samples with same

stoichiometry were deposited as a periodic structure of $BaTiO_3$ (BTO) and $SrTiO_3$ (STO) layers. The layer thickness was chosen so as to not exceed the critical thickness required for epitaxial growth. In order to obtain a specific Ba/Sr stoichiomeric ratio in the sample, the number of laser pulses shot to BTO and STO targets was adjusted according to the ratio. This enabled a series of STO and BTO layers to be deposited in which the layer thickness could be varied. All samples were made under same conditions, maintaining the same total number of laser pulses. The structural properties of all samples were investigated using X-ray diffraction and SEM. The elemental composition of the samples was investigated using an EDXA attached to a Hitachi SEM. To prevent a signal from the substrate a low accelerating voltage was used. For RF (10MHz) and microwave (1-10GHz) electrical properties examination a simple capacitor structure was patterned on the film surface. The measurements were performed in a temperature range between 250K and 350K. The XRD analysis shows that all films (made from a single as well as those made from two targets) are single crystal with (001) orientation. The XRD peaks measured for two targets films were broader than those measured for single target made films. However, their a, b, and c lattice parameters evaluated were almost identical but slightly larger than the lattice parameters of corresponding single target. This is believed to be due-to the residual strain caused by the film-substrate lattice parameter misfit. The difference in RF and microwave properties of the films is also discussed in the paper. An attempt to correlate it with the film processing and microstructure is made.

C8.15
Dielectric Properties of Ba0.96Ca0.04Ti0.88Zr0.12OX(BCTZ) Deposited by RF Sputtering. Thottam S. Kalkur, N. Cramer, Elliott Philofsky and Lee Kammerdiner; Electrical and Computer Engineering, University of Colorado at Coloardo Springs, Colorado Springs, Colorado.

Ba0.96Ca0.04Ti0.88Zr0.12O (BCTZ) is a high-K material commonly used in discrete capacitors based on thick film technology. As a thin film, BCTZ has recieved minimal attention. Previous studies have made of spin-on metalorganic deposition(MOD) or sol-gel techniques. To the best of authors knowledge, this is the first study to utilize RF sputtering to deposit thin film BCTZ. BCTZ exhibits dielectric properties that are very similar to barium strontium titanate (BST), a very commonly studied material. Dielectric constant, K values for BCTZ are similar to those of BST deposited under similar conditions. Leakage current in BCTZ was found to be less than in similar BST films. Both BCTZ and BST exhibit high tunability and low loss tangent, but BCTZ exhibits combinations of these two qualities that outperform similar BST films. Thus BCTZ is a possible replacement for BST in certain applications.

C8.16
Dielectric and Ferroelectric Properties of Modified $BiFeO_3$-$PbTiO_3$ Thin Films Derived from Sol-gel Processing. Jinrong Cheng[1,2] and L.Eric Cross[1]; [1]Materials Research Institute, Penn State University, State College, Pennsylvania; [2]School of materials Science and Engineering, Shanghai University, Shanghai, Shanghai, China.

In this paper, La and Ga- modified $BiFeO_3$-$PbTiO_3$ (BF-PT) morphotropic phase boundary (MPB) solid solution has been developed into the thin films using sol-gel processing. The annealing temperature of BF-PT based thin films is of 750°C. XRD analysis reveal that we have obtained the perovskite BF-PT based thin films without detectable pyrochlore phase. The dielectric constant and loss tangent of about 600 and 4% respectively are achieved for the modified BF-PT thin films, using a measurement frequency of 1 KHz. Ferroelectric hysteresis loops are also observed. Our preliminary experiments indicate that the sol-gel derived BF-PT based thin films have good insulation resistance and measurable dielectric and ferroelectric responses.

C8.17
Microstructural and Electrical Characterization of BST Thin Films Fabricatd by a New Carboxylate Free Chemical Solution Deposition (CSD) Route. Sandip Halder[1], Theodor Schneller[1] and Rainer Waser[1,2]; [1]Institut fur Werkstoffe der Elektrotechnik, RWTH -Aachen, Aachen, NRW, Germany; [2]Institut fur Festkoerperforschung, Forchungzentrum Juelich, Juelich, NRW, Germany.

A new type of alkoxide precursor was developed to avoid the formation of oxocarbonate phase as an intermediate phase during crystallization. The formation of the oxocarbonate phase is believed to be the cause for the high crystallization temperature of BST. The precursors were sythesized from Ba metal, Sr metal and aminoethanol. The new precursors were found to be more stable as compared to the carboxylate precursors and were soluble in a number of organic solvents. The precursors were deposited on platinum coated silicon wafers and crystallized between 550 and 700 degree centigrade. The films were found to crystallize above 600 degrees. After crystallization Pt top electrodes were deposited by lift off processing. FT-IR studies performed on the films showed no oxo-carbonate phase formation during crystallization. Microstructural studies involving XRD, SEM and AFM were performed on the films. The films were found to have a dielectric constant of 400 and a tunability of 37%. The frequency and temperature dependence of the dielecric constant were studied. in addition leakage studies were performed on the films.

C8.18
Comparative studies on $BaZrx_{Ti1-xO3}$ thin films deposited by sol-gel and pulse laser deposition. Anju Dixit, Pijush Bhattacharaya, Subhashish Basu Majumder, Ram S Katiyar and Amar Singh Bhalla; Physics, University of puertorico, Sanjuan, Puerto Rico.

In the present work, ferroelectric thin films of $BaZrx_{Ti1-xO3}$ were deposited on platinum (Pt) and lanthanum aluminate ($LaAlO_3$) substrates by sol-gel and pulse laser deposition technique. The structure and preferred orientation of the films were examined by x-ray diffraction measurements. The phase formation of sol-gel derived highly textured BZT films on $LaAlO_3$ substrate found to be at high temperature while the pulse laser deposited BZT films were formed at low temperature. The films were highly oriented on $LaAlO_3$ substrate. Polycrystalline films were observed in case of platinum (Pt) substrates by both techniques. Ferroelectric nature of the films was confirmed by hysteresis and capacitance-voltage characteristics using top electrodes. The phase transition behavior of $BaZrx_{Ti1-xO3}$ (x= 0.0 to 1.0) thin films has been investigated by temperature dependent Micro-Raman and dielectric measurements. BZT films prepared by both technique showed strong compositional dependence. Normal ferroelctric to relaxor behavior has been observed in the composition range (x = 0 to 0.60). From temperature dependent Raman scattering it was found that the cubic to tetragonal transition temperature decreases while the lower phase transitions temperatures increase. For films with Zr contents of 10% all transition temperatures coalesce into one at Tc $\sim$ 280k. The dielectric measurements confirm this observation. Above 15% Zr the dielectric constant measurements show a broad maximum at the transition temperature. For Zr concentration above 25% the material shows relaxor properties. Above 60% no relaxation is observed in BZT films. Transition temperatures as well as dielectric constant were found to be decrease by increasing Zr contents. Several comparative aspects will be discussed from the studies of both sol-gel and pulse laser deposited films.

C8.19
Growth and study of $BaZrO_3$ thin films by pulsed laser ablation. Rajasekarakumar Vadapoo[1], P. Victor[1], R. Ranjith[1], S. B. Krupanidhi[1], S. Rajagopalan[2] and A. K. Tyagi[2]; [1]Materials Research Centre, Indian Institute of Science, Bangalore, karnataka, India; [2]Materials Science Devision, Indira Gandhi Center for Atomic Research, kalpakkam, India.

Thin films of $BaZrO_{3}$ (BZ) were grown using a pulsed laser deposition technique on platinum coated silicon substrates. Films showed a polycrystalline perovskite structure upon different annealing procedures of in-situ and ex-situ crystallization. The composition analyses were done using Energy dispersive X-ray analysis (EDAX) and Secondary Ion Mass Spectrometry (SIMS). The SIMS analysis revealed that the ZrO_{2} formation at the right interface of substrate and the film leads the degradation of the device on the electrical properties in the case ex-situ crystallized films. But the in-situ films exhibited no interfacial formation. The dielectric properties have been studied for the different temperatures in the frequency regime of $40 Hz$ to $100 kHz$. The response of the film to external AC stimuli was studied at different temperatures, and it showed that AC conductivity values in the limiting case are correspond to oxygen vacancy motion. The electrical modulus is fitted to a stretched exponential function and the results clearly indicate the presence of the non- Debye type of dielectric relaxation in these materials.

C8.20
Enhancing Tunability and Decreasing Temperature Sensitivity. A Tauber[2,1], S C Tidrow[1], D M Potrepka[1], B J Rod[1], K W Kirchner[1], M H Ervin[1] and F J Crowne[1]; [1]AMSRL-SE-RE, Army Research Laboratory, Adelphi, Maryland; [2]Geo-Centers, Inc., Newton Upper Falls, Massachusetts.

The employment of judicious substitution on B-sites in the perovskite oxide, $BaTiO_3$, has yielded materials suitable for relatively temperature insensitive electric field tunable microwave devices. The properties, single-phase cubic perovskites with tunabilities as large as 30% at 1 V/μm and room temperature that possess low temperature coefficient of dielectric constant and tunability over the majority of the military specified temperature range, -55 to 125 °C, have been

achieved in the charge compensated system $Ba_{1-x}Sr_xTi_{1-2y}C_yD_yO_3$ where C is Ho, Er, Tm, Lu, Sc, Y, In and D is Ta, Sb with $0 \leq x \leq 0.2$, and $0 < y \leq 0.10$. The average ionic radius for C ions is 1 $\AA$, and that for D ions is 0.8 $\AA$ or the average for all substitutions is 0.9 $\AA$. The Goldschmit tolerance factor, T, for $BaTiO_3$ is close to 1.0, an instability point. Substitutions with ionic radii larger than Ti^{4+} result in compositions with more stable T. Substitutions with ionic radii much smaller or larger than 0.9 $\AA$ result in compositions with smaller tunabilities. These materials are being used in a novel device structure that has been shown to provide broadband variable true time delay and thus can be used for broadband electronic scanning antennas applications over the military specified temperature range.

C8.21

Optimization of Strontium Titanate Thin Films For Low Loss Tunable Superconducting Microwave Filters. Gerd Fischer, Luke S.-J. Peng and Brian H. Moeckly; Superconductor Technologies, Inc., Sunnyvale, California.

Nonlinear ferroelectric thin films allow the possibility of tuning resonant circuits by changing the capacitance with an applied electric field. SrTiO3 thin films can exhibit a large tunability at low temperatures and hence are good candidates for tuning HTS filters, which operate at about 65 K. We have optimized the growth conditions of SrTiO3 thin films to obtain low loss and high tunability for use as variable capacitors in such filter circuits. We grew our thin films by reactive coevaporation, and we investigated their properties using in-situ RHEED, x-ray diffraction, low frequency capacitance-loss measurements, and high frequency resonator coupled measurements. We will discuss the influence of the growth conditions on the thin film properties. Additionally, we present data from a YBCO cross-coupled 6-pole, 0.2% bandwidth filter centered at about 800 MHz (modified cellular A-prime band) with insertion loss less than 1dB over the band. The use of SrTiO3 allows this filter to be electrically tuned by about 1 MHz while maintaining a high Q value. This work was funded by DARPA as part of the FAME program, Contract No. N00014-98-C-0287.

C8.22

Properties of amorphous $Zr_{0.2}Sn_{0.2}Ti_{0.6}O_2$, a high-performance dielectric. Sara Barron, Lynn F. Schneemeyer and R. Bruce van Dover; Materials Sci. & Eng, Cornell University, Ithaca, New York.

While many dielectric materials are known to have a permittivity higher than that of amorphous SiO_2, ϵ_r=3.9, few have breakdown fields nearly so high, E_{br}=10~20 MV/cm. For many purposes, such as storing charge on a DRAM node or gating charge into single-molecule transistors or other nanoscale entities, the critical parameter is the product $\epsilon E_{br}=Q_{max}/A$, where Q_{max}/A is the maximum charge density that the material can induce on its electrodes. Amorphous $Zr_{0.2}Sn_{0.2}Ti_{0.6}O_2$ (aZTT) can deliver values as high as ϵE_{br} =35 μC/cm2 (equivalent to a surface electron density of >2 x 10^{14} cm^{-2}), compared to 3~7 $\mu C/cm^2$ for SiO_2 and ~8 $\mu C/cm^2$ for optimized Al_2O_3. We have prepared aZTT using two different vacuum deposition systems, using two radically different sputtering geometries (90° off-axis and conventional on-axis), and using two types of plasma power sources (RF and pulsed-dc), obtaining comparable results in each case after optimizing the deposition conditions (pO_2, pAr, substrate temperature, etc.). We have measured the frequency and temperature dependence of the permittivity over the range 100 Hz < $2\pi\omega$ < 1 MHz and 4.2 < T <300 K. The results indicate that the polarizability is due to electronic and lattice contributions, with no low-frequency orientational or ionic contributions. We have also studied the effect of processing (annealing in oxidizing and reducing ambients) on the properties of this material. While aZTT may not be suitable for conventional Si-IC DRAM applications that involve subsequent high-temperature processing, its superior performance makes it uniquely attractive for applications where the thermal budget is limited, such as in scientific studies or polymer-based integrated electronics.

C8.23

Electrode effect on microwave properties of ferroelectric $Ba_{0.8}Sr_{0.2}TiO_3$ thin film. Won-jeong Kim[1], Sang-Soo Kim[1], Tae-Kwon Song[1], Seung Eon Moon[2], Eun-kyoung Kim[2], Su-Jae Lee[2], Seok-Kil Han[2], Young-Tae Kim[2], Han-Chul Ryu[2] and Min-Hwan Kwak[2]; [1]Physics, Changwon National University, Changwon, South Korea; [2]Electronics and Telecommunications Research Institution, Daejeon, South Korea.

Microwave properties of coplanar waveguide (CPW) transmission lines fabricated on high dielectric materials, such as ferroelectric $Ba_{1-x}Sr_xTiO_3$ films, are highly sensitive on the dimension and shape of electrodes. A small change in the edge angle of the cross-sectioned electrode affects the total electrical length of the CPW, which may mislead the effective dielectric constant of the dielectric layer. Furthermore, extracting dielectric constant of high-k thin films from the measured microwave properties, such as S-parameters, are very difficult. The well known a modified conformal mapping method frequently exhibits inconsistent dielectric constant for CPW on high-k materials. In this presentation, CPW transmission lines were fabricated on high-k thin films, ferroelectric $Ba_{0.8}Sr_{0.2}TiO_3$, which were deposited by the pulsed laser deposition with partial oxygen backgrounds. The physical characteristics of the films were investigated by XRD and SEM. Microwave properties of the CPW phase shifter were measured using a HP 8510C vector network analyzer from 0.045 ~ 20 GHz. A large phase shift angle of 100o was observed from the CPW (gap=5um, length=3mm) with 40V of dc bias, which support the idea of the tunable microwave device application using ferroelectrics. The dielectric constant of the thin ferroelectric film was extracted from the dimension of the CPW (gap, width, length) and the measured S-parameter by a modified conformal mapping. However, the dielectric constant of the ferroelectric thin film exhibits a gap dependency; dielectric constant (1210 ~ 960) decreases with increasing gap size (4 ~ 19um, respectively). For comparison, dielectric properties have been extracted by extensive EM-simulation using a HFSS (Ansoft) with observed dimension of CPW. By changing the edge angle of the cross-sectioned electrode, the ferroelectric thin film exhibits a unique dielectric constant of 950 ± 20 in the entire gap size. In this presentation, effect of the dimension of CPW on the microwave properties of the ferroelectric thin film will be discussed in detail.

C8.24

Integration Of Passive Components In Power Electronics. Ferroelecric Films Prepared From Soft Chemistry Powders. Sophie Guillemet[1], Madona Boulos[1], Christophe Calmet[1], Bernard Durand[1], Vincent Bley[2] and Thierry Lebey[2]; [1]Material Science, Universite Paul Sabatier, Toulouse, France; [2]Electrical Engineering, Universite Paul Sabatier, Toulouse, France.

The trend in electronic industries is to offer smaller and lighter products of lower costs and increased features. Nevertheless, passive components miniaturization is an important challenge in the field of power electronic integration since they occupy more than 70% of the substrate surface. One of the possible integrated passive technologies is a multilayer ceramic construction combining different functional ceramics in a 3D architecture. A particular structure of filter has been proposed in a previous paper. It consists in a structure of alternative layers of both metal and dielectric materials. In the present work, we have focused on the elaboration of the ferroelectric film started from the powder synthesis. Barium titanate is the material of choice which presents the best trade-off between the desired electrical characteristics and the compatibility with the other materials that form the overall structure. Nanoparticles of BaTiO3 powders have been elaborated from 2 different soft chemistry methods, namely co-precipitation and hydrothermal synthesis. A particular attention is paid to the optimisation of the synthesis parameters in order to increase the powder quality. In the 2 cases, the most important characteristics of the powders necessary to obtain a good slurry were determined and compared. These are Ba/Ti ratio, structure, specific surface area, H2O and C content. Different pastes have been prepared by mixing the powders with organic materials. The paste containing the BaTiO3 powder is deposited by the doctor blade method, and sintered. The structural and dielectric properties of the films are determined and correlated with the powder characteristics. Films prepared from co-precipitation powders present improved characteristics, compared to those obtained from hydrothermal powders.

C8.25

Tunable Microstrip Bandpass Filters Using Ferroelectric Thin Films With Constricted Gaps. Carl Henry Mueller[1], Fredrick W Van Keuls[2], Robert R Romanofsky[3] and Felix A Miranda[3]; [1]Analex Corporation, Cleveland, Ohio; [2]Ohio Aerospace Institute, Cleveland, Ohio; [3]NASA Glenn Research Laboratory, Cleveland, Ohio.

Microstrip bandpass filters are attractive at K-band (12 to 18 GHz) and higher frequencies because of their small size. A problem that plagues microstrip filters at these frequencies is the inability to tune the inter-resonator capacitance without introducing excessive losses as a result of the tuning mechanism. At a basic level, tuning is required to correct for manufacturing tolerances, and thus enable the filter to operate at the design frequency. At a more advanced level, tuning across several frequency bands would enable a single device to serve as a multi-channel filter bank. Previous efforts to introduce ferroelectric tuning into microstrip bandpass structures are hampered by dielectric losses in the ferroelectric films. This paper expands on our previous efforts regarding the use of selectively etched ferroelectric films to minimize RF losses without degrading tunability. Patterning the films so as to form a constriction in the ferroelectric film, near the center of the gap, causes the electric field to be concentrated in the constricted region, thus creating a region with relatively low (as compared to the

non-constricted regions) dielectric constant and loss. By designing the constricted region so that its width changes as a function of dc bias, capacitive tuning is achieved while maintaining low loss. Using this principle, we have designed, fabricated and tested coupled one-pole microstrip bandpass filters with fundamental resonances at 7.2 GHz, and well-defined first and second harmonic resonances. For one of the filters, we observed experimental results verified that the center frequency was tunable by 538 MHz at a center frequency of 21.957 GHz, with insertion losses varying from 4.3 to 2.5 dB, at tuning bias values of 0 and 3.5 volts/micron, respectively. More extensive experimental and modeling data to clarify the role of the constricted layer to improve device performance will be presented.

