SYMPOSIUM Y

Ferroelectric Thin Films VIII

November 28 – December 2, 1999

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TUTORIAL

FTY: FERROELECTRIC THIN FILMS
Sunday, November 28, 1999
1:00 - 5:00 p.m.
Room 203 (H)

There has been a rapid rise in the extent of R&D activities leading to the integration of ferroelectric thin films in commercial devices. This tutorial covers the following topics:

- Introduction to material types, ferroelectric films, and a brief history of the field
- Applications of ferroelectric films, including recent commercial developments, and materials science issues. This section will be divided into the following categories:
  - Ferroelectric nonvolatile materials (device principles, material types, primary properties)
  - Ferroelectric films for DRAMs and other capacitor applications (device principles, materials needs, material types, physical properties, impact on capacitor performance, processing and composition effects, obstacles to Gbit integration)
  - Piezoelectric and pyroelectric applications
  - Miscellaneous applications
- Processing: summary of deposition methods and issues with emphasis on CSD, MOCVD, and PVD methods; application to PZT, SBT, and BST
- Integration issues: using nonvolatile memories and DRAMs as examples
- Outlook

Instructors:
Angus I. Kingon, North Carolina State University
Seshu B. Desu, University of Massachusetts-Amherst

SESSION Y1: BST THIN FILMS AND DRAM
Chairs: Scott R. Summerfelt and In Kyung Yoo
Monday Morning, November 29, 1999
Room 304 (H)

8:30 AM *Y1.1
CHEMICAL VAPOR DEPOSITION AND ELECTRODE TECHNOLOGIES FOR (Ba,Sr)TiO_3 CAPACITOR USED IN GIGA-BIT DRAM. Kazuhiro Eguchi, Katsuhiko Hieda, Masahiro Kiyotoshi, Tomonori Aoyama, Mitsuaki Izuha, Soichi Yamazaki, Syoko Niwa, Hiroshi Tomita, Kenro Nakamura, Yusuke Kohyama, Yutaka Ishibashi, Yoshiaki Fukuzumi, Tsunetoshi Arikado, Katsuya Okumura, Toshiba Corporation Semiconductor Company, Microelectronics Engineering Laboratory, Yokohama, JAPAN; Junya Nakahira, Masaaki Nakabayashi, Jun Lin, Akihiro Shimada, Fujitsu Limited, Semiconductor Group, Technology Development Division, Mie-ken, JAPAN; Kohji Tsunoda, Fujitsu Laboratories Limited, Atsugi, JAPAN.

(Ba,Sr)TiO_3 (BST) is a promising candidate for the cell capacitor in gigabit generations (0.10 - 0.13μm design rule) of dynamic random access memory (DRAM). There are many issues to be solved for application of BST in DRAM cell capacitor. In this talk, two important issues among them, i.e. chemical vapor deposition (CVD) of BST film and electrodes technology, are discussed. The requirements for deposition method of BST are good step coverage and good electrical characteristics (low leakage current and high permittivity). The low temperature CVD around 400°C is required to obtain conformal coverage of BST. However, the electrical characteristics of BST films deposited at low temperature are not so good because of carbon and hydrogen incorporation. To solve this problem, we proposed In-situ Multi-Step deposition (IMS), which is a repetition of low temperature deposition of ultra thin BST film (<10nm) and high temperature annealing (~650°C). By using IMS process, we improve electrical characteristics with conformal step coverage. An electrode material selection is also important issue to obtain good electrical characteristics of BST capacitor. We have been proposed All PErovskite Capacitor (APEC) technology, in which $SrRuO_3$ (SRO) films are used as both top and bottom electrodes of BST capacitor. SRO electrode has several advantages compared with a novel metal electrode (Pt, Ru, etc.), i. e., lower leakage current, higher reliability, and higher resistance against H_2 anneal. Moreover, during CVD of BST on SRO, SRO reveals good adhesion with underlying layer and BST easily crystallize on SRO, because SRO and BST have the same crystal structure and the lattice parameter of SRO is very close to that of BST. By combination of IMS process and APEC technology, we achieved low leakage current of ~10^{-7}A/cm^2, high permittivity of 350, and good step coverage over 90% in the 0.2μm concave storage node structure (hole pattern) with the aspect ratio of 2.5, simultaneously.

9:00 AM Y1.2
PRECURSOR CHEMISTRY AND FILM-FORMATION MECHANISMS IN MOCVD GROWTH OF (Ba,Sr)TiO_3 THIN FILMS. Y. Gao, M. Henderson, S. He, T. Tran, and M. Engelhard, Pacific Northwest National Laboratory, Richland, WA; P. Alluri, Materials Technologies Laboratories, Motorola Inc., Austin, TX.

Precursor reaction kinetics, film-formation mechanisms, and their effects on step coverage of MOCVD (Ba,Sr)TiO_3 (BST) thin films have been studied using isotopic oxygen and diketonate-based precursors both in an UHV surface science study and in typical MOCVD processing. The surface science approach was used to determine precursor reaction pathways, ligand substitution, specific bond cleavage in the precursors, and sticking coefficients of the reactive species. The isotopic labeling experiments under the typical MOCVD conditions revealed two film-formation reactions: oxidation and thermal decomposition of the precursor molecules. For example, about two thirds of M-O bonds in the original precursors are preserved in the BST films grown at 700°C in O_2. However, more precursor molecules are oxidized by O_2 at 625°C, indicating that the ligand substitution by O_2 plays an important role in the film-formations at lower temperatures. This is presumably due to a decrease in thermal decomposition rate of the precursors as decreasing the growth temperatures. A much improved understanding of the film-formation mechanisms and kinetics in the MOCVD processing has been achieved by linking the precursor chemistry and kinetics obtained from the surface science study to the film-formation reactions and growth rate observed in the MOCVD growth of BST thin films. These results were found to be very useful to understand the step coverage of BST thin films on 3D Pt and Ir electrodes, which varies from ~60% to >85% for the diketonate-based precursors with different ligands and/or adducts or under different growth conditions.

9:15 AM Y1.3
MOCVD OF (Ba,Sr)TiO3 USING SINGLE SOURCE OF Ba(methd)2,Sr(methd)2, AND Ti(mpd)(thd)2 IN A NEW WARM WALL REACTOR FOR LARGER WAFER PROCESS. DooYoung Yang, Cheol-Hoon Yang, Young-Ki Han, and Chul-Ju Hwang, JuSung Engineering Co., Kyunggi-Do, Korea Cheol Seong Hwang and Jaehoo Park, School of Material Science and Engineering, Seoul National University, Seoul, SOUTH KOREA.

New metal organic precursors of Ba(methd)2 (methd=methoxyethoxy-tetramethylheptanedionate), Sr(methd)2, and Ti(mpd)(thd)2 (mpd=methylpentanediol, thd=tetramethylheptanedionate) were dissolved in methanol and made into a single mixed source. The liquid source was supplied through a liquid mass flow controller and vaporizer to an unprecedented warm wall type CVD reactor in which the source vapor and oxidant gases are pre-heated and reacted on a 8 inch substrate. The source vapor and the oxidant gas were not introduced through the conventional showerhead type injector to simplify the condensation, decomposition, and premature reaction control of precursors. The kinetic study of the BST CVD process with the new source shows that the surface reaction-controlled regime can be maintained up to 500C and Titanium incorporation increases ubruptly when mass trasport-controlled regime starts. BST thin films with 15 to 30 nm thickness were deposited in the surface reaction-limited regime to ensure better step coverage. The uniformities of BST thickness and composition across 8 inch wafer were able to be well maintained by adjusting the relative heights of the gas injector and the substrate position without showerhead within the tolerance of the mass production. The wafer to wafer repeatibility and the the long lifetime of the MOCVD system are attributable to the single source and hence the simplest design of the single LDS(Liquid Delivery System).

9:30 AM Y1.4
PREPARATION OF Ru THIN FILMS BY CHEMICAL VAPOR DEPOSITION USING A LIQUID Ru(EtCp)$_2$ SOURCE. Yuichi Matsui, Masahiko Hiratani, Yasuhiro Shimamoto, Shinichiro Kimura, Hitachi, Ltd, Central Research Laboratory, Tokyo, JAPAN; Toshihide Nabatame, Hitachi, Ltd, Hitachi Research Laboratory, Ibaraki, JAPAN.

Ruthenium (Ru) thin films were regarded as promising for use as

electrodes for (Ba,Sr)TiO_3 [BST] capacitors in Gbit-scale dynamic random access memories (DRAMs). In Gbit-scale DRAMs, a three-dimensional capacitor is required even if high-dielectric oxides are applied. Therefore, a chemical vapor deposition (CVD) method having excellent step coverage will be necessary to fabricate a Ru electrode. In this paper, we report on a Ru thin film that was successfully fabricated using a liquid bis-ethylcyclopentadienyl ruthenium [$Ru(EtCp)_2$] precursor with the bubbling transfer method. The $Ru(EtCp)_2$ precursor was vaporized at 50°C; at that temperature the vapor pressure was about 0.02 Torr. Argon gas was used as a transfer carrier of the precursor, and a reactive oxygen gas was mixed with the carrier gas just before the reaction chamber. The total pressure was kept at 0.5 Torr. The deposition temperature and the oxygen partial pressure were varied from 220°C to 350°C and from 1.3% to 25%, respectively. The deposition rate rose, and the amount of residual carbon fell, as the oxygen partial pressure and the deposition temperature increased. This was because the precursor became more oxidized and dissociated more easily. Under the low oxygen partial pressure (1.3%), increasing the deposition temperature enhanced the crystallization of the Ru metal film. On the contrary, under the high oxygen partial pressure (25%), the crystallinity was degraded as the deposition temperature rose, because the oxygen ions contaminated the Ru film. The Ru films deposited at low temperatures (below 230°C) showed excellent step coverage of almost 100%. The electrical properties of a BST capacitor with a CVD-Ru bottom electrode were as good as those of one with a sputter-deposited electrode. Thus, we consider the CVD-Ru film to be suitable for use as the bottom electrode of BST capacitors.

9:45 AM Y1.5
IN-SITU STUDIES OF CARBON CONTAMINATION AT $Ba_{1-x}Sr_xTiO_3$ AND Pt FILM SURFACES AND ITS EFFECT ON THE ELECTRICAL PROPERTIES OF BST CAPACITORS. J. Im,[1], O. Auciello,[1], A.R. Krauss,[2], S.K. Streiffer[1]. [1]Materials Science Division, Argonne National Laboratory, Argonne, IL, [2]Material Science and Chemistry Division, Argonne National Laboratory, Argonne, IL.

It has been speculated that C / H containing species at the film-electrode interfaces of BST capacitors may contribute to the BST thickness dependence of the leakage currents and permittivity. However, no direct evidence of the degree to which this contamination affects capacitor performance or the conditions under which it can be eliminated has been presented. Therefore, we have investigated surfaces of Pt and $Ba_{1-x}Sr_xTiO_3$ (BST) films using the highly surface sensitive mass spectroscopy of recoiled ions (MSRI) technique. Specifically, hydrogen- and carbon-containing species on Pt and BST surfaces were monitored under typical processing conditions used to fabricate BST capacitors by magnetron sputter-deposition. MSRI analysis of the surface of Pt films deposited on Si substrates, heated at 500°C in vacuum (10^{-7} Torr), show an increase in the C signal concurrently with the disappearance of the Pt peak, indicating total coverage of the Pt surface by C, probably due to hydrocarbon cracking on the surface. On the contrary, complete removal of hydrogen and carbon from the Pt surface occurs during heating in 10^{-3} Torr of oxygen at 200°C. For BST films, carbon contamination was present during heating up to 700°C in vacuum of 10^{-7} Torr to 5 x 10^{-4} Torr of oxygen, and it was only removed by heating at 500°C in 10^{-3} Torr of oxygen. These results imply that under typical deposition conditions, the top Pt electrode-BST film interface is contaminated with carbon, while the bottom Pt electrode-BST film interface is carbon-free. These results may explain why post-deposition annealing in oxygen or air to 500°C is required to minimize leakage current and dielectric loss in BST capacitors. The impact of carbon contamination on the electrical properties of BST film capacitors fabricated under the typical and optimized conditions found by MSRI will be discussed. *Work supported by the U.S. Department of Energy, BES-Material Sciences, under Contract W-31-109-ENG-38, and by the DARPA-FAME Program.

10:30 AM *Y1.6
INTEGRATION ISSUES OF (Ba,Sr)TiO_3 (BST) THIN FILMS IN HIGH DENSITY DRAM DEVICES. Cha-Young Yoo,Hong-Bae Park, Doo-Sup Hwang, Hideki Hori, Wan-Don Kim, Jin-Won Kim, Sang-Don Nam, Seok-Jun Won, Chang-Seok Kang, Young-Wook Park, Sang-In Lee, Moon-Yong Lee, Samsung Electronics Ltd, Yong-In, KOREA.

(Ba,Sr)TiO_3 (BST) thin film has been paid much attention as the promising candidate for capacitor dielectric material for Gbit DRAMs due to its high dielectric constant. There are, however, several problems to be overcome in order to apply the BST thin films to the real device. Recent progress will be shown in this presentation. Most of them result from the noble metal electrodes which are required for the BST thin films. First, barrier metal is needed to prevent the reaction between the electrode and poly-Si plug. It must have oxidation-resistant properties because post-annealing at high temperature under atmosphere containing oxygen is preferred in order to enhance the leakage current. Ternary barrier metal is evaluated and proved to be superior to TiN barrier. Making 3-D structure of bottom electrode is the other challenge. Noble metal, especially Pt is very difficult to etch. It has been throught that Pt stack capacitor over 0.5μ thick is impossible to make. We applied the electroplating process to make Pt stack, and were able to make the stack Pt capacitor successfully. Also, concave-shape Pt electrode is developde by the simple etch-back process. We conclude that 3-D structure capacitor can be made with both Pt and Ru. Besides the problems related to the electrode, MOCVD BST film must deposit uniformly on the bottom electrode which have complex 3-D structure to obtain sufficient capacitance. Its composition must also be same over the entire area of bottom electrode. We developed low temperature deposition process below 420°C. Because the deposition temperature is low, deposited BST film is amorphous and have to be annealed in O_2 atmosphere to crystallize. Toxeq of $3.5\AA$ could be achieved by deposition and annealing process. We also confirmed that deposited BST film in concave structure have the same electrical properties as the planar structure. It means that its composition as well as the thickness of deposited BST film is uniform. In conclusion, we have developed the MOCVD BST process, the barrier metal and 3-D structure of Pt electrode and could give solutions to apply the BST films to real devices.

11:00 AM Y1.7
INTEGRATION OF BSTO STACKED CAPACITOR FOR GIGABIT-SCALE DRAM APPLICATION. H. Shen, D. Kotecki, S. Athavale, M. Gutsche, J. Lian, G. Kunkel, L, Economicos, F. Jamin, R. Wise, S. Mathad , G. Kaplita, Y. Wang, R. Laibowitz, K. Saenger, T. Shaw, Infineon Technologies, Inc, Hopewell Junction, NY.

A new stacked capacitor structure using BSTO (barium strontium titanate) as the dielectric material has been developed for gigabit-scale DRAMs. Pt bottom electrode is deposited by PVD and patterned by RIE process. It is shown that it is possible to achieve almost vertical angle of bottom Pt electrode at small feature size. It is also shown that barrier materials are capable of preventing both diffusion and oxidation. Further more, the BSTO film deposited by MOCVD process shows good composition and thickness uniformity and good comformality. SEM, TEM and electrical results including capacitance and leakage are presented.

11:15 AM Y1.8
UNIVERSAL DYNAMIC RESPONSE OF THE POLARIZATION CURRENTS AND A.C. CONDUCTIVITY IN PEROVSKITE-TYPE TITANATES. J.D. Baniecki, Columbia Univ., New York, NY, and IBM Research, Yorktown Heights, NY; R.B. Laibowitz, T.M. Shaw, IBM Research, Yorktown Heights, NY; Q.Y. Ma, Columbia Univ., New York, NY.

Perovskite-type titanate dielectrics, such as Barium Strontium Titanate (BSTO), are being actively considered as replacements for the conventional silicon oxynitride dielectrics in DRAM capacitors and for tunable microwave devices. Characterizing the dynamic response of BSTO and understanding the factors which control dielectric relaxation and loss is crucial for device applications. The dynamic response of perovskite-type titanate thin films is generally regarded as being different from their bulk and single crystal counterparts; thin films fully depleted of free charge carriers exhibit dielectric relaxation currents which follow a power-law time dependence (Curie-von Schweidler law), while bulk ceramics and single crystals show a Maxwell-Wagner type relaxation. In the talk, we present measurements of the dynamic response of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films, bulk ceramics, and $SrTiO_3$ single crystals over a very wide range of temperature (4.2-633K). This approach allows us to distinguish between dielectric relaxation contributions from the bulk lattice, grain boundaries, and electrode interfaces. Our results show that after removal of Maxwell-Wagner polarization, and independent of the particular microstructure or thickness, perovskite-type titanate capacitors exhibit a common dynamic response with the polarization currents and a.c. conductivity following power-laws. Possible mechanisms for this "universal" behavior and the implications of such behavior occurring in bulk polycrystalline as well as single crystal perovskite-type titanates on relaxation mechanisms in thin films will be discussed. The influence of low oxygen partial pressure anneals (vacuum and forming gas) on the magnitude of the power-law dispersion in both thin film and bulk samples will also be presented.

11:30 AM Y1.9
RESISTANCE DEGRADATION IN BARIUM STRONTIUM TITANATE THIN FILMS. Sufi Zafar, Peir Chu, B. Hradsky, D. Gentile, R.E. Jones and S. Gillespie, Motorola, Matls Technology Laboratory, Austin, TX.

Experimental and modeling results for resistance degradation in barium strontium titanate (BST) thin film capacitors with platinum (Pt) electrodes are reported. The main experimental results are as

follows. Under a constant applied voltage, the current density is observed to increase with time until it reaches a maximum value. Once the maximum value is reached, the current density becomes constant with time. The barrier height at the BST/Pt (cathode) interface is observed to decrease after prolonged electrical stressing. The resistance degradation effect is observed to be reversible, particularly at elevated temperatures. Based on the experimental results, a quantitative model for resistance degradation is proposed. In this model, the increase in the current density is attributed to a decrease in the barrier height at the cathode and this decrease is assumed to have stretched exponential dependence on time. Using experimentally determined parameters, the model calculates the current density as a function of time at various temperatures. The calculated results are verified and the model is shown to be self-consistent. Hence the model provides an accelerated method for determining the lifetime of thin BST films at the operating conditions for advanced memory applications.

11:45 AM Y1.10
INTERFACE PROPERTIES BETWEEN $SrTiO_3$ THIN FILMS AND ELECTRODES. Anna M. Clark, Jianhua Hao, Weidong Si, and X.X. Xi, The Pennsylvania State University, Department of Physics, University Park, PA.

$SrTiO_3$ (STO) thin films were grown by pulsed laser deposition on $LaAlO_3$ substrates with a $SrRuO_3$ buffer layer, which also serves as a bottom electrode. Measurements of the low frequency dielectric properties were performed in a parallel plate capacitor configuration for a range of temperatures using different top electrode materials. The contribution to the interfacial potential from Schottky barriers was investigated. In comparison to STO single crystals, thin films have continued dielectric non-linearity above T$\sim$70K. This complicates conventional Schottky barrier height measurements using C-V curves because both Schottky barriers and dielectric non-linearity result in a decrease in dielectric constant under applied electric fields. However, by using I-V data, difficulties related to field dependence of the dielectric constant may be removed. Barrier height measurements for both metal and oxide electrodes were performed for T>70K.

SESSION Y2: FUNDAMENTAL PROPERTIES OF THIN-FILM FERROELECTRICS
Chairs: Angus I. Kingon and Paul C. McIntyre
Monday Afternoon, November 29, 1999
Room 304 (H)

1:30 PM *Y2.1
THE DEVELOPMENT OF MICROSTRUCTURE IN THIN FILMS OF BARIUM STRONTIUM TITANATE GROWN BY MOCVD AND ITS EFFECT ON THEIR ELECTRICAL PROPERTIES. T.M. Shaw, R.B. Laibowitz, K.L. Saenger, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY; J.D. Baniecki, S-W. Chan Columbia University, NY; D.E. Kotecki, IBM Microelectronics Division, Hopewell Junction, NY; H. Shen, J. Lian Infineon Technologies, Hopewell Junction, NY.

Barium Strontium Titanate (BSTO) films grown by MOCVD deposition are currently being evaluated for use as an alternative dielectric in DRAM capacitors. Under typical growth conditions the films have a fine grain structure (15-20nm) and thus contain a high density of grain boundaries. Also films with different grain orientations can be produced under different deposition conditions. It is therefore important to understand the influence, if any, grain boundaries and film texture have on the leakage and dielectric properties of BSTO films. In the talk I will present observations of how the grain structure develops during growth of MOCVD films. The results show that in the early stage of film deposition the film often consists of multiple grain orientations that have no crystallographic orientation relationship with the underlying Pt electrode. In the later stages of growth often a single texture dominates and grains grow with a columnar morphology. The effects of texture and grain structure on the leakage and dielectric properties of thin BSTO films will be presented.

2:00 PM Y2.2
EFFECTS OF GRAIN BOUNDARY ON THE FERROELECTRIC PROPERTIES OF SELECTIVELY GROWN PZT THIN FILMS. Jang-Sik Lee, Eung-Chul Park, Jung-Ho Park, Byung-Il Lee and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

It is generally accepted that the grain boundaries of oxide films are mainly responsible for poorness in electrical performance and the PZT thin films are no exception. In this study, PZT thin films were prepared on Pt substrate using crystallized PZT dots as a seed for formation of large grained PZT thin films through lateral growth. It has been found that about 40μm sized PZT single grains can be obtained after annealing at 600°C for 2 hours. Effects of the grain boundary on the electrical properties of thus obtained PZT thin films were investigated by locating the upper Pt electrode of about 8μm in a diameter right on the grain boundaries in a controlled manner. It turned out that when there was no grain boundary, the best ferroelectric and electrical performance could be obtained as expected. P_r(remanent polarization)=30μC/cm^2, J_L(leakage current density)=1×10^{-7}A/cm^2 at 5V and E_{BD}(breakdown field)=1.24MV/cm. When one-grain boundary was contained in the area measured, P_r=21μC/cm^2, $J_L=2.35\times10^{-6}$A/cm^2 at 5V and E_{BD}=0.785MV/cm and when four-grain boundaries were contained in the area measured, P_r=11μC/cm^2, $J_L=9.76\times10^{-3}$A/cm^2 at 5V and E_{BD}=0.64MV/cm. More drastic change could be observed in fatigue test. No appreciable degradation in the ferroelectric performance could be observed in grain boundary free PZT films up to 2×10^{11} cycles at 1MHz. However serious degradation could be observed at 4.4×10^6 cycles when one-grain boundary was contained and at 1.4×10^4 cycles when four-grain boundaries were contained in the area measured at 1kHz. This is the first qualitative investigation about the effect of the grain boundary on the ferroelectric performance of PZT thin films and the microstructure of the laterally grown single PZT grain as well as the growth mechanism will be introduced in the discussion.

2:15 PM Y2.3
OBSERVATIONS OF DOMAIN STRUCTURE AT INTIAL GROWTH STAGE OF $PbTiO_3$ AND $Pb(Zr,Ti)O_3$ THIN FILMS GROWN BY MOCVD. H. Fujisawa, K. Morimoto, M. Shimizu and H. Niu, Himeji Institute of Technology, Department of Electronics, Himeji, JAPAN; K. Honda and S. Ohtani, Fujitsu Laboratory Ltd, Atsugi, JAPAN.

Domain structure and growth mechanism of $PbTiO_3$(PTO) and $Pb(Zr,Ti)O_3$ films were investigated using an atomic force microscope(AFM) and a transmission electron microscope (TEM) from the viewpoint of size effects. PTO and PZT thin films were prepared on a (111)$Pt/SiO_2/Si$ substrate by metalorganic chemical vapor deposition (MOCVD). At initial growth stage of (111)-oriented PTO films, triangle-shaped islands were observed by AFM. Triangle-shaped islands grew gradually in a lateral dimension. The height of them was approximately 20nm and did not changed through the growth. This result indicates that PTO films grew two-dimensionally at initial growth stage. From cross-sectional TEM observations, domain walls were observed in some PTO islands. These domain walls were dependent on the size of islands and the minimum island which had domain walls was 20nm high and 40nm length. This means that island-shaped PTO nuclei had spontaneous polarization. Observation of domain structure of PZT islands will also be reported.

2:30 PM Y2.4
SCANNING PROBE MICROSCOPY STUDIES OF DOMAIN DYNAMICS IN EPITAXIAL THIN FILMS OF $Pb(Zr_{0.3}Ti_{0.7})O_3$. K. Ghosh, S.K. Streiffer, O. Auciello, G.R. Bai, Materials Science Division, Argonne National Laboratory, Argonne, IL; Q. Gan, C.B. Eom, Dept. of Mechanical Eng. and Materials Science, Duke University, Durham, NC; C. Thompson, Materials Science Division, Argonne National Laboratory, Argonne, IL and Department of Physics, Northern Illinois University, DeKalb, IL.

Most previous applications of scanning probe microscopy (SPM) techniques elucidating domain structure and evolution in ferroelectric thin films, have been performed on polycrystalline and textured films. We present recent results of our piezoresponse SPM studies of domain statics and dynamics in very high crystal quality, epitaxial thin (40-200nm) films of $Pb(Zr_{0.3}Ti_{0.7})O_3$(PZT). The films were deposited by metal organic chemical vapor deposition (MOCVD) on substrates consisting of epitaxial layers of $SrRuO_3$ sputter deposited on $SrTiO_3$ substrates. Piezoresponse images of the virgin domain structure in these samples indicate a strongly preferred polarization direction over macroscopic distances, corresponding to a natively poled state. These observations are consistent with conventional electric measurements on the films, which reveal that the polarization hysteresis loops are also imprinted. In contrast to sputtered films where similar effects have been observed, both poled states have been found to occur in different specimens. The size and polarization retention characteristics of domains switched using the SPM tip as one electrode, have been investigated as a function of the pulse voltage and time. We attribute at least some component of domain decay with time to poor polarization saturation of regions switched far from the tip and thus at lower field
This work is supported by U.S. Department of Energy, Basic Energy Sciences - Materials Science under contract W-31-109-ENG-38, State of Illinois under HECA, David & Lucile Packard Fellowship, and NSF Young Investigator Award.

2:45 PM Y2.5
CHARACTERIZATION OF FERROELECTRIC $BaTiO_3$ (100)

SURFACE BY VARIABLE TEMPERATURE SCANNING SURFACE POTENTIAL MICROSCOPY. Sergei V. Kalinin, Dawn A. Bonnell, The Univ. of Pennsylvania, Dept. of Mat. Sci. Philadelphia, PA.

Properties of the thin-film and nanocrystalline ferroelectric materials are long known to be different from that of the bulk crystals due to the significant contribution of surface layers to the overall properties of material. In the present research we applied variable temperature scanning surface potential microscopy (SSPM) together with intermittent mode AFM for the characterization of model $BaTiO_3$ (100) surface. The influence of domain structure of the sample on surface topography and surface potential distribution is discussed. Dependence of apparent surface potential of the tip-sample separation in the SSPM was used to quantify the details of contrast formation in the SSPM on ferroelectric surface. The potential contrast formation mechanism is briefly discussed and surface domain structure consistent with experimental observation is proposed. The domain induced surface corrugations were found to disappear above the Curie temperature in full agreement with theoretical expectations. Relaxation of apparent surface potential after the transition to paraelectric state on heating and during the transition to ferroelectric state on cooling was observed. The kinetics of potential relaxation was quantified and compared with existing models of relaxation mechanisms.

3:30 PM Y2.6
NEAR-FIELD SECOND HARMONIC MICROSCOPY OF THIN FERROELECTRIC FILMS. I.I. Smolyaninov, H.Y. Liang, C.H. Lee, C.C. Davis, Electrical and Computer Engineering Department, University of Maryland, College Park, MD; L.D. Rotter, D.L. Kaiser, NIST, Gaithersburg, MD.

Near-field second harmonic microscopy [1] is ideally suited for studies of local nonlinearity and poling of ferroelectric materials at the microscopic level. Its main advantages in comparison with the other scanning probe techniques are the possibility of fast time-resolved measurements, and substantially smaller perturbation of the sample under investigation caused by the optical probe. We report second harmonic imaging of the surface of thin $BaTiO_3$ films obtained in a near-field microscopy setup using a Ti:sapphire laser system consisting of an oscillator and a regenerative amplifier operating at 810 nm. Optical resolution on the order of 80 nm has been achieved. Switching between P- and S- polarized excitation light leads to substantial changes in the near-field second harmonic images. This allows us to analyze the local poling direction of individual submicrometer size crystalline grains of the film.
[1] I.I. Smolyaninov *et al.*, Appl. Phys. Lett. 74, 1942 (1999)

3:45 PM *Y2.7
FREQUENCY DEPENDENCE OF THE COERCIVE VOLTAGE OF FERROELECTRIC THIN FILMS. Rainer Waser, IFF, Research Center Juelich, GERMANY; Stephan Tiedke, aixACCT Systems, Aachen, GERMANY; Oliver Lohse, Ulrich Boettger, IWE II, RWTH University of Technology Aachen, GERMANY.