C8.26
Piezoelectric and Dielectric Properties of Thin Film $BaTi_{1-x}M_xO_3$ (M=Zr, Hf). Ytshak Avrahami, Il-Doo Kim and Harry L Tuller; MIT, Cambridge, Massachusetts.

Recent studies have shown that $BaTi_{1-x}M_xO_3$ (M=Zr, Hf) solid solutions stabilized in orthorhombic and rhombohedral phases exhibit enhanced piezoelectric and distinctive dielectric properties. There is, however, limited research on the properties of these materials in thin film form. $BaTi_{1-x}M_xO_3$ films were grown by Pulsed Laser Deposition (PLD) on a number of thin film electrodes, including $(La,Sr)CoO_3$ and Pt deposited on MgO and Si substrates. Textured films with controlled orientations were obtained. The effects of growth parameters (substrate temperature, oxygen partial pressure, laser fluency) and film composition on the ferroelectric and piezoelectric properties are discussed and compared with values obtained in the bulk.

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

8:30 AM *C9.1
Lanthanum Oxide Thin Films For Advanced Gate Dielectrics. Blech Vincent[1], Marie-Christine Hugon[2], Bernard Agius[2], Michel Touzeau[2] and Vincent Le Goascoz[1]; [1]Reseach & Development, STMicroelectronics, Crolles, France; [2]Plasma et Materiaux, LPGP, Orsay, France.

For the past two years, the researches on advanced gate dielectrics have gained considerable attention since the technology roadmaps predict the need of a sub-2nm gate dielectric for sub-0.13μm MOSFET devices in 2002. The thinning of the gate dielectric required by scaling rules, currently between 2 and 2.5nm in fabrication, will give origin to unacceptably high gate current arising from electron tunneling through the SiO_2 films. One possible solution is to use an alternative material to SiO_2 with dielectric constant (K) much higher than 3.9. Due to its high permittivity (K=38), La_2O_3 appears to be a good candidate. La_2O_3 films are deposited on Si substrates by rf magnetron sputtering of a La_2O_3 target in argon atmosphere. Thin film properties are studied as a function of deposition (rf power density, process pressure) and thermal annealing parameters(temperature, time). One of the most important steps in our searching of La_2O_3 film properties is to correlate the physical properties of the material (composition, density) determined by Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Analysis (NRA) [$^{16}O(d,p1)^{17}O$ at 850keV] and X-reflectometry to the plasma characteristics investigated by optical diagnostics (Optical Emission and Absorption Spectroscopy). Whatever the deposition conditions, the film composition is O/La=1.3 $\pm$ 0.1 and their density is 7 $\pm$ 0.7g/cm^3 (ρbulk=6.5g/cm^3). We have performed high frequency (1MHz, 100kHz, 1kHz) capacitance-voltage C-V measurements on $RuO_2/La_2O_3/Si$ MIS structure. With the device biased in accumulation regime, a permittivity of 30 was deduced. The C-V curves exhibit well defined accumulation, depletion and inversion regimes which indicate a low interface state density.

9:00 AM C9.2
Liquid Injection MOCVD of Rare-earth Oxides Using New Alkoxide Precursors. Paul Andrew Williams[1], Anthony C Jones[1,2], Helen C Aspinall[2], Jeffrey M Gaskell[2], Paul R Chalker[3], Paul A Marshall[3], John L Roberts[2] and Lesley M Smith[1]; [1]Epichem Limited, Bromborough, Wirral, United Kingdom; [2]Chemistry, University of Liverpool, Liverpool, Merseyside, United Kingdom; [3]Materials Science and Engineering, University of Liverpool, Liverpool, Merseyside, United Kingdom.

Thin films of rare earth oxides such as, La_2O_3, Pr_2O_3, Gd_2O_3 and Nd_2O_3 have potential applications as alternative high-κ gate dielectric layers in silicon-based field effect transistors. MOCVD is an attractive technique for the deposition of these materials, but progress has been restricted due to lack of suitable precursors. There are some reports on the use of metal-β-diketonate precursors, but these often require high growth temperatures and carbon contamination is a potential problem. Although metal alkoxides have been widely used in MOCVD, there have previously been no reports in the literature into the use of rare-earth alkoxide precursors in MOCVD. This is because the large ionic radius of the highly positively charged lanthanide (III) ions leads to the formation of bridging intermolecular metal-oxygen bonds, resulting in many of the simple alkoxide complexes being polymeric or oligomeric, with a corresponding low volatility. However, the sterically hindered donor functionalised alkoxide ligand 1-methoxy-2-methyl-2-propanolate, $OCMe_2CH_2OMe$ [mmp], facilitates the formation of the volatile metal alkoxide complexes $[M(mmp)_3]$ (M = La, Pr, Gd etc?). In this paper the synthesis of a number of these new complexes is described together with their use in liquid injection MOCVD.

9:15 AM C9.3
Composition dependence of crystallization in alternative gate oxides. R. Bruce van Dover[1], Martin L Green[2], Lalita Manchanda[3] and Lynn F Schneemeyer[1]; [1]Materials Sci. & Eng, Cornell University, Ithaca, New York; [2]Agere Systems, Allentown, Pennsylvania; [3]SRC, Research Triangle Park, North Carolina.

Thin films comprising group-IV metal oxides are likely candidates for replacing SiO2 in high-performance/low power Si electronics where the effective electrical thickness of the gate oxide must be less than the equivalent of 1.0 nm of SiO2. Elemental oxides such as ZrO2 and HfO2 have dielectric constants that are in the suitable range, $\epsilon \sim$20-30, but crystallize readily under standard process conditions (1000 °C for 5-20 seconds) required to activate ion-implanted dopants. It is known that crystallization can be suppressed by alloying with a main-group oxide such as SiO2 or Al2O3, although these oxides have a much smaller dielectric constant and therefore strongly decrease the dielectric constant of the mixture. We have investigated the post-annealed crystallinity of various mixed transition-metal/main-group oxides using a composition-spread approach. This technique allowed us to determine that the mole fraction of main group oxide in the Zr-Si-O, Zr-Al-O, and Hf-Si-O systems must be greater than 83%, 65%, and 78%, respectively, in order to avoid crystallization. The kinetics of transformation suggest that this conclusion is not sensitive to the anneal time, though it is quite sensitive to the peak temperature. Evaluation of the dielectric constant in the same systems leads us to conclude that the useful dielectric constant is therefore limited to $\epsilon < 6.9$, 12.7, and 6.6, respectively. We conclude that the silicate systems are not likely to be useful as replacements for SiO2, while aluminates are more promising.

9:30 AM C9.4
Epitaxial thick film heterostructures of Pb(Mg1/3Nb2/3)O3-PbTiO3 relaxor ferroelectric films on silicon for high performance electromechanical systems. Dong Min Kim[1], Sang Don Bu[1], Chang Beom Eom[1], Valanoor Nagarajan[2], Jun Ouyang[2], Ramamoorthy Ramesh[2], Venu Vaithyanathan[3], Susan Trolier-Mckinstry[3], Darrell G. Schlom[3], W. Tian[4] and Xiaoqing Pan[4]; [1]Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; [2]Materials and Nuclear Engineering, University of Maryland, College Park, Maryland; [3]Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania; [4]Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT) single crystal relaxor ferroelectrics yield significantly higher electromechanical coupling coefficient than conventional polycrystalline ferroelectric materials. A major challenge is to fabricate epitaxial PMN-PT thick films between epitaxial metallic oxides and integrate them into microelectromechanical systems on silicon wafer. We have created epitaxial thin films with the highest longitudinal piezoelectric tensor coefficient ever realized on silicon substrates by (1) using Pb(Mg1/3Nb2/3)-PbTiO3 (PMN-PT), the material which in single crystal form is known for its giant piezoelectric response, (2) using epitaxy to orient it optimally, and (3) nanostructuring it to reduce the constraint imposed by the underlying silicon substrate. When subdivided by focused ion beam processing to reduce mechanical constraints, a 4 μm thick film shows a low-field d33 of 425 pm/V that increases to over 700 pm/V under bias, which is a factor of 4 higher than the highest strain achieved in Pb(Zr,Ti)O3 thin films on silicon. These epitaxial heterostructure can be used for multilayered MEMS devices with high strain and low driving voltage for miniature devices, high frequency ultrasound transducer arrays for medical imaging, tunable dielectrics, and capacitors for charge and energy storage. We will discuss the effect of substrate constraint and thermal strain on the piezoelectric responses in heteroepitaxial PMN-PT thick films on silicon.

9:45 AM C9.5
c-axis oriented Epitaxial $BaTiO_3$ Films on (001) Si.
Venugopalan Vaithyanathan[1], James Lettieri[1], Darrell G. Schlom[1], Jeremy Levy[2], Wei Tian[3] and Xiaoqing Q. Pan[3]; [1]Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania; [2]Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania; [3]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

We have been investigating the epitaxial growth of c-axis oriented $BaTiO_3$ on (001) Si for a novel quantum computing architecture in which an epitaxial ferroelectric film in close proximity to silicon is desired.[1] Silicon is used because of its weak spin-orbit coupling for electrons and relatively long transverse decoherence time. The ferroelectric must be oriented such that its switching results in an electric field effect to confine the electrons laterally in the underlying silicon. The 4.5% lattice mismatch between $BaTiO_3$ and (001) Si at a typical growth temperature of 600 °C, coupled with the much smaller thermal expansion coefficient of silicon than $BaTiO_3$, have until now prevented the growth of c-axis oriented epitaxial $BaTiO_3$ films on (001) Si. This large lattice mismatch leads to the rapid relaxation of the lattice constant of the $BaTiO_3$ film to its bulk cubic lattice constant at the elevated growth temperature. As such a relaxed $BaTiO_3$ film is cooled from its growth temperature, it experiences biaxial tension due to the larger thermal expansion coefficient of the $BaTiO_3$ film compared to the silicon substrate. When the film cools through the Curie temperature of the $BaTiO_3$, the c-axis of the $BaTiO_3$ aligns in the plane of the substrate (a-axis oriented $BaTiO_3$) to reduce the biaxial tension. To achieve the desired c-axis oriented epitaxial $BaTiO_3$ film on (001) Si for our application, a buffer layer of relaxed $Ba_xSr_{1-x}TiO_3$ is introduced between the Si and $BaTiO_3$ and the $BaTiO_3$ films are maintained thin enough that they are commensurately strained to the underlying relaxed $Ba_xSr_{1-x}TiO_3$ buffer layer. The films are grown by reactive MBE. *Insitu* characterization of the films by RHEED and *exsitu* characterization by XRD and TEM reveal epitaxial c-axis oriented $BaTiO_3$ films with rocking curve widths (FWHM in ω) as narrow as 0.44°. The orientation relationship between film and substrate is $BaTiO_3$ (001) // Si (001) and $BaTiO_3$ [100] // Si [110]. By applying a voltage between a conductive AFM tip and the silicon substrate, domains with up and down polarization have been written in the film at locations specified by the user. Piezo-response AFM has been used to to observe the written domains, which have lateral extent down to ~100 nm. [1] J. Levy, Phys. Rev. A **64**, 052306 (2001).

10:30 AM *C9.6
Long Retention Performance of a MFIS Device Achieved by Introducing High-k Al_2O_3/Si_3N_4/Si Buffer Layer.
Yoshihisa Fujisaki[1,2], Kunie Iseki[1] and Hiroshi Ishiwara[1]; [1]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan; [2]Reaearch and Development Association for Future Electron Devices, Tokyo, Japan.

We introduced high-k Al_2O_3/Si_3N_4 buffer layer in MFIS (Metal-Ferroelectric-Insulator-Semiconductor) devices to realize long retention characteristics and succeeded to achieve a retention time longer than 2×10^6 sec. This long retention character is mainly due to the high insulating property of the buffer layer by reducing the loss of retained charges with minimizing the leakage current. We prepared thin Si_3N_4 (0.9 nm) buffer layer by directly nitridizing Si substrate with atomic nitrogen radicals.[1] The nitridation was carried out at 700 °C. Then we deposited Al_2O_3 thin films on the buffer Si_3N_4 with atomic layer deposition (ALD) technique using $Al(CH_3)_3$ and H_2O precursors.[2] Since the ALD depositions were carried out at low temperature (300 °C), we had to anneal the film to eliminate the defects in the film. The post oxidations were performed at 1000 °C for 30 sec in 5%-O_2/95%-N_2 ambient. On this stacked buffer layer, we deposited 150 nm-thick $Bi_{3.45}La_{0.75}Ti_3O_{12}$ (BLT) ferroelectric films using LSMCD (Liquid Source Misted Chemical Deposition) technique. The BLT film were crystallized at 800 °C in oxygen ambient. The deposited BLT films oriented mainly along the c-axis of BLT crystal lattice normal to the Si substrate. Since our Si_3N_4 buffer layer is highly dense, it prevents the underlying Si substrate from being oxydized during the post oxidation of Al_2O_3 film and the crystallization of BLT film. Therefore, the stacked Al_2O_3/Si_3N_4 buffer layer can preserve high capacitance density and low leakage current even after highly oxidizing thermal treatments.[3] The interface state density between the ALD-Al_2O_3/Radical-Si_3N_4 stacked insulator and a Si substrate is as low as 10^{11} $cm^{-2}eV^{-1}$. The current density less than 10^{-9} A/cm^2 is realized under the 1V bias application using films with the capacitance density of 12fF/μm^2. The memory window larger than 2V was realized in C-V characteristics with ± 6V voltage scan. With this MFIS diode, we found that more than 60% charges are retained for 17 days. This excellent retention character is attributable to the high insulating property of the ALD-Al_2O_3/Radical-Si_3N_4 stacked insulator and also attributable to the perfect elimination of defects at the interfaces in the MFIS structure. This work was done under the auspices of the R&D Projects in Cooperation with Academic Institutions (Next-Generation Ferroelectric Memory), supported by the New Energy and Industrial Technology Development Organization (NEDO), and managed by the R&D Association for Future Electron Devices (FED). Reference 1. Y. Fujisaki and H. Ishiwara, Jpn. J. Appl. Phys. **39**, L1075 (2000). 2. A. Paranjpe. S. Gopinath, T. Omstead and R. Bubber, J. Electrochem. Soc. **148**(**9**), G465-G471(2001). 3. Y. Fujisaki, K. Iseki ,H. Ishiwara, M. Mao and R. Bubber, Appl. Phys. Lett. **82**, 3931 (2003).

11:00 AM C9.7
Investigation of Retention Properties for $YMnO_3$ Based Metal/Ferroelectric/Insulator/Semiconductor Capacitors.
Takeshi Yoshimura, Daisuke Ito, Hironori Sakata, Norimiti Shigemitsu, Kohei Haratake and Norifumi Fujimura; Graduate School of Engineering, Department of Applied Materials Science, Osaka Prefecture University, Sakai, Osaka, Japan.

Ferroelectric gate field-effect transistors (FETs) have been investigated for the applications to nonvolatile memory devices due to the nondestructive read operation and the advantages of decreasing memory cell size. Because of the difficulty to obtain the excellent ferroelectric-semiconductor interface, ferroelectric gate FETs with a metal-ferroelectric(-metal)-insulator-semiconductor (MF(M)IS) structure have been widely studied. We have investigated $YMnO_3$ films for MFIS type ferroelectric gate FET, because YMnO3 has suitable properties for this application such as small spontaneous polarization and low permittivity. We have succeeded in fabricating $YMnO_3$ epitaxial films with $2P_r$ of 3.4 μC/cm^2 on (111)Pt/sapphire substrates and epitaxially grown (0001)$YMnO_3$/(111)Y_2O_3/(111)Si capacitors with ferroelectric type C-V hysteresis loops. In this study, the degradation mechanism of memory retention for Pt/$YMnO_3$/Y_2O_3/Si capacitors are discussed using the leakage current analysis and the pseudo isothermal capacitance transient spectrum (pseudo ICTS) and others. Although the retention time of as-deposited capacitors was 10^3 s, it was prolonged up to 10^4 s when the leakage current density was reduced from 4×10^{-8} A/cm^2 to 2×10^{-9} A/cm^2 by the annealing under N_2 ambience. For the leakage current of the Pt/$YMnO_3$/Y_2O_3/Si capacitors, it was revealed that Schottky emission was dominant at memory retention state however Poole-Frenkel emission occurred when high voltage was applied. Since the activation energy of the Poole-Frenkel emission of the Pt/$YMnO_3$/Y_2O_3/Si capacitors agreed with that of Pt/$YMnO_3$/Pt capacitors, the origin of the Poole-Frenkel emission existed in the $YMnO_3$ layer. It was also found that applied voltage with unnecessarily long time to polarize the ferroelectric layer generated Poole-Frenkel defects in the ferroelectric layer and that the amount of the defects greatly affected the memory retention time. These results suggest that Poole-Frenkel defects work as trap sites of the charge and that the charge injection to the Poole-Frenkel defects occurs gradually until it neutralizes the remanent polarization of the Pt/$YMnO_3$/Y_2O_3/Si capacitors.

11:15 AM C9.8
Characterization of Metal-Ferroelectric-Metal-Insulator-Semiconductor (MFMIS) FETs using $(Sr,Sm)_{0.8}Bi_{2.2}Ta_2O_9$ (SSBT) Thin Films.
Hirokazu Saiki[1] and Eisuke Tokumitsu[1,2]; [1]Precision & Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; [2]RIEC, IT-21, Tohoku University, Sendai, Miyagi, Japan.

Metal-ferroelectric-metal-insulator-semiconductor (MFMIS) structure has attracted considerable attention for ferroelectric-gate transistor applications. MFMIS structure has a merit that one can design the area of an MFM capacitor (S_F) and that of an MIS diode (S_I) independently. To match the ferroelectric polarization with the charge of FET channel, a large area ratio (S_I/S_F) is usually used in MFMIS-FETs. However, $S_I/SF=1$ is desirable for large-scale integration. We previously reported that $Sr_{0.8-1.5x}Sm_xBi_{2.2}Ta_2O_9$ (SSBT) thin film has small remanent polarization and large coercive field, which are suitable for MFMIS structures. In this work, we have fabricated and characterized Pt/$Sr_{0.5}Sm_{0.2}Bi_{2.2}Ta_2O_9$(SSBT)/Pt/Ti/$SiO_2$/p-Si MFMIS-FET (W/L=50/5μm). The crystallization of SSBT was done in O-2 ambient at 850°C. The thickness of SSBT and SiO_2 is 130nm and 10nm, respectively. A memory window of about 2V was obtained with an applied gate voltage of ±5V from drain current-gate voltage (I_D-V_G) characteristic of MFMIS-FET even with $S_I/S_F=1$. This value of memory window agrees with the product of coercive field and thickness of SSBT films. This indicates that the saturated hysteresis loop of SSBT is available even if the MFM capacitor and the MIS diode have same area. This work was supported by a Grant-in-Aid for Scientific Research (No.14040208, No.14655117, and No.15360157) from the Ministry of Education, Science, Sports, and Culture. This work was performed under the auspices of the R&D Projects in Cooperation with Academic Institutions (Next-Generation

Ferroelectric Memory), supported by NEDO and managed by FED.

11:30 AM C9.9
Selective Deposition Of C-Axis Oriented Pb5Ge3O11 On Patterned Hi-K Gate Oxide By MOCVD Processes.
Tingkai Li, Bruce Ulrich, Dave Evans and Sheng Teng Hsu; PTL, Sharp Labs. of America, Inc., Camas, Washington.

MFIS (Metal/Ferroelectrics/Insulator/Silicon) transistor ferroelectric memory devices have been fabricated. C-axis oriented Pb5Ge3O11 (PGO) thin films showed very good ferroelectric and electrical properties for 1T-memory device applications. Extremely high c-axis oriented PGO thin films can be deposited on high k gate oxide, and functional 1T-memory devices with PGO MFIS memory cell have been fabricated. The integration process-induces damage such as etching damage that degrades the properties of FRAM devices and high surface roughness resulted in difficulty for alignment. In order to solve this problem, selective deposition processes have been developed to simplify integration processes and improve the properties of MFIS transistor ferroelectric memory devices. Based on different deposition rates of ferroelectric materials on high-k oxide and silicon dioxide, we selective deposited a c-axis oriented PGO film on patterned high-k oxide such as ZrOx (x=0-2), HfOx (x=0-2), TiO2, etc. and their mixtures other than on SiO2. By patterning the high-k dielectric, the PGO deposition is limited to just the preferred pattern area. SEM, EDX and x-ray measurements further confirmed that c-axis oriented PGO thin films selectively deposited on high-k gate oxide other than on field SiO2. Sometimes during annealing of the PGO, staining of the field oxide occurs. This can be eliminated by not depositing PGO in the field area. The morphology of the PGO film can be very rough which can cause subsequent alignments to be very difficult if not impossible. Again by confining the PGO deposition to just the patterned area will also eliminate the roughness problem for alignments. Also etching damage is eliminated since there is no need to etch the PGO film, which improved the properties of FeRAM devices.

SESSION C10: Piezolectric, Optical and Pyroelectric
Chairs: Susanne Hoffmann-Eifert and Paul Muralt
Thursday Afternoon, December 4, 2003
Room 203 (Hynes)

1:30 PM *C10.1
Ferro- and piezoelectric properties of $Bi_{4-x}Pr_xTi_3O_{12}$ polycrystalline thick films with Ps-vector orientation.
Hirofumi Matsuda, Sachiko Ito and Takashi Iijima; SSRC, AIST, Tsukuba, Ibaraki, Japan.

A principle to synthesize Ps-axis-oriented films with $Bi_4Ti_3O_{12}$ (BIT)-type structure on Si substrate was presented and the alignment of the spontaneous polarization Ps vector along the film normal was demonstrated as the key role of ferroelectric polarization of BIT-based ferroelectric films. 1.2 μm-thick and Pr^{3+}-substituted $Bi_{4-x}Pr_xTi_3O_{12}$ (BPT, x=0.0, 0.3, 0.5, 0.7) films with preferred orientation of Ps were grown on Ir(111)/Ti/SiO2/Si(001) substrates by chemical solution deposition (CSD) method. BPT film of x=0.3 exhibited superb ferroelectric properties of remnant polarization 2Pr=92 $\mu C/cm^2$, saturation polarization Psat=50 $\mu C/cm^2$, and coercive field 2Ec=184 kV/cm. These values of polarization manifested the alignment of Ps-vector along the film normal. The film also exhibited uniform response of electrical field induced displacement with an improved piezoelectric coefficient of AFM-d_{33}=36 pm/V. During the decomposition of precursor solutions, IrO_2 oxidized layers were formed at the surface of Ir bottom electrode and the nucleation of grains with a- and b-axis orientation was accelerated by lattice matching to the (101) plane of IrO_2 with rutile type structure. On cooling after annealing above the Curie temperature Tc for grain growth, in addition, the differential thermal expansion between film and substrate Si introduced in-plane lateral stress squeezing the Ps-vector out of plane. The facts that a relatively poor value of 2Pr=26 $\mu C/cm^2$ was measured in BIT film while monotonous decrease in Pr values with increasing x in the range of 0.3-0.7 was observed suggested that the lattice matching alone was insufficient to explain the separation between grains with a-axis orientation and b-axis orientation. The one part of these orientations doesn't contain Ps component along the film normal, the degradation of polarization can be expected in the films of BIT-type structure with mixed orientation of a- and b-axis.

2:00 PM C10.2
Thickness and Composition Dependence of Piezoelectric Properties of PZT Thin Films for MEMS Devices.
Seung-Hyun Kim, Chang Young Koo, Jung-Hoon Yeom, Jong-Hyeon Cheon and Jowoong Ha; R&D Center, INOSTEK Inc., Ansan, Gyeonggi, South Korea.

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

2:15 PM C10.3
Thickness dependence of structural and piezoelectric properties of epitaxial Pb(Zr0.52Ti0.48)O3 Films on Silicon and SrTiO3 substrates.
Dong Min Kim[1], Chang Beom Eom[1], Valanoor Nagarajan[2], Jun Ouyang[2], Ramamoorthy Ramesh[2], Venu Vaithyanathan[3] and Darrell G. Schlom[3]; [1]Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin; [2]Materials and Nuclear Engineering, University of Maryland, College Park, Maryland; [3]Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

We have studied the lattice distortions and piezoelectric properties of epitaxial Pb(Zr0.52Ti0.48)O3 (PZT) films in the thickness range of 0.04 μm and 4μm. The films were grown on both (100) SrTiO3 and (100) Si substrates by on-axis magnetron sputtering. As film thickness increased, the out-of-plane lattice parameter decreased and the in-plane lattice parameter increased. These lattice parameters approached to a rhombohedral lattice parameter values although the composition is in the tetragonal region. The polarization and piezoelectric coefficient increased with film thickness. The polarization and piezoelectric coefficient of 4 μm thick PZT film on SrTiO3 which is continuous film capacitor was 50mC/cm2 and 180 pm/V. When subdivided by focused ion beam processing to reduce mechanical constraints, a 4 μm thick film shows a low-field d33 increases to 376 pm/V under bias, which is twice higher than the clamped value in Pb(Zr,Ti)O3 thin films on silicon. This is attributed by substrate constraint and material getting softer from rhombohedral composition. The PZT films on silicon exhibit less tetragonality than PZT on SrTiO3, which explains the higher piezoelectric coefficient of PZT on silicon. However, the PZT films on SrTiO3 show higher polarization than the PZT films on silicon because of their higher tetragonality. These are attributed to the film microstructure formed by strain relaxation and thermal expansion mismatch between the films and substrates.

2:30 PM C10.4
Modeling of Piezoresponse of Nanostructured PZT Films.
J-H Li, V Nagarajan, L Chen, R Ramesh and A L Roytburd; Department of Materials Science and Engineering, University of Maryland, College Park, Maryland.

Patterning thin ferroelectric (FE) films into discrete islands is an effective way to release the constraint imposed by a substrate and to enhance film piezoresponse. The converse piezoresponse measured by the surface displacement of FE islands, with lateral size changing from a nanoscale to a substrate dimension, has been modeled using Finite Element Method. The modeling and the theoretical analysis have shown that piezodeformation of the islands results in a local bending of a substrate in the vicinity of island. The bending deflection is larger when the substrate is softer. The bending, together with clamping by the substrate, decreases the effective d33 of the island. We also discuss the effect of the top electrode to the contribution of the measured d33, when using the converse method. Piezoresponse of different size island capacitors with PbZr0.5Ti0.5O3(50/50)/STO/Si and PbZr0.2Ti0.8O3(20/80)/STO heterostructures has been calculated. The results of modeling are in good agreement with experimental data on d33 obtained by piezoresponse microscopy. This work is supported by the NSF-MRSEC under contract No. DMR-00-80008.

2:45 PM C10.5
Bi-Based Perovskite Piezoelectrics. Juan Nino and Susan Trolier-McKinstry; Materials Research Institute and Materials Science and Engineering Dept., Penn State, University Park, Pennsylvania.

To date, most MEMS sensors and actuators employing ferroelectric films use lead zirconate titanate (PZT) films as the transducer. Randomly oriented PZT films (1 - 8 micron thick) show piezoelectric $e_{31,f}$ coefficients of ~ -7 C/m^2. Enhanced piezoelectric response with good temperature stability can be achieved in (001) rhombohedrally-distorted perovskites. However, ultimately, the temperature stability of the piezoelectric response is governed by the transition temperature of the compound. Thus, it is interesting to consider alternative piezoelectrics based on $BiMeO_3$ - $PbTiO_3$ systems with higher transition temperatures. This paper focuses on the growth and electromechanical properties of films, where Me = Sc, Fe, and $Mg_{1/2}Ti_{1/2}$. Thin films were grown by pulsed laser deposition on $SrRuO_3$/(100) $LaAlO_3$ as well as Y_2O_3/YSZ/CeO_2/biaxially textured NiW substrates. Targets used for the growth were Bi and Pb rich to compensate for loss during growth. It was found that the $SrRuO_3$ phase was unstable in the presence of too much Bi. High quality films could be prepared from targets 10mole% rich in Bi_2O_3 and 20 mole% rich in PbO. For example, $BiScO_3$ - $PbTiO_3$ films grown at 730C, a target to substrate distance of 4 cm, in a 90% O_2, 10% O_3 ambient on $SrRuO_3$/(100) $LaAlO_3$ were phase pure perovskite. It was found that many of the films are somewhat deficient in Pb and excess in Bi. The resulting films were good electrical insulators, with room temperature dielectric constants of 850, and loss tangents of 0.08. The best piezoelectric properties were observed in epitaxial $0.6BiScO_3$ - $0.4PbTiO_3$ / $SrRuO_3$ / (100) $LaAlO_3$ films, which show $e_{31,f}$ = -12 C/m^2, coupled with a transition temperature of 460C.

3:30 PM C10.6
Shape of Piezoelectric Hysteresis Loop for Non-Ferroelastic Switching. Alexander K. Tagantsev[1], Paul Muralt[1] and Jan Fousek[2]; [1]Ceramics Laboratory, EPFL, Swiss Federal Institute of Technology, Lausanne, Switzerland; [2]Department of Electrical Engineering and Electromechanical Systems, Technical University of Liberec, Liberec, Czech Republic.

The shape of piezoelectric hysteresis loops (piezoelectric coefficient d vs. applied dc electric field E) is typically different from that of polarization hysteresis loops (polarization vs. applied electric field). The features of the piezoelectric hysteresis loops, which are often come across, are: (i) a "hump", i.e. when E decreases from the tip of the loop down to zero, d passes through a maximum, (ii) a self-crossing of the loop close to its tips. Despite wide experimental observations of these features, they have not been entitled to a theoretical explanation yet. In this paper, we show that the origin of these phenomena is the motion of non-ferroelastic domain walls. We develop a theoretical scheme that enables a calculation of the piezoelectric loops in the case of non-ferroelastic switching, the case typical for ferroelectric thin films. The scheme yields the piezoelectric loop using the polarization loop, C-V curve, and information of the lattice contribution to the dielectric permittivity. It is shown that a large enough value of the domain contribution to the dielectric permittivity necessitates the appearance of the hump and self-crossing. The theory is compared to the experimental data on piezoelectric thin films.

3:45 PM C10.7
Fabrication and Characterization of $BaTiO_3$ Optical Waveguides. Il-Doo Kim, Ytshak Avrahami, Harry L Tuller, Luciano Socci, Francisco Lopez-Royo and Peter T. Rakich; Microphotonic Center, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The possibility of creating $BaTiO_3$ waveguides and optical components on oxide substrates has been demonstrated in recent years. There is a great incentive to try and replicate these achievements on silicon based wafers for integrated optical applications. The buffer layer between Si and $BaTiO_3$ plays a major role in determining the quality of the film and its optical properties. Films of $BaTiO_3$ were grown on Si using Pulsed Laser Deposition (PLD) with a number of buffer layers, including MgO. The effect of growth conditions and buffer layer on the crystallographic quality of the $BaTiO_3$ films was investigated. Waveguides were formed by e-beam lithography. The optical properties of the films and the waveguides (insertion and absorption loss, index of refraction and birefringence) will be presented and correlated with film quality and orientation

4:00 PM C10.8
Submicron Ferroelectric Domain Engineering in $LiNbO_3$ Thin Films grown by Liquid Phase Epitaxy. Ji-Won Son[1], Yin Yuen[3], Sergei S. Orlov[2], Bill Phillips[2], Ludwig Galambos[2], Lambertus Hesselink[2] and Vladimir Ya. Shur[4]; [1]Materials Science and Engineering, Stanford University, Stanford, California; [2]Electrical Engineering, Stanford University, Stanford, California; [3]Applied Physics, Stanford University, Stanford, California; [4]Institute of Physics and Applied Mathematics, Ural State University, Ekaterinburg, Russian Federation.

We describe novel grating structures of submicron domains in $LiNbO_3$ films. Domain engineering in $LiNbO_3$ has been studied intensively for various electro-optic device applications. Recently, submicron domain engineering has drawn much attention because of the possibility of implementing it in backward wave parametric generation and tunable Bragg grating structures. We demonstrate submicron ferroelectric domain engineering in liquid phase epitaxy (LPE) $LiNbO_3$ thin films grown on $LiNbO_3$ and $LiTaO_3$ substrates using a direct-write electron beam poling for waveguide applications. $LiNbO_3$ thin films of several-micron thickness were grown using a flux melt of 20 mol% $LiNbO_3$-80 mol% $LiVO_3$. The typical growth temperature was 900~910°C, and resulting films have a single crystal structure with the crystallinity comparable to that of the substrates. The films grown on $LiTaO_3$ substrates are planar waveguides supporting both TE and TM modes at λ=632.8nm, and exhibit a step index profile. The films are single domain, -Z oriented on both +/- Z surface of $LiNbO_3$ substrates, and also on $LiTaO_3$ substrates. To engineer domain structures in -Z oriented LPE $LiNbO_3$ films, a direct-write electron beam poling was implemented. The opposite side of the e-beam exposed surface is coated with Au for a ground electrode, and LPE $LiNbO_3$ films are exposed to e-beam radiation with varying doses ranging from 50μC/cm^2 to 300μC/cm^2. For the -Z homoepitaxial $LiNbO_3$ films on -Z $LiNbO_3$ substrates, the domain orientations in both the film and the substrate are the same, therefore the inverted domain structure penetrates the substrate. On the other hand, the inverted domain structure is isolated in the homoepitaxial $LiNbO_3$ film in the -Z film/ +Z substrate system and the $LiNbO_3$/$LiTaO_3$ heteroepitaxial system. It is shown that we can engineer the domain structure of LPE $LiNbO_3$ films by using the direct e-beam poling, even though that the whole domain structure throughout the thickness is multi-layered as in the $LiNbO_3$/$LiTaO_3$ system. The domain engineering in the $LiNbO_3$/$LiTaO_3$ system is particularly interesting since it has a step-index waveguide suitable for efficient radiation guiding. We also compared e-beam poling behavior in a single crystal of $LiNbO_3$ and a LPE $LiNbO_3$ film. Using the same e-beam scan parameters, the definition of the domain structure is enhanced in LPE films compared with domains in a single crystal $LiNbO_3$. Moreover, merging of domains is prevented in LPE $LiNbO_3$ films, resulting in submicron domain structures. We obtained structures with a 0.9μm period consisting of ~400nm width domains extending 30μm in the LPE $LiNbO_3$ films, which could not be obtained in a single crystal. We propose that the defect structure, such as the misfit between the film and the substrate and point defects in the LPE films can possibly explain these positive results. Further optimization of the domain structures by changing scanning parameters and materials is presently under study.

4:15 PM C10.9
Pyroelectric Properties of Ferroelectric Thin Films: Effect of Internal Stresses. Zhigang Ban, Anuj Sharma and S Pamir Alpay; Metallurgy and Materials Engineering, Univ. of Connecticut, Storrs, Connecticut.

The role of internal stresses on the pyroelectric properties of ferroelectric thin films is analyzed theoretically via a thermodynamic model. The pyroelectric coefficient as a function of the misfit strain is calculated for (001) $Ba_{0.6}Sr_{0.4}TiO_3$ epitaxial thin films. The effect of applied electric field on the pyroelectric coefficient is also discussed. It is shown that the pyroelectric response is highly dependent on the misfit strain in epitaxial thin films. Enhanced pyroelectric coefficient as high as 0.65 μC/cm^{2}K can be achieved by adjusting the misfit strain especially in the vicinity of the ferroelectric to paraelectric phase transformation. The analysis shows that internal tensile stresses are particularly not desirable with significant degradation close to an order of magnitude in the pyroelectric response. Discussion on integration of the ferroelectric thin films with Si-based technology of ICs for pyroelectric device applications is provided.

4:30 PM C10.10
The piezoelectric effects under large electric field in the epitaxial ferroelectric thin films. Lang Chen, V Nagarajan, J Ouyang, R Ramesh and A L Roytburd; Department of materials Science and Engineering, Univ. of Maryland, College Park, Maryland.

We present the theoretical and experiment results of piezoelectric-related effects induced by large electric field in thin ferroelectric (FE) single domain and 180 degree polydomain films. The nonlinear electric field dependences of piezoresponse in epitaxial FE lead zirconate titanate (PZT) thin films have been reported and

calculated by using a Landau-Devonshire-type phenomenological thermodynamic approach for tetragonal single domain case. The tunability of piezoelectric responses by external electric field and its dependence on film/substrate misfit and elastic compliance of thin films are characterized quantitatively. The experiment results of piezoresponse scanning microscopy (PFM) of PZT epitaxial single domain thin films matches well within the range of our theoretical estimation.In the second part we present work on the theoretical modeling of the converse piezoelectric effects in the FE 180 degree c-domains with opposite polarization vector. In such case, due to opposite polarities, the applied large electric field induces large internal stress and thereby changes the dielectric properties of thin films. Since the coercive field of ultra thin films can be close to intrinsic one, the domain clamping effect is important for domain switching. Our theoretical calculation shows that domain clamping effects may inhibit the nucleation of 180 degree domain when a large negative pulse is applied to a single domain. As an evidence of the relaxation of piezostress due to this domain clamping effect, we have discussed the observation of newly formed 90 degree elastic domains (twins) at local poling under a biased AFM conductive tip in epitaxial Pb (Zr0.2Ti0.8) O3 thin films via PFM.This work is supported by the NSF under Grant DMR 0210512 and NSF-MRSEC under contract No. DMR-00-80008.