Recent progress in the measuring techniques based on a combination of a quasistatic P-V analysis, conventional dynamic hysteresis measurements, and fast pulse characterization allow to determine the coercive voltage as a function of the frequency over a range of more than seven orders of magnitude. In this review, we explain the experimental techniques and present the results for the competitive thin film systems of SBT and PZT.Theoretical models of the correlation between the ferroelectric relaxation and the coercive voltage is discussed in the light of the new data.

4:15 PM Y2.8
TEMPERATURE DEPENDENCE OF THE REVERSIBLE AND IRREVERSIBLE POLARIZATION CONTRIBUTIONS IN FERROELECTRIC THIN FILMS. D. Bolten, M. Grossmann, O. Lohse, IWE II, RWTH Aachen University of Technology, GERMANY; R. Waser, IFF, Research Center Juelich, GERMANY.

The origin of the ferroelectric hysteresis is the existence of irreversible polarization processes, the nature of which is still subject to debate. A detailed knowledge of the polarization processes in ferroelectric materials, however, is of special interest for the development of non-volatile ferroelectric memory devices (FeRAMs). Mainly two conceivable mechanisms for irreversible processes exist. First, lattice defects which interact with the domain wall and hinder it from returning into its initial position. Second, the nucleation and growth of new domains. Reversible contributions in ferroelectrics are due to ionic and electronic displacements and to domain wall motions with a small amplitude. The reorientation of defect dipoles and charged defects or free charges also contributes to the total polarization. In this paper the temperature dependence of reversible and irreversible polarization contributions in the temperature range between 223 K and 473 K is investigated to elucidate the microscopic mechanisms responsible for reversible and irreversible changes in the ferroelectric polarization. Small signal capacitance measurements under dc-bias are used to measure the reversible contributions. Quasi-static hysteresis measurements are used to obtain the total polarization, i.e. the sum of the reversible and irreversible contributions. The combination of both measurements allows the separation of the reversible and irreversible parts. Measurements of Rayleigh loops which allow a direct separation of the reversible and irreversible parts in the sub-coercive regime were carried out to supplement the information obtained by the other measurements. The reversible and irreversible contributions are demonstrated for $SrBi_2Ta_2O_9$ (SBT) thin films and compared to tetragonal $Pb(Zr,Ti)O_3$ (PZT) thin film capacitors.

4:30 PM Y2.9
ACTIVATION FIELD IN PLZT FERROELECTRIC THIN FILMS. I.-Wei Chen, University of Pennsylvania, Department of Materials Science and Engineering, Philadelphia, PA.

Coercive field in ferroelectrics is often frequency dependent, reflecting the underlying kinetics of domain wall movement. We have found that Merz equation adequately describes the coercive fields and their frequency dependence in several PLZT films that show very different ferroelectric characteristics and fatigue tendencies. A particularly important feature of our data is that they point to a universal prefactor in the Merz equation. This prefactor corresponds to the vibration frequency of domain walls. The Merz equation is then left with only one parameter, the so-called activation field, and this parameter can be used to uniquely specify the coercive state of the ferroelectric, fresh or fatigued. A constitutive equation can thus be obtained to describe the fatigue damage of ferroelectric thin films. A further examination of the Merz equation also suggests that the dielectric degradation at the electrode/ferroelectric interface, which raises the depolarization energy and hence the activation field, is the source of fatigue in Pt/PLZT/Pt thin films.

4:45 PM Y2.10
REVERSIBLE AND SWITCHING PARTS OF POLARIZATION IN PZT FILMS. Vladimir Petrovsky, Harlan U.Anderson, Tatiana Petrovsky, University Missouri-Rolla, EMARC, Rolla, MO; Alexander Grishin, Royal Institute of Technology, Dept of Condensed Matter Phys, Stockholm, SWEDEN.

Ferroelectric thin film are of interest for use in nonvolative memory chips because the polarisation can be switched by an electric field thereby making it possible to store information over extended periods without the need for sustaining fields. The switching of the polarisation is the common method for information readout. However, nondestractive readout without the switching the polarisation is certainly of great interest. Previously, we analyzed different ways of accomplishing nondestractive readout. This report expands on our early work by making a more detailed investigation of the behavior of PZT films in electrical fields. A special pulsing technique was developed to separate the reversible and switching parts of the polarization, that gives us the possibility of obtaining more information about the behavior the ferroelectrics in the electrical field, than from the standart Sawyer-Tower technique. Laser ablation, sol-gel and polymeric precursor techniques were used to prepare the PZT films. It was found that the ratio between the reversible and the switching parts of the polarisation depend upon the crystallographic structure of the film and the contact material. The possibility of the nondestructive readout of the information was also demonstrated. The value of the signal charge for this type of readout depends on the parameters of the sample and the value of the readout voltage. Under optimum conditions it was found that signal charges as high as 20% of the switching polarization charge could be obtained without the destruction of the stored information, thereby making it possible to accomplish an unlimited number of the readout processes.

SESSION Y3: POSTER SESSION:
ELECTRODES AND INTEGRATION
Chairs: Stephen R. Gilbert and Theodore S. Moise
Monday Evening, November 29, 1999
8:00 P.M.
Exhibition Hall D (H)

Y3.1
THERMAL STABILITY OF Ir/TaN ELECTRODE/BARRIER ON THIN GATE OXIDE FOR MFMOS ONE TRANSISTOR MEMORY APPLICATION. Fengyan Zhang, Sheng Teng Hsu, Tingkai Li, Yoshi Ono, Jer-shen Maa, Hong Ying, Lisa Stecker, Sharp Laboratories of America, Inc., Camas, WA.

The MFMOS (Metal Ferroelectric Metal Oxide Silicon) one transistor memory needs to have metal electrode on top of thin gate oxide. The gate oxide used in our present MFMOS one transistor memory processing is 30-35 Å SiO_2. By choosing Ir as the bottom electrode,

TaN has been used as the barrier layer between Ir bottom electrode and the gate oxide. The purpose of TaN barrier layer is to prevent the formation of iridium silicide. It is also important that the TaN itself is stable and will not react with gate oxide during ferroelectric material deposition and annealing process. In this paper, TaN barriers with different deposition conditions have been deposited on 30 $\AA$ gate oxide. 2000 $\AA$ Ir was deposited on TaN barrier layer. The capacitors were defined by dry etching. Series RTP annealing were performed in oxygen from 500-650°C and annealing time from 5 min to 2 hours. C-V and I-V characterizations were used to characterize the stability of the Ir/TaN/Gate Oxide structure. It has been proved that the Ir/TaN/Gate Oxide is very stable during above mentioned annealing conditions. The consumption and further oxidation of the gate oxide is very small and would depend on the deposition condition of the TaN barrier layer. With optimized deposition conditions, 220 $\AA$ TaN barrier layer can effectively prevent any iridium silicide formation and will not degraded the gate oxide during annealing. The interface between the TaN and gate oxide can be further improved by forming gas annealing.

***Y3.2**
PROPERTIES AND DECOMPOSITION BEHAVIORS OF REACTIVELY SPUTTERED Pt(O) ELECTRODE MATERIALS. Katherine L. Saenger and Stephen M. Rossnagel, IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY.

The possibility that oxygen-containing Pt might be superior to conventional Pt as an electrode for high-epsilon (HE) and ferroelectric (FE) perovskites has led to renewed interest in the family of Pt(O) materials. Here we report on the properties and decomposition behaviors of reactively sputtered PtOx electrode materials having x in the range 0 to ~1.4. Phases of Pt(O) identified included $<111>$-textured cubic Pt ($x < 0.2$), tetragonal PtO ($x \sim 1$), and amorphous platinum oxide a-PtOx ($x \sim 1.4$). Film texture, morphology, resistivity, adhesion, and oxgyen content were examined before and after annealing in O_2 and N_2 at temperatures approximating those of HE/FE deposition and processing (400 - 650°C). After annealing at 650°C for 5 min, all Pt(O) films lost oxygen and showed growth in metallic Pt phases whose orientations were often $<200>$ or $<220>$ rather than the $<111>$ orientation typically produced by physical vapor deposition of the pure metal. Pt(O) films having a PtO-like structure typically showed only surface oxygen loss, with close to original oxygen levels left in the film bulk, suggesting that the oxygen in these films may be retained long to have a beneficial effect on HE/FE layers at later stages in processing.

Y3.3
(100)-ORIENTED $LaNiO_3$ BOTTOM ELECTRODES FOR GROWTH OF FERROELECTRIC THIN FILMS. Zhenshan Zhang and Susan Trolier-McKinstry, Materials Research Laboratory, Pennsylvania State University, University Park, PA.

Highly (100)-oriented thin films of $LaNiO_3$ (LNO) were deposited by DC magnetron sputtering onto Si substrates. The target powder was prepared using a molten salt technique with $NaCO_3$ as a flux. The final target density was greater than 85% of theoretical density. The best results were obtained when sputtering was carried out at a power of 186 W and a working pressure of 45 mtorr with a gas composition of 50% O_2+ 50% Ar. The thickness of the deposited films was proportional to the sputtering time, and the growth rate was 300 angstroms per hour. The resulting LNO films had a resistivity of 6 $\mu\Omega$·m at room temperature. Highly {100}-oriented thin films of lead zirconate titanate $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) were fabricated by a sol-gel method on (100)-textured LNO metallic oxide electrodes. Orientation of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ films on these electrodes will also be discussed.

Y3.4
FERROELECTRIC PROPERTIES OF BARIUM STRONTIUM TITANATE (BST) CAPACITOR WITH LANTHANUM NICKELATE (LNO) ELECTRODES. M. Vedawyas, Rajesh Katare, T. Potts, Ashok Kumar and M. Shamsuzzoha*, Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL. *Department of Metallurgical and Material Engineering, University of Alabama, Tuscaloosa, AL.

Barium Strontium Titanate (BST) thin films are promising high dielectric materials in fabricating cell capacitors for high density dynamic random access memory (DRAM) devices. In this study, the growth, structure and the ferroelectric properties of BST with lanthanum nickelate (LNO) as top and bottom electrodes is discussed. Epitaxial LNO films are deposited on $LaAlO_3$ (100) substrates by pulsed laser deposition technique. LNO is a metallic oxide with a perovskite structure, having a resistivity of less than 1 mohm.cm. Then BST film is grown on the LNO layer, again utilizing the pulsed laser deposition technique. We are able to grow high quality oriented films of BST on LNO, since BST is also a material of same perovskite. The morphology and the structure of the multi-layers are studied by scanning electron microscopy (SEM) and the X-ray diffraction respectively. The cross-sectional transmission electron microscopy(TEM) results show smooth interface among different layers. The ferroelectric properties of the multilayer cell are measured using the RT66A tester under the virtual ground conditions.

Y3.5
PREPARATION OF $SrRuO_3$ AND $CaRuO_3$ FILMS BY MOCVD AND ITS APPLICATION TO ELECTRODES OF FERROELECTRIC THIN FILM. Hiroshi Funakubo, Norikazu Okuda, Noriyuki Higashi, Katsuyuki Ishikawa, Tokyo Institute of Technology, Dept. of Innov. Eng. Mater., Yokohama, JAPAN.

$SrRuO_3$ and $CaRuO_3$ thin films were prepared by MOCVD from $Sr(C_{11}H_{19}O_2)(C_8H_{23}N_5)$ - $Ru(C_{11}H_{19}O2)$ - O_2 and $Ca(C_{11}H_{19}O_2)(C_8H_{23}N_5)$ - $Ru(C_{11}H_{19}O2)$ - O_2 systems, respectively. (001)-, (110)- and (111)- oriented $SrRuO_3$ films were epitaxially grown on (100), (110) and (111) $SrTiO_3$ substrates at 750°C, respectively. The full width of the half maximum of (200) diffraction of $SrRuO_3$ phase was fairly narrow to be 0.046^0 when the (100)-oriented $SrRuO_3$ film was deposited on (100)$SrTiO_3$ substrate. Its resistively was about 280 $\mu\Omega$·cm regardless of the film thickness from 50 to 200 nm. This value was compatible to the reported value for the single crystal. (001)-oriented $CaRuO_3$ film was also epitaxially grown on $(100)SrTiO_3 substrate at 750°C$. Its resistively was about 200 $\mu\Omega$·cm. On (100)$SrRuO_3$‖(100)$SrTiO_3$ substrate, (001)-oriented $SrBi_2Ta_2O_9$ film was epitaxially grown above 620°C. On the other hand, (116)-oriented $SrBi_2Ta_2O_9$ film was epitaxially grown on (110)$SrRuO_3$‖(110)$SrTiO_3$ substrate above 820°C.

Y3.6
HETEROEPITAXIAL GROWTH OF Ir FILM ON EPIRAXIAL (100)ZrN/(100)Si SUBSTRATE FOR FERROELECTRIC CAPACITOR. Sadayoshi Horii*, Seiji Yokoyama and Susumu Horita, Japan Advance Institute of Science and Technology, School of Material Science, Ishikawa, JAPAN, *Delegated from Kokusai Electric Co., LTD., Toyama, JAPAN.

For the electric devices, a single crystalline thin film is more attractive than polycrystalline one because it exhibits greater stability, uniformity of the material properties and high performance of device, in particular, on Si substrates. In order to obtain a 1T-1C ferroelectric memory with an epitaxial ferroelectric film, the epitaxial bottom electrode must be prepared on Si directly. In this study, we tried to produce the heteroepitaxial growth of an Ir film on a (100)Si substrate covered with an epitaxial ZrN(Zirconium mononitride) film. ZrN film is an attractive candidate for diffusion barriers in microelectronics because of its high thermal and chemical stabilities and low bulk resistivity of 7-13.6 $\mu\Omega$·cm. The 100-nm-thick ZrN film was deposited by rf sputtering with the N_2/Ar flow rate ratio of 5~100% at substrate temperature of 850°C on (100)Si. The rf power was 50 W for 4 inch Zr metallic target and the deposition rate was 10 nm/min. The sputtering chamber was pumped down to a base pressure of less than 7×10^{-6} Pa. At N_2/Ar = 20%, we obtained the epitaxial (100)-oriented ZrN film on Si with a cube-on-cube relationship. However, at N_2/Ar more than or equal to 50%, no ZrN film was deposited because the sputtering yield of nitrogen ion is very small. The Ir thin film was deposited by rf sputtering at substrate temperature of 575 or 600°C on the epitaxial (100)ZrN/(100)Si structure. Its thickness was 20nm. At the substrate temperature of 600°C, the deposited Ir film was reacted with ZrN film and the surface became rough. However at 575°, the epitaxial (100)-oriented Ir film was obtained on the epitaxial ZrN film with a cube-on-cube relationship and the surface was relatively smooth.

Y3.7
STUDIES OF BARRIER AND OXIDE ELECTRODE THIN FILM GROWTH AND INTERFACES VIA IN SITU SURFACE SENSITIVE ANALYTICAL TECHNIQUES. A.M. Dhote, A.R. Krauss, and D.M. Gruen, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; O. Auciello, Materials Science Division, Argonne National Laboratory, Argonne, IL; S. Aggarwal and R. Ramesh, Materials and Nuclear Engineering Department, University of Maryland, College Park, MD.

Low-density non-volatile ferroelectric random access memories (NVFRAMs) have been introduced into the market in "smart cards". The next major step is the development of high density memories. In this case, diffusion barrier layers will play a critical role since the ferroelectric capacitors will be fabricated directly on top of CMOS transistors. Therefore, it is relevant to study the growth, processing and interaction of diffusion barrier and bottom electrode layers used for integration of ferroelectric capacitors with CMOS devices. For PZT film-based capacitors, conductive oxide electrodes are necessary to minimize fatigue. We have recently demonstrated that $La_{0.5}Sr_{0.5}CoO_3$/Ti-Al alloy heterostructure can be used as bottom

electrodes for PZT capacitors. The Ti-Al layer can provide the double functionality of diffusion barrier and bottom electrode. The LSCO/Ti-Al layer exibits a good ohmic bahavior when the Ti-Al layer has an amorphous microstructure, and a diode-type bahavior when the structure is polycrystalline. Therefore, it is critical to study the growth and interface of the LSCO/Ti-Al layer to determine the processing conditions that make this heterostructure work as a potential good bottom electrode for NVFRAMs. Three different types of samples were investigated, namely: (a) magnetron sputter-deposited LSCO/Ti-Al at high deposition rate (polycrystalline Ti-Al), (b) magnetron sputter-deposited LSCO/Ti-Al at low deposition rate (amorphous Ti-Al), and (c) ion-beam sputter deposited LSCO/Ti-Al. These layers were investigated using in situ mass spectroscopy of recoil ions (MSRI) and XPS. The MSRI analysis revealed that the amorphous Ti-Al layer has a Ti-rich surface, while the polycrystalline Ti-Al film shows segregation of Al to the alloy surface. XPS revealed the information of a partially oxidized Ti layer in the first case, and an Al_2O_3-rich layer in the second case. Possible mechanisms for the different bahavior of the Ti-Al layers and the implications for the electrical properties of PZT-based capacitors with bottom LSCO/Ti-Al electrodes will be discussed. *(This work was supported by US-DOE, BES Material Sciences, under contract W-13-109-ENG-38; NSF-MRSEC under Grant #DMR-96-32521; the NSF/ONR under contract N00014-89-J-1178).

Y3.8
THE MASKING EFFECT OF TiN IN DRY ECTHING OF PZT FILMS. T.B. Wu, T.P. Liu, M.C. Chiang, Y.H. Lee, Natl Tsing Hua University, Dept of Materials Science & Engineering, TAIWAN ROC.

The pursuit of an appropriate mask material having a significant etching selectivity with respect to the electrode and ferroelectric thin films is important in the development of dry etching technique for the fabrication of high density ferroelecrtric random access memories. In this work, the masking effect of TiN thin film was investigated in dry etching of the PZT films with Helicon wave plasma using a gas mixture of Ar, O_2 and CF_4. A high etch rate of 75 $\sim$ 70 nm/min can be obtained for the etching of PZT with the gas mixture having $Ar/O_2/CF_4$ in a range of 80/20/20 $\sim$ 30/20/50. On the contrary, the TiN has a low etch rate around 20 nm/min although the etch rate increases with increasing the CF_4 content in the gas mixture. A high etching selectivity of 5.6 is thus reached for the ecthing of PZT with respect to TiN in Helicon wave plasma with $Ar/O_2/CF_4$ = 60 /20 /20, and a steep etching profile of $\sim$70° is obtained. Moreover, a fine capacitor in Pt/PZT/Pt stacked structure is also successfully fabricated by using TiN as the only mask in the etching process.

Y3.9
HIGH DENSITY PLASMA ETCHING OF (Ba,Sr)TiO_3 AND $LaNiO_3$. K.P. Lee, K.B.Jung, A. Srivastava, D. Kumar, R.K. Singh, S.J. Pearton, University of Florida, Dept of Materials Science and Engineering, Gainesville, FL.

$LaNiO_3$ (LNO) is a potentially advantageous electrode material for use with BST films. We have investigated ICP etching of both BST and LNO thin films in Cl_2/Ar and $CH_4/H_2/Ar$ plasma chemistries. The rates were very low (= 100 $Å \bullet min^{-1}$) with $CH_4/H_2/Ar$, but rates up to 900 $Å \bullet min^{-1}$ and selectivities of 16 for BST and 7 for LNO over Si were achieved in Cl_2/Ar. Smooth (root-mean-square-roughness 0.6-0.7nm) surfaces were achieved for both materials in Cl_2/Ar and sub-micron ($\sim$ 0.5 μm CD) patterns were transferred using photoresist masks.

SESSION Y4: POSTER SESSION:
FUNDAMENTAL PROPERTIES OF THIN-FILM FERROELECTRICS
Chairs: Hiroshi Ishiwara and John Robertson
Monday Evening, November 29, 1999
8:00 P.M.
Exhibition Hall D (H)

Y4.1
THERMODYNAMIC STUDY OF STRESS DISTRIBUTION IN EPITAXIAL Pb(Zr,Ti)O_3 (PZT) THIN FILMS. S. Hoon Oh, H.J. Kim, Hyun M. Jang, Dept. of Materials Science and Engineering, Pohang Univ. of Science and Tech. (POSTECH), Pohang, KOREA.

The effects of the stress distribution over the thickness direction on various ferroelectric properties of epitaxial Pb(Zr,Ti)O_3 (PZT) thin films were examined using the Landau's phenomenological thermodynamic approach. Because the rate of the stress variation over the thickness direction ($d\sigma(z)/dz$) is likely to be proportional to the local stress itself, we have introduced an exponentially decaying function for $\sigma(z)$. The modified Landau's thermodynamic formalism predicts that the spontaneous polarization, the para-ferro transition temperature, and the dielectric stiffness all decrease with decreasing film thickness under a tensile stress. In order to experimentally examine the present theoretical predictions, we have fabricated epitaxial PZT thin films with various film thicknesses using pulsed laser deposition method. The comparison suggests that the extrinsic stress caused by the cubic-tetragonal 1st-order phase transition is significantly greater than the thermal stress originating from the difference in the thermal expansion coefficient between the film and the MgO (001) substrate. This further implies that a tensile stress dominates over a compressive stress in the epitaxially oriented tetragonal PZT thin film.

***Y4.2**
DOMAIN IMAGES AND RETENTION BEHAVIOR OF PZT THIN FILMS OBSERVED BY ELECTROSTATIC FORCE MICROSCOPY. William Jo and Dong-Cheon Kim, LG Corporate Institute of Technology, Seoul, KOREA; Jae Wan Hong, PSIA, Seoul, KOREA.

We report results on domain retention in preferentially oriented $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) thin films on Pt and on $LaNiO_3$ (LNO) electrodes. Domain images are obtained by detecting an electrostatic force exerted on the biased conductive probe. We demonstrate that polarization loss of PZT domains on LNO electrodes occurs less under no external field rather than that of PZT on Pt. The time dependence of the remnant polarization is found to follow a stretched exponential decay. On PZT/LNO heterostructures, it was observed that the output signal by positive voltage at top surface shows larger values than that by negative one. Furthermore, if the inside part of the domain is switched as a reverse direction, the backswitched area retains its value for more than 10^5 sec. These asymmetric switching characteristics are related to defect states and depolarization field in the film and the interface.

***Y4.3**
DOMAIN IMAGING, POLARIZATION HYSTERESIS AND SWITCHING IN NANO-SIZE FERROELECTRIC STRUCTURES. C. Harnagea, A. Pignolet, M. Alexe, D. Hesse, and U. Goesele, Max Planck Institute of Microstructure Physics, Halle/Saale, GERMANY.

The last decade has seen a surge of interest for ferroelectric thin films due to the wide range of their potential applications in microelectronics, especially in non-volatile memories. For a 1 Gbit memory the lateral dimension of a memory cell is about 160 nm. Further decrease of the size of ferroelectric capacitors to the nanometeric scale raises both the problem of patterning and the question of size effects in very small ferroelectric structures. In order to study the size effects in ferroelectrics, local piezoelectric hysteresis loops were recorded on PZT structures with lateral size ranging from 1 μm^2 to 100 nm^2. The PZT nanostructures, as well as regular arrays of $SrBi_2Ta_2O_9$ (SBT) mesas 100 nm in lateral size were fabricated using *electron-beam direct writing*. Using pulsed laser deposition (PLD) we also produced thin films of various Bi-layered perovskites having epitaxial (110)- and (100)-oriented grains of nanometric size embedded in a c-oriented matrix. Measurements of the polarization and of the piezoelectric properties of individual structures at the nanoscale level were performed by scanning force microscopy (SFM) used in piezoresponse mode. The piezoresponse SFM mode was also used to investigate the polarization at the nanoscale of (110)-, (100)- and c-oriented Bi-layered perovskite films. It was demonstrated for instance, that the polarization of SBT has indeed no component along its crystallographic c-axis. The ferroelectric domains were visualized by the same method and it was shown that more than two ferroelectric domains could coexist within a nano-size structure or within a single Bi-layered perovskite nano-size grain, each domain not exceeding 100 nm in lateral size. Fatigue measurements on these nano-size structures were also performed and will be discussed.

Y4.4
CRITICAL FACTORS CONTROLLING DOMAIN STRUCTURES IN EPITAXIAL PZT THIN FILMS. Kyeong-Seok Lee, Sunggi Baik, Pohang Univ. of Science and Technology, Dept. of Materials Science and Metallurgical Engineering, Pohang, KOREA.

The initial status of stress developed during PZT film growth was controlled by selecting proper substrates and film composition through careful consideration on lattice mismatching and thermo-elastic interaction in each system. Partial relaxation of the built-in stresses at and below growth temperature in epitaxial Pb(Zr,Ti)O_3 (PZT) thin films was extensively analyzed using $in-situ$ and $ex-situ$ synchrotron X-ray diffraction techniques. Various single crystal substrates such as MgO (001), $KTaO_3$ (100), and $SrTiO_3$ (001) were selected, and Zr concentrations were adjusted to 0 and 32 mol%. The film growth was processed using a pulsed laser ablation method. In the case of PZT(0/100) films, each system showed the characteristic domain structures depending on substrate selection. Perfectly *c*-axis oriented films were obtained on $SrTiO_3$ (001) substrates, while the films grown on $KTaO_3$ (100) showed

a-domain dominant structures with a small amount of c-domains embedded in matrix a-domains. However, these domain structures were drastically changed in somewhat complex manner depending on the sign as well as the magnitude of coherent strain at the growth temperature when Zr was added. Especially, PZT(32/68) films grown on $KTaO_3$(100) showed highly c-axis oriented domain structure contrary to the case of PZT(0/100) film. Consequently, even above a certain equivalent value of critical film thickness, misfit strain is only partially relaxed, and expected to play an important role on the formation of domain structures in comparison to the thermal strains that could also be varied by the selection of substrates.

Y4.5
DOMAIN IMAGING AND LOCAL PIEZOELECTRIC PROPERTIES OF $Pb(Zr_{0.53}Ti_{0.47})O_3$ THIN FILMS. J.B. Xu, G.D. Hu, X. Wang, Z. Xie, E.Z. Luo and I.H. Wilson, Dept. of Electronic Engineering and Materials Science and Technology Research Center, The Chinese University of Hong Kong, NT, HONG KONG.

The domain structure of polycrystalline $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) thin films was studied by a modified atomic force microscope (AFM) both in the constant force mode and in the piezoelectric mode. It is found that some grains are split by polydomains. The domain types formed in the grains were identified by analyzing the dependence of the piezoelectric coefficient on the electric field (d_{33}). To study the switching properties, the sample was additionally polarized and imaged over a large area. No grain was found to be effectively clamped.

Y4.6
COMPARISON OF LEAKAGE CURRENT MECHANISMS IN LEAD BASED PEROVSKITE CAPACITORS WITH DIFFERENT ELECTRODES. Brindha Nagaraj, S. Aggarwal, H. Leblanc, R. Ramesh, Univ of Maryland, College Park, MD; G. Velasquez, L. Boyer, J.T. Evans Jr, Radiant Technologies Inc, Alburquerque, NM.

Electrodes and hence interfaces play an important role in determining the characteristics and performance of devices. We have compared the leakage current mechanisms in sputtered $Pb(Nb,Zr,Ti)O_3$ [PNZT(4,28,68)] capacitors with Pt, $La_{0.5}Sr_{0.5}CoO_3$(LSCO), $SrRuO_3$(SRO) electrodes. We find that the dominant leakage current mechanism in both LSCO and SRO capacitors is the bulk limited Poole-Frenkel emission with an activation energy of 0.6eV. This leakage current mechanism is consistent with the simplistic energy band scenario of these heterostructures. Similarly, the energy band diagram for Pt/PNZT suggests no depletion. However there are several studies which report Schottky type emission for such an interface. Our results with true leakage current also indicate Schottky type emission with an interfacial barrier height of 0.9eV. We have analyzed the leakage current in detail in these heterostructures and determined that it has interesting time dependent features. We believe the origin of Schottky barrier is hidden in this relaxation. We propose that the slow leakage current relaxation is due to trapping of injected carriers by deep traps at or near the interface. Furthermore, we observe interesting correlations between leakage current relaxation and switched polarization loss during bipolar cycling i.e. fatigue. In this presentation, we will present results of the experiments and the correlations between the interface conditions (i.e. electrode type) and reliability properties.

Y4.7
CALCULATION OF THE FERROELECTRIC RESPONSE OF BARIUM TITANATE NANOPARTICLES. Juan Romero and Luis F. Fonseca, Dept of Physics, University of Puerto Rico, San Juan, PR.