4:45 PM C10.11
Investigation of the piezoelectric properties of PZT films.
Jun Ouyang[1], V Nagarajan[1], H M Zheng[1], Z K Ma[1], S Y Yang[1], L Chen[1], J Melngailis[1], A L Roytburd[1], R Ramesh[1], D M Kim[2] and C B Eom[2]; [1]Dept. of Materials Science and Engineering, University of Maryland, College Park, Maryland; [2]Dept. of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin.

Lead Zirconate Titanate ($PbZr_{1-x}Ti_xO_3$) thin films with compositions close to the morphotropic boundary (x$\sim$0.5) (MPB-PZT) have interesting applications in micromechanical systems due to their high piezoelectric coefficients. Recent *Abinitio* calculation by Cohen and single crystal work on PZN-PT by Shrout and others suggest enhanced piezoelectric performance in ferroelectric materials if a field-induced phase transformation occurs. However, in thin films, the phase transition is inhibited by substrate induced constraint. The motivation of our work is to investigate such field induced transition in PZT films by creating nanostructured islands, which are not clamped by substrate. We report on the measured out-of-plane piezoelectric coefficient for PZT films with composition close to the MPB. The film thickness is kept at 1.5 μm in order to have a full range of aspect ratio (island lateral size/film thickness). To investigate the possibility of inducing a phase transition by using a suitable template, $SrTiO_3$ substrates with 3 different crystallographic orientations -(100), (110), (111), are utilized. We have studied in detail the effect of crystallographic orientation on the piezoelectric performance of PZT films. By using a combined approach of phenomenological theory and tensor mathematics, the theoretical piezoelectric coefficients for both clamped and unclamped capacitors in different orientations are calculated, assuming a monodomain condition. Our experimental results indicate that it may be necessary to have films oriented away from the polar axis to achieve a field induced phase transition. This work is supported by the NSF-MRSEC under contract No. DMR-00-80008
and partially supported by the NSF under contract No. DMR-02-10512.

SESSION C11: Poster Session
Chairs: Susanne Hoffmann-Eifert, Vikram Joshi and Angus Kingon
Thursday Evening, December 4, 2003
8:00 PM
Exhibition Hall D (Hynes)

C11.1
Fatigue Behavior and Influence of the Surface Morphology on Polarization Reversal in MOCVD Ir/PZT/Pt Films.
Vladimir Ya. Shur[1], Ivan S. Baturin[1], Ekaterina V. Nikolaeva[1], Eugene I. Shishkin[1], Dmitrii Kuznetsov[1], Paul McIntyre[2], Lawrence Schloss[2] and Maxim Kelman[2]; [1]Institute of Physics&Applied Mathematics, Ural State University, Ekaterinburg, Russian Federation; [2]Materials Science and Engineering, Stanford University, Stanford, California.

The fatigue effect during cyclic switching has been studied in MOCVD PZT films with different thickness. The switching current data analysis allows to extract the evolution of the internal bias field distribution function. Important role of the surface morphology on the switching current shape has been demonstrated. We have investigated experimentally the fatigue phenomena by analysis of the switching current data during cycling in metalorganic chemical vapor deposition grown Pb(Zr-{0.35}Ti-{0.65})O-3 thin films ranging in thickness from 70 to 400 nm with Ir bottom and Pt top electrodes. Atomic force microscopy in contact mode has been used to measure the surface morphology with high resolution. The hysteresis loops and switching currents have been measured in triangular pulses in frequency range from 10 to 100 Hz. The original mathematical treatment of switching current data recorded during hysteresis measurement allows to extract the evolution of internal bias field distribution function during long-time cyclic switching. It was shown that increasing of switching time and changing of the switching current shape is correlated with growth of the internal bias field dispersion. All results are in accordance with the model of self-organized frozen domain evolution during cyclic switching proposed by us recently. The proposed fatigue mechanism is related to spatially inhomogeneous imprint effect. The influence of the film morphology on the spatial distribution of the electric field in the bulk has been calculated and taken into account while analyzing the current data. The strong effect of nonuniform spatial distribution of applied field has been demontrated. The obtained results are correlated with the crystallographic phase distribution in these films, which has previously been shown to depend on film thickness and thermal history. Preliminary results on the effects of UV light exposure on fatigue of these PZT films will be presented also. The research was made possible in part by RFBR (Grant 01-02-17443), by RFBR-DFG (Grant 02-02-04006), by Ministry of Education RF (Grant E02-3.4-395) and by program "Basic Research in Russian Universities" (Grant UR.06.01.031), and by Award No.REC-005 of CRDF.

C11.2
Crystallization of Sub-100 nm-Thick $Bi_{4-x}La_xTi_3O_{12}$ Films on Silicon Substrates and Their Electrical Properties.
Atsushi Kohno[1,2], Fumitake Ishitsu[1], Kazuhiro Matuo[1] and Hiroyuki Tomari[1]; [1]Applied Physics, Fukuoka University, Fukuoka, Japan; [2]Advanced Materials Institute, Fukuoka University, Fukuoka, Japan.

Poly-crystalline $Bi_{4-x}La_xTi_3O_{12}$ (BLT) thin films were formed on silicon substrates, and crystallization of the films was investigated by X-ray diffraction (XRD) and X-ray Reflection (XRR) analysis. After chemical cleaning and HF treatment of p-type Si(100) substrates, a precursor solution for BLT was spin-coated on the silicon substrates and the samples were dried at 150 °C in the atmosphere. Subsequently, the samples were annealed in a furnace. Furthermore, in the case of electrical measurement Au electrodes were formed on the film. The film thicknesses after the crystallization annealing were evaluated to be 40-50 nm by XRR analysis. When the films were annealed in the temperature range from 550 to 650 °C the crystallization into bismuth-oxide layered perovskite structure was confirmed by XRD. The diffraction intensities increased and the peak widths decreased as the annealing time increased from 10 to 120 min. Also, atomic force microscope (AFM) observations indicated that grain growth occurred during the crystallization. X-ray reflectivity analysis and FT-IR measurements indicated that an interfacial layer was formed during the crystallization. Furthermore, growth of (001)-oriented grains was observed by pole figure measurements. There is a difference of orientation of the grains between the films crystallized at 550 and 600 °C. Current-voltage (I-V) and capacitance-voltage (C-V) characteristics of Au/BLT/p-Si structures were measured at room temperature. The leakage current was lower than 25 nA/cm^2 at the gate voltage Vg of 3 V. Hysteresis loops were observed in C-V characteristics at frequency range from 10 kHz - 1 MHz. The hysteresis voltage width depended on the crystallization annealing temperature, and so it may be related to the orientation of crystals in the film. The hysteresis width of the C-V curve for the MFS structure, the BLT thin film of which was crystallized at 550 °C, was about 0.3 V with the sweep gate voltage of $\pm$3V at 1 MHz. This seems to indicate that the coercive field (Ec) was about 33 kV/cm. From the analysis of the flat-band voltage shift, fixed charges and traps in the film and the interfacial layer were discussed.

C11.3
Frequency-Dependent Electromechanical Response in Ferroelectric Materials Measured via Piezoresponse Force Microscopy.
Andrei Kholkin[1], Igor Bdikin[1], Vladimir Shvartsman[1] and J. Manuel Herrero[2]; [1]Dept. of Ceramics and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal; [2]Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain.

Piezoelectric properties of ferroelectric materials are frequency-dependent, which can be a limiting factor for their applications as sensors and actuators operating at high speed. The frequency dependence of the piezoelectric response is generally attributed to the reversible motion of the ferroelectric domain walls moving in the random potential of defects. In most cases, this dependence can be described by the logarithmic law until very high frequencies where the domain motion is not fast enough to respond to the external driving field. In the last years, the piezoelectric response is intensively investigated at the nanoscale using so-called Piezoresponse Force Microscopy (PFM) capable of imaging domains

with the nm resolution and measuring piezoelectric properties just under the PFM tip, i.e., over distances comparable with the domain wall width. In this paper, we will present our recent findings related to the frequency-dependent piezoelectric response measured using PFM setup where the properties of the individual domain walls can be, in principle, accessed. Several materials have been tested such as piezoelectric ceramics, thin films (lead zirconate titanate and lead titanate doped with La) and piezoelectric single crystals. The mechanical properties of the PFM cantilevers in the contact with the piezoelectric media will be taken into account. It will be shown that the frequency dependence of the piezoelectric effect is strongly influenced by the mechanical resonances in the PFM. It will be shown that, using stiff cantilevers, the frequency dependence of the piezoresponse in ferroelectric materials can be determined. It will be also demonstrated that the electrostatic interaction that frequently masks the piezoelectric response in PFM can be eliminated by using stiff cantilevers and sharp tips.

C11.4

Ferroelectric Domain Studies In PZT Thin Films With Different Compositions By PFM. Aiying Wu, Paula Vilarinho, A. Kholkin and Isabel Salvado; University of Aveiro, Aveiro, Portugal.

Due to growing field of applications of ferroelectric thin films it is of great interest to study the ferroelectric properties on a nanometer scale. The integration of ferroelectric thin films into microelectronic devices requires substantial improvement in the understanding of the physical properties of ferroelectric materials at the submicron level, as well as an implementation of new tools suitabl for an in situ testing ferroelectric nanostructures. Piezoresponse Force microscopy (PFM) has been receiving significant attention in the field of ferroelectric materials due to its powerful capabilities for monitoring domain features and investigating electrical properties locally at a nanoscale level. The use of PFM to characterize the domain behavior of ferroelectric thin films is of importance from both the technological and scientific point of view. Successful experiments have been performed to nanocharacterize ferroelectric thin films, such as domain structure and switching behavior. However, the PFM studies in the PZT system have been mainly concentrated near the morphotropic phase boundary compositions and a few of them in the tetragonal region. In the current work, PFM based technique is applied to analyze the domain structure as a function of film composition in a systematic way. Polycrystalline PZT thin films were deposited onto a commercially available Pt/Ti/SiO2/Si substrate via sol-gel technique. Ferroelectric domain structure, asymmetric domain switching, polarization distribution and piezoelectric non-linearity by PFM are studied in ferroelectric PZT thin films with different compositions (from PZT20/80 to PZT 60/40), which cover the tetragonal to rhombohetral crystallographic symmetry. The stability of the local piezoelectrical response of the PZT thin films of different composition is presented and discussed in terms of grain size, annealing temperatures, presence of defects and charge accumulation. Simultaneously, the macroscopic electrical characteristics of the films are analyzed. The comparison of the domain structure and electrical response at a nanoscale provided by PFM with the macroscopic electrical properties is presented and discussed.

C11.5

Kinetics of phase transformation of PZT thin film by sol-gel method using Scanning Force Microscopy. Bongki Lee[1], Changdeuck Bae[1], Seunghyun Kim[2] and hyunjung Shin[1]; [1]advanced material engineering, kookmin university, seoul, South Korea; [2]Inostek Inc, seoul, South Korea.

Lead zirconate titanate (PZT) thin films are prepared by sol-gel techniques onto platinized Si substrates (Pt/Ti/SiO2/Si). The sol-gel process draws much technological attentions because of its unique advantages on changing compositions and ease to dope with impurities, and ability to make large coatings. Understanding the mechanisms of the nucleation and growth in ferroelectric PZT thin film will be of vital importance in optimizing the sol-gel process. Scanning Force Microscopy modified to detect the piezoresponse from ferroelectric thin films is used in this study. We have investigated the piezoelectric response of sol-gel PZT(52/48) thin film with 300nm in thickness. The as-prepared PZT films were annealed in conventional tube furnace at from 430°C to 470°C with holding time of 10∼60min. Isolated ferroelectric phases were found in the surroundings of pylochlore matrix upon heating between 430°C and 470°C. The amount of phase transition from pyrochlore to perovskite characterized by SFM was found to increase rapidly with annealing time and to be saturated. The kinetic process of growth was modeled using the Avrami equation. The Avrami coefficient n was determined to be ∼0.34. The activation energy will be determined. The results of the perovskite surface coverage taken from SFM are more reliable than other microscopic techniques, such as TEM or SEM, because of capability to scan larger scan size and to detect in high resolution (∼10nm in lateral). Moreover, kinetic studies of phase transformation from pyrochlore to perovskite are help to develop low-temperature processing.

C11.6

Dielectric anomaly in epitaxial strontium bismuth tantalate thin films. Kenta Kotani, Iwao Kawayama and Masayoshi Tonouchi; Research Center for Superconductor Photonics, Osaka University, Suita, Osaka, Japan.

$SrBi_2Ta_2O_9$ (SBT) has attracted much attention from the viewpoint of application to ferroelectric random access memory (FeRAM) because of their high fatigue endurance, low coercive fields. Recently, it was reported that cation substitution for Sr^{2+} site and Bi^{3+} site strongly affects the ferroelectric and the dielectric properties of SBT. Meanwhile, most of the research have been done for polycrystalline thin films on conductive Pt coated Si substrates for memory applications or polycrystalline ceramics for investigating fundamental properties. Therefore it is difficult to compare these results because of the difference in the quality and the orientation of each sample. We consider that it is important for understanding their properties to systematically measure the temperature dependence of the dielectric properties with epitaxial SBT thin films. In this study, we constructed measurement systems which can operate in wide temperature range from -250 °C to 600 °C, to measure temperature dependent dielectric properties of SBT thin films of different compositions using interdigital surface electrodes. We found that the peak of dielectric constant vs. temperature depend on frequency and dielectric peak shift from 275 °C to 307 °C when the measurement frequency changes from 100 kHz to 10 MHz. Such a behavior is typically seen in relaxer materials and found with stoichiometoric SBT for the first time. The relaxer behavior, however, disappeared in 20% Sr-deficient Bi-excess SBT and measured T_C of the off-stoichiometric SBT thin films were 450 °C, independent of the frequency. We considered that the relaxer behavior was led by the substitution of Sr^{2+} for Bi^{3+} in Bi_2O_2 layers. On the other hand, the measurement below room temperature shows a discontinuity of the dielectric constant at about 100 K, and the results from dielectric constant as a function of DC bias voltage show that variation of permittivity remarkably decreases below the temperature. These phenomena imply the presence of paraelectric phase in the low temperature region. The details of dielectric properties of epitaxial SBT thin films as a function of temperature and frequency will be discussed.

C11.7

Charge Retention Characteristics of PZT Thin Films for High Density FeRAM Devices. Jung-Hoon Yeom[1], Seung-Hyun Kim[1], Chang Young Koo[1], Jong-Hyeon Cheon[1], Jowoong Ha[1] and Cheol Seong Hwang[2]; [1]Inostek Inc., Ansan-si, Gyeonggi-do, South Korea; [2]School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

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

C11.8

Ti-site Substitution Using the Higher-valent Cations for Enhancing the Ferroelectric Properties of Nd^{3+}-substituted Bismuth Titanate Thin Films. Hiroshi Uchida[1], Seiichiro Koda[1], Hirofumi Matsuda[2], Takashi Iijima[2], Takayuki Watanabe[3] and Hiroshi Funakubo[3]; [1]Department of Chemistry, Sophia University, Tokyo, Japan; [2]Smart Structure Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; [3]Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Japan.

Thin films of neodymium-substituted bismuth titanate,

(Bi,Nd)4Ti3O12 (BNT), have excellent ferroelectric properties comparable with those of Pb-base ferroelectrics (e.g., Pb(Zr,Ti)O3, etc.). In this study, defect-control in bismuth titanate (BIT) crystal was attempted for improving the ferroelectric properties of the BNT films. Ti-site ions in BNT thin films were substituted by other ions with higher charge valences in order to compensate the charge valence of oxygen vacancies in BIT crystal. Solutions for the spin-coating were prepared using bismuth nitrate, neodymium nitrate, metal (i.e., Ti^{4+}, V^{5+}, etc.) alkohoxides and 2-methoxyethanol as starting materials. The solutions were spin-coated on (111)Pt/Ti/SiO2/(100)Si substrates, followed by a drying process at 150°C for 3 min in air and a pyrolysis process at 400°C for 3 min in air. After repeating these processes several times, the resulting films were heat-treated for crystallization at 750°C for 5 min in air. The films were fabricated from the spin-coating solutions with chemical compositions of (Bi3.50Nd0.50)1-(x/12)(Ti3.00-xVx)O15 (x = 0 ~ 0.09). Results of XRD analyses indicated that all of the films consisted of single phase having BLSF crystal structure (m = 3) without preferred orientation. The SEM observation showed that those films had isotropic granular structure with diameters of ~ 100 nm. These results suggested that Ti-site substitution did not affect both the microstructure and the crystal structure of the BNT films. V5+-substitution enhanced the remanent polarization (Pr) of BNT film from 30 μC/cm^2 (x = 0) up to 35 μC/cm^2 (x = 0.02), while both films possessed similar coercive field (Ec) of approximately 120 kV/cm. Leakage current density of the BNT film was suppressed by V^{5+}-substitution from ~ 10^{-7} A/cm^2 (x = 0) down to ~ 10^{-8} A/cm^2 (x = 0.02) at an applied field of 100 kV/cm, that would be ascribed to the charge compensation of oxygen vacancies by Ti-site substitution using the higher-valent cation.

C11.9

Preparation, Microstructure and Physical Characteristics of Ferroelectric Pb5Ge3O11 Thin Films for Memory Application. Yanxiang Liu[1], Christine Caragianis-Broadbridge[2], Ann Hein Lehman[3] and Tso-Ping Ma[1]; [1]Electrical Engineering, Yale Univ., New Haven, Connecticut; [2]Physics, Southern Connecticut State Univ., New Haven, Connecticut; [3]Facility for Electron Microscopy, Trinity College, Hartford, Connecticut.

Ferroelectric thin films have great potential for memory applications. The transistor with metal-ferroelectrics-insulator-semiconductor (MFIS) gate structure has many desirable properties, such as small cell size, low-voltage operation, fast writing time, and non-destructive reading. It is one of the promising candidates for future high-density, high-speed, and low power memory technology. However, the desired low-voltage operation and long retention time demand the ferroelectric film have as small a dielectric constant as possible. Therefore, the Pb5Ge3O11 (PGO) film with a relatively low dielectric constant and preferred c-axis orientation is a promising ferroelectric material that offers the possibility of increased retention time and reduced memory-writing voltage. We report our sol-gel process of PGO as well as the microstructure and physical properties of ferroelectric PGO films on SiO2 and Pt substrates. The PGO sol is prepared from lead acetate hydrate, germanium isopropoxide, and di(ethylene glycol) ethyl ether. The reactions taking place during the sol-gel process are examined in detail. The method that we have developed to maintain the desired species ratio and prevent germanium oxide precipitation is presented. We have found that the orientation of the PGO thin films are well controlled by the heating and reflux procedures in the sol-gel preparation process. Additionally, to examine the impact of post-deposition processing, selected samples are oxygen annealed at temperatures ranging from 450-650°C, and characterized with X-ray diffraction (XRD), non-contact (cross-sectional and planview) atomic force microscopy (nc-AFM), and cross-sectional transmission electron microscopy (TEM). These data indicate that the microstructure and physical properties of PGO films depend strongly on the precursor preparation as well as the post deposition annealing temperature.

C11.10

Novel PZTN Thin Film for High-Density FeRAM. Takeshi Kijima, Yasuaki Hamada, Koji Ohashi, Hiromu Miyazawa, Taku Aoyama, Eiji Natori and Tatsuya Shimoda; Technology Platform Research Center, SEIKO EPSON Corporation, Nagano-ken, Japan.

Ferroelectric random access memories (FeRAMs) have attracted considerable attention due to the recent development of portable computer technology. However, fabrication of FeRAMs is still difficult, because of problems such as the ferroelectric film quality. Therefore, we have investigated Si-substituted films with spin-coating [1]. In this experiment, we tried to substitute 20% of B-site Ti-ion of Pb(Zr,Ti)O3 (PZT) to only Nb-ion. The crystallization temperature increased than 800C. We obtained a only pyroclore phase. Therefore, we added a 3mol% Si and 20mol% Nb in PZT at the same time. At last, we were able to obtain the (111) highly oriented PbZr0.2Ti0.6Nb0.2O3 (PZTN) thin film with perovskite single phase lower than 650C. Our new Si substituted 150-nm-thick PZTN thin film has a good square-shaped hysteresis loops. The polarization is well saturated at an applied voltage of 1.5V. Additionally, it shows an excellent reliability, such as a leakage current property. In the Nb-added PZT film, the leakage current density decreased at least by 4-orders-of magnitude in comparison with usual PZT, and it was less than 10-9 A/cm2 at 3V with high-breakdown voltage over than 20V. Moreover, as a result of the static imprint test, good imprint resistance was shown that the shifted quantity of hysteresis loops were less than 3%. Therefore, we investigated a more detailed structural change of the PZTN film quality using Secondary Ion Mass Spectrometry (SIMS). The oxygen defects were decreased about 10% in comparison with one of PZT. The excess coordinate number of Nb comparison with one of Ti was compensated for oxygen deficit prevention. [1] T. Kijima and H. Ishiwara, Jpn. J. Appl. Phys. 41(2002)L716

C11.11

Ferroelectric memory in La doped $Bi_4Ti_3O_{12}$ thin films. R.E. Melgarejo, Maharaj Singh Tomar and S. P. Singh; Physics, University of Puerto Rico, Myayaguez, Puerto Rico.

The recent demonstration of large ferroelectric memory in rare earth doped $Bi_4Ti_3O_{12}$ attracted a lot of research interest in this material. $Bi_{4-x}La_xTi_3O_{12}$ for different compositions (x = 0.00, 0.26, 0.46, 0.56, 0.75, 0.85, 1.0 and 1.5)has been synthesized by sol-gel method and thin films were deposited using spin coating on Pt ($Pt/TiO_2/SiO_2/Si$) substrate. Thin films were post annealed at 700 ^{0}C . Structural studies based on X-ray diffraction and Raman spectroscopy shows well oriented films. The prominent effect of La substitution observed in low frequency Raman modes. Ferroelectric response shows high remnant polarization (P_r = 48 μC/Cm^2) for x= 0.56 and fatigue free response is observed up to 10^9 switching cycles. The ferroelectric response for seven other compositions will be presented.

C11.12

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

The study of ferroelectric-gate controlled devices has been vigorously pursued since this device is expected to have versatile advantages such as very small memory cell size, non-destructive read out, high-speed operation, and low-power consumption. However, there is no reliable memory device fabricated yet because of the difficulty in the complicated integration processes for one transistor memory device fabrication. Especially, annealing under O2 atmosphere for the crystallization of ferroelectric material induces the formation and growth of interfacial layers such as silicate and SiO2 between insulator and silicon substrate. In this case, if the thickness of the interfacial layers is thick, because most of the applied voltage drop occurs across these layers, an effective applied field on the ferroelectric layer could not be enough for the polarization reversal. To overcome aforementioned problems, in this work, we successfully synthesized the ferroelectric Ce2Ti2O7 (CTO) by annealing under vacuum. CTO films were deposited on Y2O3/Si (100) by chemical solution method. The crystalline property of the film with anneal temperature was characterized and the ferroelectric and electric properties were also monitored by measuring the capacitance-voltage and current-voltage relations.

C11.13

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

Ferroelectric-gate controlled devices, such as metal-ferroelectric-semiconductor (MFS) FET, were studied as early as 1950s. However, conventional MFS structure has many problems such as difficulty of deposition of ferroelectric thin films directly on silicon, increase of trap density, and diffusion of elements into silicon, and so on. In order to avoid these problems, metal-ferroelectric-insulator-semiconductor (MFIS) FET structure has been extensively investigated, then the interfacial problems have been solved to a certain extent. However, in designing the MFISFET structure, there are several matters to be attended, such as thermal stability of buffer layer on silicon substrate, and so on. Among these matters, we have paid attention to the permittivity of each layer such as ferroelectric, insulator, and silicon dioxide layer. Since the MFIS structure consists of a series connection of capacitors, the applied voltage of each layer is in inverse proportion to the permittivity and thickness of each layer. The amount of interfacial layer depends on the process condition for formation of ferroelectric layer, i.e., ferroelectric material. Then effective applying field for polarization reversal of ferroelectric layer should be considered on the point of view of

permittivity and thickness of interfacial layers including ferroelectric layer itself. In this work, from a point of view described above, we fabricated MFIS structures using various ferroelectric materials such as Pb(Zr,Ti)O3, SrBi2Ta2O9, and Nd2Ti2O7 which have different permittivity and process condition, and discussed the relationship between the constitutional structure and the operating conditions of field effect transistor.

C11.14
Abstract Withdrawn

C11.15
Structural And Electrical Investigations Of Ferroelectric Lead Strontium Titanate Thin Films And Ceramics. M. Jain[1], P. Bhattacharya[1], Yu. I. Yuzyuk[1], R. S. Katiyar[1] and A. S. Bhalla[2]; [1]Department of Physics, University of Puerto Rico, San Juan, PR, Puerto Rico; [2]Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania.

$SrTiO_3$ and $PbTiO_3$ are known to form the solid solution in the entire range. The Curie temperature and lattice constants of $Pb_{1-x}Sr_xTiO_3$ (PST) were found to be dependent on Pb/Sr composition ratio. PST compositions with x$\geq$ 0.3 are paraelectric at room temperature and exhibit ferroelectric phase transition below room temperature. The properties like high dielectric constant and low leakage current densities of ferroelectric PST thin films are attractive for applications in dynamic random access memories. Lead strontium titanate ($Pb_{1-x}Sr_xTiO_3$) (x=0.3-1.0) targets were prepared by the conventional powder processing method. Thin films of these compositions were deposited on various substrates like platinized silicon, MgO etc by pulsed laser deposition technique. These films were characterized for their phase purity, surface morphology, dielectric, and leakage current characteristics. X-ray diffraction and surface microscopy were used for the structural characterization of these materials. The room temperature x-ray diffraction studies for x=0.3 indicated a stabilized cubic perovskite phase. Raman spectroscopy was used to study lattice dynamics of the bulk ceramics and thin films on different substrates. Soft mode behavior in films is discussed in comparison with the bulk data. The grain size of PST thin films was observed to be reduced with the increase in strontium contents. The room temperature dielectric constant decreased while the leakage current densities reduced with the increase of strontium contents of PST thin films. The changes in the thin film properties with varying composition were investigated and compared with the bulk properties.

C11.16
Ferroelectric Properties Of $PbZr_{0.4}Ti_{0.6}O_3$ Film Spin-Coated On Pt Bottom Electrode Using A $La_{0.5}Sr_{0.5}CoO_3$ Buffer Layer. Jai-Hyun Kim[1], Woong Kil Choo[1] and Kyoung Shin Koh[2]; [1]Material Science and Engineering, KAIST, Taejon, South Korea; [2]Chemistry, Chungang Univ., Seoul, South Korea.

We have studied ferroelectric properties of $PbZr_{0.4}Ti_{0.6}O_3$ [PZT 40/60] films grown on $Pt/TiO_2/SiO_2/Si(100)$ bottom electrode using a $La_{1/2}Sr_{1/2}CoO_3$ [LSCO] buffer layer. It is approved that the conductive perovskite LSCO thin film (about 5nm thick) which consist with fine grain (less than 20nm) is grown on the $Pt/TiO_2/SiO_2/Si$ substrate at relatively low temperature (450°C) by d.c. magnetron sputtering and shows the ohmic contact to the Pt bottom electrode. In order to investigate the ferroelectric properties of spin-coated PZT 40/60 films, we measured the P-V hysteresis loop vs. temperature. Different from the general decrease of remanent polarization(P_r) with temperature, it shows an increasing Pr up to 373K. Also, in fatigue test, it shows a smaller decrease in Pr up to $2x10^{10}$ switching cycle at 323K than 298K. We measured the J-V curve vs. temperature. Different from the general increase of leakage current with temperature in the schottky or ohmic contact, it shows a very small increase up to 373K. However, above 373K, the increase appears in different aspect. The current density is dependent on the square of the applied voltage and exponential of temperature. This is new type of space charge limited conduction from the existence of thin LSCO buffer layer.

C11.17
Hydrogen Effects in MFSFET and MFISFET with $Pt/SrBi_2Ta_2O_9/Si$ and $Pt/SrBi_2Ta_2O_9/Y_2O_3/Si$ Gate Structures. Sun Il Shim[2], Young Suk Kwon[1], Seong-il Kim[1], Yong Tae Kim[1] and Jung Ho Park[2]; [1]systems technology division, Korea Institute of Science and Technology, Seoul, South Korea; [2]Electronics Engineering, Korea University, Seoul, South Korea.

The single transistor type ferroelectric memory has many advantages over the capacitor type because of its nondestructive read operation and small cell size. Many kinds of attempts have been tried to fabricate metal ferroelectric semiconductor or metal ferroelectric insulator semiconductor field effect transistor (MFSFET or MFISFET). In this study, we have studied the hydrogen annealing effects on the single transistor type ferroelectric memory devices. It is well known that the hydrogen annealing degrades the ferroelectric properties but the leakage current and interface trap density are improved. The MFSFET ($Pt/SrBi_2Ta_2O_9/Si$) and MFISFET ($Pt/SrBi_2Ta_2O_9/Y_2O_3/Si$) were fabricated with direct etching process by using the inductively coupled plasma reactive ion etch (ICP-RIE) system. The memory windows of MFSFET and MFISFET were 0.74 V and 1.0 V at 7 V, respectively. Then, after hydrogen annealing at 400 °C for 30 min, memory windows were degraded. But, the leakage current was rather improved, which affected the retention characteristic of the single transistor type ferroelectric memory. The threshold voltage was shifted toward positive bias, which resulted from the reduction of the interface trap density of the MFSFET and MFISFET. These results are well consisted with the electrical results of the MFS and MIFS capacitor structures. The hydrogen annealing effects are more dominant in the MFISFET than in the MFSFET and MFS capacitor structure.

C11.18
Charicteristics And Calculation Of One Transistor Memory Devices. Tingkai Li, Sheng Teng Hsu, Bruce Ulrich and Dave Evans; PTL, Sharp Labs. of America, Inc., Camas, Washington.

One transistor memory devices with MFMPIS (M: Metal, F: Ferroelectrics, M: Metal, P: polysilicon, I: insulator, S: silicon) structure have been fabricated. The working functions of memory window, retention, imprint, switching characteristics, and thermal stability have also been measured and evaluated using various methods. One-transistor memory devices show excellent memory working functions. The typical MFMPIS one transistor memory devices show memory windows around 2 - 3V. The memory windows are almost saturated from operation voltage of 3V. For the one transistor memory device, after writing off state (-5 V), the drain current (ID) at VD of 0.1V and VG of 0, 0.5, and 1 V was about 2 x 10-14 A. After writing on state (+5 V), the drain current (ID) at VD of 0.1V and VG of 0, 0.5, and 1 V was about 1.00 x 10-5 A. The on state current to the off state current ratiois about 9 orders of magnitude. However, the one-transistor memory devices also show poor retention and switching properties, especially at higher temperatures. Compared with calculation data based on circuit modeling of 1T memory device, most experimental results are consistent with the calculation data. The challenges for one-transistor memory devices are switching properties and retention properties at higher temperatures. The effects of depolarization field and leakage current on the retention properties at higher temperatures have also been calculated and discussed.

C11.19
Low Temperature Aluminum Oxide Mocvd Films For Ferroelectric Film Passivation. Catherine Rice[1], J. Cuchiaro[1], S. Sun[1], G. Provost[1], G. Tompa[1], T. Davenport[2], G. Fox[2], F. Chu[2] and S. Sun[2]; [1]Structrured Materials Industries, Inc., Piscataway, New Jersey; [2]Ramtron, Colorado Springs, Colorado.

A long-term consideration in the application of ferroelectrics for device production is hydrogen-induced failures. Protection of the active ferroelectric layer through covering the capacitor with a dense dielectric can mitigate these failures. However, the dielectric deposition temperature should be sufficiently low so as not to degrade underlying transistor plug layers, or react with the memory capacitor to degrade performance. Further, the addition of elements to the base silicon process for construction of a barrier need to be minimized so that transistor properties remain reliable. In part, a design solution to this problem is to employ an aluminum oxide hydrogen diffusion barrier in the device structure. We have focused on MOCVD of the barrier layer using an array of precursors, including trimethylaluminum and aluminum iso-propoxide, among others. The effects of RF plasma on deposition rate and film properties have been examined. We have successfully reduced the deposition temperature from 600C to 350C without sacrificing film quality and deposition rate. Produced films are uniform over 8" diameter wafers and are highly reproducible. Films are produced in a "SpinCVD${TM}$" cluster tool rotating disk low pressure MOCVD reactor. The electrical characterization and physical properties of these films will be discussed.

C11.20
Lead Barium Titanate Thin Film Based Positive Temperature Coefficient of Resistance Thermisters. RaviPrakash Jayaraman and Susan Trolier-McKinstry; Materials research Institute, Pennsylvania State University, University Park, Pennsylvania.

Positive Temperature Coefficient of Resistance (PTCR) thermistors typically employ donor doped compositions of BaTiO3. The PTCR phenomena is thought to be due to the formation of insulating grain boundary barriers separating conducting grains. The barrier is

modulated by ferroelectric polarization and the dielectric permittivity of the material. In this work, (Ba, Pb)TiO_3 were investigated as high temperature PTCR materials. Lead barium titanate thin films ($0.35\mu m$) prepared by a sol-gel technique showed a T_c of 240°C with around 50 at% lead content. XRD of these films indicate that the films do have the perovskite structure. The room temperature dielectric constant for the films was found to be around 400, with a dielectric loss of around 5%. A remanent polarization of 20 $\mu C/cm^2$ and a coercive field of 900 KV/cm was obtained. The PTCR characteristics of films based on this solid solution series will be reported.

C11.21
Magnetic and Ferroelectric Behaviors of Multi-Ferroic RMnO3 (R: yttrium or rare earth ion) Thin Films.
Norifumi Fujimura, Hironori Sakata, Takeshi Yoshimura and Hironori Shigemitsu; Graduate School of Eng., Osaka Prefecture Univ., Osaka, Japan.

Ferroelectric materials with magnetic properties have several advantages when the materials use for memory devices. Hexagonal yttrium and rare earth manganites form an interesting class of materials known as ferroelectro-magnet in which the ferroelectric and magnetic orders coexist at low temperatures. We have demonstrated that YMnO3 thin films show ferroelectric and antiferromagnetic behaviors and demonstrate a relationship between carrier concentration and magnetic properties of YMnO3 films. However, little interaction was observed between the magnetic spin and dipole moment. Although YMnO3 films exhibit antiferromagnetic magnetization behavior regardless of the crystallographic orientation and the carrier concentration, Li doped sample displays parasitic ferromagnetic behavior (weak ferromagnetism). Substituting Y for Yb enhances the ferromagnetic interaction. This paper describes that the effect of A-site substitution on the magnetic and ferroelectric properties of RMnO3 films and also demonstrates electric-field control of magnetic properties of the films.

C11.22
Characterization of layer-transferred single crystal $BaTiO_3$ thin film by H^+ and He^+ ions co-implantation.
Young-Bae Park, Jennifer L. Ruglovsky, James M. Zahler and Harry A. Atwater; Applied Physics, California Institute of Technology, Pasadena, California.

We have investigated ion-induced layer transfer of $BaTiO_3$ thin films onto various substrates to obtain high quality single crystal ferroelectric thin films. We will report thermodynamic criteria for cavity nucleation and ferroelectric properties of transferred single crystal $BaTiO_3$ thin films. Bulk single crystal $BaTiO_3$ was processed by high dose H and He ion implantation. The ion implantation energy was 20 $\sim$ 115 keV and dose ranged from $5x10^{16} \sim 1x10^{17}/cm^2$ for H^+ and energy was 30 $\sim$ 200 keV with dose of $1x10^{17}/cm^2$ for He^+, respectively. After substrate cleaning, $BaTiO_3$ was bonded to various substrates (Si, Si_3N_4 and Al) at a room temperature. To investigate cavity growth and layer splitting, anneals were performed in the range from 300 $\sim$ 500 $^\circ$C in various ambient and pressure conditions. Single crystal $BaTiO_3$ layers with the area of 40 x 200 um^2 were transferred onto Si_3N_4/Si substrates. Transferred layers exhibited single crystalline structure with tetragonal phase. Film stoichiometry did not change compared to bulk $BaTiO_3$ but transferred layer exhibited stacking faults and polarization change. RMS surface roughness of transferred layer was in the range $\sim$ 30 nm. Ferroelectric domain size ranged from 1 $\sim$ 2 μm and showed typical ferroelectric domain switching behavior with a coercive field $\sim$ 20 kV/cm. Cavity nucleation before layer transfer was observed by optical microscopy and SEM. FRES analysis was conducted to obtain hydrogen depth profiles in the implanted region. AFM was used to characterize surface roughness and measured the size of surface blisters, cavity radius and height. Raman spectroscopy was used for structure and chemical disorder. Microstructural analysis was performed using plan view TEM. For the oxide layer stoichiometry, RBS was performed before and after layer splitting. PFM was used to investigate the ferroelectric domain and switching property. The initial stages of layer splitting were studied with thermodynamic modeling and prospects for large-area single crystal ferroelectric layer transfer onto various substrates will also be discussed.

C11.23
Deposition Of $BaTiO_3$ Thin Films And MgO Buffer Layers On Patterned GaAs Substrates for Integrated Optics Applications.
Ding-Yuan Chen, Timothy E Murphy and Jamie D Phillips; Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan.