The progressive reduction in size of the new devices requires to understand how the bulk properties as ferroelectricity change when the material is prepared with such a small dimensions. We report our calculations of the averaged electrical polarization of $BaTiO_3$ nanoparticles using Monte Carlo simulations. The bulk phase transition of the material is checked by running the simulations with a model hamiltonian and including the proper interaction coefficients. Then, the ferroelectric response of the nanoparticles is studied as a function of their size and at different temperatures. Of main importance is the study of the surface effects in this kind of particles. We found that the surface interactions can shift the critical temperature to upper values according to the relative strength of those interactions.

Y4.8
FERROELECTRICITY IN EPITAXIAL $LaTiO_{3.5}$ THIN FILMS. J.W. Seo[1,2], J. Fompeyrine[2], S. Molitor[3], P. Guethner[3], S. Gariglio[4], J.-M. Triscone[4], H. Siegwart[2] and J.-P. Locquet[2]; [1]Université de Neuchâtel, Institut de Physique, Neuchâtel, SWITZERLAND; [2]IBM Zurich Research Laboratory, R, SWITZERLAND; [3]Omicron Vakuumphysik GmbH, Taunusstein, GERMANY; [4]Université de Genève, DPMC, Genève, SWITZERLAND.

Ferroelectricity only appears in non-centrosymmetric crystals such as $LaTiO_{3.5}$ which is a uniaxial (along the b axis) ferroelectric compound. The structure of this compound is made up of four $LaTiO_3$ units: two regular units sandwiched between two distorted units that share an additional oxygen layer. The resulting dipole moment is localized around this additional layer. Unfortunately, during the epitaxy precisely this additional layer is difficult to incorporate since it has to be inserted under two $LaTiO_3$ units, below the actual film surface. This process is only possible with appropriate oxidation channels. Such channels have been identified by high resolution TEM and epitaxial films were successfully grown, albeit with a distorted lattice. The fundamental question is whether such distorted films are still ferroelectric. TEM results confirm the non-centrosymmetry and predicts the direction of the polarization axes in the different domains. Additional evidence was obtained using electrostatic force microscopy. Domains could be written only when a high enough voltage pulse 5-8 V - beyond the coercive field - was applied, suggesting ferroelectric behavior.

SESSION Y5: POSTER SESSION: Pb-BASED THIN FILM FERROELECTRICS

Chairs: William Jo and Ramamoorthy Ramesh
Monday Evening, November 29, 1999
8:00 P.M.
Exhibition Hall D (H)

Y5.1
THE MICROSTRUCTURE, PHASE AND FERROELECTRIC PROPERTIES OF PZT THIN FILMS ON ORIENTED MULTILAYER ELECTRODES. Tingkai Li, Weiwei Zhuang, Fengyan Zhang, Hong Ying, Sheng Teng Hsu, Sharp Laboratory of America, Camas, WA; Yufei Gao and Mark H. Engelhard, Pacific Northwest National Laboratory, Richland, WA.

Three kinds of oriented electrodes of Pt, Ir and multilayer Pt/Ir electrodes were prepared for deposition of PZT thin films. The oriented Pt, Ir and multilayer Pt/Ir electrodes have been prepared by electrical beam evaporation techniques. First, 100 - 200 nm thick Ir electrodes were grown on $Ti/SiO_2/Si$ substrates with preferred (111) orientation. Then the very thin Pt electrode from 10 - 50 nm was partially epitaxial grown on Ir electrode. The X-ray pattern confirmed the formation of partially epitaxial multilayer Pt/Ir electrodes. An oxide MOCVD reactor with liquid delivery system was used for the growth of PZT thin films. $[Pb(thd)_2]$, $Zr(TMHD)_4$ and $Ti(IPO)_4$ were dissolved in a mixed solvent of tetrahydrofuran or butyl ether, isopropanol and tetraglyme to form a precursor source. The deposition temperatures and pressure were 500 - 650°C and 10 Torr separately. The experimental results showed PZT thin film deposited on various electrodes had different composition, phase formation, microstructure and properties. The X-ray patterns showed the perovskite phase of PZT films grown on both of Ir and epitaxial Pt/Ir electrodes at 550°C, and only grain size increased after a higher temperature annealing. But as-deposited PZT on Pt electrodes showed existed pyrochlore phase at 550°C, then transferred to perovskite phase completely after 650°C annealing. Compared with the PZT thin films deposited on Pt and Ir electyrodes, the MOCVD PZT thin films on multilayer Pt/Ir had the best ferroelectric and electrical properties. The hysteresis loop with 2Pr value of 40 $\mu C/cm^2$ and 2Ec 73 kV/cm was well saturated and symmetrical at an applied voltage of 5 V. The hysteresis loop of the PZT thin film was almost saturated from 3 V. A low leakage current 6.16 x 10^{-7} A/cm^2 at 100 KV/cm is also found. The effect mechanism of electrodes on ferroelectric properties of PZT thin films was also investigated.

Y5.2
PROCESSING OF LANTHANUM DOPED PZT THIN FILMS: INFLUENCE OF SOLVENTS. Marija Kosec, Mira Mandeljc, Barbara Malič, Goran Dražič, Jožef Stefan Institute, Ljubljana, SLOVENIA.

Thin films of ferroelectric ceramic materials have been recently extensively studied for possible microelectronic and micromechanical applications. Currently, donor doped PZT solid solutions are of interest but it is recognized that donor dopants modify crystallization and the microstructure of thin films and effect the ferroelectric response as compared to undoped PZT films. Our aim was to obtain high quality, perovskite-phase lanthanum-doped PZT ($Pb_{0.925}La_{0.05}Zr_{0.30}Ti_{0.70}O_{0.3}$) thin films by emphasizing the role of solution chemistry. The sols were prepared from lead oxide, lanthanum nitrate hydrate, zirconium and titanium n-butoxides in various ether-alcohols, namely in 2-ethoxyethaol, 2- butoxyethanol and in the most commonly used 2-methoxyethanol. The 0.5 molar sols were spin-coated on platinized silicon substrates ($2nmTiO_2/100nmPt/20nmTiO_2/SiO_x/Si$), dried at 200°C, pyrolysed at 350°C or 400°C and annealed at 550°C to 650°C. The films were

characterized by X-ray diffraction, thermal analysis and optical, scanning and transmission electron microscopy. Various solvents strongly influence thermal decompositions of the respective sols dried at 60°C, both the weight losses and thermal effects upon functional group removal. In the case of 2-ethoxyethanol derived thin films, the pyrolysis at 400°C results in crystallization of the perovskite phase as observed by XRD and TEM. The comparison with 2-methoxyethanol and 2-butoxyethanol derived thin films will also be reported.

Y5.3
EFFECT OF CRYSTALLOGRAPHIC TEXTURE ON FERROELECTRIC PERFORMANCE OF PZT THIN FILMS.
Glen R. Fox, Ramtron International Corporation, Colorado Springs, CO.

Two methods for characterizing the crystallographic texture of PZT were used to determine what effect texture has upon the ferroelectric properties of PZT thin films. The first method of texture characterization employed the measurement of the XRD rocking curve peak width for the PZT 222 peak. The second texture characterization method utilized peak intensity ratios to calculate the volume fraction of {111}, {100}, and randomly oriented material. A large set of films with textures ranging from fully random to fully {111} texture were generated using the ULVAC ZX-1000 production sputter deposition machine. It was found that the switched polarization could be significantly altered by changing the PZT oriented volume fractions. Fatigue was also monitored as a function of PZT texture. For highly {111} textured films, it was determined that the degree of texture, i.e., the rocking curve peak width, has no effect on PZT performance for FRAM^{TM} applications. A model relating the PZT texture and switching performance was developed from the experimental results.

Y5.4
EFFECT OF La DOPANT ON MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF PZT THIN FILM CAPACITORS.
Chang Jung Kim and Ilsub Chung, Samsung Advanced Institute of Technology, Material & Device Sector, Microelectronics Lab, Suwon, KOREA.

Lanthanum doped PZT(40/60) thin films have been prepared on $Pt/IrO_2/Ir/Ti/SiO_2/Si$ substrates by sol-gel method. The microstructure and electrical properties of the PZT capacitors were evaluated as a function of La content in the range of $0 \sim 1$ at.%. The crystalline orientation was appreciably influenced by the addition of La in PZT thin films. The microstructure of films in the range of La $= 0 \sim 0.5$ at.% was a single perovskite phase, but above La = 0.5 at.%, the second phase was detected by SEM observation. The best ferroelectric and retention properties for ferroelectric random access memory were obtained at La = 0.5 at.%.

Y5.5
A STUDY ON THE SELECTIVE NUCLEATIONS FOR FORMATION OF LARGE SINGLE GRAINS IN PZT THIN FILMS.
Jang-Sik Lee, Eung-Chul Park, Jung-Ho Park, Byung-Il Lee and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

There have been extensive efforts to integrate ferroelectric thin films with existing Si technology to fabricate reliable non-volatile memories. However several issues still need attention such as high leakage current, fatigue and aging phenomena of the PZT thin films. The degradation of ferroelectric properties has been correlated with the grain boundaries which are randomly generated during phase transformation. In this work, we will report a new fabrication method for large single grained PZT thin films by selective nucleation and growth method to eliminate the degradation due to grain boundaries and growing behavior and size of grains are investigated according to the annealing temperature and time. Polarization, electrical, fatigue and retention characteristics of the thus formed PZT thin films are investigated as well. Ta-doped PZT thin films for seeding layer were deposited on $Pt/SiO_2/Si$ substrates by a reactive co-sputtering method and then crystallized at 700°C for 30 seconds by RTA. Perovskite PZT thin film dots were formed by a lithographic patterning and etching. PZT thin film was deposited on the substrates having PZT array island. Nucleation of the PZT films were selectively occurred on the seeding PZT island at the temperatures around 540°C which is lower temperature for the nucleation of PZT films without seeding layer. Nucleation between seeding island was suppressed at those temperatures. By annealing at 600°C for 2 hours in air, single grains of which size were grown up to 40μm could be obtained. Single grained PZT thin films showed polarization properties of P_r(remanent polarization)=30μC/cm^2, electrical properties of J_L(leakage current density)=8×10^{-8}A/cm^2, E_{BD}(breakdown field)=1240kV/cm and no degradation up to 2×10^{11} cycles at 1MHz in fatigue test. The switchable polarization exhibited no loss with 10V write/read voltage after 30000 seconds retention time.

Y5.6
PREPARATION OF Al DOPED PZT THIN FILMS USING A SOL-GEL METHOD.
Takashi Iijima, Norio Sanada, Tohoku National Industrial Research Institute, AIST, MITI, Sendai, JAPAN; Kunio Hiyama, Hideki Tsuboi, Masuhiro Okada, YAMAHA Co, Material & Component Development Center, Toyoka, JAPAN.

We have reported that Al substitution for Ti site of $PbTiO_3$ improved the ferroelectric properties elsewhere. In this work, Al substitution for ZrTi site of PZT was attempted using a sol- gel method, and the ferroelectric properties of Al doped PZT were compared with those of non- doped PZT. The precursor solutions were synthesized from trihydrated lead acetate, titanium iso- propoxide, zirconium iso-propoxide and aluminum iso- propoxide, and 2- methoxyethanol was used as a solvent. The nominal composition of the solutions were equivalent to those of $Pb_{1.1}(Zr_{0.52}Ti_{0.48})O_3$ and $Pb_{1.1}((Zr_{0.52}Ti_{0.48})_{0.98}\ Al_{0.02})O_3$. To control the microstructures of PZT or Al doped PZT thin films, sol- gel derived seed layer of $PbTiO_3$ or Al doped $PbTiO_3$ were deposited onto the 6'' Pt /Ti /SiO_2 /Si substrate respectively, before coating process. The sequence of spin coating at 3000rpm and pyrolysis at 400°C was performed several times, and the films were fired at 700°C for 15 min in Air. The film thickness of the fired samples was 200nm. To fabricate the 200μm square top electrode, Pt layer was sputtered onto the film surface, and then iron etching were performed. Finally SiO_2 passivation layer was deposited on the top surface to simulate the device structure. The Al doped PZT thin films showed well saturated P- E hysteresis curve at 5V, and Pr was 22μC/cm. The dielectric constant and leakage current did not show remarkable difference comparing with those of PZT, and those values were 1070 and 2×10^{-7}A/cm^2 at 5V respectively. On the other hand, the fatigue property of Al doped PZT thin films showed a little progress, because the reduction rate of the fatigue was smaller than that of PZT.

Y5.7
CHANGES IN PREFERRED ORIENTATION OF SOL-GEL DERIVED $Pb(Zr_{0.53}Ti_{0.47})O_3$ THIN FILMS ON Ti-FREE $Pt(111)/SiO_2/Si$ AND $Pt(200)/SiO_2/Si$ SUBSTRATES.
Song-Yi Lee, Dong-Su Lee, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA; Dong-Yeon Park, INOSTEK, Inc., Seoul, KOREA; Euijoon Yoon and Byungwoo Park, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA.

The preferred orientation of $Pb(Zr_{1-x}Ti_x)O_3$ thin films is one of the important factors that affect the ferroelectric and pyroelectric properties. In general, sol-gel derived PZT films on $Pt(111)/Ti/SiO_2/Si$ are (100)-orientated, since the (100) plane is the lowest-energy surface. However, (111)-oriented PZT films on the same substrate have been reported when the films were pyrolyzed at low temperatures (~350°C) and for short times less than 5 min. The origin of the (111) preferred orientation in PZT films is still unknown. It has been proposed that Ti atoms from the adhesion layer diffuse through the Pt layer and form Pt_3Ti or TiO_2 precipitates that act as nucleation sites for (111)-oriented perovskite films at the interface. We have grown PZT(53/47) thin films on Ti-free $Pt(111)/SiO_2/Si$ and $Pt(200)/SiO_2/Si$ substrates through a modified sol-gel process ($Pb(CH_3CO_2)_2{\cdot}3H_2O$, $Zr(OC_4H_9)_4$, and $Ti(i\text{-}OC_3H_7)_4$ in 2-methoxyethanol). Pyrolysis temperature was varied from 300 to 420°C. After the pyrolysis for various times (1-30 min.), the samples were finally annealed in a tube furnace at 650°C for 20 min. in air. Subsequently, x-ray diffraction, scanning electron microscopy and transmission electron microscopy were used to investigate the texture and the microstructure of films. Although most of films showed (100) preferred orientation on Pt(111) substrates, (111) preferred orientation developed when the film was pyrolyzed for 1 min. regardless of pyrolysis temperature. It is speculated that the perovskite phase could nucleate directly at the interface and grow with an epitaxial relationship with the Pt(111) substrate, since it was impossible for Pt_3Ti or TiO_2 seeding layers to form without a Ti glue layer. On the other hand, films with (100) preferred orientation were observed on Pt(200) substrates. The role of pyrolysis in determining the preferred orientation of the PZT films will be addressed.

Y5.8
EFFECT OF Pb EXCESS CONTENT ON MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF SOL GEL DERIVED PZT THIN FILMS.
Zhanjie Wang, Ryutaro Maeda, Kaoru Kikuchi, Mechanical Engineering Laboratory, Dept of Manufacturing Systems, Tsukuba, JAPAN.

PZT thin films were fabricated using the addition of -10, 10, and 20 mol % excess of Pb to the starting solution and spin coating onto Pt/Ti/SiO2/Si substrates. The crystalline phases as well as preferred orientations in the PZT films were investigated using X-ray diffraction analysis (XRD). The microstructure and composition of the films were studied by scanning electron microscopy (SEM), Transmission

electron microscopy and electron probe microanalysis (EPMA), respectively. The well crystallized perovskite phase and the (100) preferred orientations were obtained using the addition of 10% excess of Pb to the starting solution. It was found that the PZT films used the addition of 10% excess of Pb had better electric properties. The remnant polarization and the coercive field of this film were 34.8 uC/cm2 and 41.7kV/cm, while the dielectric constant and loss value measured at 1kHz were approximately 1600 and 0.04, respectively. Dielectric and ferroelectric properties were correlated to the microstructure of the films. The effect of the thickness on texture of the films was also investigated, and it is clear that the (100) texture gradually increases and the (111) texture decreases with increasing film thickness. A PtxPb intermetallic metastable phase was observed by X-ray diffraction, and it is found that the position of this peak shifted from 38.30 degree ;(d:0.23481 nm) to 37.10 degree (d:0.4213 nm) with increasing firing temperature from 350 degree C to 550 degree C. The (111) preferred orientation in the PZT film was promoted by the metastable PtxPb phase. The formation of the (100) texture of perovskite phase in the multilayer films was mainly attributed to the effects of both substrates and crystal growth rates which dependent on orientation of crystal.

Y5.9
EFFECT OF ELECTRODES ON THE SWITCHING DYNAMICS OF LEAD BASED THIN FILM FERROELECTRIC CAPACITORS. I. Jenkins, S. Aggarwal, B. Nagaraj, N. Valanoor, C. Kerr and R. Ramesh, Univ of Maryland College Park, Dept of Materials and Nuclear Engineering, College Park, MD.

The microstructure and interface properties of ferroelectric capacitors are significantly influenced by the selection of electrode materials. These structural properties have been shown to play a major role in affecting reliability properties such as fatigue and imprint. Little work, however, has been reported on the effect of the electrode materials on the switching dynamics of ferroelectric thin film capacitors. Fast polarization logic state switching will become increasingly significant in future generations of nonvolatile ferroelectric random access memories with higher bit densities. With this in mind, we are studying the effects of systematic variations in the thin film microstructure, tetragonality and contact electrodes on the switching performance. The ease of switching of a ferroelectric capacitor can be quantified by a parameter termed the activation field introduced by Merz in the 1960's in his study of barium titanate single crystals. In our study, we compare pulse width dependence and activation field measurements of niobium doped Pb(Zr,Ti)O_3 (PZT) capacitors with $SrRuO_3$ (SRO), $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) and Pt electrodes to determine the role of the electrodes on the switching characteristics.

Y5.10
ORIENTATION EFFECTS IN CHEMICAL SOLUTION DERIVED PZT THIN FILMS ON FERROELECTRIC PROPERTIES. Seung-Hyun Kim, J.G. Hong, D-J. Kim, J-P. Maria, A.I. Kingon, North Carolina State Univ., Dept of Materials Science and Engineering, Raleigh, NC; D.-S. Lee, J.W. Ha, Inostek Inc., Seoul National Univ., Seoul, KOREA.

Ferroelectric materials are anisotropic, thus there may be an optimal crystallographic orientation for electronic devices making use their properties. In the absence of single crystal data for PZT compositions, one method of determining orientation-property relationships is through the study of strongly textured thin films. Unfortunately, however, producing sets of thin films having a series of distinct orientations with an arbitrary degree of chemical and physical similarities can be difficult. Typically, for example, changing process parameters to produce (111) vs. (100)-texture will concomitantly change characteristics such as grain size, roughness, or density. As such, solely orientation-related effects can not be isolated. We report on an investigation where (111) and (100)-textured PZT (30/70) thin films were prepared on (111) and (100)-textured Pt substrates respectively. In this investigation, the processing conditions used were identical for all samples. As a result, the film composition, microstructure, and topography were highly similar in all cases. Electrical properties were measured, and comparisons were made in reference to orientation differences. We find that the remanent polarization values and loop squareness are improved in (111)-textured films, while permittivities are higher in the case of (100) orientations as compared to (111)-textured films. Fatigue characteristics were also evaluated, however, negligible orientation effects were observed. Detail results and possible mechanisms are discussed here.

***Y5.11**
PHENOMENOLOGICAL BEHAVIORS OF FATIGUE AND VOLTAGE OFFSETS IN PZT THIN FILMS. Seung-Hyun Kim, D.-J. Kim, J.-P. Maria, A.I. Kingon, North Carolina State Univ., Dept of Materials Science and Engineering, Raleigh, NC; J.A. Christman, North Carolina State Univ., Dept of Physics, Raleigh, NC.

Although a number of experimental and theoretical contributions have been made concerning the issues of fatigue and imprint, no clear consensus has emerged regarding their origins or potential solutions. The purpose of this research is to investigate aspects of fatigue and imprint which have been observed in recent experimental results, and to define a phenomenological explanation which describes this behavior. In an approach to address these issues we have performed an extensive series of experiments on (111)-textured PZT (30/70) film on Pt electrodes. This is chosen for the present as it is the preferred composition and orientation for non-volatile memories. Electrical measurements include polarization hysteresis, imprint, fatigue, voltage dependent permittivity, and leakage current density. All electrical measurements are performed before and after achieving the fatigued and imprinted states. Results to emphasize include the fact that more severely fatigued samples show larger imprint. In addition, fatigued samples show lower leakage current density, in contrast to several reports. Furthermore, coercive field is found to decrease slightly with fatigue, but only in one switching direction. Detail results and possible mechanisms are discussed here.

***Y5.12**
CHARACTERISTICS AND APPLICATIONS OF Sr-MODIFIED FERROELECTRIC Pb(Zr,Ti)O_3 THIN FILMS. K.B. Lee, H.S. Lee, Sangji Univ, Dept of Physics, Wonju, Kangwondo, KOREA; B.K. Ju, Division of Electronics and Information Technology, Korea Institute of Science and Technology, Seoul, KOREA; Seshu B. Desu, Department of Electrical and Computer Engineering, University of Massachusetts, Amherst, MA.

We have investigated the electrical characteristics of Sr-modified Pb(Zr,Ti)O_3 thin films. Sol-gel derived $(Pb_{1-x}Sr_x)(Zr_{0.53}Ti_{0.47})O_3$ (PSZT) films were deposited by means of spin casing onto platinized silicon wafers. XRD patterns of these films showed perovskite single phase without any extra peak corresponding to $SrTiO_3$, which implies the successive substitution of Pb into Sr. Dielectric constant as well as remanent polarization of PSZT capacitors decreases with increasing Sr for x larger than 0.1. Otherwise, polarization fatigue loss after 10^{11} switching repetitions as well as leakage resistivity increases with increasing Sr. In this paper, we also discuss the applications of these PSZT thin films.

Y5.13
ELECTRICAL PROPERTIES OF LOW-TEMPERATURE PROCESSED PZT THIN FILMS WITH PREFERRED ORIENTATIONS. Hisao Suzuki, Yasuhiro Kondo, Shoji Kaneko, Shizuoka Univ, Dept of Materials Science, Hamamatsu, JAPAN; Takashi Hayashi, Shonan Inst of Technology, Fujisawa, JAPAN.

Ferroelectric PZT has a perovskite structure and therefore, PZT thin films with good ferroelectricity have a polarization axis, showing the different electrical properties depending on the crystal orientations of the resultant films. Consequently, orientation control is essential for the PZT films to apply various electronic devises with high performance. In this paper, ferroelectric PZT thin films with preferred orientations and good electrical properties, which had morphotropic phase boundary composition to show the superior ferroelectric properties for FE-RAM, were deposited on the silicon wafer with platinum electrode at low temperature. Chemical solution deposition from molecular-designed alkoxide precursor solution was applied for low-temperature processing of PZT thin films. This technique involved the addition of excess amount of lead in the precursor solution and the controlled pre-annealing process. The orientation of the resultant film was successfully controlled by changing the pre-annealing temperature. As a result, (111)-oriented PZT film exhibited relatively good ferroelectric and dielectric properties than the (100)-oriented PZT film, whereas the leakage current of the (111)-oriented film was larger than that of the (100)-oriented film. In addition, the resultant films had composition slightly rich in lead and zirconium than that of the stoichiometry, having the rhombohedral symmetry. All these films show the potential for the FE-RAM.

SESSION Y6: POSTER SESSION:
Bi-BASED THIN FILM FERROELECTRICS
Chairs: Harald Bachhofer and Bryan C. Hendrix
Monday Evening, November 29, 1999
8:00 P.M.
Exhibition Hall D (H)

Y6.1
FLUORITE AND LAYERED PEROVSKITE PHASES IN Sr-Bi-Ta-O FILMS. Jeong Soo Lee, Hyun Ja Kwon, Young Woo Jeong, Hyun Ha Kim, LG Corporate Institute of Technology, Seoul, KOREA; S.J. Hyun, T.W. Noh, Seoul National University, Seoul, KOREA.

The phase formation and microstructural evolution of Sr-Bi-Ta-O films grown on $LaAlO_3$ substrate by pulsed laser deposition were investigated using x-ray diffraction and cross-sectional transmission electron microscopy. At the as-deposited (deposition temperature = 600°C and 650°C heat-treated (1h) states, the epitaxially grown fluorite phase with a face-centered-cubic symmetry (Fm3m) was found. The crystallographic orientation relationships between the film and substrate were fluorite (0 0 1) || $LaAlO_3$ (0 0 1) and fluorite [1 1 0] || $LaAlO_3$ [1 0 0]. From the electron diffraction patterns for the fluorite phase, 1/2 1/2 1/2 and {1 0 0}-type superlattice spots were observed, which indicates that the fluorite phase has an ordered structure. After heat treatment at 750°C for 1h, the fluorite phase was gradually encroached upon by polycrystalline layered perovskite $SrBi_2Ta_2O_9$ (SBT) grains. The resultant SBT grains were highly (001) prefer oriented. The similarities of atomic structures between fluorite and layered perovskite SBT will be also discussed.

Y6.2
TEMPERATURE DEPENDENCE OF FERROELECTRIC PROPERITES OF BISMUTH LAYERED PEROVSKITES. S. Tirumala, S.B. Desu, Department of Electrical and Computer Engineering, University of Massachusetts, Amherst, MA.

We investigated the P-E hysteresis characteristics of $(SrBi_2Ta_2O_9)_{1-x}$: $(Bi_3TiNbO_9)_x$ solid solution thin films as a function of measuring temperature. $(SBT)_{1-x}$: $(BTN)_x$ solid solutions with x varying from 0.0 to 0.4 were prepared using metal organic solution deposition method and were spin coated on to platinized silicon substrates. All the films were processed at 750°C in oxygen atmosphere in order to obtain well crystallized single phase perovskite structures, and the ferroelectric properties were measured in the temperature range of 25°C to 200°C. While the remnant polarization of $SrBi_2Ta_2O_9$ thin film capacitor was reduced by 50% as the measuring temperature was increased from 25°C to 100°C, the remnant polarization of $(SrBi_2Ta_2O_9)_{0.6}$: $(Bi_3TiNbO_9)_{0.4}$ thin film capacitor remained unchanged at 100°C. However, coercive field of all the films decreased with the increasing measuring temperature. Additionally, we found that for a given measuring temperature, the coercive field of $SrBi_2Ta_2O_9$ thin film was always the lowest as compared to that of other compositions. Such a trend could be attributed to the low Curie temperature of $SrBi_2Ta_2O_9$ as compared to that of other compositions.

Y6.3
EFFECT OF POST-DEPOSITION ANNEALING ON THE DIELECTRIC PROPERTIES OF $SrBi_2Ta_2O_9$ THIN FILMS PREPARED BY PLD. M. Cruz, Centro de Investigacion Cientifica y de Educacion Superior de Ensenada, Ensenada, BC MEXICO; J.M. Siqueiros, Centro de Ciencias de la Materia Condensada-UNAM, Ensenada, BC MEXICO; J. Portelles, Facultad de Fisica-IMRE, Universidad de la Habana, La Habana, CUBA.

Well adhered $SrBi_2Ta_2O_9$ (SBT) thin films were prepared on $Pt/TiO_2/SiO_2/Si$ substrates by PLD. The films were deposited at 450°C and then annealed in an air atmosphere at temperatures between 450°C and 850°C. Scanning (SEM) and transmission (TEM) electron microscopy as well as x-ray diffraction (XRD) techniques were used for their microstructure characterization. The x-ray spectra of the deposited films showed a BiO_{2x} crystalline phase a result that was confirmed by TEM studies. No interdiffusion of the Pt bottom electrode in the PLD layer was detected in these films. The development of the SBT layer perovskite phase with preferential (115) orientation was observed as the temperature of the annealing process was increased. An increase in the mean grain size with heat treatment was also observed by SEM images. After a sputter deposition of a Pt top electrode, the microstructural results previously obtained were correlated to the ferroelectric properties.

Y6.4
PREPARATION OF C-AXIS-ORIENTED FERROELECTRIC $SrBi_2Ta_2O_9$ THIN FILMS. T.B. Wu, C.L. Liu, Natl Tsing Hua University, Hsinchu, TAIWAN ROC.

The $SrBi_2Ta_2O_9$ (SBT) thin films have attracted much interest for non-volatile memory application due to its minimal polarization fatigue. In this study, highly (100) oriented $LaNiO_3$ (LNO) electrode was deposited on $Pt/Ti/SiO_2/Si$, and SBT thin films were subsequently deposited on the LNO electrode by RF magnetron sputtering at temperatures of 500-600°C. The SBT films were found to have a strongly C-axis-oriented texture and the crystallization temperature of SBT films can be reduced to 560°C. The C-axis-oriented SBT thin films have a dielectric constant of 120, and the leakage current is about 10^{-7} A/cm^{-2} at 130 KV/cm. The remnant polarization and the coercive filed are 0.352 uC/cm^2 and 52.35 KV/cm, respectively, at an applied voltage of 3V. Such a low remnant polarization of SBT is believed to be due to the C-axis preferred orientation, which is not the primary polarization orientation of SBT. It was also found that the C-axis preferred orientation can be further enhanced by a post annealing at temperature of 700°C. However, the annealing does not affect the remnant polarization and coercive field, but the leakage current increased with increasing the annealing temperature.

Y6.5
LOW-TEMPERATURE PROCESSING USING TRIPLE ALKOXIDE PRECURSORS FOR LAYER-STRUCTURED PEROVSKITE THIN FILMS: PREPARATION AND CHARACTERIZATION OF $MBi_2Ta_2O_9$ (M: Ca or Ba) THIN FILMS. Kazumi Kato, National Industrial Institute of Nagoya, Nagoya, JAPAN; Tokyo Institute of Technology, Yokohama, JAPAN.

Thin films of layer-structured perovskite, $MBi_2Ta_2O_9$(M: Ca or Ba), were prepared on Pt-passivated silicon substrates by a spin-on deposition method using triple alkoxides which contained three metals of M(M: Ca or Ba), Bi, and Ta with an atomic ratio of 1:2:2. The M-Bi-Ta triple alkoxides were found to be synthesized by the same method as a Sr-Bi-Ta triple alkoxide [1,2]. The M-Bi-Ta triple-alkoxy-derived gel films crystallized at relatively low temperatures by rapid thermal annealing in an oxygen flow. The crystallinity of the films improved with annealing temperatures. The crystallization behavior and the ferroelectric and endurance properties will be discussed. References [1] K. Kato, et al., J. Am. Ceram. Soc., 81, 7, 1869 (1998). [2] K. Kato, Jpn. J. Appl. Phys., 37, 9B, 5178 (1998).

Y6.6
A STRUCTURAL STUDY OF $SrBi_2Ta_2O_9$-Bi_3TiNbO_9 FERROELECTRIC THIN-FILMS. E. Ching-Prado, W. Pérez[1], P.S. Dobal[1], R.S. Katiyar[1], S. Tirumala[2], and S.B. Desu[2] Faculty of Science and Technology, Technological University of Panamá, PANAMÁ; [1]Department of Physics, University of Puerto Rico, San Juan, PR; [2]Department of Electrical and Computer Engineering, University of Massachusetts, Amherst, MA.

Thin films of ferroelectric $(SrBi_2Ta_2O_9)_x(Bi_3TiNbO_9)_{1-x}$ layered structure were prepared for x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0, by metal organic solution deposition method on $Pt/TiO_2/SiO_2/Si$ substrates. The samples were studied by Raman spectroscopy, X-ray diffraction, atomic force microscopy (AFM), and electrical measurements. All of these techniques are sensitive to the inclusion of $SrBi_2Ta_2O_9$ (SBT) into the Bi_3TiNbO_9 (BTN) system. The Raman spectra show frequency shifts and broadening of the bands as x changes from 0.0 to 0.4, which is related to the nature of Sr and Bi in the A-sites, and Ta, Ti, and Nb in the B-sites. A temperature Raman study is presented and discussed. AFM study, in all samples except for x = 1 shows a smooth surface with no cracks and defects. Also, the AFM images indicate that the grain size in the films increase with increasing SBT material in the BTN compound. Electrical measurements show that the remanent polarization (Pr) and the coercive field (Ec) increase from 2 C/cm^2 and 30 KV/cm, for x = 0.0, to 12.5 C/cm^2 and 125 KV/cm, for x = 0.6. A decrease in these parameters are found for higher x-values. Possible correlation between Pr and Ec, and the Raman spectra are investigated. Finally, a comparison between the films and those in the bulk form are established and discussed. Partially supported by NSF-INT 9604988 and NSF-DMR 9801759 grants.

Y6.7
PREPARATION OF NEW SBT CHEMICAL SOLUTIONS USING CROWN ETHER AND ITS THIN FILM DEPOSITION. Yo-Sep Min, June key Lee, In-sook Lee, Samsung Advanced Institute of Technology, Microelectronics Lab, Yongin, KOREA.

New chemical solution for $SrBi_2Ta_2O_9$ (SBT) thin films using crown ether is proposed. Crown ether-coordinated metal acetates enhance the solubility of metal acetates in acetic acid, which make one solvent solution possible. Metal acetate based SBT precursor solution was prepared in acetic acid solvent using 18-crown-6 coordinated bismuth acetates, strontium acetates and tantalum ethoxides. The perovskite phase SBT ferroelectric thin films were formed on $Pt/TiO_2/SiO_2/Si$ substrates by spin-coating and annealing at 800°C. Hysteresis loop obtained from a 200 nm thick film with Pt electrodes showed ~3 μC/cm^2 of remanent polarization and ~50 kV/cm of coercive voltage.

Y6.8
LOW TEMPERATURE PREPARATION OF $Sr_2(Ta_{1-x}, Nb_x)_2O_7$ FERROELECTRIC THIN FILM BY PULSED LASER DEPOSITION FOR APPLICATION TO FERROELECTRIC MEMORY MFIS-FET. Minoru Noda, Toshiyuki Nakaiso, Hideki Sugiyama, Tomofumi Kiyomoto and Masanori Okuyama, Graduate School of Engineering Science, Osaka Univ, Osaka, JAPAN.

Preferentially (151)-oriented $Sr_2(Ta_{1-x}, Nb_x)_2O_7$ (STN) thin films on Pt have been prepared at temperatures as low as 600 and 550 degree Celsius, in O_2 and N_2O atmospheres, respectively, by pulsed

laser deposition (PLD). The temperatures are quite lower than those of other methods such as sol-gel method, where 950 degree Celsius was reported. It is noted, on the other hand, that STN thin film is suitable as a ferroelectric material for ferroelectric memory FETs, because it has a low dielectric constant(ε), low coercive force(E_c), thermal stability and enough D-E hysteresis, compared to bismuth-layer-structured ferroelectric materials such as $SrBi_2Ta_2O_9$. Moreover this includes no toxic volatile and viscous elements such as Pb and Bi. Low temperature methods, however, are still needed because some conventional standard Si IC processes cannot endure process temperatures as high as about 900 degree Celsius. In this work composition ratio (x) in target material used is decided to be 0.3 from a point of Curie temperature and ferroelectric property. In PLD, active oxygen generated when using N_2O atmosphere is found to be very effective by observations of X-ray Diffraction and Raman spectroscopy to decrease growth temperature of crystallized STN film and to improve crystallinity in the film. It is also confirmed by surface AFM and cross-sectional SEM observations that the film has a columnar-shaped structure with grain size ranging from 50 to 100 nm. Finally, we expect the low temperature STN film prepared by PLD is a promising ferroelectric one for the application to ferroelectric memory FET.

Y6.9
X-RAY PHOTO ELECTRON SPECTROSCOPY AND MICRO-RAMAN STUDIES OF $SrBi_2Ta_{0.8}Nb_{1.2}O_9$ THIN FILMS. Srinivas Sathiraju, Rasmi R. Das, Estevao R. Fachini, Juan Mercado, William Perez and Ram S. Katiyar, Spectroscopy laboratory, Univeristy of Puerto Rico, San Juan, PUERTO RICO.

It has been well established that Bismuth based ferro-electric compounds such as $SrBi_2Nb_2O_9$ (SBN), $SrBi_2Ta_2O_9$(SBT) and $SrBi_2Ta_{0.8}Nb_{1.2}O_9$ (SBTN) have a significant advantage over Pb-based ferro-electric materials which usually show fatal fatigue failures with Pt electrodes. Inorder to understand the role of oxygen ions, in this paper, we report the effect of growth conditions such as substrate temperature (25-850°C) and oxygen partial pressure (50-450 mTorr) on the microstructure-property relationship of pulsed laser deposited SBTN thin films on Si (100) and MgO(100) substrates. Films were characterized using X-ray diffraction (XRD), X-ray photo emission spectroscopy (XPS), Atomic force microscopy (AFM) and micro-Raman spectroscopy. As deposited thin films below 500°C were amorphous. AFM studies indicated that average grain size of the films varied between 0.08 μm to 0.1μm with the increase in the growth temperature. XPS studies of as-deposited films reveals that the oxygen vacancies are preferably present near the Bi ions at the Bi_2O_2 layers and varies with substrate temperature and oxygen partial pressure. Also, XPS studies of Sr3d core level for SBTN films suggests that the oxygen ions at the $Sr(Ta/Nb)_2O_7$ perovskite layers are much more stable than those at the Bi_2O_2 layers. Micro-Raman studies of SBTN films revealed the fact that shifting of Raman modes, which corresponds to the BO_6 octahedron symmetry to higher frequencies, is in accordance with the different ionic radii of the B site ions and thus affecting the force constants involved due to Nb doping at Ta sites.

SESSION Y7: Pb-BASED THIN-FILM FERROELECTRICS
Chairs: Yoichi Miyasaka and Dirk J. Wouters
Tuesday Morning, November 30, 1999
Room 304 (H)

8:30 AM *Y7.1
COMPOSITIONAL HETEROSTRUCTURES AND ORIENTATION EFFECTS IN PZT FILMS FOR NONVOLATILE MEMORIES. Angus I. Kingon, SeungHyun Kim, JoonGoo Hong, Jon-Paul Maria and Stephen K Streiffer*, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC. *Materials Science Division, Argonne National Laboratory, Chicago, IL.

Within the $Pb(Zr,Ti)O_3$ system, research and development groups have typically concentrated upon the Ti-rich tetragonal compositions with (111) orientation, in particular to achieve square hysteresis loops with high values of switchable polarization. In this study, we have addressed two issues. Firstly, we have made a careful comparison of (111) and (100) oriented PZT films with tetragonal symmetry. The P-E hysteresis loops are a little squarer for the (111) films, this well-defined onset of switching being ascribed to the small ferroelastic strain contribution. Other properties are very similar for the two orientations, and these results are discussed in the light of current models of switching, fatigue and imprint. Secondly, we have prepared a series of CSD PZT films in which the composition is varied through the thickness. The heterostructures were prepared by various sequential combinations of two endmembers, these being a tetragonal 70/30 and a rhombohedral 35/65 composition. It was clear from separate diffraction peaks in the x-ray diffraction analysis that significant interdiffusion did not occur, and that B-site cation compositional heterogeneity was maintained. As expected, there was no observed anomaly in the switchable polarization. The property characterization of the samples showed a surprisingly simple relationship to the endmembers. Once again the results are analyzed in terms of current fatigue and imprint models. The utility of compositional heterostructures as a strategy for ferroelectric memory is discussed.

9:00 AM Y7.2
EFFECT OF Pb STOICHIOMETRY ON SWITCHING BEHAVIOR OF SOL-GEL PREPARED PZT THIN FILMS. G. Norga, Laura Fe, D. Wouters, IMEC, Leuven, BELGIUM; J. Maes, O. Van der Biest, MTM - KU Leuven, Leuven, BELGIUM.

Reduction of the switching voltage of PZT thin films is an important milestone on the road to high density FERAMs based on PZT. In this paper we demonstrate that Pb excess, apart from its well known effects on crystallization behavior and texture selection, can have a large influence on ferroelectric switching behavior as well. By performing PZT crystallization in a closed system (quartz ampoule) containing $PbZrO_3$ powder, the lead loss which is inherent to furnace crystallizations can be prevented. Films crystallized by this method showed improved squareness of the hysteresis loop, along with a considerable reduction in switching field. For 20/80 PZT, this resulted in a switching voltage reduction from 2.5 V to 1.9V, while maintaining P_r = 30 $\mu C/cm^2$. For 30/70 and 40/60 PZT, switching voltages of 1.5 V and 1.3 V were obtained, with P_r = 30 and 25 $\mu C/cm^2$, respectively. A simple defect chemistry model is presented, which illustrates the need to strictly maintain Pb stoichiometry at the PZT/topelectrode interface in order to suppress bandbending and reduce switching voltage. In conclusion, opportunities for further reducing switching voltage by reducing PZT layer thickness will be discussed.

9:15 AM Y7.3
LOW OXYGEN PRESSURE CRYSTALLIZATION OF $Pb(Zr,Ti)O_3$ FOR EMBEDDED FERAMS. Yoshikazu Fujimori, Toshiyuki Takeda, Takashi Nakamura, Hidemi Takasu, Device Technology Div. Semiconductor Research and Development Headquarters, Rohm Co., Ltd. Kyoto, JAPAN.

Ferroelectric memory (FeRAM: Ferroelectric Ramdom Access Memory) has been expected as a non-volatile RAM, and FeRAMs have been produced in mass production level. Embedded FeRAMs have been intensively studied because the FeRAM has high potential for low-power, high-speed operation, and high switching endurance compared to conventional non-volatile memories. To realize the embedded FeRAMs, lowering the temperature during fabricaton of the ferroelectric capacitors is essential not to affect the parameters of metal oxide semiconductor (MOS) transistors. In this study, lowering crystallization temperature was succeeded in the sol-gel method by using low pressure annealing. The oxygen (partial) pressure dependence were investigated, and the mechanism of lowering temperature was considered. the low crystallization temperature led to low thermal stress and sharp interface. Thus the endurance and retention characteristics of the PZT capacitor were greatly improved.

9:30 AM Y7.4
HIGH-ENDURANCE SCALABLE PZT CAPACITORS USING THIN SRO/Pt STACKED ELECTRODES. Koji Yamakawa, Osamu Arisumi, Osamu Hidaka, Toyota Morimoto, Iwao Kunishima, Shin-ichi Tanaka and Tsunetoshi Arikado, Microelectronics Engineering Laboratory, Toshiba Corp. Semiconductor Company, Yokohama, JAPAN.

Effects of SRO(SrRuO3) electrode have been studied for high-endurance PZT capacitors, 90nm-thick PZT capacitors using Pt/thinSRO stacked electrodes showed 2V operation capability, no remanence degradation after more than 1E10 switching cycles, and less imprint.
In order to achieve low voltage operation, PZT film thickness must be reduced though it causes serious fatigue degradation by higher electric fields. We introduced SRO electrode which has the same crystal structure (perovskite) as PZT. It is expected to promote domain switching at lattice-matched PZT/SRO interfaces in addition to fatigue performance.
PZT films crystallized on SRO showed smaller coercive voltage Vc (2/3 of that for PZT/Pt) with random orientation. There was no polarization decrease observed after more than 1E10 cycles. Ferroelectric P-V hysteresis was obtained down to 90nm-thick films. To investigate the role of SRO, capacitors with only top SRO electrodes were studied. This case the SRO increased polarization and improved saturation property compared to Pt electrode PZTs. Fatigue and imprint degradation was observed by Pt bottom electrode interface deterioration. The fatigue was found to occur not by DC voltage but by polarization reversal.

It is believed that oxygen vacancy created along with Pb vacancy is determinant in endurance and retention. SRO layers block Pb diffusion and supply oxygen, thereby resulting in less oxygen vacancies at PZT interfaces. A model is proposed in which oxygen vacancy induces strain and causes domain pinning with less nucleation at electrode interfaces. Partially epitaxial PZT/SRO interfaces give more nucleation sites for domain reversal. 1.8*1.8um PZT capacitors with thin SFRO/Pt stacked electrodes were formed through integration processes. Functional operation was confirmed in 1MFRAM devices using the developed capacitors. It is shown this technique has potential for application in the coming Mbit FRAM generation.

9:45 AM Y7.5
BOTTOM ELECTRODE EFFECTS IN CONTROLLING ORIENTATION OF LEAD ZIRCONATE TITANATE FILMS DEPOSITED BY CHEMICAL SOLUTION DEPOSITION.
Deborah A. Neumayer, Katherine L. Saenger, Robert B. Laibowitz, Thomas M. Shaw, Rebecca Mih, Alfred Grill, IBM T.J. Watson Research Center, Yorktown Heights, NY.

The microstructure and electrical properties of lead zirconate titanate $Pb(Zr,Ti)O_3$ (PZT) films prepared by chemical solution deposition (CSD) with and without lead titanate seed layers was examined as a function of iridium/iridium oxide electrode type. The novel PZT CSD solution was prepared from a mixture of zirconium and titanium butoxyethoxides and lead ethylhexanoate dissolved in butoxyethanol. The use of a lead titanate seed layer was found to promote (111) orientation on iridium but not on iridium oxide. Remanent polarization ($2P_r$) was found to vary with film orientation and thickness. A 230 nm PZT film with iridium top and bottom electrodes had a $2P_r$ of 45 $\mu C/cm^2$ at 5V. The effect of various iridium/iridium oxide bottom electrodes on fatigue was investigated.

10:30 AM Y7.6
THICKNESS DEPENDENCE OF CRYSTALLINE AND ELECTRICAL PROPERTIES OF PZT ULTRATHIN FILMS GROWN ON $SrRuO_3/SrTiO_3$ BY MOCVD.
M. Shimizu, Y. Ishii, K. Morimoto, H. Fujisawa and H. Niu, Himeji Institute of Technology, Department of Electronics, Himeji, JAPAN.

In order to realize the low voltage operation and high density integration of non-volatile ferroelectric random access memories (NV-FeRAMs), the dependence of film thickness on the crystalline and electrical properties was investigated for PZT thin films with thicknesses ranging from 40 to 400nm grown on $SrRuO_3/SrTiO_3(100)$ (SRO/STO) by MOCVD. Epitaxial PZT thin films were successfully grown on SRO/STO substrates at a deposition temperature of around 580°C. Lattice constants of c-axis were increased and those of a-axis were decreased as the film thickness decreased. Dielectric constant of epitaxial films gradually decreased as thickness decreased, while strong thickness dependence of dielectric constant was observed for polycrystalline PZT grown on $SRO/SiO_2/Si$. Epitaxial PZT thin films obtained showed well saturated D-E hysteresis loops even when film thickness was 40nm. Remanent polarization and coercive field of the 40nm-thick PZT film were around 35$\mu C/cm^2$ and 370kV/cm, respectively. Current densities and switching fatigue characteristics were also influenced by film thickness and these were poorer for thinner films than for thicker films. Comparison with the thickness dependence of polycrystalline PZT films and TEM observations of domain structure will also be reported.

10:45 AM *Y7.7
OBSERVATION OF DOMAIN SWITCHING IN EPITAXIAL $Pb(Zr,Ti)O_3$ THIN FILMS IN REAL TIME USING X-RAY SCATTERING.
A. Munkholm[a], C. Thompson[b,c], K. Ghosh[c], S.K. Streiffer[c], G.B. Stephenson[c], O. Auciello[c], J.A. Eastman[c], G.R. Bai[c], Q. Gan[d] and C.B. Eom[d]; [a]Chemistry Division, Argonne National Laboratory, Argonne, IL; [b]Dept. of Physics, Northern Illinois University, IL; [c]Materials Science Division, Argonne National Laboratory, Argonne, IL; [d]Dept. of Mechanical Eng. and Materials Science, Duke University, Durham, NC.

X-ray scattering measurements performed simultaneously with electrical switching allow real-time observation of domain structure dynamics in epitaxial ferroelectric thin films. Interference between the scattering from the ferroelectric film, the epitaxial bottom electrode, and the substrate gives rise to strong oscillatory modulations in the crystal truncation rod. These oscillations are sensitive to the structure and polarity of the film and allow us to probe structural changes during switching. We have characterized 25-40 nm thick $Pb(Zr,Ti)O_3$ films grown by MOCVD on epitaxial $SrRuO_3$ bottom electrodes, which were sputter-deposited onto vicinal $SrTiO_3(001)$ substrates. Using synchrotron radiation from the Advanced Photon Source, we measured the scattering from the active element beneath a 250 μm diameter top electrode. Measurements of the ferroelectric response of the film in real time during switching will be presented.

11:15 AM Y7.8
STOCHIOMETRY AND INTERDIFFUSION IN PZT $(Pb(Zr,Ti)O_3)$ THIN FILMS STUDIED BY TRANSMISSION ELECTRON MICROSCOPY (TEM).
Laurent Sagalowicz, Paul Muralt, Thomas Maeder, Keith Brooks and Nava Setter, Laboratoire de Cèramique, Swiss Federal Institute of Technology (EPFL), Lausanne, SWITZERLAND.

Electrode stability, interdiffusion, phase purity and deviation from stochiometry at the PZT-electrode interface are key issues in PZT thin film integration. Oxidation reactions, diffusion through the electrode layers are often non homogeneous as they depend on grain boundaries and thin film morphology. This article highlights the use of Transmission Electron imaging and diffraction combined with Energy Dispersive Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS) for the investigation of these phenomena. The accuracy of the EDS analysis is discussed. It will be shown that using a standard PZT sample and controlled conditions, reliable analysis can be performed. Diffusion mechanisms have been studied for Pt based electrode systems and RuO_2 based electrode systems developed for direct integration onto silicon. The materials studied were composed of stacks of silicon-silicon oxide, an adhesion layer, an electrode (Pt or RuO_2) and PZT (45/55). The PZT was deposited by sol gel using the same parameters to really compare the different electrodes. Four different adhesion layers-electrode materials were compared (Ti-Pt, TiO_2-Pt, Ta-Pt and TiO_2- RuO_2). In the case of Pt, lead and oxygen diffusion through the electrode is observed. While the initial Ta layer transforms into a homogeneous pyrochlore phase, the Ti adhesion layer is heavily deformed. In the case of TiO_2 the lead is mainly incorporated at the interfaces with Pt and with SiO_2. The mechanisms of diffusion responsible for this behavior will be discussed. No lead diffusion to the adhesion layer is observed for the RuO_2 electrode. It will be also shown that direct contact of PZT on reactive substrates (such as W, Mo, TiN) can be made using RuO_2. The RuO_2 electrode associated with a Cr adhesion layer plays a role of diffusion barrier for oxygen till 800°C. The Cr forms a passivating layer.

11:30 AM Y7.9
STATISTICAL ANALYSIS OF HIGHLY ACCELERATED LIFETIME TESTS (HALT) ON PIEZOELECTRIC LEAD ZIRCONATE TITANATE THIN FILMS.
Ronald G. Polcawich*, Cheng-Ning Feng, Stewart Kurtz[1], Steve Perini, Susan Trolier-McKinstry, Clive Randall, The Materials Research Laboratory, The Pennsylvania State University, University Park, PA, *currently at The Army Research Laboratory, Adelphi, MD. [1]Electrical Engineering, The Pennsylvania State University, University Park, PA.

Lead zirconate titanate ($PbZr_{0.52}Ti_{0.48}O_3$) thin films have high dielectric and piezoelectric constants and as a result are extremely attractive for capacitive and MEMS applications. The reliability of PZT thin films under dc electric fields can be assessed using highly accelerated lifetime tests (HALT). To date, though, there has been limited statistical analysis of HALT experiments using dc electric fields on PZT thin film capacitors. Thus, a series of HALT experiments were conducted on sets of 30 samples at temperatures ranging from 120°C to 180°C and fields ranging from 250 kV/cm to 400 kV/cm. Assuming a lognormal distribution of the failure times, it was found that breakdown occurred by two distinct failure modes. Early freak failures were mostly likely due to extrinsic defects, with later failures representing the limit on reliability. The shape parameter of the distribution for failure times, σ_{ln}, remained relatively constant for various voltage and temperatures stresses. The relative independence of this parameter allowed for a direct determination of the activation energy for failure, ~0.78 eV, and the voltage acceleration factor, ~7.8. Lastly, analysis of the samples that failed during the HALT experiments revealed that microcracking, film/electrode delamination, and arcing all contribute to failure.

11:45 AM Y7.10
EFFECTS OF ACTIVE AMMONIA GAS CRACKED IN CATALYTIC-CVD ON PZT FERROELECTRIC CAPACITORS.
Toshiharu Minamikawa[1,2], Yasuto Yonezawa[2], Yoshikazu Fujimori[1,3], Takashi Nakamura[3], Atsushi Masuda[1], Hideki Matsumura[1]; [1]Japan Advanced Inst. of Science and Technology, Ishikawa, JAPAN, [2]Industrial Research Inst. of Ishikawa, Ishikawa, JAPAN, [3]Rohm Co., Ltd., Kyoto, JAPAN.

We investigated the effects of exposure in active ammonia gas on ferroelectric $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) capacitors. In generally, SiN_x or SiN_xO_y films are employed for passivation films of ferroelectric nonvolatile random access memories (FRAMs) in order to prevent moisture corroding aluminum from penetrating them. It has been reported that device quality SiN_x films are prepared by catalytic chemical vapor deposition (Cat-CVD) using a gaseous mixture of SiH_4 and NH_3 at low substrate temperature. It is also known that such SiN_x films have low hydrogen content below a few at.%, low stress below 10^9 dyn/cm^2 and low etching rate below a few nm/min.

These results suggest that Cat-CVD SiN_x films are one of the promising candidates for passivation films of FRAMs. However, deoxidization hydrogen exist on the substrate surface in Cat-CVD processes since SiH_4 and NH_3 gases are decomposed by catalytic cracking reaction with a heated catalyzer. Therefore, it is very important to know the effects of exposure in active ammonia gas generated in Cat-CVD system on PZT properties in order to apply Cat-CVD SiN_x films to passivation films for ferroelectric FRAMs. The exposure in active ammonia was carried out for PZT film capacitors with three kinds of electrodes on Si wafer at various substrate temperatures. The capacitor with Pt/IrO_2 bottom electrode peeled off from substrate during the exposure over 200°C. On the other hand, the ferroelectricity of the capacitors with IrO_2 or Ir/IrO_2 bottom electrode gradually degraded from 200°C to 300°C. As a result, it is found that no degradation of the ferroelectricity is detected for the exposure below 200°C. It is concluded that the Cat-CVD method is promising candidate for preparation of the SiN_x passivation film on ferroelectrics, since it is a low stressed film with low hydrogen content.

SESSION Y8: Bi-BASED THIN-FILM FERROELECTRICS
Chairs: Jeffrey F. Roeder and Robert W. Schwartz
Tuesday Afternoon, November 30, 1999
Room 304 (H)

1:30 PM Y8.1
MOCVD OF $SrBi_2(Nb, Ta)_2O_9$ FOR INTEGRATED FERROELECTRIC CAPACITORS. Bryan C. Hendrix, Timothy E. Glassman* and Jeffrey F. Roeder, Advanced Technology Materials, Inc., Danbury, CT. *Present address: Intel Corp., Hillsborough, OR.

The Bi layered perovskites are promising materials for ferroelectric random access memories (FeRAM's) because of their inherently high resistance to fatigue and imprint. Liquid delivery, flash vaporization metalorganic chemical vapor deposition (LD-MOCVD) is an attractive process for these materials, because it offers the ability to produce high quality, conformal films of controlled composition for both high and low density memory applications. We have developed a well-controlled process to deposit Nb-substituted $SrBi_2Ta_2O_9$ (SBNT) using a mixed alkoxide-β-diketonate precursor $Nb(O\text{-}i\text{-}Pr)_4(thd)$ that is compatible with a previously developed precursor suite for SBT ($Sr(thd)_2$-lewis base, $Bi(thd)_3$, and $Ta(O\text{-}i\text{-}Pr)_4(thd)$). In this study, wavelength dispersive x-ray fluorescence has been used to characterize composition and thickness. As-deposited films are smooth, with a surface roughness of 1.5 nm RMS. After a post-deposition annealing treatment, a high quality layered perovskite crystal structure was obtained. The resultant ferroelectric properties including fatigue and imprint are compared to SBT films without substitution.

1:45 PM Y8.2
EFFECT OF FILM COMPOSITION ON LOW TEMPERATURE PROCESSING OF SBT DEPOSITED BY MOCVD.
Harald Bachhofer, Frank Hintermaier, Manfred Hauf, Oswald Spindler, Thomas Haneder, Christine Dehm, Infineon Technologies, Memory Products, Munich, GERMANY; Henning von Philipsborn, University of Regensburg, Physics Department, GERMANY; Rainer Waser, IFF, Forschungszentrum Juelich and RWTH Aachen, GERMANY.

For stacked capacitor FeRAM applications a major challenge is to combine the diffusion barrier with the high temperature annealing of the strontium bismuth tantalate (SBT) process. Thus, it is desirable to lower the SBT processing temperature. This paper summarizes the effect of film composition on microstructure and electrical properties of a low temperature SBT process. SBT thin films (90 nm) of various compositions were grown on Pt/Ti electrodes by metalorganic chemical vapor deposition (MOCVD). Starting from a film composition of Sr/Bi/Ta = 0.85/2.20/2.00 the Sr and Bi content have been varied systematically from 0.55 to 1.00 and 2.00 to 3.00, respectively. The SBT films were annealed in oxygen ambient at temperatures ranging from 650°C to 800°C and then, phase transition, orientation, microstructure, polarization and leakage current of the thin films were evaluated. High temperature X-ray diffraction studies show that the required temperature for the phase transition from fluorite-type to ferroelectric phase and the formation of 2^{nd} phases strongly depend upon film composition. For highly Sr-deficient films a pyrochlore-type phase is already present at 700°C. Excess Bi allows decreasing the crystallization temperature. At the same time, high remanent polarization values of 20 $\mu C/cm^2$ and low leakage current values of 10^{-7} A/cm^2 at an applied electric field of 220 kV/cm are achieved. The orientation of the SBT grains in the films was found not only to be dependent upon Sr but also on Bi content. Overall, it could be shown that for a low temperature process precise composition control is even more important than for higher annealing temperatures.