The integration of ferroelectric thin films with semiconductors is of high interest for integrated optics and optoelectronic integrated circuits (OEIC). Ferroelectric oxides such as $BaTiO_3$ are transparent in the visible and infrared and possess strong electro-optic coefficients making them attractive for active and passive optical components. Highly oriented $BaTiO_3$ thin films on GaAs have been previously demonstrated using MgO buffer layers. The $BaTiO_3$/MgO/GaAs structures have been problematic for integrated optics applications due to the inability to obtain thick MgO cladding layers for optical waveguiding and the presence of cracking in the thin films that are likely a result of thermal expansion mismatch. In this work, we present the deposition of $BaTiO_3$ thin films with MgO buffers on patterned GaAs substrates as an approach to achieve crack-free optical waveguiding structures. $BaTiO_3$ and MgO thin films were deposited by pulsed laser deposition on pre-patterned GaAs substrates. The GaAs substrates were patterned into stripe geometries with widths ranging from 1 to >100 μm and depths of up to 1-2 μm using reactive ion etching to achieve vertical sidewalls. We observe cracking and peeling of the thin films on patterns with lateral dimensions exceeding several microns or with etch depths significantly less than the $BaTiO_3$/MgO film thickness ($\sim$0.5-1.0 μm). We observe crack-free thin films for patterns with lateral dimensions of a few microns and etch depths similar to the film thickness. We believe that the patterned features provide strain relief to prevent cracking due to thermal expansion mismatch during heating and cooling steps of the deposition process. The structures obtained are suitable for single-mode optical waveguiding structures, where optical characterization will be presented. Furthermore, we will report on the inclusion of Al_xO_y buffer layers obtained through wet-oxidation of AlGaAs prior to $BaTiO_3$/MgO deposition as a means of enhancing optical cladding.

C11.24
Parametric studies on Suppressing Secondary Phases in Lithium Niobate thin films deposited by Pulsed Laser Depostion.
Ji-Won Son[1], Sergei S. Orlov[2], Bill Phillips[2] and Lambertus Hesselink[2]; [1]Materials Science and Engineering, Stanford University, Stanford, California; [2]Electrical Engineering, Stanford University, Stanford, California.

We performed parametric studies to suppress secondary phases in lithium niobate thin films by pulsed laser deposition (PLD). A KrF excimer laser (λ=248nm) was used as a PLD source and c-oriented sapphire and $LiTaO_3$ were used as substrates for waveguide applications. The main limitation in producing single phase $LiNbO_3$ films by PLD is that secondary phases such as a Li-deficient phase ($LiNb_3O_8$) are easily mixed. In our previous research, we deposited lithium niobate films on sapphire (0006) substrates in two different deposition geometries, on-axis and off-axis. Under the same growth conditions, it was found that the on-axis geometry was prone to produce a Li-deficient phase while the off-axis geometry produced single phase $LiNbO_3$. The main differences between the on and off-axis geometries are the growth rate and scattering of materials in the plume that reach the surface of the substrate. By reducing the growth rate and changing the ambient gas pressure in the on-axis geometry, we found that the main factor that can reduce the secondary phase is controlling the plume strength, rather than the growth rate. To investigate the relation between the film phases and the plume strength, extensive parametric studies were performed by changing the oxygen ambient pressure, the target to substrate distance, and also the Li content in the target. The structure, phase, and composition of the films were investigated by XRD and XPS. It is shown that there is an optimum range of ambient pressure and target-substrate distance to produce single phase $LiNbO_3$ films. As the ambient oxygen pressure or target-substrate distance increases, i.e. the plume strength decreases, the phase of the lithium niobate films changes from Li-deficient mixtures of $LiNbO_3$, to the $LiNbO_3$ single phase. Further reducing of the plume strength passing through the optimum condition induces the appearance of the Li-excess phase (Li_3NbO_4). The trend of the phase change is consistent in lithium niobate films produced by using either $LiNbO_3$ or Li-rich targets, but the Li-rich target has an optimized condition with a stronger plume than a $LiNbO_3$ target. From these results, we postulate that the main reason for the change in Li content in the film is caused by different elemental scattering in the plume, and/or the knock-out of Li from films by a high energy plume. The surface morphology and structural evolution of single-phase films and Li-deficient phase mixed films are also studied by AFM and TEM, and related to the growth mechanism with a lattice misfit.

C11.25
Abstract Withdrawn

C11.26
Structure, Dielectric and Piezoelectric Properties of $0.5Pb(Yb_{1/2}Nb_{1/2})O_3$-$0.5PbTiO_3$ Thin Films Prepared via Sol-Gel.
Nazanin Bassiri Gharb and Susan Trolier-McKinstry; Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania.

(1-x)$Pb(Yb_{1/2}Nb_{1/2})O_3$-x$PbTiO_3$ (PYbN-PT) has one of the highest

Curie temperatures (~360°C) near the morphotropic phase boundary (x~0.5) among the relaxor-PT solid solution systems. This should yield good temperature stability of the piezoelectric properties and a wide working temperature range, which are promising for transducers and actuators. In this work, 0.5PYbN-0.5PT thin films were deposited on platinized silicon substrates by sol-gel processing. Films with strong (111) and (001) orientation were obtained by controlling the process parameters. The films exhibited good ferroelectric and piezoelectric properties. The dielectric permittivities were around 820 and 1160 and the dielectric losses around 4% and 2.5% respectively for the (111) and (001) orientations. The effective transverse piezoelectric coefficient $e_{31,f}$ was measured using a modified wafer flexure method and was as high as -4.8 C/m^2 and -8.4 C/m^2 when poled with the top electrode positive at room temperature for (111) and (001) films respectively. Grazing angle X-rays showed an increase in the unit cell parameter near the surface for the (001) oriented films probably due to either a composition or stress gradient through the thickness of the film. An oscillating composition gradient was observed through the thickness of the films where alternating layers roughly 80nm thick rich in Yb and Nb and depleted in Ti were followed by the reverse.

C11.27

PZT Thick Film deposited by improved Hydrothermal Method for Thickness Mode Ultrasonic Transducers.

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

C11.28

Mist Deposition of Micron-Thick Lead Zirconate Titanate Thin Films.

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A majority of the work published on liquid source misted chemical deposition (LSMCD) has focused on the fabrication of thin ferroelectric films for random access memory (RAM) applications. However, the ability of LSMCD to combine the characteristically good stoichiometric control of a chemical solution deposition process with good film conformality, makes this a desirable technique for other applications, including microactuators and integrated passive components. For these applications, though, LSMCD is limited by its low throughput. This paper describes the feasibility of depositing micron-thick lead zirconate titanate (PZT) films using the LSMCD tool. PZT films of 52/48 composition were deposited on both platinized silicon and platinized alumina substrates. The chamber temperature and the delivery geometry of the LSMCD tool were identified as limiting factors in the rate at which micron-thick samples can be prepared. By switching to a focused nozzle delivery geometry and increasing the chamber temperature from room temperature to 60°C, the total process time for 1 μm thick films can be reduced from 480 min to 90 min. In addition, polarization hysteresis measurements indicated a 60% higher remanent polarization for PZT films deposited on platinized alumina substrates (33 μC/cm^2) compared to those deposed on platinized silicon substrates (20 μC/cm^2). The polarization loop for the silicon substrate sample was also tilted. These observations are evidence of higher tensile stresses in the PZT films deposited on silicon substrates due to a larger mismatch in the thermal expansion coefficients of the film and the substrate.

C11.29

Sample Geometry Effects on Electric-Field-Induced Displacements in Piezoelectric Thin Films Measured by Atomic Force Microscopy.

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A remarkable interest in electric-field-induced displacements in ferroelectric thin films has arisen for application and integration of ferroelectric microelectromechanical systems. Currently, several techniques such as atomic force microscopy (AFM), interferometry and direct methods have been employed to evaluate the electric-field-induced displacements. Among these techniques, AFM is the most effective technique for materials research, because AFM is easy to operate and has sufficient sensitivity. However, there have been few reports on sample geometry influence on electric-field-induced displacements in piezoelectric thin films measured by AFM. In this study, we report detailed investigation of electric-field-induced displacements calculated by finite element method (FEM), and compare the calculations with experimental results. 3-D FEM analyses were performed using a commercial software (Dynus Co. Ltd., PiezoPLUS). Electric field-induced displacements were calculated using static analysis mode, because applied field frequencies for AFM measurements (Hz – kHz) were sufficiently lower than the mechanical resonance frequencies of thin film specimens (MHz –). Columnar FEM models consisted of 5 layers: Pt(0.1μm)/PZT(5μm)/Pt(0.1μm)/SiO_2(1μm)/Si(299μm). The radii of the whole FEM models were 10 times as long as the radii of top electrodes (TE) ranging from 0.1 μm to 500 μm. Piezoelectric constant ($d_{ij}{}^T$), stiffness ($s_{ij}{}^E$), permittivity ($\epsilon_{ij}{}^T$) and density of pure PZT(52/48) ceramics were substituted for these constants of PZT thin films. Here, d_{33} of PZT thin films was 223×10^{-12} m/V. After the FEM calculation, $d_{33(AFM)}$ was computed from displacement at the center of TE surface. $d_{33(net)}$ were also estimated from PZT thin film deformation at the center of the model. If the TE radius was longer than 5μm, $d_{33(AFM)}$ included a contribution of the bending motion of substrate[1]. This bending motion contradicted the net displacement of PZT thin film. Accordingly, if the TE radius was longer than 200μm, $d_{33(AFM)}$ became negative, while $d_{33(net)}$ still remained to be positive. Besides, as the TE radius decreased from 1μm to 0.1μm, $d_{33(AFM)}$ (almost equal to $d_{33(net)}$ in this case) reduced from 201 to 104×10^{-12} m/V. This was because surrounding PZT film outside TE area prevented electric-field-induced displacements. Hence, "side-etching" (etching PZT film excluding TE area) effect was also investigated. If the TE radius was lager than 10μm, the results of side-etched models were almost the same as non-side-etched models. Nevertheless, as the TE radius decreased from 10μm to 0.1μm, $d_{33(AFM)}$ and $d_{33(net)}$ became close to the bulk value rapidly. Therefore, necessary conditions to measure intrinsic d_{33} by AFM were shorter TE radius than the thickness of ferroelectric films and side-etching treatment. [1] A. L. Kholkin, Ch. Wütchrich, D. V. Taylor, and N. Setter, Rev. Sci. Instrum. **67**, 1935 (1996)

C11.30

The Synthesis and Structure of New Piezoelectric Materials Niobate Processed in Millimeter Wave Field.

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A new niobate materials Ba5LixTixNb10-xO30 , which could be as candidate of piezoelectric materials, were synthesized by doping Li+ in the system BaO- TiO2- Nb2O5 in millimeter wave field. XRD quantitative and scanning transition spectroscopy (SEM) analysis were employed to study crystal structure and microstructure of reaction products. It was found that pure reaction products could be obtained at temperature 900, 8 min. The results of XRD shown the crystal belongs to tetragonal tungsten bronze structure with space group P4bm and it cell parameters : a=b=1.2512(2) nm,c=0.4008(5) nm. The reaction mechanism in millimeter wave field was analyzed based on the XRD quantitative data. The theoretical calculations are

agreement with experiment data.

C11.31
Ferroelectric Properties of a Lead Zirconate Titantate Film Deposited by a Hydrothermal Method. Takeshi Morita[1], Yasuo Wagatsuma[1], Hitoshi Morioka[2], Hiroshi Funakubo[2], Nava Setter[3] and Yasuo Cho[1]; [1]Research Institute of Electrical Communication, Tohoku University, Sendai, Japan; [2]Tokyo Institute of Technology, Yokohama, Japan; [3]Swiss Federal Institute of Technology, Lausanne.

Among various methods, a hydrothermal method is a unique method to deposit a ferroelectric thin film below 200 degrees Celsius. Concerning a PZT thin film, a chemical reaction of solution containing lead, zirconium and titanium ions is utilized with high alkali concentration. Shimomura *etal.* adopted a titanium metal as a substrate and polycrystalline PZT thin film was successfully obtained[1] and this film was applied to a micro ultrasonic motor by *T.Moritaetal*[2]. Automatically polarization alignments indicated a fine crystallites film and can be thought to have good purity due to direct synthesis under low temperature. Indeed, SEM photograph verified the deposited film consisted of cubic shaped crystals. A.T. Chien *etal.* have studied an epitaxial hydrothermal PZT films using a $SrTiO_3$ single crystal 100 as a substrate. XRD measurements revealed film alignment of 001; although 100 peak was also detected. Electrical properties including a piezoelectric performance could not be measured because of non-conductivity of the $SrTiO_3$ substrate. In this study, an epitaxial $SrRuO_3$ thin film was sputtered on $SrTiO_3$ 100 as a bottom electrode. Then, a PZT thin film was deposited on $SrRuO_3$ by a hydrothermal method. With a suitable heating method and suspending substrate condition, crystal quality was improved. A PE hysteresis curve and a strain induced by an inversely piezoelectric effect could be measured. The poling direction distribution were measured using a nonlinear dielectric microscopy (SNDM) and it was confirmed that poling directions were aligned parallel to the thickness direction during the deposition process without a poling treatment. [1]K. Shimomura, T. Tsurumi, Y. Ohba, M. Daimon, Preparation of lead zirconate titanate thin film by hydrothermal method, Jpn. J. Appl. Phys., vol. 30-9B, pp.2174-2177 (1991). [2]T. Morita, MK. Kurosawa and T. Higuchi, "A Cylindrical Shaped micro ultrasonic motor utilizing PZT thin film", Sensors and Actuators, vol. 83, pp.225-230 (2000). [3]A.T. Chien, J.S. Speck, and F.F. Lange, "Hydrothermal Heteroepitaxial of $Pb(Zr_xTi_{1-x})O_3$ at 90-150 deg.C", J. Mat. Res., vol. 12-5, 1176-1178 (1997).

C11.32
Local Hysteresis Behavior of Ferrelectric Thin Films of Si Added $PbTiO_3$. Vaijayanti Raghunath Palkar[1], M. Higgins[2], S. C. Purandare[1], R. Pinto[1] and S. Bhattacharya[1,2]; [1]Condensed Matter Physics & Materials Science, Tata Institute of Fundamental Research, Mumbai, Maharashtra, India; [2]NEC Research Institute, Princeton, New Jersey.

2 Mole percent Si added $PbTiO_3$ thin films have been deposited on $Pi/TiO_2/SiO_2/Si$ substrate by pulsed laser deposition technique. Phase purity of the films is checked by X-ray diffraction (XRD). The ferroelectric properties are determined by using ferroelectric loop tracer. The piezo-response in various local regions on the film has been studied using Atomic Force Microscope (AFM) with a conducting tip. XRD results indicate that the films are single phase and polycrystalline in nature. Saturated ferroelectric hysteresis loop and well-defined local piezoelectric loops obtained on different films demonstrate excellent properties equivalent to any other established ferroelectric material like PZT. Deflection, amplitude and phase images obtained by using AFM with conducting tip yield the following important conclusions. ♦ The first more fundamental conclusions that the structural defects especially spatially correlated ones such as the grain boundaries are dominant pinning centers. These pinning centers are significantly more important than random point defects that may exist throughout the sample in both intra and inter-granular space. ♦ The second, more technologically significant, conclusion is that for better and reliable performance as NV-FRAM the cell size should match with the grain size and for higher memory cell densities the grain size should be smaller. ♦ Si segregates at the grain boundaries without affecting $PbTiO_3$ matrix. Moreover, it restricts the grain growth. The optimization of Si concentration could therefore help to control the grain size and achieve higher memory cell densities in NV-FRAM.

C11.33
An Effective Way to Suppress the Pyrochlore Phase Formation in SBT Thin Films. Yun-Mo Sung, Se-Yon Jung, Woo-Chul Kwak and Seung-Joon Hwang; Materials Sci. & Eng., Daejin University, Pochun-koon, South Korea.

Sr0.7Bi2.4Ta2O9 (SBT) layer with ~40 nm thickness was introduced as a seed layer for the phase formation of SBT thin films with the same chemical composition. The influence of seed layer on the phase formation characteristics of SBT thin films was investigated using x-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. Formation of pyrichlore as well as Aurivillius phase was observed in both the unseeded and seeded SBT thin films heated at 740C. However, it was revealed that Aurivillius phase formation was enhanced in seeded SBT thin films and pyrochlore phase formation was highly suppressed. In this study two possible mechanisms for the suppression of pyrochlore phase formation were proposed from the perspectives of activation energy difference for Aurivillius and pyrochlore phase formation and Bi-ion diffusion to pyrochlore phase.

C11.34
Growth Reorientation with the Annealing Temperature of SrBi2Ta2O9 Films Deposited by PLD. Ma. de la Paz Cruz[1], Jorge Portelles[2], Oscar Raymond[1] and Jesus Siqueiros[1]; [1]Optical Properties, CCMC-UNAM, Ensenada, B.C., Mexico; [2]Facultad de Fisica, IMRE, La Habana, Cuba.

The ferroelectric properties of SrBi2Ta2O9 (SBT) films are highly dependent on crystallographic orientation due to its highly anisotropic structure. In particular, the spontaneous polarization vector is directed along the a-b crystal plane, perpendicular to the c-axis. For SBT films prepared over the more widely used Pt/TiO2/SiO2/Si substrates, the preferential growth direction in our films is (115) rendering modest values for the polarization. It is therefore important to increase the fraction of crystallites with the a-b plane directed as close as possible to the normal to the substrate surface. In this work, SBT films produced by the Pulsed the Laser Deposition (PLD) technique, in an oxygen pressure of 450mT at different temperatures, were heat treated after deposition in an air atmosphere, at a temperature of 750C. At a deposition temperature of 610C, the X-ray diffraction pattern shows a pure SBT crystalline phase with the presence of peaks associated to (00l) planes. The intensity of these peaks is increased with the deposition temperature up to 715C. Nevertheless, the heat treatment of the films deposited at 610C induces a growth reorientation favoring the formation of (00l) planes parallel to the film plane and improving the ferroelectric properties. Polarization values, 2Pr, of 9.1 $\mu C/cm^2$ and coercive fields, Ec, of 52 KV/cm at a voltage of 5V are typically obtained. This work was partially supported by grants of DGAPA-UNAM, Proj. IN104000 and CoNaCyT Proj. 33586-E. Thanks are due to E. Aparicio, P. Casillas, J. Díaz, I. Gradilla, P. Ruiz and G. Vilchis for technical help.

C11.35
Electrical and Structural Features of $Pb_{0.6}Sr_{0.4}TiO_3$ Thin Films on LSCO/MgO and LSCO/$SrTiO_3$. Eduardo Martinez[1], Oscar Blanco[1], Abel Fundora[3] and Jesus M. Siqueiros[2]; [1]Fisica de Materiales, CICESE, Ensenada, Baja California, Mexico; [2]Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, Baja California, Mexico; [3]Facultad de Fisica, Universidad de la Habana, La Habana, La Habana, Cuba.