2:00 PM *Y8.3
RELATIONSHIPS BETWEEN Bi/Ti COMPOSITION RATIO AND O_2 CONCENTRATION FOR ORIENTATION CONTROL OF $Bi_4Ti_3O_{12}$ THIN FILM USING MOCVD METHOD. Takeshi Kijima, Sharp Corporation, Kashiwa-shi, JAPAN.

We obtained a pillar-shaped structure MOCVD-$Bi_4Ti_3O_{12}$ thin films from (001) to (117) orientation changing oxygen concentration and a Bi/Ti composition ratio. When a Bi/Ti composition ratio was 0.65 and not stoichiometry, a (001) film obtained the value with Pr=0.8μC/cmBi^2, υ_r=40. $Pt/Bi_2SiO_5/Si$(MIS) and Pt/200-nm-$Bi_4Ti_3O_{12}$/Pt/30-nm-Bi_2SiO_5/ Si(Metal/Ferroelectric/Metal/Insulator/Semiconductor) structures were prepared by MOCVD method. When the capacitance-vs-voltage(C-V) characteristics of the $Pt/Bi_2SiO_5/Si$ structure was measured, the inversion layer formation could be confirmed by the electron of the minor career. On the other hand, the C-V characteristics of $Pt/Bi_4Ti_3O_{12}/Pt/Bi_2SiO_5/Si$ structure has ferroelectric switching property, and the memory window was about 2.0V. Furthermore, it is shown that the capacitance at zero-bias shows almost constant for 24 h.

2:30 PM Y8.4
PLASMA ETCHING DAMAGE TO FERROELECTRIC $SrBi_2Ta_2O_9$ (SBT) THIN FILMS AND CAPACITORS. Jun Hee Cho, Il Young Kwon, Chanro Park, Chang Ju Choi, Yeo Song Seol, D.S. Pyun and Il Hyun Choi, Memory Research and Developement Division, Hyundai Electronic Industries Co. Ltd., Kyungki-do, KOREA.

The reactive ion etch (RIE)-induced degradation of Pt/SBT/Pt capacitor performance has been investigated. SBT thin films were deposited on Pt electrode-coated substrate by metal organic decomposition method (MOD). After the top surface of the SBT/Pt layers was pretreated by Cl_2/Ar plasma with various gas ratios in RIE reactor, another Pt electrodes were deposited on the top of SBT/Pt layer by sputter deposition. Then the Pt/SBT/Pt-stacked layers were etched by Cl_2/Ar plasma in RIE reactor to form ferroelectric capacitors feasible for electrical evaluation. After annealed at high temperature in O_2 ambient, polarization-voltage characteristics of the Pt/SBT/Pt capacitors were measured and correlated to the surface composition of the plasma-pretreated SBT/Pt layers using XPS method. The remanent polarization of the plasma-pretreated samples was found to be significantly smaller than the one without pretreatment, at worst, by ~60%. The remanent polarization of the pure Cl_2 plasma-pretreated capacitor was 9.8$\mu C/cm^2$ (16.3 $\mu C/cm^2$ without pretreatment) and further decreased in the presence of Ar, which obviously is not explained by the SBT thickness reduction induced by pretreatment. The surface composition study of the plasma-pretreated SBT/Pt samples revealed that oxygen concentration is deficient near the surface compared to the bulk, which is thought to be due to the energetic ions and free radicals bombardment during pretreatment. The pretreatment also caused shift in polarization hysterisis curve along the voltage axis. The magnitude of voltage shift correlates to the amount of Cl_2 in plasma. The surface analysis results show that voltage shift is caused by oxygen deficiency and chlorine ion accumulation in the SBT surface which would contribute the internal E-field built-up in SBT layer.

2:45 PM Y8.5
PROCESSING OF REDUCTION RESISTANT $SrBi_2Ta_2O_9$ (SBT) CAPACITORS USING IRIDIUM BASED ELECTRODES.
S. Tirumala and S.B. Desu, Department of Electrical and Computer Engineering, University of Massachusetts, Amherst, MA; K.B. Lee, Department of Physics, Sangji University, Wonju, KOREA.

An attempt is made to reduce the degradation of ferroelectric properties of SBT based capacitors, caused by annealing in forming gas, by using Ir and IrO_2 top electrodes. A metal organic solution deposition technique is used to fabricate 0.25mm thick SBT film on platinized silicon wafer. Using SBT/Pt thin films processed at 750°C in oxygen atmosphere, three types of capacitors were fabricated, namely, Pt/SBT/Pt, Ir/SBT/Pt, IrO_2/Ir/SBT/Pt. All the three capacitor structures were annealed in forming gas at temperatures ranging from 25°C to 400°C. The remnant polarization of Pt/SBT/Pt capacitor was found to decrease by 65% after annealing in forming gas at 400°C. For the same annealing temperature, loss of polarization of Ir/SBT/Pt was observed to be 8%, while that of IrO_2/Ir/SBT/Pt was as low as 3%. Reduced catalytic activity of these electrodes as compared to that Pt could be a reason for the reduced degradation of SBT capacitors during forming gas annealing.

3:30 PM *Y8.6
CRYSTAL STRUCTURES, FERROELECTRIC PROPERTIES, AND CHEMICAL REACTIONS OF $SrBi_2Ta_2O_9$: SOLID STATE CHEMISTRY OF SBT MATERIALS FOR FeRAMs.
Yuichi Shimakawa and Yoshimi Kubo, Fundamental Research Laboratories, NEC Corporation, Tsukuba, JAPAN.

We describe some aspects from solid state chemistry of ferroelectric $SrBi_2Ta_2O_9$ (SBT). Crystal structure analysis by high-resolution neutron diffraction revealed considerable structural distortion in the SBT materials. This distortion, which consists of displacements of Bi^{3+} ions in the Bi_2O_2 layers and distortions of TaO_6 octahedra, causes large ferroelectric spontaneous polarization. The structural distortion is increased in a Sr-deficient-and-Bi-excess material, $Sr_{0.8}Bi_{2.2}Ta_2O_9$. This result is consistent with observations in thin-film capacitors, where the Sr-deficient-and-Bi-excess materials show remanent polarization larger than that of the stoichiometric sample. The enhanced distortion is explained in terms of an "ionic size effect" at the *A*-cation site, which is apparently seen in a series of compounds of $ABi_2Ta_2O_9$ (*A*=Sr, Ca, and Ba). Analysis of chemical reactions gives important information for degradation of the SBT capacitors and reaction between a Pt electrode and the SBT materials during device fabrication process. The degradation of SBT in an H_2-containing reduced atmosphere and its recovery by subsequent annealing in oxygen have been reproduced in experiments by using bulk ceramics and analyzed by thermogravimetric and x-ray-diffraction measurements. SBT decomposes into Bi metal and Sr-Ta oxide(s) in H_2 at above 300°C, and is recovered through oxidation of Bi metal into β-Bi_2O_3 and then reaction of β-Bi_2O_3 and Sr-Ta oxide(s). In the presence of Pt, in contrast, Bi-Pt alloy and Bi-Pt oxide are produced in the reduced and oxidized conditions, respectively. Velocities of the SBT degradation are also reported.

4:00 PM Y8.7
STUDIES OF HYDROGEN-INDUCED DEGRADATION PROCESSES IN $SrBi_2Ta_2O_9$ THIN FILMS USING COMPLEMENTARY TRANSMISSION ELECTRON MICROSCOPY AND IN SITU MASS SPECTROSCOPY OF RECOILED IONS ANALYSIS.
N. Poonawala and V.P. Dravid, Northwestern University, Dept. of Materials Science & Engineering, Evanston, IL; J. Im and O. Auciello, Argonne National Laboratory, Materials Science Division, Argonne, IL; A.R. Krauss, Argonne National Laboratory, Materials Science and Chemistry Divisions, Argonne, IL.

It is known that the forming gas (N^2-H^2 mixture) annealing process required for microcircuit fabrication results in electrical degradation of $SrBi^2Ta^2O^9$ (SBT) ferroelectric capacitors, mainly due to the interaction of H^2 with the ferroelectric layer. In our prior work, mass spectroscopy of recoiled ions (MSRI) analysis revealed a depletion of Bi on the surface of SBT layers exposed to hydrogen at high temperatures (~500°C), resulting in very high leakage currents and/or low polarization. Annealing in oxygen at 700-800 °C resulted in the replenishment of Bi to the SBT surface and recovery of electrical properties. X-ray Diffraction (XRD) analysis did not show any significant change between the virgin, H^2 annealed and O^2 recovery annealed samples. We have now performed cross-section Transmission Electron Microscopy (TEM) studies on pristine, H^2 annealed and O^2 recovered SBT/Pt/TiO^2/SiO^2/Si heterostructures to investigate the microstructural and microchemical changes induced by hydrogen and oxygen annealing. In our TEM methodology, we have exploited the high spatial resolution of a STEM-EDS probe (~2 nm diameter) to perform microanalysis combined with imaging, to highlight the effect of the SBT layer microstructure on the microchemical changes and the resulting electrical properties of the SBT capacitors. The cross-section TEM samples were prepared using a Focussed Ion Beam system. EDS line profiles for Bi/Sr, Bi/Ta and Sr/Ta ratios were obtained in the SBT layer from the film surface into the bulk and from the center of one grain to another across grain boundaries. The TEM data revealed a Bi depletion layer up to ~30 nm underneath the SBT surface of the hydrogen annealed sample, and a slight excess of Bi at the grain boundaries. The oxygen-annealed sample revealed that Bi has been replenished in the previously depleted near surface region, with some loss of Bi at the grain boundaries. We believe that the resurgence of Bi at the surface on O^2 annealed samples is due to grain boundary diffusion.
Work supported by the U.S. Department of Energy, BES-Material Sciences, under Contract W-31-109-ENG-38.

4:15 PM Y8.8
IN-SITU TEM STUDY OF DOMAIN DYNAMICS IN FERROELECTRICS.
A. Krishnan, P. Chandra, M.E. Bisher and M.M.J. Treacy, NEC Research Institute, Inc., Princeton, NJ.

In an effort to understand the role of domain motion in ferroelectric fatigue, we have conducted in-situ TEM experiments on thinned single crystal barium titanate and potassium niobate wherein we have observed the effect of an external applied field on domain nucleation and propagation. Our experiments indicate that domain configurations that were hitherto believed to be uncharged can possess significant amounts of displacement charge. The interaction of this charge with other domains and crystal defects is observed to play a significant role in their motion and pinning. In addition, we have also probed the role of various length scales in domain reorientation and displacement charge patterns in these materials. In this paper, we present a model for the displacement charge density on a pinned domain wall, and we show in-situ TEM video data of domain wall motion under an applied electric field.

4:30 PM Y8.9
EPITAXIAL GROWTH OF $SrBi_2Nb_2O_9$ FILMS ON $SrTiO_3$ (110).
J. Lettieri, M.A. Zurbuchen, Y. Jia, A.H. Carim, D.G. Schlom, Penn State University, University Park, PA; W. Tian, X.Q. Pan, University of Michigan, Ann Arbor, MI; G.W. Brown, M.E. Hawley, Los Alamos National Laboratory, Los Alamos, NM.

The ability of polycrystalline $SrBi_2Nb_2O_9$ films to withstand repeated ferroelectric switching cycles (in excess of 10^{12}) without degradation makes it an excellent candidate material for ferroelectric memories. Presently the mechanisms for this fatigue resistance, believed to be anisotropic, are not entirely understood. Previous attempts to grow films with appropriate orientation to explore the anisotropic properties of these ferroelectrics has proven extremely difficult due to the propensity of the material to grow with a (001) orientation. In this study we exploit the tendency for (001) growth to grow films in more favorable orientations (i.e., with the polarization vector not entirely parallel to the direction of measurement) through growth on a $SrTiO_3$ (110) surface. The resulting films can be characterized as having the polarization vector at ~45° to the substrate normal and no low index plane parallel to the substrate surface. Atomic force microscopy (AFM), transmission electron microscopy (TEM), 4-circle x-ray diffraction, and dielectric measurements for films grown on epitaxial (110) $SrRuO_3$ electrodes will be discussed. This characterization indicates that the $SrBi_2Nb_2O_9$ films grow with two symmetry-equivalent orientations in which the c-axis is rotated by approximately ±45° from the substrate normal. However, by growing on vicinal (110) $SrTiO_3$ substrates, this epitaxial degeneracy is removed and one orientation relationship dominates.

4:45 PM Y8.10
ORIGINS FOR THE FATIGUE-FREE BEHAVIOR OF $SrBi_2Ta_2O_9$: A NEW FERROELECTRIC MATERIAL APPLICABLE TO FRAM DEVICES.
Bae Ho Park, Bo Soo Kang, Sang Don Bu, Tae Won Noh, Seoul National Univ, Dept of Physics, Seoul, KOREA; Hyung-Do Kim, Univ of Seoul, Dept of Physics, Seoul, KOREA; Tae Hyung Kim, LG Corporate Institute of Technology, Seoul, KOREA.

X-ray photoemission spectroscopy measurements were executed to compare nature of defects in $SrBi_2Ta_2O_9$(SBT) and $Bi_4Ti_3O_{12}$(BTO) films. In the SBT film, it was found that the oxygen ions at the metal-oxygen octahedra were much more stable than those at the Bi_2O_2 layers. On the other hand, for the BTO film, oxygen vacancies could be induced both at the titanium-oxygen octahedra and at the Bi_2O_2 layers. We suggested that the difference in chemical stability of the metal-oxygen octahedra should be related to different fatigue behaviors of the SBT and the BTO films. In order to ascertain the above suggestion, we changed chemical stability of SBT films by substituting ions in metal-oxygen octahedra. Bi_3TiTaO_9(BTT) is a modified material whose Bi ions and Ti ions were substituted for Sr ions and Ta ions of SBT in order to reduce chemical stability, respectively. As expected, the BTT films showed serious fatigue failures. Therefore, we concluded that the stability of the perovskite layers, as well as an important role of the Bi_2O_2 layers, should be considered as origins for the fatigue-free behavior of SBT films. According to the conclusion, we modified BTO by substituting Bi ions. As a result, we found a new ferroelectric material which showed fatigue-free property and large remnant polarization in spite of low processing temperature.

SESSION Y9: INTEGRATION AND ELECTRODES
Chairs: Takeshi Kijima and Katherine L. Saenger
Wednesday Morning, December 1, 1999
Room 304 (H)

8:30 AM *Y9.1
EMBEDDED NON-VOLATILE FERROELECTRIC MEMORIES.
Ted Moise, Scott Summerfelt, Francis Celii, Luigi Colombo, Guoqiang Xing, Tomoyuki Sakoda, Texas Instruments, Dallas, TX; Steve Bilodeau, Stephen Johnston, Michael Russell, Dan Vestyck, Peter Van Buskirk, ATMI, Danbury, CT.

As a potential alternative to conventional embedded memory technologies, scaled ferroelectric memory (FeRAM) has attracted significant attention over the past several years. The desire to combine the read/write speed of DRAM with the non-volatility of EEPROM motivates the development of this technology. To be cost-effective, the FeRAM module must be embedded with a minimum number of additional masks while achieving a competitive cell area. Further, the FeRAM module process must cause no (or minimal) disruption to the

standard CMOS logic devices. A few specific areas of concern are thermal budget, operating voltage, and hydrogen sensitivity. In this presentation, we will review the motivations for scaled, embedded FeRAM technology and highlight some of the issues associated with integration into submicron CMOS. We will also describe the electrical properties of low-voltage (<1.5V) TiAlN/Ir/PZT/Ir/TiAlN capacitors which have been formed using MOCVD PZT. The integration of these films within a low-temperature backend process will also be discussed.

9:00 AM Y9.2
NARROW RESONANCE PROFILING STUDY OF THE OXIDATION OF $Ti_xAl_{1-x}N$ BARRIER LAYERS. M.C. Hugon, J.M. Desvignes, B. Agius, Laboratoire Charles Fabry, Groupe Physique des Films Minces, Universite Paris Sud, Orsay, FRANCE; I. Vickridge, GPS, Universite Paris 6 et 7, Paris, FRANCE; A.I. Kingon, Dept. of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

The preparation of ferroelectric and high dielectric constant perovskite materials, which is performed at high temperature (550-750°C) in oxidising environments, provides strong limitations on the choice of electrode materials which have to be used for integration with semiconductor devices. To minimize interdiffusion and oxidation reactions, diffusion barrier must be deposited between Si substrate or Si plug and electrode material (Pt, IrO_2, RuO_2O). $Ti_xAl_{1-x}N$ thin films, deposited by reactive sputtering, are promising as electrically conductive layers and robust diffusion barriers. The stability of these films has been investigated at conditions typical for crystallization of perovskite dielectrics: films with various Al composition (x=1, 0.8 and 0.4) have therefore been annealed by RTA (rapid thermal annealing) in $^{18}O_2$ at 550-750°C. The as deposited and annealed samples were characterized using Rutherford Backscattering Spectroscopy and nuclear reaction analysis ($^{14}N(d,p)^{15}N$) for chemical composition. The concentration depth profiles of both ^{18}O and ^{27}Al were measured before and after the RTA treatments via the narrow resonances of $^{18}O(p,\alpha)^{15}N$ at 150 keV (fwhm=100eV) and $^{27}Al(p,\gamma)^{28}Si$ at 992keV (fwhm=100eV). The depth profiles were deduced from the measured excitation curves with the aid of the SPACES simulation program. RBS analysis indicates that RTA caused no change in Ti content of the film. The different ^{18}O excitation curves show that the oxidation resistance increases with Al incorporation. The loss of N is concomitant with O-in diffusion driven by oxidation. The Al excitation curves indicate an uniform Al content for as deposited $Ti_xAl_{1-x}N$, and reveal Al diffusion to the surface during the oxidation process, which indicates the formation of an Al rich oxide layer at the $Ti_xAl_{1-x}N$.

9:15 AM Y9.3
OXIDATION AND PROPERTIES OF BARE AND Pt COVERED TiAlN. Scott R. Summerfelt, Si Technology Research, Texas Instruments Inc., Dallas, TX; Paul C. McIntyre, Dept. MS&E, Stanford U., Palo Alto, CA; Paul Schuele, WaferTech, Camas, WA.

Electrodes for high dielectric constant materials have several severe requirements for high density devices DRAM or FeRAM devices. In order to achieve these conflicting requirements, the electrode has two layers. An oxygen stable layer next to the high dielectric constant layer and an diffusion barrier underneath. One of the biggest problem is the oxidation of the diffusion barrier (traditionally TiN) which can cause several problems such as high contact resistance or roughening of electrode and degraded leakage current. TiAlN is a proposed oxidation resistant diffusion barrier. This paper will discuss the properties of TiAlN (resistivity, stress) and oxidation rate for bare Ti(1-x)AlxN (x=0-0.6). Oxidation kinetics are reported for TiAlN thin film diffusion barriers beneath polycrystalline Pt films of 50-200 nm thickness annealed in dry O2/N2 ambients of varying oxygen partial pressure and total pressure near 1 atm. Oxygen resonance backscattering spectrometry was used to detect thin oxide layers at the Pt/TiAlN interface produced by oxidation annealing at 475-650C. Over part of this temperature range, a linear oxidation rate law was observed for short times and a parabolic oxidation rate was observed for longer time. Various possible rate-controlling oxidation mechanisms are critically analyzed in light of the kinetic data and results from microstructural studies of the Pt/TiAlN bilayers.

9:30 AM Y9.4
PLATINUM FILM GROWTH WITH $PT(PF_3)_4$ AND DIMETHYL(1,5-CYCLOOCTADIENE) PLATINUM. Y.-M. Sun, N. Mettlach, J. Lozano, J.G. Ekerdt and J.M. White, The University of Texas at Austin, Texas Materials Institute, Austin, TX; S. Madhukar, R.L. Hance, Embedded Systems Technology Laboratories, Motorola, Austin, TX.

We have investigated platinum film growth using the platinum precursors $Pt(PF_3)_4$ and dimethyl(1,5-cyclooctadiene) platinum (Me_2PtCOD). The study focused on three aspects of film growth: conformality, adhesion and selective growth. Two delivery methods, gas phase delivery and direct liquid injection, were applied to $Pt(PF_3)_4$ and Me_2PtCOD, respectively. $Pt(PF_3)_4$ deposits pure Pt films over a wide range of deposition temperatures (~200 to 400°C). However, the step coverage over an aspect ratio of three is poor, even at 200°C. Lower growth temperatures also show a significant decrease in the growth rate. In addition, these films show poor adhesion to the substrate as indicated by separation between the Pt films and substrates in the cross sectional scanning electron microscopy (SEM) images. Me_2PtCOD did not deposit pure Pt film unless oxygen was added during film growth. Adding oxygen during Pt film growth for $Pt(PF_3)_4$ shows improvement in both film conformality and adhesion. With oxygen, the step coverage on the side wall reaches > 90% for both precursors. The dependence of the film growth rate on oxygen for $Pt(PF_3)_4$ varies with the growth temperature; the growth rate increases at 150°C, while it decreases at 200°C when oxygen is added. The substrate effect on the initial growth rate using $Pt(PF_3)_4$ was studied on various substrates. It is clear that the initial growth rate on metals is much faster than that on other substrates. The growth rate decreases in the order of Pt > TiN > BST > Si_3N_4 > SiO_2.

9:45 AM Y9.5
Abstract Withdrawn.

10:30 AM Y9.6
ANISOTROPIC PLASMA ETCHNG OF BARIUM-STRONTIUM-TITANATE THIN FILMS FOR DRAM INTEGRATION.
Stefan Schneider[1], Mark Kennard[2], Rainer Waser[1]; [1]Institut für Festkörperforschung, Forschungszentrum Jülich, Jülich, GERMANY; [2]Lam Research Corporation, Fremont, CA.

Reactive Ion Etching of $Ba_{0,7}Sr_{0,3}TiO_3$ (BST)- thin films was studied using a Lam TCP^{TM} 9400SE high density, low pressure plasma reactor. The BST thin films were etched with a variety of reactive gas combinations in a transformer coupled plasma (TCP) by varying the etching parameters such as plasma density, DC bias to wafer susceptor, gas pressure, flow, and gas composition. Etching effects were investigated in terms of etch rate, etch selectivity to photo resist and SiO_2, etch profiles, sidewall deposition (fence), and etch product residues.
The etch process of BST is known to be sputter dominated. With the chemistries used, the etch products have little or no volatility. Such a processes regime is expected to contaminate the wafer with sidewall depositions(fences) and residues which are both detrimental for further processing and may cause a possible particle problem and a low MTBC. The BST films were prepared by chemical solution deposition. This method produced films typically 120 nm thick, as compared to 20-50 nm normally used for ULSI DRAM applications. Films were intentionally made thicker to exaggerate the effects and aid the understanding of the plasma etching phenomena.
The photoresist masks thickness and slope were varied to characterize the relationship between profile and residue observed in the BST etch. Photoresist mask was also sloped using in situ plasma processing. Through optimization of mask and etch parameters, an etch process suitable for BST capacitors integration was achieved.

10:45 AM *Y9.7
HYDROGEN-INDUCED DEGRADATION OF (Ba,Sr)TiO_3 THIN FILMS. S.R. Gilbert, Y. Okuno, L. Colombo, P. Chen, S.P. Tang, T.S. Moise, and S.R. Summerfelt, Silicon Technology Research, Texas Instruments, Dallas, TX.

High dielectric constant materials, particularly (Ba,Sr)TiO_3 (BST), have attracted considerable attention for use as the charge storage dielectric in giga-bit scale DRAMs. Significant technical challenges, however, must be overcome to integrate BST capacitors with sub-micron CMOS. For example, during a typical back-end-of-line process flow, the capacitor arrays are subjected to numerous hydrogen-containing ambients. It is well known, however, that exposing high-k materials to hydrogen severely degrades capacitor leakage. This phenomenon has been the subject of intensive study, and potential strategies for mitigating its effects include the use of recovery anneals, barrier layers, optimized electrode structures, and modified deposition processes for contact metals and inter-layer dielectrics. The emphasis of this presentation will be on investigating the mechanisms for hydrogen-induced degradation of Pt/BST/Pt capacitors using a combination of electrical analysis and secondary ion mass spectroscopy (SIMS). BST thin films were deposited by metalorganic chemical vapor deposition (MOCVD) onto (111) Pt, and capacitors defined by e-beam deposition of Pt top electrodes through a shadow mask. Samples were annealed in deuterated forming gas (N_2:D_2 = 90%:10%) between 200 and 500°C. Use of deuterium as a diffusion marker facilitated SIMS analysis because of the high concentration of residual hydrogen in the as-grown BST films. It will be shown that, upon annealing in N_2:D_2, deuterium piled up at the Pt-BST interfaces, and diffused into the bulk of the BST layer. The results are consistent with the dissociation of molecular D_2 into D^+ species, a reaction that appeared to be catalyzed by the Pt electrodes.

Further, our computer simulations support the notion that the D^+ (or H^+) species are incorporated into the perovskite lattice as positively charged hydroxyl donor centers. Presumably, the increased leakage current is caused by the incorporation of these defects in the BST layer and at the Pt - BST interfaces.

11:15 AM Y9.8
THE EFFECT OF FORMING GAS ANNEALING ON (Ba,Sr)TiO_3 THIN FILMS: SIMS ANALYSIS AND ELECTRICAL CHARACTERIZATION. Joon-Hyung Ahn and Paul C. McIntyre, Department of Materials Science and Engineering, Stanford University, Stanford, CA; Laura Wills-Mirkarimi, Solid State Technology Laboratory, Hewlett-Packard, Palo Alto, CA.

High dielectric constant thin films including (Ba,Sr)TiO_3 (BST) have been widely studied as a capacitor material for giga-bit DRAM and other on-chip capacitor applications. It is known that forming gas annealing may cause severe degradation of the leakage current resistance of BST thin films. Such degradation is a significant obstacle to integration of BST in CMOS devices. To clarify the mechanism of forming gas degradation of thermal MOCVD-grown BST thin films, we performed quadrupole-based SIMS analysis of specimens annealed in a forming gas, combined with detailed electrical characterization. Deuterated forming gas (D_2:N_2 = 5:95) was chosen for improved SIMS sensitivity over that obtained with hydrogen forming gas. A drastic increase of leakage current density was measured and the movement of deuterium ions across the BST dielectric was observed after deuterated forming gas annealing. The as-deposited MOCVD-grown BST was found to contain a substantial concentration of hydrogen impurities that remained relatively immobile during the forming gas anneals. The effect of heat treatment of the BST films (both before and after forming gas anneal) on the electrical properties and the deuterium ion profiles in the BST will be discussed.

11:30 AM Y9.9
RECOVERY OF FORMING GAS DAMAGED Pb(Nb,Zr,Ti)O_3 CAPACITORS. S. Aggarwal, S.R. Perusse, C.J. Kerr, R. Ramesh, Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD; D.B. Romero, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD; G. Velasquez, L. Boyer, J.T. Evans, Jr., Radiant Technologies, Inc. Albuquerque, NM.

We report on the recovery of fully integrated Pb(Nb,Zr,Ti)O_3 ferroelectric capacitors damaged during forming gas (4% H_2, balance N_2) annealing. In such capacitors oxygen loss, lead loss and hydrogen incorporation are three degradation mechanisms that have been identified. The capacitors were encapsulated using TiO_x and SiO_2 as inter-level dielectrics to prevent any loss of oxygen or lead. Hydrogen however diffused into the ferroelectric film leading to the loss of ferroelectricity. To recover the properties of the capacitor, the fully integrated structure was annealed in VLSI grade N_2 ambient to drive the hydrogen out. Raman scattering experiments performed in the high frequency regime to detect the [OH^-] stretching vibration mode confirmed the removal of hydrogen after annealing in VLSI grade N_2. The ferroelectric properties including polarization and resistivity of the capacitors was restored to their initial values prior to damage. This shows that the process of hydrogen damage is reversible with the time to recovery being dependent on the amount of hydrogen in the forming gas.