$Pb_{0.6}Sr_{0.4}TiO_3$ (PST60) thin films have been grown on LSCO/$SrTiO_3$(100) and LSCO/MgO(200) substrates using the RF Ion Sputtering Technique. The structural and ferroelectric characteristics of PST60 thin films grown on both kinds of substrates are determined to evaluate the potential of this heterostructure for non-volatile memory applications. Epitaxy of LSCO films was confirmed before depositing PST60 films on both of the above mentioned substrates through 4-Circle X-Ray Diffraction analysis ($\theta/2\theta$, ω and ϕ scans). The same analysis performed on the ferroelectric PST60 layer showed that the films are textured and entirely perovskite phase. LSCO and PST60, crystallize in the perovskite structure and their lattice parameters are well matched (within 1.3% for $SrTiO_3$. This fact renders favorable structural and chemical conditions for the growth of PST60 on LSCO. Rutherford Backscattering Spectrometry (RBS) was also used to analyze interfaces and the chemical environment for the PST60 films. TEM studies show the interaction between the LSCO textured electrodes and the PST60 layer. The electrical performance of the Pt/PST60/LSCO/$SrTiO_3$(100) and Pt /PST60/LSCO/MgO(200) capacitors was evaluated through polarization-Voltage (P-V) and Fatigue measurements. It is concluded that textured LSCO provides a favorable environment for the growth of PST60 but ferroelectric fatigue is still present.

C11.36
Effects of Sol-Gel Processing Parameters on Solid Solution $Pb_{1-x}Ba_xTiO_3$ Powders and Thin Films. Stacey W Boland and Sossina M Haile; Materials Science, California Institute of Technology, Pasadena, California.

A series of sol-gel processes for producing $Pb_{1-x}Ba_xTiO_3$ (PBT), a ferroelectric material of interest for sensor and actuator applications, is investigated. Precursor chemistry, water for hydrolysis, and lead:barium composition were systematically varied and the resulting sols and powders were studied using TGA/DSC, FTIR, and XRD. Thin films were prepared by spin coating onto single crystal (100)

MgO. Acetic acid, acetylacetone, and diethanolamine were used as chelating agents for titanium isopropoxide and titanium butoxide, and the effect of using particular titanium/chelating agent combinations on the resulting powders and thin films is examined. The importance of thermal processing was studied through varying heating rate, holding time, and ambient atmosphere during calcination, using conventional furnace annealing and rapid thermal annealing. Films were subsequently characterized by XRD and SEM to determine orientation and surface morphology. Ferroelectric properties are also examined. The chelating agent used was found to significantly influence the calcination temperature required to produce phase pure PBT. Thermal treatments were found to strongly affect the orientation and grain size of the resulting films. Under optimized conditions, highly oriented films were obtained for a range of Pb:Ba compositions.

C11.37
Ir Thin Films for PZT Capacitors Prepared by MOCVD Using a New Ir Precursor. Masaru Shimizu[1], Soichi Watari[1], Hironori Fujisawa[1], Hirohiko Niu[1] and Noriaki Oshima[2]; [1]Department of Electrical Engineering and Computer Sciences, Himeji Institute of Technology, Himeji, Japan; [2]Tokyo Reserch Center, Tosoh Corporation, Kanagawa, Japan.

Ir-based electrode materials, such as Ir and IrO2 have been extensively investigated for PZT memory applications. For the future realization of FeRAMs with very high integration, the structural design of ferroelectric capacitors is one of most important key issues and alteration of capacitor structures from planar to three-dimensional structures will be required. For this alteration of capacitor structure, MOCVD technique will be indispensable because of its highly conformal growth, high growth rate and compatibility of LSI process. In this paper, preparation of Ir and IrO2 films by MOCVD using a new Ir precursor, Ir(EtCp)(CHD), and electrical properties of PZT capacitors with Ir electrodes solely by MOCVD are reported. In our experiments, a new Ir precursor, Ir(EtCp)(CHD) ((ethylcyclopentadienyl) (cyclohexadiene)iridium), was used to prepare Ir and IrO2. This precursor is a liquid at room temperature (m.p. : 15°C) and the thermal decomposition temperature is 300°C. PZT films were also prepared by MOCVD. (111)-oriented Ir films with highly reflecting surfaces were successfully grown at 300-350°C on SiO2/Si. When Ir(EtCp)(CHD) was used as a precursor, higher nucleation density and shorter incubation time were observed than when conventional Ir precursor, Ir(EtCp)(COD), was used. IrO2 films with smooth surfaces were also grown at 400°C on Ir/SiO2/Si. IrO2 films obtained showed smaller grains and smoother surfaces than those of films grown using Ir(EtCp)(COD). Ir films deposited on stepped substrate showed good step coverage higher than 80%. Electrical properties of Ir/PZT/Ir capacitors fabricated on three-dimensional structures solely by MOCVD will be compared with those of planar capacitors.

C11.38
Alkoxy-Derived Nucleation Layers For Control Of Phase Transition In Bismuth-Based Layer-Structured Ferroelectric Thin Films. Kazumi Kato[1,2], Kazuyuki Suzuki[1], Kiyotaka Tanaka[1], Desheng Fu[1], Kaori Nishizawa[1] and Takeshi Miki[1]; [1]Ceramics Research Institute, National Institute of Advanced Industrial Science and Technology, Nagoya, Aichi, Japan; [2]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan.

Thin films of Bi-based layer-structured ferroelectrics (BLSFs) are expected as candidate materials for application to a variety of integrated devices such as non-volatile memories, high capacitance condensers and also piezoelectric devices. However, the high-temperature processing is still needed for the BLSF thin films because of the existence of non-ferroelectric intermediates and is severe for the integration into Si semiconductor. Pyrochlore phase is a major of the non-ferroelectric intermediates, which often crystallizes initially at the interface between the thin films and Pt bottom electrodes. In this paper, nucleation layers of TiO_2 were inserted between $CaBi_4Ti_4O_{15}$ thin films and the Pt bottoms by chemical solution deposition technique. Several tens nanometer in thickness of the alkoxy-derived TiO_2 layers were found to be critical for acceleration of the phase transition in the thin films. Unlike the thin film crystallized directly on the highly (111)-oriented Pt bottom electrode, the thin film on 650°C-crystallized TiO_2 layer was almost single phase of perovskite and showed random orientation. The phase purity depended on the crystallinity of the TiO_2 layer. Also, the crystallinity of the BLSF thin film was much higher than that crystallized directly on the Pt bottom electrode. These crystallization behaviors of the BLSF thin films may associate with the phase transformation in the TiO_2 nucleation layer itself. The dielectric and ferroelectric properties of the $CaBi_4Ti_4O_{15}/TiO_2$-stacked thin films on Pt-coated Si substrates will be discussed. Thereby the potential of the nucleation layer for the integrated devices would be primarily addressed.

C11.39
Low Temperature Preparation by Pulsed Laser Deposition and Polarization Enhancement of Nd Modified Bismuth Titanate. Minoru Noda, Wenbiao Wu, Akira Shibuya and Masanori Okuyama; Graduate School of Engineering Science, Osaka university, Toyonaka, Japan.

Neodymium-modified $Bi_4Ti_3O_{12}$(BNdT) thin films have been prepared by pulsed laser deposition (PLD), aiming to realize low temperature growth by considering various PLD conditions. When deposited at 500 degree C, $P-E$ hysteresis shows twice remanent polarization $2Pr$ of 69.9 $\mu C/cm^2$, coercive force Ec of about 200 kV/cm, and the leakage current of less than 10^{-7} A/cm^2 from -50 to +50 kV/cm. Recent studies [1-3] revealed that Bi^{3+} ions in $Bi_4Ti_3O_{12}$ structure could be substituted by trivalent rare earth ions, such as La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}, for the improvement of its properties. Especially, BNdT has been receiving great attention for its very large remanent polarization. However, the deposition temperature is high (about 650 degree C) and so is sincerely expected to decrease for device application. The Nd-doped $Bi_4Ti_3O_{12}$ (BIT) films have been prepared on $Pt/TiO_2/SiO_2/Si$ at low temperatures ranging from 400 to 550 degree C, O_2 gas pressure was 0.1 Torr. XRD patterns showed preferential c-axis oriented growths of the film when deposited at higher than 400 degree C. Grain size was around 100 nm in the temperature range from AFM images. The dependence of the structure and ferroelectric properties of BNdT on repetition frequency of laser shot were found to be large. The $2Pr$ value of BNdT films at deposited 3, 5, 7 and 10 Hz, are 30.3, 69.9, 47.9 and 38.4μC/cm^2, respectively. When applied pulses are 500 kHz bipolar square with electric field ranging from -250 to +250 kV/cm, good fatigue properties of BNdT films deposited at 5 Hz have been obtained up to 10^{10} cycles, where decrease in the value of $+Pr$ and $-Pr$ are less than 25 %. [1] T. Kojima et al, Appl. Phys. Lett. 80, 2746 (2002), [2] H. Uchida et al, Appl. Phys. Lett. 81, 2229 (2002), [3] Uong Chon et al, Phys. Rev. Lett. 89, 087601 (2002)

C11.40
Hydrothermally deposited thin films with vertically oriented columnar growth. Scott E. Solberg, Palo Alto Research Center, Palo Alto, California.

A novel growth mode for hydrothermal films of lead zirconium titanate (PZT) has been discovered. Previously reported hydrothermal PZT films have had a loosely-packed cubic morphology, and indeed that is the most common growth mode. However, under special growth conditions, with much more dilute reagent concentrations than previously reported, substantially vertically oriented, long rod-like grains may be grown. Metal-organic reagents such as lead acetate trihydrate, zirconium propoxide, and titanium isopropoxide were used along with potassium hydroxide mineralizer. The hydrothermal process involves simultaneous deposition and etching, and it is believed that the amorphous metal-organic components deposit, and are converted to inorganic oxides insoluble in the alkaline solution. Metal and metal-coated substrates with appropriate seed layers, such as lead titanate (PT) and PZT were used. The hydrothermal process does not require high deposition temperatures, for example 160 degrees C reactor temperature was used in these experiments. The unique vertical rod-like films may be useful in electrical devices such as capacitors.

C11.41
Energetic Mechanisms Operant During Pulsed Laser Deposition (PLD). Aaron Fleet[1], Darren Dale[2], H.H. Wang[1], Y. Suzuki[3] and J.D. Brock[1]; [1]School of Applied & Engineering Physics, Cornell University, Ithaca, New York; [2]Department of Materials Science & Engineering, Cornell University, Ithaca, New York; [3]Department of Materials Science & Engineering, UC Berkeley, Berkeley, California.

The plume of material ablated from a target in PLD contains a distribution of neutral, ionic, and polyatomic species, with energies of up to 100 eV. Previous growth studies have described the growing film according to standard statistical thermodynamics, and have interpreted experimental results in the context of well-known growth modes. Our group previously demonstrated the activation of energetic atomistic mechanisms during hyperthermal ion epitaxy [1]. For example, incident ions with energies near 20eV insert themselves near terrace edges during Cu homoepitaxy, given sufficient surface step-edge density. We are investigating whether similar processes occur during PLD of perovskite materials. While growing $EuTiO_3$ two-dimensionally on $SrTiO_3$, we diffract synchrotron x-rays off of the film, with ms time resolution. Differences in the transient x-ray intensity following laser pulses at varying surface coverage probe whether step edge density affects morphological evolution. In this talk, I will present experimental data on this issue. This work is

supported by the Cornell Center for Materials Research, under National Science Foundation Grant No. DMR-0079992, and uses facilities at the Cornell High Energy Synchrotron Source, NSF Grant No. DMR-9311772. [1]J.M. Pomeroy, A.J. Couture, M.V.R. Murty, E.N. Butler, and B.H. Cooper. Hyperthermal ion beam system for studying the effects of kinetic energy on thin-film growth. Review of Scientific Instruments, 73, 3846 (2002)

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

It is crucial to control grain boundaries for good lead zirconate titanate (PZT) thin films because the grain boundaries play a critical role in the degradation such as fatigue and high leakage current. We previously suggested selectively nucleated lateral crystallization (SNLC) of PZT thin film as a method of controlling grain boundaries. But this process needs additional high temperature annealing for PZT seed crystallization. We investigated selectively nucleated lateral crystallization (SNLC) of lead zirconate titanate (PZT) thin film using titanium(Ti) island seed layer. Ti island seed layer($\sim 50\AA$) was used to avoid additional high temperature annealing for crystallization of seed layer. Ti island seed layer was deposited on $Pt/SiO_2/Si$ by radio frequency magnetron sputtering and lift-off process at room temperature. The lateral crystallization of PZT thin film deposited on seeded substrate was completed after 570°C, 2hour furnace annealing. The maximum lateral growth length was 20um and lateral growth region had good ferroelectric properties. In this work, ferroelectric properties of PZT thin film crystallized by lateral crystallization will be shown and mechanism of lateral crystallization of PZT thin films will be discussed in detail through microstructure analysis.

C11.43
Laser Annealing of MOCVD Deposited Ferroelectric $SrBi_2Ta_2O_9$, $Pb(Zr_xTi_{1-x})O_3$ and $CeMnO_3$ Thin Films. Nick M Sbrockey[1], L. Gary Provost[1], Catherine E Rice[1], S Sun[1], Joseph D Cuchiaro[1], Gary S Tompa[1], Robert L DeLeon[2] and T. S Kalkur[3]; [1]Structured Materials Industries, Inc., Piscataway, New Jersey; [2]AMBP Tech Corporation, Amherst, New York; [3]University of Colorado, Colorado Springs, Colorado.

Thin films of ferroelectric oxides are being investigated for application in ferroelectric memory (FeRAM) devices. The advantages for these devices include high storage density, non-volatility and improved radiation hardness. However, many of these ceramic oxide films require high temperatures, to crystallize and to achieve optimum ferroelectric properties. For example, $SrBi_2Ta_2O_9$ films are typically post-deposition annealed at 750 C in an oxidizing environment. This step is not compatible with silicon CMOS fabrication. Integrating ferroelectric thin films with silicon based microelectronics requires development of low temperature ($\leq$ 550 C) processes. This study investigated laser annealing, as a low temperature alternative for processing of ferroelectric $SrBi_2Ta_2O_9$ (SBT), $Pb(Zr_xTi_{1-x})O_3$ (PZT) and $CeMnO_3$ (CMO) thin films. We used metal organic chemical vapor deposition (MOCVD) films of SBT, PZT and CMO, plus samples of sol-gel deposited SBT. All samples were prepared on silicon wafers with either platinum or iridium lower electrode layers. Laser annealing was done in air, using a KrF (wavelength = 248 nm) excimer laser, as a function of laser power and total number of laser pulses. Selected samples were alternatively furnace annealed, for comparison of results. The films were characterized by x-ray diffraction for crystallinity and texture and by wavelength dispersive electron microprobe analysis for composition. Capacitor structures were formed in the films to determine their electrical properties, including capacitance versus voltage (CV) and polarization versus electric field (PE) behavior. The results show SBT films can be easily crystallized by laser annealing. The resulting ferroelectric properties are highly dependent on composition and processing conditions. PZT and CMO films deposited by MOCVD in the temperature range of 500 C to 600 C were crystalline as deposited. Depending on the processing conditions, laser annealing could further improve crystallinity and ferroelectric properties without exposing the substrate to a high temperature processing step.

C11.44
Pyroelectricity in Quasi-Amorphous $BaTiO_3$ Thin Films. Yshay Feldman[1], Vera Lyahovitsky[1], Iliya Zon[1], Sidney Cohen[2], Ellen Wachtel[2], Alexander K. Taganstev[3] and Igor Lubomirsky[1]; [1]Materials & Interfaces, Weizmann Institute, Rehovot, Israel; [2]Research Support, Weizmann Institute, Rehovot, Israel; [3]Ceramics Laboratory, Ecole Polytechnique Federale De Lausanne, Lausanne, Switzerland.

Spontaneous or stress-induced polarization, signifying pyroelectricity and piezoelectricity respectively, can appear in ionic solids solely due to a non-centrosymmetrical spatial distribution of ions in a polar crystalline structure. We have investigated formation and properties of quasi-amorphous pyroelectric $BaTiO_3$ films. It has been found that amorphous $BaTiO_3$ films prepared by sputtering on bare Si do not crystallize if passed through a steep temperature gradient. Instead, they form an amorphous phase that demonstrates strong pyro- and piezo-electricity. Thus, this "quasi-amorphous" pyroelectric phase of $BaTiO_3$ represent a polar ionic solid without spatial periodicity inherent to ionic crystals. Sharp increase of the dielectric constant during the transformation of the amorphous into the quasi-amorphous films suggests that polarity of the quasi-amorphous $BaTiO_3$ is associated with directional ordering of crystal motifs formed in the steep temperature gradient. Once formed, quasi-amorphous phase remains stable with respect to heating up to 800 °C. As-deposited films crystallize into randomly oriented cubic $BaTiO_3$ if subjected to heating under isothermal conditions. The films deposited on a MgO seeding layer crystallize irrespective of the heating conditions. The development of high in-plane compressive stress and the decrease of the refractive index during the formation of the quasi-amorphous films suggested the existence of an intermediate low-density phase. Thermodynamic description based on this hypothesis quantitatively reproduces the data on thermal stability of the quasi-amorphous films. Furthermore, the hypothesis also explains the mechanism of formation of the pyroelectric phase. The ratio of pyroelectric coefficient/dielectric constant for quasi-amorphous $BaTiO_3$ is close to or surpasses that of $LiNbO_3$, making it very attractive for pyroelectric detector applications.

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

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

C11.46
Preparation and Characterization of Ba1-xSrxTiO3 Based Thin Films for Pyroelectric Applications. Clifford W Hubbard[1], M W Cole[1], P C Joshi[1], M Ervin[2] and M Wood[2]; [1]US Army Research Laboratory, APG, Maryland; [2]US ARMY RESEARCH LABORATORY, Adelphi, Maryland.

The use of pyroelectric thin films in uncooled IR detectors have many advantages over the present IR detector technology, which requires extensive cooling for operation. These include reduced weight, reduced footprint, reduced complexity, increased reliability, and decreased maintanance. Ba1-xSrxTiO3 (BST), both doped and undoped, based thin films are ideal candidates for use in these devices due to their tailorable materials properties. These properties include a high dielectric constant, low dielectric loss, high electrical resistivity, as well as a high pyroelectric constant. BST thin films were doped with Mg from 0 to 20mol%. The thin films were deposited via metalorganic solution deposition on Pt/Ti/SiO2/Si substrates. Annealing temperatures ranged from 500 to 7500C. The films were then characterized for structural, microstructural, compositional, surface morphological, dielectric and insulating properties. Glancing angle x-ray diffraction (GAXRD) was used to determine crystallinity, phase formation and film orientation. Field emission scanning electron microscopy (FESEM) and cross sectional transmission electron microscopy (TEM) were employed to access surface morphology, as well as plan- view and x-sectional grain formation. TEM was also used to detail film-substrate interface. The Materials Detectivity Figure of Merit (FOM), $D^*_{FOM}=(p_i)\div(C_V*(\epsilon_0*\epsilon_r*\tan\delta)\hat{1}/2)$,was used to evaluate the films detectivity response. Capacitance (Cp), dissipation factor (tan d) and dielectric permittivity (er) were measured with a HP4192A impedance/gain analyzer. Permittivity values ranged from 450 at 0% Mg to 205 at 20%Mg. Dissipation factor ranged from .01 at 0% to .007 for the 20% film. The films insulating properties, leakage current/film resistivity (IL/ r), were evaluated via I-V measurements using a HP4140B semiconductor test system. Pyroelectric currents were measured by the Byer and Roundy method.