11:45 AM Y9.10
EVALUATION OF CONDUCTIVE REGION IN PZT FILM INDUCED BY LOW TEMPERATURE HYDROEGN TREATMENT ON Pt/PZT/Pt CAPACITOR. Hiroyuki Kanaya, Yoshinori Kumura, Iwao Kunishima and Shin-ichi Tanaka, Microelectronics Engineering Laboratory, Toshiba Corp. Semiconductor Company, Yokohama, JAPAN; Tsuyoshi Iwamoto, Corporate Manufacturing Engineering Center, Toshiba Corp., Yokohama, JAPAN; Yukio Takahagi, Environmental Engineering & Analysis Center, Toshiba Corp., Yokohama, JAPAN.

Conductive region in PZT induced by low temperature (60C) hydrogen treatment was evaluated by SIMS and electrical measurements. A novel charged-up SIMS analyses were performed on Pt/PZT/Pt capacitor. The charged-up SIMS profiles were useful to evaluate the conduction region in PZT film. The conductive region in the PZT was found to increase by the hydrogen treatment. Pt/PZT/Pt (180/240/180nm) capacitor was prepared by sputtering method. PZT was crystallized by RTA. Only top electrode was patterned to the size of 0.7mm x 0.9mm by RIE. Oxygen annealing at 650C was performed to recover the RIE damage. Hydrogen treatment at 60C was applied to the sample. After that, the detailed SIMS analyses and electrical measurements were performed. From the charged-up SIMS analyses of Pb, Zr and Ti of virgin sample, it is found that PZT near the bottom Pt electrode was not charged up but PZT near top electrode was charged up. It indicates that conductive region existed in PZT near the bottom Pt electrode whereas PZT near the top electrode was insulative. After the hydrogen treatment, the charged-up region decreased in PZT, indicating that the conductive region increased in PZT. The hydrogen in Pt/PZT/Pt was expected to reduce PZT both at grain boundaries and interfaces, and to form the conductive region. This result was consistent with an increase of leakage current of the sample after the hydrogen treatment. We found that the hydrogen treatment formed conductive region in PZT from the charged-up SIMS profile for the first time. The hydrogen in the capacitor reduces the PZT and form the conductive region.

SESSION Y10/KK4: JOINT SESSION:
HIGH-FREQUENCY APPLICATIONS OF FERROELECTRICS
Chairs: Quanxi Jia and Susan Trolier-McKinstry
Wednesday Afternoon, December 1, 1999
Room 304 (H)

1:30 PM *Y10.1/KK4.1
MATERIALS ISSUES IN ELECTRIC FIELD TUNABLE RF AND MICROWAVE DIELECTRICS. L. Eric Cross, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

Ferroelectric crystals are in general highly nonlinear dielectrics, but in the ferroelectric phase extrinsic domain wall processes generally give rise to very high dielectric loss levels. To achieve dielectric tunability under electric field, but retain low dielectric loss there has been a focus upon the paraelectric phase in incipient ferroelectrics in the perovskite structure oxides. Strontium titanate ($SrTiO_3$) and Potassium Tantalate ($KTaO_3$) are favorable candidates and solid solutions based on these end members, such as $(Ba_xSr_{1-x})TiO_3$ and $K(Ta_{1-x}Nb_x)O_3$ and composites containing these solid solutions are under study for room temperature application.
The focus on the paraelectric phase is understandable as both theory and experiment confirm low loss ($\tan\delta \sim 0.00065$ at 10 GHz) and high tunability in single crystal $SrTiO_3$. In thin film form however, which is essential for many important device applications, both dielectric loss levels and E-field tunability are significantly compromised although adequate tunability is maintained because of the enhanced dielectric strength of the thin films. Recent improvements in film processing and performance will be reviewed and the developing understanding of the importance of crystal quality in the films underscored.
Strontium titanate has been an excellent vehicle for the study of the roles of both isovalent and aleovalent substituents in the perovskite lattice and these works will be summarized and discussed. New work to explore the low temperature pyrochlore structure ferroelectrics will be described and measurements showing promising results for both loss levels and tunability presented.
With molecular beam techniques it is possible to develop completely new single phase examples of the strontium titanate Ruddleston Popper phase crystals and to make new layer structure compounds in the $(SrTiO_3)_x$ $(BaTiO_3)_{1-x}$ compositions. Work on these systems will be described and the dielectric properties of these new artificial compounds briefly reviewed.

2:00 PM *Y10.2/KK4.2
DIELECTRIC PROPERTIES OF (Ba,Sr)TiO_3 THIN FILMS TAILORED FOR TUNABLE MICROWAVE APPLICATIONS. C.L. Canedy, M.R. Burr, D. Steinhauer, S. Anlage, T. Venkatesan and R. Ramesh, Materials Research Science and Engineering Center (MRSEC), University of Maryland, College Park, MD; F.W. Van Keuls, R.R. Romanofsky, N.D. Varaljay and F.A. Miranda, NASA Glenn Research Center, Cleveland, OH.

Ferroelectric materials enjoy a large nonlinearity in their dielectric response, which gives rise to an electric field dependent permittivity. This feature makes them particularly attractive for use as electronically tunable microwave components. However, early studies have reported prohibitively large dielectric losses in the microwave frequency regime. Recently though, progress in materials processing and deposition techniques has dictated the fabrication of thin ferroelectric films of high crystalline quality and corresponding losses which make them competitive for use as resonators, filters or phase shifters. Nonetheless, it is still unclear as to how basic material properties are correlated with dielectric losses and/or the degree of tunability. In this study, we report on the evolution of the dielectric properties in epitaxial $Ba_{1-x}Sr_xTiO_3$ (BSTO) thin films with varying extrinsic parameters, such as stress and oxygen defect concentration. The films were grown on four separate substrates using pulsed laser deposition. These included $LaAlO_3$,MgO,$(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$ (LSAT) and $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ (YSZ) coated Si. In addition, the defect chemistry was altered in a controlled fashion by annealing in reducing atmospheres of oxygen. The dielectric properties at low frequency were measured using Au/Ti interdigitated electrodes. Furthermore, assessment of the BSTO films at microwave frequencies

was accomplished by incorporating the films in an actual microwave phase shifter device based on a novel coupled microstripline phase shifter (CMPS) geometry. Strain relaxation in the films was studied using glancing x-ray diffraction while oxygen defect concentration was inferred using positron annihilation studies. Finally, a novel scanning microwave microscope was used to detail the local microwave response of our films. This work was partially funded by NSF-MRSEC.

2:30 PM Y10.3/KK4.3
COPLANAR CAPACITORS WITH HIGH DIELECTRIC CONSTANT $BaSrTiO_3$ FOR MICROWAVE APPLICATION. Wei Hu, Valdimir Fouflyguine, Jim Chi, NZ Applied Technologies, Inc. Woburn, MA.

MIM Capacitors with BST dielectrics normally exhibits a nonsymmetrical IV characteristics. This nonsymmetrical behavior can be primarily attributed to the thermal degradation of the bottom BST-electrode interface during film preparation. High leakage current and low breakdown voltage in one direction of bias are resulted. The present work examined the IV nonsymmetry and proposed a solution for this problem. For this study, MIM structures were fabricated on Si and GaAs substrates. The BST film was prepared by the sol-gel method. The deposition temperature was varied from 400 to 600 C. The relative dielectric constants are typically around 300 and can be as high as 470. The bottom electrode is Pt e-beam deposited on several combination of metals and dielectrics to minimize the stress in the BST film. After capacitor fabrication, the IV characteristics were measured over a temperature range from room temperature to 200C with voltage varied from -15 V to 15 V. The IV characteristics are analyzed assuming Schottky emission mechanism. It is found that the barrier height for the bottom interface is significantly lower than the top. This barrier lowering may be explained by the thermal degradation during the film deposition. Since the lowered barrier height will cause a higher large leakage current in one direction, it needs to be avoided for circuit applications. To solve this problem, a novel electrode structure is proposed to eliminate the nonsymmetrical IV characteristics by putting the two electrodes both on the top side of the BST film. This structure is seen to be effective in reducing the leakage current and increasing the breakdown voltage. The capacitance per unit area, however, is reduced by a factor of four. Such a reduction is tolerable, since the BST capacitors is still one order of magnitude higher than the conventional capacitors with the silicon oxynitride as the inter-electrode dielectrics. In addition to reducing the leakage and increasing the breakdown voltage, an additional benefit for the present structure is the extremely low parasitic inductance compared with the standard MIM structure. Such a low parasitic results in excellent high frequency properties. Both these benefits with the present structure may advance the application of BSTs to the microwave devices and circuits.

2:45 PM Y10.4/KK4.4
DOPED BARIUM STRONTIUM TITANATE THIN FILMS FOR INTEGRATED CAPACITORS. Gregory T. Stauf, Phil S. Chen, Witek Paw and Jeffrey F. Roeder, Advanced Technology Materials Inc., Danbury, CT.

There has been significant interest recently in use of $BaSrTiO_3$ (BST) thin films for integrated capacitors; these devices have benefits for high temperature and high frequency operations, particularly when electrically tunable devices are required. We will discuss the electrical properties of BST thin films which make them suitable for these applications, as well as the impact of processing conditions on specific film properties. Voltage withstanding capability and high frequency loss are particularly important parameters for determining applications for these devices. By addition of a dopant to BST films grown by metalorganic chemical vapor deposition (MOCVD), we have increased breakdown voltages in BST films by as much as a factor of two, to approximately 2 MV/cm, potentially raising their energy storage density values significantly.

3:30 PM *Y10.5/KK4.5
THE COMBINATORIAL APPROACH TO TUNABLE FERROELECTRIC MATERIALS. XiaoDong Xiang, Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, CA.

We have established a comprehensive combinatorial methodology in order to search for novel and improved ferroelectric materials for tunable microwave devices. Using a discrete combinatorial scheme, we perform systematic doping study where up to thousands of different combinations of dopants and host materials are generated on individual chips. We have identified several dopants that help reduce the microwave loss in $(Ba,Sr)TiO_3$. Alternatively, we have also developed a continuous-compositional-spread technique where refined compositional search is performed in a given chip. We have identified a novel low loss compositional region from a $(Ba,Sr,Ca)TiO_3$ "ternary-phase-diagram" chip. We use the scanning evanescent microwave microscope (SEMM) to rapidly scan and screen our combinatorial samples. SEMM allows quantitative electrical impedance microscopy of ferroelectric/dielectric materials with high spatial resolution (< 0.1 micron. The microscopy is also used to investigate tunability by applying a voltage to a localized spot in a film.

4:00 PM Y10.6/KK4.6
BISMUTH PYROCHLORE FILMS FOR DIELECTRIC APPLICATIONS. Wei Ren, Ryan Thayer, Clive A. Randall, Susan Trolier-McKinstry, Materials Research Laboratory and Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA.

Bismuth pyrochlore ceramics have low temperature coefficients of capacitance, good microwave properties, and can be prepared at relatively modest temperatures (~1000 - 1100°C). This work focuses on the preparation and characterization of thin films in this family for the first time. A sol-gel procedure using bismuth acetate in acetic acid and pyridine, in combination with zinc acetate dihydrate and niobium ethoxide in 2-methoxyethanol was developed. The solution chemistry was adjusted to prepare $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ and $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ films. Solutions were spin-coated onto platinized Si substrates and crystallized by rapid thermal annealing. In both cases, crystallization occurred by 550°C into the cubic pyrochlore structure. $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ films remained in the cubic phase up to crystallization temperatures of 750°C, while the structure of the $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ thin films is dependent of the firing temperature: cubic below 650°C and orthorhombic above 750°C. A mixture of cubic and orthorhombic structures is found at 700°C. The resulting BZN films are dense, uniform, smooth (rms roughness of < 5 nm) and have a very small leakage current. In terms of the dielectric properties, cubic bismuth zinc niobate films show dielectric constants up to 150, a negative temperature coefficient of capacitance, TCC, (= - 400 ppm/°C), tan δ < 0.01, and a field tunable dielectric constant. Orthorhombic films showed smaller dielectric constants (~80), low tan δ (1%), positive TCC, and field independent dielectric constants. TCC could be adjusted to new 0 ppm/°C using a mixture of orthorhombic and cubic material.

4:15 PM Y10.7/KK4.7
STRUCTURAL AND DIELECTRIC PROPERTIES OF PULSED LASER DEPOSITED PYbN-PT THIN FILMS. Veronique Bornand, Susan Trolier-McKinstry, The Pennsylvania State University, Department of Materials Science and Engineering, Materials Research Laboratory, University Park, PA.

The demonstration of high strain, high piezoelectric coefficients, and high electromechanical coupling constants in relaxor ferroelectric single crystals in the $Pb[B'B'']O_3$-$PbTiO_3$ family make them promising candidates for micro-electromechanical systems (MEMS). Thus, this study focuses on the preparation and characterization of epitaxial (1-x) $Pb[Yb_{1/2}Nb_{1/2}]O_3$ - x $PbTiO_3$ (PYbN-PT) thin films. The high Curie point (~360°C) at the morphotropic phase boundary (x ~ 0.5) should greatly improve the high temperature capabilities of piezoelectric driven MEMS relative to the lead magnesium niobate-based compounds. Heterostructures consisting of (100) $LaAlO_3$ substrates, a $SrRuO_3$ metallic oxide bottom electrode and PYbN-PT ferroelectric film were deposited by pulsed laser deposition. The influence of deposition parameters such as the chamber pressure, the substrate temperature, the laser frequency, and the target composition on the microstructural and dielectric properties was investigated. High quality films could be grown in the 600-660°C temperature range, with a dynamic O_3/O_2 pressure of 300 mTorr and high laser repetition rates. 4-circle X-ray diffraction analyses, performed on optimized samples, confirmed the (001) orientation of the perovskite sub-cells in each layer, as well as the < 110 > PYbN-PT || [110] $SrRuO_3$ in-plane heteroepitaxial relationships. Scanning electron microscopy studies revealed well-defined and homogeneous microstructures. Most of the films show room temperature dielectric constant greater than 1500 associated with low dielectric losses (~ 0.03-0.05) and exhibit saturated hysteresis loops with remanent polarizations up to P_r = 40 $\mu C.cm^{-2}$. Furthermore, the stabilization of the < 001 >-orientation was observed to enhance the fatigue resistance. <c>-axis oriented PYbN-PT thin films do not show polarization fatigue up to 10^{11} cycles, making these heterostructures attractive for non-volatile ferroelectric memories, in addition to ferroelectric actuators or sensors.

4:30 PM Y10.8/KK4.8
PULSED LASER DEPOSITED $Na_{0.5}K_{0.5}NbO_3$ THIN FILMS: FROM SUPERPARAELECTRIC STATE TO FERRO-ELECTRICITY. Choong-Rae Cho and Alex Grishin, Condensed Matter Physics, Dept of Physics, Royal Institute of Technology, Stockholm, SWEDEN.

$Na_xK_{1-x}NbO_3$ is the continuous solid solution of potassium and sodium niobates, which shows a number of ferroelectric phases experienced coupled structural-polarization phase transitions. $Na_{0.5}K_{0.5}NbO_3$ (NKN) possesses a high spontaneous polarization of 30 $\mu C/cm^2$, high piezoelectric constant d_{33} of 160 pC/N, strong dependence of dielectric permittivity on electric field with low loss. Therefore it is considered as a promising candidate for various applications as piezoelectric micro-sensors and actuators, electrically tunable micro- and millimeter waveguides, surface and bulk acoustic wave devices. Recently we have reported *self − assembled* highly c-axis oriented single-phase NKN thin films pulsed laser deposited (PLD) onto polycrystalline and amorphous substrates (Appl. Phys. Lett., 75, July 12, 1999) and epitaxial NKN/(La,Sr)MnO_3 heterostructures on $SrTiO_3$ single-crystal (Mat. Res. Soc. Symp. Proc., MRS Spring 1999 meeting). Here we present improved as well as extended crystalline and electrical properties of PLD-NKN thin films on polycrystalline Pt and oxidized Si substrates. Phase composition and microcrystalline properties of fabricated NKN films have been found to be crucially dependent on ambient gas pressure, laser fluence and repetition rate, substrate temperature and target-to-substrate distance. These effects will be discussed in the framework of the model of *discriminated thermalization* of laser-ablated ions and neutral species in laser plume. Electrical performance of NKN films has been successfully tailored from low loss - high electrically tunable superparaelectric state to ferroelectric state characterized by high remnant polarization and piezoelectric activity. Films deposited at low oxygen pressure regime contain NKN nanocrystallites embeded in the sodium poor potassium niobate matrix, exhibit low loss tanδ of 0.3%, dielectric permittivity of 175 which is frequency independent (from audio frequencies up to 100 kHz) and 5% tunable at the field of 100 kV/cm. Films grown at high oxygen pressure have been found to be single-phase as well as strongly c-axis oriented due to the effect of self-assembling: FWHM of NKN-200 reflection is less than 2° while Pt-200 substrate reflection was about 15°. Ferroelectric measurements yield remnant polarization of 20 $\mu C/cm^2$, spontaneous polarization of 30 $\mu C/cm^2$ at electric field of 80 kV/cm, electric resistivity of 100 GΩ·cm at 10 kV/cm, dielectric permittivity of 500 and tanδ less than 3%. Results of piezoelectric measurements for ferroelectric films also will be presented.

4:45 PM Y10.9/KK4.9
A SYSTEMATIC STUDY OF FERROELECTRIC $Ba_xSr_{1-x}TiO_3$ FILMS. Hua Jiang, Vladimir Fouflyguine, Wei Hu, Jing Zhao and Peter Norris, NZ Applied Technologies, Woburn, MA; A. Drehman, S. Wang and P.Yip, Air Force Research Laboratory, Hanscom AFB, MA.

Metal-Organic Chemical Liquid Deposition (MOCLD) has many advantages in fabricating ferroelectric films. Its simplicity and economic nature made it most suitable for doping and multicomponent materials development. Using MOCLD technology, we have systematically grown $Ba_xSr_{1-x}TiO_3$ (BST) films (x = 0, 0.1, 0.25,0.4, 0.5, 0.6, 0.75, 0.90, and 1) on a variety of substrates and at different temperatures. Excellent epitaxial BST films have been obtained. The c-axis and a-b plane alignments of the BST films grown on $LaAlO_3$ substrates were about 0.06° and 0.5°, respectively, measured by a four-circle high resolution x-ray diffractometer. The correlation of film quality (in terms of orientation, grain size, dielectric constant, dielectric tunability, dielectric loss and leakage) to the growth temperature and oxygen treatment have been investigated. We also doped BST films with Ca, Mg, and rare earth elements, and studied the film structures and dielectric properties influenced by the doping. This work demonstrated that MOCLD can be used to grow very low loss (tan δ < 0.003) BST ferroelectric films. We also grew multilayer of alternating $BaTiO_3/SrTiO_3$ and BST1/BST2 (BST1 has different composition from BST2) using the same MOCLD method. We found that the dielectric constant value of the $BaTiO_3/SrTiO_3$ multilayer structure was very similar to that of a $(Ba_{0.5}Sr_{0.5})TiO_3$ solid solution film except that it remained nearly constant over a wide temperature range (-200°C to 0°C). This structure may find a very important application where temperature variation is a key consideration.

SESSION Y11: POSTER SESSION:
FUNDAMENTALS PROPERTIES OF THIN-FILM FERROELECTRICS; FERROELECTRIC GATE MATERIALS
Chairs: Alain Pignolet and Yuichi Shimakawa
Wednesday Evening, December 1, 1999
8:00 P.M.
Exhibition Hall D (H)

Y11.1
UNIAXIAL FERROELECTRIC FILMS ON Pt(111)/SiO_2/Si FOR FRAM APPLICATION. J.H. Song, J.W. Song, K.-B. Lee, Y.H. Jeong, Dept. of Physics, Pohang Univ. of Science and Technology, Pohang, S KOREA.

Perovskite ferroelectric PZT is a promising material for FRAM applications; however, there are problems with PZT, most notably fatigue, that must be solved. As a result, there have been intense efforts in search for other candidate materials. Here we report our study on uniaxial ferroelectrics with only 180 domain walls, as opposed to cubic ones with both 90 and 180 domain walls. We first deposited (111) oriented Pt films on SiO_2/Si substrates, and then uniaxial ferroelectric films (hexagonal $YMnO_3$ or $Pb_5Ge_3O_{11}$) were deposited using the Pulsed Laser Deposition method. X-ray diffraction analysis showed that we obtained high quality oriented films in both cases. Despite the structural high quality, the shape of ferroelectric hysteresis loops varied widely depending on the deposition conditions. We will focus on the correlation between the deposition conditions and the quality of the ferroelectric switching behavior, and discuss about realistic possibility of these ferroelectrics as a FRAM material.

Y11.2
MICROSTRUCTURE OF FERROELECTRIC SUPERLATTICES GROWN BY A MOLECULAR BEAM EPITAXY. W. Tian,* J.C. Jiang,* J.H. Haeni,** D.G. Schlom,** and X.Q. Pan*; *Department of Materials Science & Engineering, The University of Michigan, Ann Arbor, MI, **Department of Materials Science & Engineering, Penn State University, University Park, PA.

Molecular beam epitaxy (MBE) has been used to synthesize epitaxial $BaTiO_3/SrTiO_3$ and $PbTiO_3/SrTiO_3$ superlattices with and without composition gradients. The atomic structure of these films and the related heterostructural interfaces as well as their structural instabilities at high temperatures have been investigated by a combination of high-resolution transmission electron microscopy (HRTEM) and computer image simulations. Both superlattice thin films were found to be single crystals with a coherent epitaxy on the (001) $SrTiO_3$ substrates. The interface between neighboring layers in the heterostructure was atomically abrupt and free of dislocations. The c/a ratios were measured to be 1.061 for $PbTiO_3$ and 1.045 $BaTiO_3$ in the superlattices, which are greater than the values of bulk materials. The lattice mismatch between $BaTiO_3$ and $SrTiO_3$ layers will result in ~3.0% strain in the heterostructure which makes $BaTiO_3$ / $SrTiO_3$ superlattices an excellent candidate for exploring stress-effect in ferroelectrics. Quantitative HRTEM investigations indicate an enhanced displacement of Ti cations with respect to oxygen octahedra in $BaTiO_3$ layers of the superlattice, which suggests a stress-induced enhancement of spontaneous polarization in the superlattice.

Y11.3
MICROSTRUCTURAL AND RAMAN SPECTROSCOPIC STUDY OF RARE EARTH DOPED $Pb_{0.85}La_{0.15}TiO_3$ THIN FILMS AND POWDERS. P.S. Dobal, R.R. Das, B. Roy*, S. Jain*, D.C. Agrawal* and R.S. Katiyar Department of Physics, University of Puerto Rico, San Juan PR; *Material Science Program, IIT Kanpur, INDIA.

The effects of Ce^{+3} and Gd^{+3} substitution on the La^{+3} sites of the sol-gel prepared $Pb_{0.85}La_{0.15}TiO_3$ were investigated utilizing x-ray diffraction, atomic force microscopy, and micro-Raman scattering techniques. With increasing content of Gd, an increase in the tetragonality ratio (c/a) was observed as a consequence of elongation of the c lattice parameter. Relatively less ferroelectric ordering was obtained in Ce doped thin films. Raman spectra exhibited features characteristics of bulk $Pb_{0.85}La_{0.15}TiO_3$, including the observation of the soft mode. Variation of the phonon modes, especially the lowest soft mode, for $Pb_{0.85}La_{0.15-x}Ce_xTiO_3$ and $Pb_{0.85}La_{0.15-x}Gd_xTiO_3$ have been investigated as a function of the composition x, in the range 0.00 to 0.15. Different behaviors were observed in the thin films and the corresponding powders in the Ce doped samples. Raman spectra of these samples will be studied as a function of temperature. The results of Raman and microstructural analysis, and change in phase transition temperature, T_c, with Ce and Gd substitution on A sites will be presented. This work is supported by #NSF-DMR-9801759 and #NSF-INT-9604988 grants.

Y11.4
LOW TEMPERATURE GROWTH OF BARIUM STRONTIUM TITANATE FILMS BY ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION. V. Craciun, J. Howard, A. Srivastava, and R.K. Singh, Department of Materials Science and Engineering, Gainesville, University of Florida, FL; J. Perriere, Groupe de Physique des Solides, Universites Paris VII et VI, Paris, FRANCE.

The properties of $Ba_{1-x}Sr_xTiO_3$ thin layers grown on (100) Si substrates using an in-situ ultraviolet (UV)-assisted pulsed laser deposition (UVPLD) technique have been studied. An excimer laser (KrF, 248 nm) emitting 25 ns long pulses was used for ablation. A vacuum compatible, low pressure Hg lamp capable of dissociating

molecular oxygen into ozone and atomic oxygen, was fitted into the PLD system. It allows for in-situ UV irradiation during both the laser ablation-growth process and the cooling stage, exposing each deposited layer to the action of more reactive gaseous species formed by UV photodissociation. The crystalline structure of the grown layers was investigated by X-ray diffraction (XRD), while the chemical composition and bonding were investigated by X-ray photoelectron spectroscopy (XPS). The optical properties of films grown on Si substrates were investigated by spectroscopic ellipsometry and those of films grown on corning glass by spectrophotometry. The surface morphology was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). These investigations showed that, with respect to conventional PLD grown films under similar conditions but without UV illumination, UVPLD grown films exhibited better crystallinity, especially for films grown at low substrate temperatures. These films also posses higher dielectric constant values by around 50%, reduced leakage currents and contained less physisorbed oxygen, having a better overall stoichiometry. A smoother surface morphology of UVPLD grown films suggests that during the ablation-growth process, UV radiation increases the surface mobility of adatoms. The UVPLD is especially effective at moderate processing temperatures, where the thermal energy available for the growth process is comparatively low.

Y11.5
FERROELECTRIC PROPERTIES OF II-VI TYPE SEMI-CONDUCTING THIN FILMS ON Si(100). Hitoshi Tabata, Mathew Joseph, Yasushi Hotta, Tomoji Kawai, ISIR-Sanken, Osaka Univ., Osaka, JAPAN.

Recently, a lot of studies have been performed on oxide ferroelectric ($BaTiO_3$, PZT etc.) thin films for electronic applications such as non-volatile memories. For realizing an ideal device structure of MFS-FET, it is required that the oxide ferroelectric thin films can be formed directly on the Si substrate. But there is serious problem of forming amorphous Si-O layer at the interface between the Si-substrate and oxide ferroelectric films due to the oxidative reaction of Si. We have demonstrated that non-oxide (II-VI type semi-conductors) ferroelectric thin films, such as (Zn,Cd)Te, (Zn,Cd)Se and (Zn,Cd)S, indicate ferroelectric properties. (thickness : 3000-5000 A) Furthermore, thin films of Li-doped ZnO of different compositions $(Zn_{1-x}Li_x)O$ (x=0.1 - 0.3) films also have been formed by a pulsed laser deposition on Si(100) substrates. They have shown the ferroelectric hysteresis feature with memory windows of 0.25V, 0.2V and 1.2V, respectively. The materials design for getting the ferroelectric nature is as follows: when the size of the replaced atom is smaller than the host atom, then the substituent atoms can occupy off-centered positions, thus locally induce electric dipoles, thereby leading to ferroelectric behavior. These II-VI wide gap semiconducting ferroelectric films will open the door for the new memory devices. ref) M.Joseph et al. Appl.Phys.Lett. 26 (1999) 2534.

Y11.6
ORIGIN OF LEAKAGE CURRENT OF $YMnO_3$ THIN FILMS PREPARED BY THE SOL-GEL METHOD. Hiroya Kitahata, Kiyoharu Tadanaga, Tsutomu Minami, Norifumi Fujimura and Taichiro Ito Department of Applied Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka, JAPAN.

Thin films of $ReMnO_3$ (Re: rare earth) are proposed as new field effect transistor type non-volatile ferroelectric memory devices since they have low dielectric constant and remanent polarization, and do not contain volatile elements such as Bi or Pb. However, they have a serious issue of relatively large leakage current due to unstable valence state of Mn ions. Kamata et al. reported that $YMnO_3$ sintered in air was in $YMnO_{3+x}$ state examined by TGA [1], and our group also suggested that the excess oxygen in the bulk $YMnO_{3+x}$ enhanced the hole generation [2]. Since the leakage current of $YMnO_3$ should be originated from the valence fluctuation of Mn ions, the atmosphere during heat treatment for $YMnO_3$ thin films is very important to control the leakage current. Very recently, we have reported on the preparation of $YMnO_3$ thin films by the sol-gel method from yttrium acetate [3] and yttrium alkoxide [4] as a starting material. In the present study, we examine the origin of the leakage current of $YMnO_3$ thin films prepared by the method. When yttrium acetate was used, the leakage currents of the films heat-treated in vacuum and air were in the order of 10^{-6} and 10^{-3} A/cm^2 at an applied voltage of 1 V. The leakage current was drastically improved by the heat treatment in vacuum. The reduction of the leakage current in the films heat-treated in vacuum should be resulted from the valence state of Mn ions being maintained at trivalent. When yttrium alkoxide was used, the formation of metal-oxygen bonds should be promoted in comparison with the use of yttrium acetate. Hence, the change of the starting material also affects the leakage current. [1] K. Kamata, et al., Mat. Res. Bull., 14 (1979) 1007. [2] T. Shimura, et al., Jpn. J. Appl. Phys., 37 (1998) 5280. [3] H. Kitahata, et al., Appl. Phys. Lett., in press. [4] H. Kitahata, et al., Jpn. J. Appl. Phys., accepted for publication.