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

Cuchiaro, G. Provost and G. Tompa; Structrured Materials Industries, Inc., Piscataway, New Jersey.

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

C11.48
Effect of the Substrate Temperature and Oxygen Partial Pressure on the Microstructural Evolution and Electric Properties of Charge-Balanced Barium Strontium Titanate Ferroelectric Thin Films Deposited on Ceramic Substrates by Pulsed Laser Deposition. Costas Fountzoulas[1], Daniel M Potrepka[2], Steven C Tidrow[2], Harry Efstathiadis[3] and Michael Hatzistergos[3]; [1]ARL, Aberdeen Proving Ground, Maryland; [2]ARL, Adelphi, Maryland; [3]The University at Albany-SUNY, Albany, New York.

Thin films, from novel B-site substituted barium strontium titanate (BST) bulk targets, have been deposited using the pulsed laser deposition (PLD) technique. The measured electrical properties of these thin films will be compared with the electrical properties of the bulk materials. In these materials, an applied electric-field can be used to change the dielectric constant of the material, hence, the phase velocity in RF/microwave devices can be tuned in real time for a particular application. The microstructure of the film influences the electronic properties that in turn influence the performance of the device. $Ba_{0.6}Sr_{0.4}Ti_{1-y}(A^{3+}, B^{5+})_yO_3$ thin films were synthesized at substrate temperatures ranging from 500 °C to 900 °C and oxygen partial pressure 20 and 50 mTorr, at 500 mJ laser fluency and 10 pulses per second on MgO (100) substrates, using the pulsed laser deposition technique. Initial shallow glazing angle x-ray diffraction (GAXRD) studies of the synthesized thin films have revealed a [100] preferred orientation. Analysis of the films microstructure deposited at 50 mTorr oxygen partial pressure by atomic force microscopy (AFM), shows increased number of cracks with increasing deposition temperature. The effect of the substrate temperature in conjunction with the effect of the oxygen partial pressure on the microstructure and mechanical properties of the thin films, as studied using x-ray diffraction, SEM, AFM, Rutherford backscattering, nanoindentation, will be discussed along with electrical properties. In addition, the film microstructure, interphase and crack nature, as studied using focused ion beam (FIB) method will be discussed.

C11.49
Hysteresis in Ferroelectric Domain Wall Dynamics in the Presence of Diffusing Impurities. Mikko Haataja[1], David J Srolovitz[1] and Yannis G Kevrekidis[2]; [1]Princeton Materials Institute and Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; [2]Department of Chemical Engineering, Princeton University, Princeton, New Jersey.

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

C11.50
Characterization Of Piezoelectricity Of (001) Oriented Ferroelectric Fresnoite Thin Films By AFM. Mankang Zhu[1,2], Wukun Dai[1], J.B. Xu[2], Yuedong Hou[1], Bo Wang[1] and Hui Yan[1]; [1]The Key Lab of Advanced Functional Materials of CHina Education Ministry, Beijing University of Technology, Beijing, China; [2]Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, China.

Fresnoite, $Ba_2TiSi_2O_8$,has been interested for its unique [TiO_5] square pyramid and layer structure. Recently, it was reported that fresnoite be a ferroelectric even its Curie temperature T_c may be over its melting temperature T_m. As a lead-free ferroelectric, its ferroelectric properties are of interest. However, few reports are available on the ferro/piezoelectricity with the domain structure for fresnoite crystal or thin films, and there is no direct observation on its ferroelectric domains. In the present study, (001) oriented fresnoite thin films have been prepared using sol-gel method. By using $Ba(Ac)_2$, $Ti(OC_4H_9)$ and $Si(OC_2H_5)$ as precursors, transparent sols with stoichiometric composition of fresnoite have been obtained and spin-coated onto $Pt/Ti/SiO_2/Si$ (100) substrates. To crystallize the thin films, all samples are post-treated at 750 ~ 850°C. FTIR spectra of the post- treated films show the signature of the isolated Si-O groups that is one of the characteristics of fresnoite. Meanwhile, the Raman spectra reveals the Ti-O vibration modes different from those in $BaTiO_3$. The XRD patterns of the thin films show two strong peaks at 17° and 34.2°, respectively, corresponding to the diffraction peaks of (001) and (002) of fresnoite, which means the C-axis orientation of the thin films. By using the piezoelectric mode AFM, the local piezoelectricity of the oriented fresnoite thin films has been characterized, presenting the domain distribution in the thin films. Besides, the ferroelectric properties of the oriented fresnoite thin films have benn studied, and the relation between the ferroelectric properties and the domain structures will be discussed.

C11.51
Formation of Stack-type PZT Capacitor for Next Generation FRAM using Rf Magnetron Sputtering Technique. Takehito Jimbo, Isao Kimura, Yutaka Nishioka and Koukou Suu; Institute for Semiconductor Technologies, ULVAC, Incorporated, Susono, Shizuoka, Japan.

Stack-type ferroelectric capacitor is expected to be FRAM cell in next generation. It is clear that thinner PZT film (~100 nm), electrode material and these stack are the key points for fabrication of next stack-type ferroelectric capacitor. While, sputtering method is brought to attention for its high stability, reproducibility and low running cost, and practically used for FRAM mass production. In this talk, fabrication and evaluation of stack-type PZT capacitor prepared by magnetron sputtering method are described. Pt/Ir system lower electrodes were deposited on thermally oxidized silicon wafers by dc magnetron sputtering. PZT thin films with around 100 nm were deposited on lower electrodes by rf magnetron sputtering at room temperature, and then annealed for crystallization by rapid thermal annealing (RTA) system (ULVAC Riko). Pt and/or IrOx films were used as top electrode. After formation of top electrodes, recovery annealing was conducted in oxygen under atmospheric pressure. As a type of result, well saturated Qtv characteristics with Qsw of about 20 $\mu C/cm^2$ at 3 V are derived in 100-nm-thick PZT capacitor

C11.52
Low Temperature Preparation by Pulsed Laser Deposition and Ferroelectric-Ferromagnetic Properties of $BiFeO_3$ Thin Films. Kwi-Young Yun[1], Minoru Noda[1], Masanori Okuyama[1], Hiromasa Saeki[2] and Hitoshi Tabata[2]; [1]System Inovation, Osaka University, Osaka, Japan; [2]ISIR, Osaka University, Osaka, Japan.

Bismuth iron oxide ($BiFeO_3$; BFO) with simple perovskite structure has attracted much attention as it shows coexistence of magnetic and ferroelectric ordering simultaneously. In this study, BFO thin films were prepared on platinized-silicon substrates in various oxygen pressures of 0.001-0.15 Torr at the temperature as low as 450°C by pulsed laser deposition (PLD), and ferroelectric and ferromagnetic characteristics of the films were confirmed by $P-E$ and $M-H$ hysteresis curves. The BFO thin films deposited at 0.01-0.1 Torr show good current density-applied voltage ($J-V$) characteristics. Leakage current density of the films decreases as the deposition pressure decreases and is 3.9×10^{-6} A/cm^2 for the film deposited at 0.05 Torr. Ferroelectric polarization-electric field ($P-E$) hysteresis curves of the BFO thin films were measured at room temperature (RT). The film deposited at 0.05 Torr shows well-saturated hysteresis characteristics, and twice remanent polarization ($2P_r$) and coercive field ($2E_c$) are 58 $\mu C/cm^2$ and 124 kV/cm for a maximum applied electric field of 114 kV/cm, respectively. The magnetization-magnetic field ($M-H$) hysteresis curve of the films measured at RT is declined as the deposition pressure decreases. BFO thin film deposited at 0.15 Torr exhibits saturated magnetic hysteresis characteristics, and $2M_r$, $2H_c$ are 0.8 emu/cm^3 and 300 Oe for a maximum magnetic field of 10 kOe, respectively.

C11.53
BiMnO3: A Multiferroic With Large Nonlinear Optical Response. Alok Sharan[1], Darell G Schlom[1,2] and Venkatraman

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Bismuth Manganite (BiMnO3), a simple perovskite structure, known to be multiferroic had been previously shown to be ferro-magnetic and a likely ferro-electric. The BiMnO3 films used were grown epitaxially on strontium titanate [111] substrate by pulsed laser deposition technique. We used optical second harmonic generated signal from such films as a probe and monitored its response to the change in its symmetry under the influence of externally electric field. This could be correlated to the rearrangement of its microstructure domains due to externally applied electric field, which strongly suggests it to be ferro-electric thus establishing it as a truly multi-ferroic. In this presentation we also show that it is also highly nonlinear optical material besides establishing its ferro-electricity. We have observed giant enhancement of the second harmonic signal by 3-4 orders of magnitude with d_{eff} ~16.5pm/V, under the influence of the electric field. Also we find that it has large third order optical nonlinearity as measured by single beam z-scan technique. The third order optical nonlinearity was measured by single beam z-scan technique. The nonlinear absorption coefficient was measured to be -0.1cm/kW. We used pulses from Ti: Sapphire mode-locked femto-second pulsed laser to measure both the second and third order nonlinear optical coefficients at 900nm. All this three properties viz. ferro-electricity, ferro-magnetism and optical nonlinearity - makes it a uniquely interesting material to study and promises to open up several new possibilities for various device applications.

C11.54
Characterization and Development of Wafer Bonded Single Crystal Thin Film $LiNbO_3$ for Waveguide Applications. Jennifer Lynn Ruglovsky, Youngbae Park, James Zahler and Harry Atwater; Applied Physics, California Institute of Technology, Pasadena, California.

Lithium niobate has been termed the 'silicon of nonlinear optics' owing to its several useful electro-optical properties, relevant for applications of modulators, switches, and waveguides. The ability to synthesize high quality single crystal $LiNbO_3$ in thin-film form could improve modulator device performance and integration possibilities by increasing modulation frequency and decreasing both device size and operating voltage. We have investigated the design of a $LiNbO_3/SiO_2/Si$ waveguide fabrication process. Beam propagation simulations were used to design a single mode waveguide of a 700nm thin film of $LiNbO_3$ on 1μm of SiO_2 on Si. Simulations show low propagation losses and mode confinement in the $LiNbO_3$. Using wafer bonding and ion implantation, we have transferred 700nm thin films of c-cut $LiNbO_3$ of approximately 100μm area onto oxidized Si substrates. Analysis via RBS and TEM shows that the transferred layer remains single crystal and stoichiometric. AFM indicates that the transferred $LiNbO_3$ surface rms roughness is 90$\AA$. We have fabricated 1cm transferred areas of bulk $LiNbO_3$ onto a 1μm thick layer of SiO_2 on a Si substrate. However, we have found that the ion implantation required for thin film layer transfer roughens the $LiNbO_3$ surface, complicating $LiNbO_3$ bond formation. Implantation with 115keV H at 8x10—*bsup—16—*esup—cm—*bsup—-2—*esup— and 175keV He at 5 x10—*bsup—16—*esup—cm—*bsup—-2—*esup— (yielding layer thickness of 700nm) the top surface of the $LiNbO_3$ increases roughness from 10$\AA$ to 79.6$\AA$. Approaches to $LiNbO_3$ roughness reduction include incorporating an intermediate layer between the $LiNbO_3$ and the substrate, growing a protective SiO_2 on $LiNbO_3$ bulk crystals before implant, as well as using a new substrate of a more compliant material, such as a rigid polymer. Each of these methods to improved large-area $LiNbO_3$ thin film fabrication will be assessed and compared. PFM measurements of $LiNbO_3$ polarization and planar waveguide loss measurements will be presented.

C11.55
Enhancement of Aurivillius Phase Formation Kinetics in SBT Thin Films using Nanoparticle Seeding. Yun-Mo Sung, Gopinathan M. Anilkumar, Woo-Chul Kwak, Se-Yon Jung and Seung-Joon Hwang; Materials Sci. & Eng., Daejin University, Pochun-koon, South Korea.

Sr0.7Bi2.4Ta2O9 (SBT) thin films were doposited on SBT nanoparticle (~60-80 nm) seeded Pt/Ti/SiO2/Si substrates via sol-gel and spin coating techniques. The SBT thin films were heated at 600C for 1 h to form the fluorite phase, and these fluorite films were further heated at 730-760C for fluorite-to-Aurivillius phase transformation. The volume fractions of Aurivillius phase formation obtained through quantitative x-ray diffraction analyses showed highly enhanced kinetics in seeded SBT thin films. Johnson-Mehl-Avrami (JMA) isothermal kinetics analyses were performed for the characterization of Aurivillius phase formation in unseeded and seeded SBT thin films using the volume fraction values. The Avrami exponents were determined as ~1.4 and ~0.9 for unseeded and seeded SBT films, respectivley, which reveals different nucleation modes. By using Arrhenius-type plots the activation energy values for the phase transformation of unseeded and seeded SBT thin films were determined to be ~264 and 168 kJ/mol, repsectively. This gives a key reason for the enhanced kinetics in seeded SBT thin films. Microstructural analyses on unseeded SBT thin films showed formation of randomly oriented needlike crystals, while those on seeded ones showed formation of clusters comprising directionally grown wormlike crystals. One the basis of the phase formation kinetics and microstructural development, a model representing different nucleation and crystal growth mechnaisms for the unseeded and seeded SBT thin films was proposed.

C11.56
Enhanced Figure-of-Merit Characteristics of PZT Thin Films for Uncooled Pyroelectric IR Sensors. Seung-Hyun Kim[1], Chang Young Koo[1], Jeong-Suong Yang[1], Euijoon Yoon[2], Jun-Shik Park[3] and Jowoong Ha[1]; [1]R&D Center, INOSTEK Inc., Ansan, Gyeonggi, South Korea; [2]School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; [3]NanoMechatronics Research Center, Korea Electronics Technology Institute, Pyung Taek, Gyeonggi, South Korea.

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

C11.57
Abstract Withdrawn

C11.58
First Prototype of High-Density Ferroelectric Data Storage System. Yoshiomi Hiranaga, Yasuo Cho and Yasuo Wagatsuma; Research Institute of Electrical Communication, Tohoku University, Sendai, Miyagi, Japan.

Scanning nonlinear dielectric microscopy (SNDM) is the purely electrical method for observing polarization distribution of ferroelectric materials with the resolution of sub-nanometer range. We have studied on ultra high-density ferroelectric data storage based on this microscopy, and reported that inverted domain dot array with areal density of 1.5 Tbit/inch^2 was successfully written in congruent $LiTaO_3$ (CLT) single crystal medium [1]. Although traditional SNDM domain engineering system, which is remodeled from commercial atomic force microscope unit, is useful for study on domain inversion characteristics in nanoscopic region, this system is inadequate to establish basic elemental technologies of high-density ferroelectric data storage, and a system equipped with all components necessary for actual read/write is required for further study aiming for practical application. Therefore, in this study, we developed the first prototype of high-density ferroelectric data storage system. The read/write head of the developed system is composed of a metal-coated conductive cantilever (typical tip radius is 25 nm) and an oscillator, which is tuned to the resonance frequency determined by the capacitance just under the tip of the cantilever and the inductance embedded in the circuit. Writing is performed by applying relatively large voltage pulse to a ferroelectric medium and locally switching the polarization direction at each point in the scan. On the other hand, reading is performed by detecting the small variation of resonance frequency caused by the capacitance variation due to the nonlinear dielectric response induced by alternating voltage applied to the medium. Firstly, we carried out a basic operation check using the developed system, and confirmed that bit data written in CLT single crystal medium is correctly read out. Subsequently, data transfer rate of this

system was evaluated. As a result, 9 kbps reading and 50 kbps writing were demonstrated with respect to 440 kbit/inch bit data array. Additionally, we also confirmed that direct bit overwriting could be realized using this system. [1] Y. Cho, K. Fujimoto, Y. Hiranaga, Y. Wagatsuma, A. Onoe, K. Terabe and K. Kitamura, Appl. Phys. Lett. 81, 4401 (2002).

C11.59

MOCVD and Electrical Properties of Hexagonal Yttrium Manganite Thin Films for Single Transistor Nonvolatile Ferroelectric Memories. J. J. Kingsley[1], David I Dalton[1], Klaus J Dimmler[1], Fred P Gnadinger[1], David G Klingensmith[1], Viorel Olariu[1], Ali J Mahmud[2], Mosiur Rahman[2] and T. S. Kalkur[2]; [1]COVA Technologies, Inc., Colorado Springs, Colorado; [2]Department of Electrical and Computer Engineering, University of Colorado at Colorado Springs, Colorado Springs, Colorado.

Hexagonal $YMnO_3$ perovskite is of interest due to its potential to be a ferroelectric material of choice for the next generation ferroelectric non-volatile memories based on single transistor cells (1T cell). Its low dielectric permittivity (about 20) and high Curie temperature (Tc > 600°C) are very suitable for achieving low operation voltages and CMOS process integration. In the present investigation, a Metal Organic Chemical Vapor Deposition (MOCVD) process was developed to deposit thin films of $YMnO_3$ on Silicon substrates and a detailed study was conducted on the relationship between the film properties and its deposition/ processing parameters. Formation of a c-axis oriented hexagonal phase of the $YMnO_3$ has been reported to be crucial for its ferroelectric performance. In the present study, it was found that while both the formation of the hexagonal phase of the $YMnO_3$ and its electrical properties depend on the film's composition and the annealing conditions the orientation of the film is profoundly influenced by the deposition parameters. The $YMnO_3$ films produced by the MOCVD process were examined using X-ray diffraction, TEM, HRTEM and EDS analysis. Its electrical properties were characterized using C-V, I-V hysteresis and pulsed-switching analysis. The results of this study along with the description of the MOCVD reactor used will be presented.

C11.60

Simulation of Phonon-Polariton Generation and Propagation in Bulk and Patterned Ferroelectric Crystals. David W Ward, Eric R Statz, Nikolay Stoyanov and Keith A Nelson; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We demonstrate a novel application of the auxiliary differential equation method of finite difference time domain ($(FD)^2TD$) simulation to describe propagation of phonon-polaritons (admixtures of polar lattice vibrations and electromagnetic waves) in ferroelectric crystals. Phonon-polariton generation by near-IR optical pump fields, phonon-polariton propagation, and phonon-polariton detection by near-IR probe pulses are simulated and compared to experimental measurements. Coupled ionic displacements and THz fields as well as phonon-polariton dispersion relations in bulk and thin film ferroelectrics are calculated. We also demonstrate simulations of phonon-polaritons in patterned ferroelectric materials and demonstrate their utility for design of patterned materials that can be fabricated using ultrafast laser machining. Additional avenues of exploration presented using this simulation approach include THz manipulation of ferroelectric domain switching, the use of electrically stressed ferroelectric domains as THz gain media, and the incorporation of quantum susceptibilities to simulate the interaction of phonon-polaritons with parabolic quantum wells and other quantal systems.