Y11.7
CHARGE RETENTION PROPERTY OF Au/BIT/PZT/BIT/Si MULTILAYER STRUCTURE. Li Xingjiao, Feng Hanhua, Zhao Jianhong, Yu Jun, Gu Haoshuang, An Chengwu, Dept. Solid State Electronics, Huazhong University of Science & Technology, Wuhan, PR CHINA; Shaoping Li, Seagate Technology, Bloomington, MN.

The multilayer structures of $Bi_4Ti_3O_{12}$(BIT)/Si,$PbZr_xTi_{1-x}O_O$(PZT)/BIT/Si, and BIT/PZT/BIT/Si have been fabricated by utilizing laser ablation method. The charge retention properties of $Bi_4Ti_3O_{12}$(BIT)/Si, $PbZr_xTi_{1-x}O_O$(PZT)/BIT/Si, and BIT/PZT/BIT/Si structures have been studied in details. The results show that the capacitance retention properties of multilayer structure of BIT/PZT/BIT/Si are much superior than those of BIT/Si and PZT/BIT/Si layers. Our experimental results indicate ferroelectric multilayer structures could be used as novel gate dielectric for ferroelectric field effect transistors (FFETs). The relevant charge retention mechanism has been also discussed.

SESSION Y12: POSTER SESSION:
BST AND DRAM
Chairs: John D. Baniecki and Cem Basceri
Wednesday Evening, December 1, 1999
8:00 P.M.
Exhibition Hall D (H)

Y12.1
EFFECT OF TiN TREATED BY RAPID THERMAL ANNEALING ON PROPERTIES OF BST CAPACITORS PREPARED BY RF MAGNETRON CO-SPUTTER SYSTEM AT LOW SUBSTRATE TEMPERATURE. Huang-Chung Cheng, Teh-Hung Teng, Chuan-Chou Hwang, Ming-Jiunn Lai, National Chiao Tung Univ, Dept of Electronics Engineering and Inst of Electronics, Hsinchu, Taiwan, ROC; Stewart C. Huang, Mosel Vitelic Inc, Science-Based Industrial Park, Hsinchu, Taiwan, ROC; Jyh-Shin Chen, Cheng-Chung Jaing, Precision Instrument Development Center, National Science Council, Hsinchu, Taiwan, ROC.

As the dimension of the charge storage node in high density DRAM shrinks, there is a need for high dielectric constant materials such as $(Ba_xSr_{1-x})TiO_3$ (BST) to keep a conventional stacked capacitor structure. In this work, $(Ba_{0.7}Sr_{0.3})TiO_3$ thin films on Pt/TiN/Ti/Si substrate were deposited by an RF magnetron co-sputter system at 300°C in Ar+O_2 mixed ambient. On the integration of BST capacitors, the diffusion barrier (TiN) under bottom electrodes was one of the key issues. To obtain a stable and excellent diffusion barrier against inter-diffusion between Pt and Si as well as being oxidized during BST deposition, TiN was treated by rapid thermal annealing (RTA) process. Experimental result indicated that proper RTA treatments resulted in superior TiN barrier layer. In addition, low substrate temperature during BST deposition suppress the phenomena of inter-diffusion and barrier oxidation. Pt hillock is another problem during BST deposition because of high thermal budget. This problem was also solved by reducing substrate temperature during BST deposition. Even though BST deposited at low substrate temperature (300°C), excellent electrical properties measured by MIM (Pt/BST/Pt) and MIMS (Pt/BST/Pt/TiN/Ti/Si/Al) structures can still be performed. High dielectric constant (k=320), low leakage current (1.5×10^{-8} A/cm^2) under 0.1MV/cm, and 10 year lifetime under 1.25MV/cm were achieved with Ar+O_2 mixed ambient at low substrate temperature (300°C) in this work. The properties of BST capacitors can fulfill the requirements of 1Gb DRAM, therefore, this technique is promising for future high-density DRAM's applications.

Y12.2
PREPARATION AND CHARACTERIZATION OF (Pb,Sr)TiO_3 THIN FILMS FOR GIGA DRAM CAPACITOR BY LIQUID SOURCE MISTED CHEMICAL DEPOSITION. Hyun Jin Chung, Jin Hong Kim, Seong Ihl Woo, KAIST, Dept of Chemical Engineering, Taejon, KOREA.

The physical and electrical properties of lead-strontium-titanate (PST) thin films prepared, for the first time, by liquid source misted chemical deposition are reported. PST thin films were deposited on a platinum-coated Si wafer. Pb acetate, Sr 2-ethylhexanoate and Ti isoproxide were used as metallic precursors. These were dissolved in 2-methoxyethnol. A fine mist of metallic precursor solution was carried into a deposition chamber by Ar carrier gas. The crystallinity of PST, estimated by X-ray diffraction, was greatly improved by heat treatment at 500°C for 5minutes in an air atmosphere after deposition of each layer. The maximum crystallinity was obtained after heat treatment at 650°C. The composition and depth profile of PST film,

measured by wavelength dispersive spectroscopy and auger electron spectroscopy, were uniform. The dielectric constant and dielectric loss of $Pb_{0.32}Sr_{0.32}TiO_3$ films of 100nm thickness were 560 (equivalent oxide thickness:0.70nm) and 0.0173, respectively. The leakage current density was greatly influenced by post heat treatment under O_2 and N_2 ambient gas after top electrode Pt was deposited on a PST thin film. The lowest leakage current density of $2.80x10^{-7}A/cm^2$ at 1V was obtained. It can be concluded that PST is better than BST for ULSI DRAM capacitor.

Y12.3
A DETAILED INVESTIGATION OF SOL-GEL DEPOSITED $Ba_xSr_{1-x}TiO_3$(BST) THIN FILMS IN TERMS OF STRUCTURE-PROPERTY CORRELATION. S.Gupta, S.B.Majumder and R.S.Katiyar, Univ. of Puerto Rico, Dept. of Physics, San Juan, PR.

Sol-Gel deposition technique has been applied to synthesize Sr-modified $BaTiO_3$ thin films (hereafter, BST) of several compositions. The crystal structure of these films and the influence of deposition parameters such as substrate materials and temperature on them have been systematically examined. Several substrates such as single-crystal MgO(100), $Al_2O3(1010), RuO_2$/Si and platinized Si have been used to study the effect of substrate in general and the applicability of RuO_2 films as a bottom electrode of DRAM capacitors. The films of RuO_2 were deposited by Sol-gel method and the surface resistivity (ρ_s) of RuO_2 was measured by Van der Pauw method. Crystallization kinetics have also been studied in detail from differential thermal analysis (DTA) and the activation energy (E_a) has been calculated around 10kcal/mole-K. However, the crystalline phase of BST thin films are obtained at relatively high temperature and we suggest but not prove that it may be due to the precursors used. A variety of structural and micro-structural techniques such as XRD, SEM, AFM and micro-Raman spectroscopy have been employed to characterize them. Elemental nature of the BST thin films have been quantified by analytical technique such as XPS and the results have been compared with the laser ablated BST thin films grown on MgO in terms of stoichiometry. Besides, the electrical and ferroelectric properties of sol-gel derived BST thin films grown on Pt as a bottom electrode have been discussed for DRAM applications. This work is supported in parts by DAAG55-98-1-0012, DE-FG02-94ER75764 and NSF-DMR-9801759 US Grants.

Y12.4
EFFECTS OF IN-SITU DC-BIAS ON THE COMPOSITION, MICROSTRUCTURES AND DIELECTRIC PROPERTIES OF RF MAGNETRON REACTIVE SPUTTERED (Ba,Sr)TiO_3 FILMS. Wen-Hao Chan, Hui-Ling Shen[1] and Lih-Hsin Chou, National Tsing Hua Univ, Dept of Materials Science and Engineering, Hsinchu, TAIWAN ROC; [1]Present address: Lead Data Inc., Fu Kou Hsiang, Hsinchu, TAIWAN ROC; Jinn-Lung Wang and Jyi-Ching Tsai, Chemical Systems Research Div, Chung-Shan Inst of Science and Technology, Lung-Tan, TAIWAN ROC.

Thin films of (Ba,Sr)TiO_3(BST) have been prepared by the rf magnetron reactive sputtering method using single alloy target. The BST films were deposited with in-situ negative DC-bias. Post annealing was applied to the as-deposited films at 893K for 2 hours. Thin film microstructures and grain sizes were studied and calculated by means of X-ray Diffraction Analyzer, while the film composition was analyzed by Electron Probe X-ray Microanalyzer (EPMA). The dielectric constant of the films was also studied. As the applied DC-bias increased, the dielectric constant increased from 176 to 912, the x-ray diffraction patterns became higher and narrower, in addition, (Ba+Sr)/Ti molar ratio increased from 0.7 to 0.83. In-situ DC-bias was observed to be a feasible fabrication process to increase the grain sizes and relative permittivity of sputtered BST films.

Y12.5
POTO-ASSISTED MOCVD GROWTH OF HIGH DIELECTRIC (Ba,Sr)TiO_3 THIN FILMS ON Ni/TiN/Si SUBSTRATE FOR DRAM APPLICATION. Yimin Chen, Naijun Wu and Alex Ignatiev, Space Vacuum Epitaxy Center and Texas Center for Superconductivity, University of Houston, Houston, TX.

High dielectric barium strontium titanium oxide (BST) thin films have been deposited on Ni/TiN/Si by photo-assisted metal organic chemical vapor deposition (PhAMOCVD). The plane capacitors based on the Ni/BST/Ni/TiN/Si heterostructure with BST-layer thickness of 50nm exhibited storage densities of about 30 $fF/\mu m^2$ and leakage current densities of less than $10^{-6}A/cm^2$ under bias bellow 2V. As bottom electrode in this newly designed capacitor structure, nickel can be easily patterned by reactive ion etching, and satisfies the requirement for integration. Test structures of stacked capacitors were fabricated using BST thin films on the sidewalls of 3-D Ni/TiN electrodes patterned by reactive ion etching.

SESSION Y13: POSTER SESSION:
Pb-BASED THIN-FILM FERROELECTRICS
Chairs: Anneli Munkholm and Masaru Shimizu
Wednesday Evening, December 1, 1999
8:00 P.M.
Exhibition Hall D (H)

Y13.1
DENSIFICATION AND STRESS DEVELOPMENT IN SOL-GEL DERIVED PZT COATINGS. Ryan J. Ong and David A. Payne, University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, Urbana, IL.

Stress effects on electrical properties are investigated further for sol-gel derived $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin layers deposited on silicon. Shrinkage behavior was examined by in-situ ellipsometry. Densification data, thermal analysis (DTA, TGA), the effect of pyrolysis, and crystallization was observed for multiple layers deposited sequentially onto silicon substrates. The resulting coating stresses were determined as a function of heat treatment by a laser reflectance technique and related to associated densification phenomena and substrate/layer thermal expansion mismatch. Dielectric behavior and piezoelectric properties are reported as a function of film stress.

Y13.2
ADVANCES IN LIQUID DELIVERY FLASH EVAPORATION SYSTEMS FOR MOCVD OF FERROELECTRICS.
Fred P. Gnadinger, G. Huebner, Cova Technologies, Inc., Colorado Springs, CO; G.S. Tompa, L.G. Provost, C. Zhang, Structured Materials Industries, Inc., Piscataway, NJ.

Chemical Vapor Deposition (CVD) is a highly desired production technology for ferroelectrics and other complex oxide films. This technique, however, has found limited application because of a lack of adequate precursor chemistries and implementation methodologies. Over the past few years, workable precursor chemistries have been developed for several materials, however they require use of liquid delivery into flash evaporators. The liquid, often referred to as a cocktail, is a mixture of dissolved precursor (solute) and solvents. The liquid must successfully evaporate the solute and solvent, and transport the evaporants into the deposition zone. The solvent itself is often a mixture of multiple precursor dissolving agents and evaporation regulating agents. Severe requirements must be met by the flash evaporator-vapor delivery system, including: vapor must be delivered in a constant and controllable manner, transport must not be hindered by decomposition or other flow constrictions, vapor transport must be variable in a controlled manner, and the unit must operate reliably and repeatably over long durations. We report herein on the design and operating improvements to our automated multi-injector system that uses a large isothermal evaporation source, volumetric damping of flux oscillations, push gas preheating, and valved and pressure controlled operation, to provide high throughput and extended service between cleanings, thus eliminating the major problems limiting usage of liquid delivery flash evaporation CVD. Specific issues addressed include cost of operation, lifetime improvements, and expansion of functional parameter ranges. The results reported herein have been enable through BMDO sponsored Air Force administered contract P33615-98-C-1326 and a Delphi R&D collaboration.

Y13.3
SPUTTERED PZT THIN FILMS FOR FERROELECTRIC CAPACITORS. Tomoyuki Sakoda, Katsuhiro Aoki, Yukio Fukuda, Texas Instruments Tsukuba R&D Center Ltd, Ibaraki, JAPAN.

The sputtered PZT thin films with superior ferroelectric properties were successfully obtained by controlling the grain structure and the film compositions. Several-nm-thick amorphous PTO was used as a buffer layer, and PZT thin films were deposited by cosputtering $Pb(Zr_{0.5}Ti_{0.5})O_3$, PbO and TiO_2 targets. We found that amorphous PTO buffer layers are effective to form PZT thin films with the fine and dense grains. The sputtered PZT thin films with Ti-rich phase showed the excellent ferroelectric properties. The remanent polarization density, the coercive field and the saturation voltage of 300-nm-thick PZT capacitors with Zr/Ti=35/65 were 42 $\mu C/cm^2$, 46 kV/cm and 3.2 V, respectively. Those of 300-nm-thick PZT capacitors with Zr/Ti=30/70 were 42 $\mu C/cm^2$, 48 kV/cm and 2.5 V, respectively. The polarization retention properties of PZT capacitors with Ti-rich phase are prominent, and the value of the retained polarization density after 10 years is expected larger than 40 $\mu C/cm^2$. Further, 150-nm-thick PZT capacitors with Zr/Ti=30/70 showed the remanent polarization density at 1.5 V more than 30 $\mu C/cm^2$, and a good retention property. These results indicate the potential of the lower voltage operation of sputtered PZT capacitors by optimizing the film composition and thickness.

Y13.4
STRUCTURAL, FERROELECTRIC AND DIELECTRIC PROPERTIES OF LASER ABLATED (Pb,La)(Zr,Ti)O_3-THIN-FILMS ON STAINLESS STEEL. Ralph Klarmann, Wolfgang Biegel, Joachim Hemberger, Bernd Stritzker, University of Augsburg, Institute of Physics, Augsburg, GERMANY.

Stainless steel with various compositions was covered with (Pb,La)(Zr,Ti)O_3 (PLZT) by Pulsed Laser Deposition (PLD). The direct deposition of the ferroelectric thin film on the conducting substrate material - without additional buffer layers or bottom electrodes beneath the PZT - leads to a simple bicomponental system with sensoric potential. Different Ni-contents of the stainless steel should influence the formation of nickeloxide at the substrate surface at the beginning of the deposition process. An improvement of the lattice mismatch by formation of such an interface layer affects the subsequent phase formation of the PLZT film. The interface was examined by TEM / XTEM studies and the phase formation by SIMS depth profile, EDX and XRD pointing out nonferroelectric secondary phases. Moreover, the crystalline quality and the texture of the films was analysed by Channeling (He^{2+}) experiments and XRD. In addition, the ferroelectric properties - i.e. P-E hysteresis, fatigue and retention behavior of PLZT on stainless steel - were measured and correlations to the structure of the films were investigated. Dielectric spectroscopy was used to examine the dependence of the permittivity ε from frequency, temperature and applied electric field. These measurements are discussed with respect to the above mentioned points.

Y13.5
MEASURING BIMODAL CRYSTALLOGRAPHIC TEXTURE IN FERROELECTRIC PZT THIN FILMS. Mark D. Vaudin, NIST, Gaithersburg, MD; Glen R. Fox, Ramtron International Corporation, Colorado Springs, CO.

A powder x-ray diffraction method has been developed to measure the volume fraction of {111}, {100}, and randomly oriented PZT in 200 nm thick films used for FRAM applications. Using a q-2q scan obtained from random (untextured) powder of the same composition as the film, the relative intensities of the 100, 111, 200 and 222 PZT peaks were determined, taking Lorentz polarization factors and multiplicities into account. The distributions of grain orientation for the {111} and {100} populations were than determined. Rocking curves were obtained from the films using the four PZT peaks listed above. The rocking curves that would be obtained from untextured films using the same peaks were calculated, using the peak profiles and the diffractometer optics to correct for defocusing. The observed rocking curves were divided by the calculated curves to give the texture profiles. To determine the total volume fraction of each population of grains, the rocking curve profiles were integrated, and these values were corrected for the relative intensities of the relevant peaks. Texture data were collected from a number of films and correlated with the ferroelectric performance of the films.

Y13.6
HYDROTHERMAL GROWTH OF EPITAXIAL THICK FILM HETEROSTRUCTURES OF FERROELECTRIC (Pb(Zr,Ti)O_3)/ CONDUCTIVE OXIDE ($SrRuO_3$). D.M.Kim, M.K. Lee, R.A. Rao, C.B. Eom, Dept of Mechanical Engineering and Materials Science, Duke University, Durham, NC.

Ferroelectric materials have been increasingly explored for use in actuators and non-volatile memories. For the ferroelectric device applications, it is desirable to have epitaxial growth of ferroelectric and conductive oxide thin films in a single heterostructure. We have grown epitaxial ferroelectric (Pb(Zr,Ti)O_3) thin films on (001) $SrTiO_3$ substrates by hydrothermal process. The hydrothermal process allows us to grow oxide films from aqueous solution at low temperature. Furthermore, it is easy to grow thick films which are necessary for the fabrication of high frequency ultrasound transducers. We prepared the mixture with titanium dioxide(anatase), zirconium oxychloride and lead nitrate in an alkaline aqueous solution. The mixture was heated to 50 - 200°C in a Teflon-lined autoclave reactor. Four-circle x-ray diffraction analysis revealed the PZT layer is purely {001} normal to the substrates with cube-on-cube in-plane epitaxial arrangement. We have also fabricated PZT/$SrRuO_3$ epitaxial ferroelectric heterostructures employing sputtered single domain $SrRuO_3$ thin film bottom electrodes. We will discuss the microstructure and electrical properties of the heterostructures.

Y13.7
ELECTRICAL PROPERTIES AND SWITCHING BEHAVIOR OF PZT THIN FILM HETEROSTRUCTURES ON SILICON BY PULSED LASER DEPOSITION. Soma Chattopadhyay, A.K. Sharma, Alex Kvit, Chunming Jin, W.J. Collis,C.B. Lee and J. Narayan, NSF Centre for Advanced Materials and Smart Structures, North Carolina A&T State University, Dept. of Electrical Engineering, Greensboro, NC; North Carolina State University, Materials Science Dept., Raleigh, NC.

Processing of PZT films with different electrodes and integration of these films with silicon for memory devices are the key issues which are being investigated extensively in the recent years. We have been successful in the fabrication of (100) oriented epitaxial PZT films on YBCO/$SrTiO_3$/MgO/TiN/Si heterostructures by pulsed laser deposition. The films were observed to be single phase by X-ray diffraction. The thickness of the films was in the range 250 - 400 nm. The surface morphology of the films was studied by contact mode Atomic Force Microscopy. The rms value for the surface roughness was found to be 20-40 nm. Dielectric measurements were performed on the films at room temperature and at a frequency of 10 kHz. P-E hysteresis loop measurements were carried out with evaporated Cr-Au electrodes. Dielectric constant for the films was found to be around 300-350. The value of saturation polarization Ps was between 20-25 $\mu C/cm^2$ and the coercive field E_c varied from 40-50 kV/cm. Growth of films for better values of P_s and E_c is in progress. Preliminary studies of polarization switching were done on some of the samples using Scanning Force Microscopy. The domain structure of the virgin state depends on the crystallinity, homogeneity and the microstructure of the films. Correlation between domain arrangement and crystallinity of the films and the thickness dependence of electrical properties are being investigated.

Y13.8
INVESTIGATION ON THE STRUCTURAL AND MICROSTRUCTURAL CHARACTERISTICS OF SOL-GEL DERIVED LEAD LANTHANUM TITANATE THIN FILMS. S.B. Majumder, S. Bhaskar, P.S. Dobal and R.S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR; Angel L. Morales Cruz, Dept of Chemistry, University of Puerto Rico, San Juan, PR.

In the present work we have successfully prepared $Pb_{1.05-x}La_xTiO_3$ (x = 0.0, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.30) thin films on sapphire (0001) and platinized silicon substrates by an acetic acid modified sol-gel technique. The thermal stability and pyrolysis characteristics of the precursors were investigated by IR spectroscopy , DSC and DTA analyses of powders derived from the precursor sol. A systematic X-ray diffraction and micro-Raman analysis were performed to understand the structural modifications with lanthanum (La) doping. La as a dopant reduces the tetragonal distortion of PT and changes its structure to cubic through a pseudocubic perovskite phase. In the Raman spectra, the soft E (1TO) phonon shifts towards the lower frequency with a sharp decrease in its intensity and a room temperature tetragonal to cubic structural transformation for 26.5 % La composition was observed. The XPS analysis confirmed the excellent surface stoichiometry of all the compositions under study. From the analysis of the chemical state of each element we have observed that Pb, Ti and O are present in the form of perovskite PT only. The growth mechanisms for the microstructural evolution of these films were analyzed by AFM and SEM. PT films were isothermally annealed at different temperatures between 500° to 700° C for various times and the evolution of the growth of columnar grains were analyzed by AFM as well as cross section SEM. The grain size of PT film was found to be reduced considerably with 5 at % La addition. With further La addition it was found that these smaller grains impinge to form larger grains. Finally, an attempt has been made to correlate the electrical properties with the structural and microstructural features of these films. This work was supported in part by DE-FG02-91ER75764, DEPSCOR DAAG55-98-1-0012 and NSF-DMR9801759 grants.

Y13.9
DENSIFICATION AND EVOLUTION OF STRESS DEVELOPMENT IN SOLUTION DERIVED PZT THIN LAYERS. Sang M. Park, Hankuk Aviation University, Dept. of Materials Engineering, Kyonggi-do, KOREA.

In this study *insitu* stress was measured for a single and multideposited PZT thin layers upon thermal cycling using laser reflectance technique. Origins of film stress are explained in terms of drying, pyrolysis, densification, and crystallization of the film during heat treatment. Stress was always tensile for a single and multi layers with its maximum in 300-350°C. The stress data indicates that actual densification of the film begins at 350-390°C, where a sharp stress reduction occurs, and is completed at near 500°C. Beyond 500°C the film stress is mainly dominated by thermal expansion mismatch between Si substrate and the film. Microhardness data for the films heat treated at various temperatures also supported the stress data with regard to film densification.

Y13.10
PROPERTIES OF FERROELECTRIC PZT THIN FILMS OBTAINED BY OXIDE PRECURSORS. Eudes Borges Araújo, José Antonio Eiras, Universidade Federal de São Carlos, Departamento de

Física, São Carlos, SP, BRAZIL.

Recently, solution deposition has been used by several researchers throughout the world to produce thin films. Solution depositions enable better stoichiometric control of complex mixed oxides than other physical techniques. The search for new routes to obtain the solution for film deposition remains as an interesting subject in order to achieve higher stability of complex compositions or cheaper processing. Lead zirconate titanate $PbZr_xTi_{1-x}O_3$(PZT is the most studied perovskite-type ferroelectric material as bulk ceramics as well thin films. PZT solid solution ceramics are well known by excellent piezoelectric, dielectric and pyroelectric properties. Thus, the preparation of PZT thin films has been attracting practical interest. Very recently, was proposed the preparation of PZT thin films from oxide precursor [1], an chemical method based on a pre-calcination of oxides or carbonates. The method was successfully applied to prepare PZT thin films on fused quartz or Pt/Si substrates [2,3]. The films showed good quality, homogeneity and high stoichiometry control. In this work, we report the structural, electrical and ferroelectric properties of PZT thin films obtained by oxide precursors. Films with 0.5 μm in thickness were deposited on Pt/Si. In these films were identified the presence of the tetragonal and rhombohedral phases. Capacitance-voltage (C-V) characteristics and P-E hysteresis loops were used to confirm ferroelectricity. The obtained remanent polarization (P_r) and coercive field (E_c) values were 6.2 μ C/cm^2 and 66kV/cm, respectively, at 100 Hz frequency. Finally, as a result of fatigue process, the P_r value decreased to 79% of its initial value after 2.6×10^7 switching cycles. [1] E.B. Araújo and J.A. Eiras, J. Mat. Sc. Letters, 17 (1998) 833. [2] E.B. Araújo and J.A. Eiras, J. European Ceram. Soc. 19 (1999) 1453. [3] E.B. Araújo and J.A. Eiras, J. Phys.: Conden. Matter 11 (1999) 1975.

SESSION Y14: POSTER SESSION:
THIN-FILM PIEZOELECTRICS, CAPACITORS AND PYROELECTRIC DEVICES
Chairs: Mareike Klee and Paul Muralt
Wednesday Evening, December 1, 1999
8:00 P.M.
Exhibition Hall D (H)

Y14.1
ELECTRICAL PROPERTIES OF Y-DOPED $BaTiO_3$ FILMS DEPOSITED IN REDUCING ATMOSPHERES USING PULSED LASER DEPOSITION. Won-Youl Choi and Susan Trolier-McKinstry, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

$BaTiO_3$-based multilayer capacitors with Ni electrodes are fired at low Po_2 to prevent the oxidation of Ni. Amphoteric dopants such as Y, Ho and Dy are used to prevent electrical degradation due to oxygen vacancy migration. This paper describes use of this approach preparing thin film $BaTiO_3$ capacitors. Tolerance of reducing atmospheres is particularly important in films which are co-processed with resistors such as TaN for integrated resistor-capacitor networks. To assess this approach, films were grown by pulsed laser deposition from $BaTiO_3$ targets containing 0.2wt% Y_2O_3. Films were deposited onto Pt/Ti/SiO_2/Si substrates using a 5Hz laser repetation, an energy density of 4.2J/cm^2 and a working pressure of 100mTorr. It was found that polycrystalline perovskite films could be grown at 700°C. Films grown in pure N_2 atmospheres had dielectric constants and losses at 1kHz of 1300 and 0.03, respectively. The temperature and field dependence of dielectric and leakage current density data will be discussed.

Y14.2
ORIENTATION AND COMPOSITION DEPENDENCE OF PIEZOELECTRIC-DIELECTRIC PROPERTIES OF SPUTTERED $Pb(Zr_x,Ti_{1-x})O_3$ THIN FILMS. Stephane Hiboux, Paul Muralt, Nava Setter, Federal Inst of Tech, Ceramics Lab, Lausanne, SWITZERLAND.

In-situ, reactively sputter deposited 300 nm thick $Pb(Zr_x,Ti_{1-x})O_3$ films on Pt/Si based substrates are investigated as a function of composition and texture. (111) PZT is grown on a (111) oriented Pt bottom electrode covered with a very thin TiO_2 layer. Highly (100) oriented PZT is grown on Pt (111) by introducing a 10 nm $PbTiO_3$ layer before the PZT deposition. The compositions at which dielectric constant and piezoelectric coefficient are peaking depend on the orientation. Pronounced deviations from known bulk PZT behavior are observed for the (111) texture. This can be explained by differences in domain wall contributions. (100) textured films exhibit a higher d_{33}. 1.3 μm (100) thick films attain the predicted d_{33} value of clamped bulk ceramics. Coercive fields and voltage offsets increase strongly with increasing Ti content. In parallel the as-grown polarization increases. Switching of domains is not possible for x $\leq$ 0.1. Post-anneals in O_2 and hot poling show that oxygen vacancies play an important role in this phenomenon. Ti-rich (100) oriented films exhibit very high and stable pyroelectric and piezoelectric coefficients without poling treatments.

Y14.3
PHASE FORMATION OF $Pb(Zr,Ti)O_3$-FILMS ON NiTi-SUBSTRATES WITH SHAPE MEMORY EFFECT. Wolfgang Biegel, Ralph Klarmann, Bernd Stritzker, University Augsburg, Institute of Physics, Augsburg, GERMANY.

It was shown in previous work, that Pulsed Laser Deposition is a proper tool to deposit $Pb(Zr,Ti)O_3$ films (PZT) with good structural and ferroelectrical properties even onto steel foils. To check the potential of a simple bicomponental system which allows actuating and sensing independently from each other, PZT was deposited onto foils of NiTi. The chosen substrate alloy with composition $Ni_{50}Ti_{50}$ shows a strong shape memory effect with a transition temperature of about 80°C. This simple bicomponental system could have the potential of an actuator device (NiTi shows a strain up to 5% during thermal cycling) with an inherent sensoric component (PZT) for the generated elongation. The phase formation of the deposited PZT films was characterized (XRD, SEM) as well as their ferroelectric behavior (P-E hysteresis). The adhesion of the PZT film on the shape memory alloy is an important point and was investigated after several numbers of temperature driven cycles (martensitic transformations) of the NiTi foil.

***Y14.4**
DIELECTRIC AND TRANSVERSE PIEZOELECTRIC CHARACTERIZATION OF SOL-GEL DERIVED $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (70/30) FILMS WITH {100} AND {111} TEXTURE. Jeong Hwan Park and Susan Trolier-McKinstry, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

Highly {100} and {111} oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (70/30) films between 0.5 and 1.5 μm thick were deposited on Pt(111)-passivated silicon substrates using a modified sol-gel process. In both cases, the degree of preferred orientation did not change with film thickness. The dielectric constant for the {100} oriented films were 2000-2500. While, the {111} oriented films were 1500-1800. In both cases tan δ was less than 0.03. It was found that the piezoelectric coefficient (d_{31}) of the PMN-PT films increased with increasing film thickness and poling voltage. The d_{31} coefficient of highly {100} oriented PMN-PT films were found to range from -60 to -80 pC/N. Highly {100} oriented PMN-PT films showed larger piezoelectric coefficient than {111} oriented films. Results on aging of the piezoelectric coefficients of the differently oriented films will also be presented.

Y14.5
IN-PLANE POLARIZED PZT THICK THIN FILMS DEPOSITED ON ZIRCONIA-BUFFERED SILICON SUBSTRATES. Baomin Xu, Yaohong Ye, L. Eric Cross, Materials Research Laboratory, Pennsylvania State University, University Park, PA; Jonathan J. Bernstein, Raanan Miller, the C.S. Draper Laboratory, Cambridge, MA.

As both d_{33} and k_{33} values of most piezoelectric ceramics are almost two times of the d_{31} and k_{31} values respectively, recently d_{33}-type unimorph benders have been developed in which the piezoelectric layer is in-plane polarized (polarization parallel to the layer surface), demonstrating great performance improvement comparing to the conventional d_{31}-type unimorph benders in which the piezoelectric layer is polarized across the thickness. As a first step to move the technology forward to fabricate micromachined d_{33}-type unimorph transducers on Si substrates for MEMS applications, ferroelectric PZT films have to be deposited on an insulating buffer layer with low dielectric constant instead of platinum buffer layer. Furthermore, this in-plane polarization configuration is especially attractive for unimorph microsensors such as micromachined unimorph sonar transducer arrays, since the diaphragm thickness and electrode spacing are now independent variables. In this work, we will report that high quality PZT (52/48) thick thin films can be prepared on ZrO_2 buffered 4-inch Si wafers. Both PZT films and ZrO_2 buffer layer are deposited by sol-gel method. PZT films with thickness from 1 to 5 μm have been fabricated showing sharp planer interfaces with the ZrO_2 layer. Using interdigitated electrode arrays on the upper surface the dielectric and ferroelectric properties of the films are characterized. Dielectric constant in the range 1000 to 1200 is achieved with dielectric loss tanδ of about 0.01. Excellent symmetric dielectric hysteresis loops are obtained with the remanent polarization P_r of 15 to 20 μC/cm^2 and coercive field of 20 to 30 kV/cm. Work is now in progress to characterize the piezoelectric d_{33} in poled films and to demonstrate unimorph structures for both actuation and sensing functions.

Y14.6
GROWTH OF EPITAXIAL $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ THIN FILMS BY MOCVD. G.R. Bai, S.K. Streiffer, O. Auciello, P.K. Baumann and K. Ghosh, Materials Science Division, Argonne National Laboratory, Argonne, IL; A. Munkholm, Chemistry Division, Argonne National Laboratory, Argonne, IL; C. Thompson, Dept. of Physics, Northern Illinois University, DeKalb, IL and Materials Science Division, Argonne National Laboratory, Argonne, IL; S. Stemmer, Department of Physics, University of Illinois at Chicago, Chicago, IL.

The relaxor ferroelectric lead magnesium niobate (PMN) and its solid solution with lead titanate (PMN-PT) have attracted much attention recently because of excellent dielectric and electromechanical properties. For many applications benefiting from integrated devices, deposition of thin film PMN-PT would be required. Here we report the preparation by metalorganic chemical vapor deposition of epitaxial PMN-PT films on $SrTiO_3$ and $SrRuO_3/SrTiO_3$ substrates, using solid $Mg(DPM)_2$ as the Mg precursor. Deposition conditions have been identified under which phase-pure perovskite PMN-PT may be grown. In contrast, in lead-poor and lead-rich environments, additional second phases of $Mg_4Nb_2O_9$ plus pyrochlore, and PbO_x, respectively, have tentatively been identified. X-ray diffraction and selected area electron diffraction indicate a cube-on-cube orientation relationship between film and substrate, with a (001) rocking curve width of 0.1°, and in-plane mosaic of 0.8°. The RMS surface roughness of a 200nm thick PMN film on $SrTiO_3$ was 2 to 3 nm as measured by scanned probe microscopy, while the refractive index was determined to be 2.519. The ferroelectric, piezoelectric, and optical properties of these samples as a function of composition will be briefly discussed.

***Y14.7**
PREPARATION OF PIEZOELECTRIC PZT THIN FILMS BY MOCVD FOR MEMS APPLICATIONS. Ing-Shin Chen and Jeffery F. Roeder, ATMI, Danbury, CT; Jon-Paul Maria and Angus I. Kingon, North Carolina State University, Raleigh, NC.

Integration of piezoelectric $Pb(Zr,Ti)O_3$ (PZT) thin films promises to furnish silicon microelectromechanical systems (MEMS) with added functionality. PZT films with compositions near the tetragonal/rhombohedral morphotropic boundary have been deposited on iridium-coated Si substrates by a thermal chemical vapor deposition (CVD) process using flash vaporized metalorganic precursors. Deposition temperatures, (A-site)-to-(B-site) ratios in the precursor mixing, and film thicknesses have been surveyed. Stoichiometric, perovskite films with nominal Zr/Ti ratios ranging from 45/55 to 60/40 were obtained. Parallel capacitor structures have been fabricated by depositing Pt top electrodes using e-beam evaporation. Ferroelectric hysteresis loops were measured by a standard ferroelectric tester and remenant polarization in the range of 15∼30 $\mu C/cm^2$ were obtained. For films of 0.5 μm or thicker, piezoelectric hysteresis loops were characterized by dual-beam interferometry. Piezoelectric coefficients (d_{33}) of 30∼50 pm/V were observed on the films deposited at 550 to 580°C.

Y14.8
EXCIMER LASER LIFTOFF OF EPITAXIAL $Pb(Zr,Ti)O_3$ THIN FILMS AND HETEROSTRUCTURES FOR PIEZOELECTRIC MEMS. Loucas Tsakalakos, Tao Su and Timothy D. Sands, University of California, Dept of Materials Science and Mineral Engineering, Berkeley, CA.

Epitaxial $Pb(Zr,Ti)O_3$-based thin films and heterostructures have been transferred intact from their sapphire and MgO growth substrates to silicon and polymer substrates utilizing a novel laser liftoff process. The heterostructures, while on their growth substrate, were bonded to the receptor substrates using one of several bonding methods, including van der Waals bonding to an elastomer receptor, and transient liquid-phase Pd-In bonding to Si substrates and a steel shim. A single 38 ns pulse from a KrF excimer laser (= 248 nm) directed through the transparent growth substrate induced localized heating of the perovskite interfacial layer. At fluences corresponding to the onset of vaporization (300-500 mJ/cm^2), the sapphire or MgO substrate was detached. Because of the short pulse length and the low thermal conductivity of Pb-based perovskite phases, heating of the top surface of the heterostructure was minimal, thus permitting film transfer to thermally-sensitive receptor substrates. X-ray rocking curves revealed slight broadening of the principal PLZT diffraction peaks (∼10-20%), suggesting local relaxation of film stress, while SEM micrographs show the presence of a quenched liquid surface layer after laser processing. Initial electrical measurements of PLZT capacitor heterostructures show the films to be nominally ferroelectric after laser liftoff, however with an increased leakage current. Possible mechanisms for this observation, as well as methods for improving the properties will be discussed.

***Y14.9**
THICKNESS DEPENDENCE OF PIEZOELECTRIC PROPERTIES OF PZT THIN FILMS. Dong-Joo Kim, Seung-Hyun Kim, Angus I. Kingon, Jon-Paul Maria, North Carolina State Univ, Dept of Materials Science and Engineering, Raleigh, NC; Hiroshi Maiwa, Shonan Institute of Technology, Dept of Materials Science and Ceramic Technology, JAPAN; Barry Chen, Jeff Roeder, Advanced Technology Materials, Danbury, CT.

For reliable application of ferroelectric thin films (primarily PZT compositions) into microelectromechanical systems (MEMS), it is necessary to understand the electromechanical response. To achieve this understanding it is important to develop reliable measurement techniques and to characterize films under a controlled series of mechanical boundary conditions. Double-beam interferometry is being developed for accurate assessment of thin film piezoelectric properties. Voltage and frequency dependent measurements of electromechanical strain have been demonstrated with sub-angstrom resolution. Specific characteristics of the measurements will be discussed. For the tetragonal sub-micron PZT films characterized, zero bias effective d_{33} measurements typically reveal values ∼ 40 pC/N, these results are discussed in context with the wide range of effective piezoelectric coefficients reported in the literature. In an attempt to isolate the effects of changing boundary conditions, tetragonal lead zirconate titanate films have been deposited by metalorganic chemical vapor deposition onto substrates with Si_3N_4 etch stop layers. Electrical and electromechanical properties for a thickness series of these PZT films will be presented. In addition to the thickness dependent analysis, property comparison will be made to films from which diaphragm structures were fabricated. Ideally, this comparison will allow assertions to be drawn regarding the effects of substrate clamping.

Y14.10
EPITAXIAL LEAD MAGNESIUM NIOBATE / LEAD TITANATE THIN FILMS DEPOSITED BY LASER ABLATION. D. Lavric, C.B. Eom, Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC.

Pure perovskite phase relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) thin films have been grown on top of $SrRuO_3$ metallic electrode on both (001) $LaAlO_3$ and miscut (001) $SrTiO_3$ substrates by the pulsed laser deposition technique. X-ray diffraction θ-2θ and off-axis ϕ scans demonstrated that the PMN-PT films are fully c-axis oriented normal to the $LaAlO_3$ and $SrTiO_3$ substrates and grow cube-on-cube on top of the $SrRuO_3$ bottom electrode, with an in-plane epitaxial arrangement, in the case of the $SrTiO_3$ substrate, of PMN-PT[100],[010] ‖ $SrRuO_3$[001] ‖ $SrTiO_3$[100] and PMN-PT[010],[100] ‖ $SrRuO_3$[$\bar{1}$10] ‖ $SrTiO_3$[010] . The crystalline quality of the PMN-PT layers was comparable with that of the bulk single crystal. The influences of the top electrodes and substrates on the dielectric and piezoelectric properties of the PMN-PT films will be discussed. This work was supported by the NSF Grant No. DMR-9802444, the NSF Young Investigator Award (CBE) and the David and Lucile Packard Fellowship (CBE).

Y14.11
DYNAMIC PYROELECTRIC RESPONSES OF MULTILAYERED PZT(30/70)/PT THIN FILMS. Liu Weiguo, Zhu Weiguang, Hybrid Microcircuits Lab., School of EEE, Nanyang Technological University, SINGAPORE.

In order to develop high performance pyroelectric detectors, it is necessary to modify the dielectric properties of the ferroelectric thin films. Multi-layered PZT(30/70)/PT thin films are prepared through a modified sol-gel process in which moisture-insensitive solid precursors are used. The thin films are composed of alternatively stacked 11 layers of PZT(30/70) and PT thin films. Total thickness of 0.8 micrometer is achieved. The PZT37Z is started from PZT and ended at PZT, while the PZT37T is started from PT and ended at PT. Microstructure of the thin films has been characterized with XRD and SEM. Both PZT37Z and PZT37T are well crystallized when they are annealed at 600 centigrade degree for 30 minutes. Dielectric properties of the films are analyzed. Different modifications of the dielectric properties have been achieved for PZT37Z and PZT37T thin films. Dynamic pyroelectric responses are measured. It is found that PZT37Z shows higher pyroelectric response. A serial model is proposed to analyze the dielectric properties of the alternatively stacked multilayer thin films. The experimental results show that multilayered thin films are good candidates for the development of high performance pyroelectric detectors.

Y14.12
LOW TEMPERATURE CRYSTALLIZATION OF $PbTiO_3$ THIN FILM BY EXCIMER LASER IRRADIATION. Toshiyuki Mihara, Shoichi Mochizuki, Tadashi Ishida, Yoshiyuki Sato, Osaka National Research Inst, Dept of Material Physics, Ikeda, Osaka, JAPAN; Junji Nishii, Osaka National Research Inst, Dept of Optical Materials,

Ikeda, Osaka, JAPAN.

Decreasing the fabrication temperature for ferroelectric film is very important not only for silicon monolithic circuits but also for various substrates use. Amorphous $PbTiO_3$ thin films were prepared on glass substrates using ArF laser ablation at rather low temperature. They were subsequently treated with a laser-induced phase transformation technique to achieve a perovskite structure. The structure, morphology and composition of the films were investigated using X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis, respectively. After irradiation with an ArF pulsed excimer laser with an energy density $50mJ/cm^2$ at frequency of 5Hz for 60min in air, the films crystallized into the perovskite structure. The surface of some films had many pits, however, the other were rather smooth. It was necessary to control the number of laser pulses for avoiding damage of films. During the whole fabrication process, the substrates were kept at room temperature. The effects of chemical composition and fabrication temperature will be discussed.

Y14.13
TEM INVESTIGATION OF PULSED-LASER DEPOSITED PLZT HETEROSTRUCTURES FOR UNCOOLED PYROELECTRIC SENSORS. Randy N. Jacobs, R.P. Godfrey, L. Salamanca-Riba, R. Ramesh, Dept of Materials and Nuclear Engineering, Univ of Maryland- College Park, MD; C.W. Tipton, U.S. Army Research Laboratory, Adelphi, MD.

Transmission electron microscopy is used as the major tool to examine the structural characteristics of $Pb_{1-x}La_xZr_{1-y}Ti_yO_3$ (PLZT) films grown on single crystal $LaAlO_3$ (LAO) substrates via pulsed excimer laser deposition. In particular, the domain orientation as a function of substrate temperature in the range 500°C to 650°C is obtained and compared to x-ray diffraction (XRD) results. The compositional dependence (i.e., lanthanum and zirconium doping) of the film epitaxial quality and structural characteristics are also examined. For simplicity, the former study involves PLZT films grown directly on LAO substrates while the latter study uses heterostructures incorporating the conducting perovskite electrodes $La_{1-x}Sr_xCoO_3$ (LSCO). In addition to TEM characterization, atomic force microscopy (AFM) is used to study film surface morphology. The dependence of the film quality on these processing parameters is reported showing a correlation with inherent pyroelectric properties.

SESSION Y15/KK5: JOINT POSTER SESSION: FERROELECTRICS
Chairs: Orlando Auciello and Quanxi Jia
Wednesday Evening, December 1, 1999
8:00 P.M.
Exhibition Hall D (H)

Y15.1/KK5.1
EFFECT OF THE OXYGEN PARTIAL PRESSURE ON THE MICROSTRUCTURE AND PROPERTIES OF BARIUM STRONTIUM TITANATE THIN FILMS SYNTHESIZED BY PULSED LASER DEPOSITION. C.G. Fountzoulas, Eric H. Ngo, C.W. Hubbard, P.C. Joshi and M.W. Cole, Army Research Laboratory, Weapons Materials Directorate, APG, MD.

Thin films of novel barium strontium titanate (BSTO), deposited by the pulsed laser deposition (PLD) technique exhibit excellent electronic properties including tunable dielectric constants and low electronic loss. The microstructure of the film influences the electronic, mechanical properties (internal stresses and adhesion), important factors affecting the mechanical integrity and reliability of a device made of these thin films, which in turn influence the performance of the film. Films of 1 μm nominal thickness were deposited simultaneously on silicon and on single crystals of sapphire. The synthesis of the films took place at 700°C and various partial oxygen pressures. The microstructure and crystallinity of the BSTO films were studied with the aid of x-ray diffraction analysis, scanning electron microscopy (SEM) and FT-Raman spectroscopy. The nanohardness, modulus of elasticity, cohesion and adhesion and wear properties of the films were studied with the aid of a nanohardness indenter and a ball-on-disk tribometer. The electronic, mechanical, physical properties and an initial microstructural zone model of these films will be discussed as a function of the partial oxygen pressure. These results will be combined with the results of our previous work[1] on the effect of substrate temperature on above electronic and mechanical properties. The substrate influence on the microstructure and properties will also be presented and discussed.

[1] 'Mechanical Properties of Ferroelectric Composite Thin Films', C. G. Fountzoulas* and Somnath Sengupta, Thin Films-Stresses and Mechanical Properties VII, MRS Vol. 505 (1998)

Y15.2/KK5.2
PARAELECTRIC COMPOUNDS BASED ON SUBSTITUTED $BaTiO_3$. S.C. Tidrow, A. Tauber*, D.D. Brickerd, A. Lee, B. Rod, E.D. Adler, M.S. Patterson, U.S. Army Research Laboratory, Adelphi, MD; *Under contract with Geo-Centers, Inc.

Cubic compounds exhibiting paraelectric behavior have been identified in systems of solid solutions between $BaTiO_3$ and perovskites that are dielectrics. Over the composition ranges studied, many compounds are cubic and their lattice parameters obey Vegard's Law. Many compositions exhibit a ferroelectric transition below room temperature. Within the paraelectric range the dielectric constant, and loss tangent are characterized with regard to temperature and microwave radiation. The variation of dielectric constant with applied dc voltage is also reported. Thin films, prepared using pulsed laser deposition, mainly grow epitaxial on $LaAlO_3$ and LSAT substrates as shown from x-ray diffraction data.

Y15.3/KK5.3
MECHANISMS OF TUNABILITY AND LOSS IN FERROELECTRIC THIN FILMS. X.X. Xi, A.A. Sirenko, Anna M. Clark, I.A. Akimov, J. H. Hao and Weidong Si, Penn State University, Department of Physics, University Park, PA.

Strain, oxygen vacancies, and interfacial effects have been recognized to play important roles in determining the tunability and loss properties in ferroelectric thin films. In this talk, I will use incipient ferroelectric $SrTiO_3$ thin films as an example to illustrate these effects in the thin films. I will present our structural, optical, and dielectric measurements in $SrTiO_3$ thin films deposited by pulsed laser deposition. We found that strain, both lattice mismatch-induced and due to local defects such as oxygen vacancies, dramatically influences the properties of the thin films. Because of strain, the thin films are in a tetragonal structure, as evidenced by the superlattice peak in x-ray diffraction due to the tilting of the Ti-O octahedron, instead of a cubic structure as observed in single crystals, at room temperature. The cubic-to-tetragonal structural phase transition, which occurs in single crystals at about 105 K, is shifted above 800 K. The Raman scattering measurements show that the symmetry-forbidden optical phonons are active in the thin films, indicating the reduction of symmetry due to the strain. The line shape of the polar phonon shows a Fano asymmetry, indicating the existence of micro polar regions, or other local polar structures around the oxygen vacancies. The dielectric properties depends on the film thickness which can be treated as the result of dead layers at the interface with the electrodes. Further, we have measured the soft mode in the thin films using far infrared ellipsometry and showed that the soft mode is considerably hardened in the thin films compared to the single crystals. The thickness dependence of the dielectric constant can be understood in the framework of lattice dynamics in the thin films.

Y15.4/KK5.4
PHASE TRANSITIONS IN $SrTiO_3$ SINGLE-DOMAIN EPITAXIAL THIN FILMS. Alexander Tagantsev, Nava Setter, EPFL Swiss Federal Institute of Technology, Ceramics Laboratiry, Materials Department, Lausanne, SWITZERLAND; Nicholas Pertsev, A.F. Ioffe Physico-Technical Institute, St. Petersburg, RUSSIA.

A Landau-Ginsburg-Devonshire-type theory is used to describe the mechanical substrate effects upon equilibrium states and phase transitions in (001) - $SrTiO_3$ single-domain epitaxial thin films. The misfit straintemperature phase diagram of $SrTiO_3$ films is developed allowing for the existence of two coupled instabilities (structural and ferroelectric) in this crystal. It is shown that $SrTiO_3$ films remain paraelectric down to 0 K only over a narrow range of small, negative misfit strains. It is found that the mechanical interaction with the substrate can result in changes in the sequence of phase transitions. For example, under certain conditions, the first transition upon cooling can be ferroelectric and only on further cooling the material undergoes the antiferrodistorsive phase transition.

Y15.5/KK5.5
MICROSTRUCTURE AND MICROWAVE RESPONSE OF YBCO AND YBCO / $SrTiO_3$ THIN FILMS ON 3-INCH DIAMETER SAPPHIRE WAFERS GROWN BY PLD. Michael Lorenz, Holger Hochmuth, Dieter Natusch, Thomas Thaerigen, University of Leipzig, Faculty of Physics and Earth Sciences, Leipzig, GERMANY; Vasily L. Svetchnikov, H.W. Zandbergen, National Center for High Resolution Electron Microscopy, Delft, THE NETHERLANDS; Gerhard Kaestner, Dietrich Hesse, Max-Planck-Institute for Microstructure Physics, Halle/Saale, GERMANY.

A highly reproducible pulsed laser deposition (PLD) process is set up for YBCO:Ag and YBCO:Ag / $SrTiO_3$ thin films on both sides of 3-inch diameter sapphire wafers to be used as tunable microwave filters for satellite and mobile communication systems. The routinely

deposited YBCO:Ag films on CeO_2 buffered sapphire show laterally homogeneous maps of microwave surface resistance R_s of about 45 mΩ at 145 GHz and 77 K. The R_s at 8.5 GHz and 77 K determined in the center position of the YBCO:Ag films is about 380 $\mu\Omega$ and remains constant up to a microwave surface magnetic field of 7-10 mT. The optimum Ag-content of the PLD-YBCO target was determined to be about 4 weight-%. The DC-electrical and microwave properties of YBCO:Ag thin films on dielectric $SrTiO_3$ films for electrically tunable microwave devices depend remarkably on the microstructure of the underlying $SrTiO_3$ layer. For deposition of YBCO / $SrTiO_3$ multilayers on CeO_2 buffered sapphire the flexible PLD technique appears as a very suitable and effective deposition technique. TEM cross sections of the large-area and double-sided PLD-YBCO:Ag thin films on R-plane sapphire with CeO_2 buffer layers show typical defects like stress modulation, stacking faults, a-axis oriented grains, precipitates and interdiffusion layers. Lower oxygen partial pressure during PLD increases the number of stacking faults in the YBCO structure, but reduces the a-axis oriented fraction, resulting in lower microwave surface resistance. The results show the state of the art and hints to a further improvement of YBCO and YBCO / $SrTiO_3$ thin films on technologically important substrates for applications as microwave devices. This work is supported by the German BMBF and by Robert BOSCH GmbH Stuttgart.

Y15.6/KK5.6

OPTIMIZATION OF RF SPUTTERED BARIUM STRONTIUM TITANATE (BST) THIN FILMS FOR HIGH TUNABILITY. T.R. Taylor[1], P. Padmini[2], J.S. Speck[1] and R.A. York[2]. [1]Materials Research Laboratory [2]Department of Electrical and Computer Engineering, University of California, Santa Barbara, CA.

Ferroelectric thin films are currently being used to develop tunable microwave circuits based on the electric field dependence of the dielectric constant. $(Ba_{0.5}Sr_{0.5})TiO_3$ films prepared on $Pt/TiO_2/SiO_2/Si$ substrates are found to exhibit a tunability {defined as $\epsilon_{r(max)}/\epsilon_{r(min)}$; $\epsilon_{r(max)}$ is the relative dielectric constant at zero bias and $\epsilon_{r(min)}$ is the relative dielectric constant at a higher or defined field} of nearly 4:1. This is the highest reported tunability to the authors knowledge for sputtered films and until now such tunabilities were only realizable by MOCVD. Our main focus has been to optimize the sputtered BST films for higher tunability for applications such as varactor-diode replacements in transmission lines and the non-linear medium in frequency triplers. BST films were systematically prepared under a range of Ar/O_2 ratios, total pressure and substrate temperature; it was found that the texture of the deposited film depended on each of these parameters. Predominatly (100) texturing results from an Ar/O_2 ratio of 90/10 (sccm), a sputtering pressure of 50 mT and a 550°C substrate temperature. The dielectric permittivity (ϵ_r) versus bias (V) characteristics of these films shows the highest tunability for (100) textured films. The large field dependence of the dielectric permittivity of the (100) textured films has been attributed to the biaxial tensile stress imposed by Si on BST making the quasi-polar axis (c-axis) oriented in-plane; thus, leading to the quasi a-axis parallel to the film normal. In a proper tetragonal ferroelectric $\epsilon_c < \epsilon_a$, which is in agreement with field induced quasi poling and lowering of the dielectric permittivity. The tensile stress in the film arises due to the difference in thermal expansion coefficients between the film ~7-8$\times10^{-6}$/°C and the Si 2.5 $\times10^{-6}$/°C substrate. This has prompted us to study growth on other substrates with low to high thermal expansion coefficient such as glass {0.75$\times10^{-6}$/°C} and sapphire {8$\times10^{-6}$/°C}.

Y15.7/KK5.7

EPITAXIAL $Ba_xSr_{1-x}TiO_3$ THIN FILMS FOR TUNABLE DEVICES: CORRELATION OF DIELECTRIC PROPERTIES WITH MICROSTRUCTURE. C.M. Carlson[1], T.V. Rivkin[2], P.A. Parilla[2], J.D. Perkins[2], J.C. Price[1], P. Ahrenkiel[2] and D.S. Ginley[2]; [1]University of Colorado, Boulder, CO, [2]National Renewable Energy Laboratory, Golden, CO.

$BaxSr_{1-x}TiO_3$ (BST) is a ferroelectric material that has a large electric-field-dependent dielectric constant and relatively low losses above the ferroelectric transition temperature, which can range from a few Kelvin to over 400 K depending on the Ba:Sr ratio. This makes BST potentially useful as the tunable element in a variety of tunable devices over a large temperature range both at RF and microwave frequencies. Using pulsed laser deposition, we have deposited high-quality epitaxial BST films on MgO and $LaAlO_3$ (LAO) substrates. These BST films exhibit peak dielectric constants $\epsilon/\epsilon_0 >$ 6000 with a change in dielectric constant of > 65% with an applied dc field of ~ 7 V/μm. We characterize the BST films both at 1 MHz and 1-2 GHz using coplanar capacitors patterned on the BST surface. We examine the correlation between structural and dielectric properties of the BST films before and after an ex-situ anneal in flowing O_2 at ~ 1100 °C for 5 hours. According to recent theories, the biaxial strain imposed on the film by the substrate affects the temperature dependence of ϵ/ϵ_0.[1,2] We attempt to accurately measure this biaxial strain before and after the anneal using x-ray diffraction and compare with the observed $\epsilon/\epsilon_0(T)$ measurements. X-ray diffraction also shows that annealing can improve the crystal orientation. Atomic force microscopy (AFM) shows that the anneal decreases the already low surface roughness to ~ 3 Å RMS, and transmission electron microscopy (TEM) shows that the density of dislocations near the substrate interface decreases from > 10^{12} cm^{-2} to ~ 10^{11} cm^{-2}, resulting in higher maximum ϵ/ϵ_0 and tuning. The optimization of the tunable dielectric properties through control of microstructure will allow the best possible device performance.
[1] S.B. Desu, V.P. Dudkevich, P.V. Dudkevich, I.N. Zakharchenko, and G.L. Kushlyan, Mat. Res. Soc. Symp. Proc. 401 (1996) 195.
[2] N.A. Pertsev, A.G. Zembilgotov, and A.K. Tagantsev, Phys. Rev. Lett. 80(9), (1998) 1988.

Y15.8/KK5.8

GROWTH AND CHARACTERIZATION OF $Ba_{1-x}Sr_xTiO_3$ (BST) THIN FILMS FOR HIGH FREQUENCY DEVICES. P.K. Baumann, S.K. Streiffer, O. Auciello, Argonne National Laboratory, Materials Science Div, Argonne, IL; D. Kaufman, R.A. Erck, J. Giumarra, Argonne National Laboratory, Energy Technology Div, Argonne, IL.

We are investigating the synthesis of $Ba_{1-x}Sr_xTiO_3$ (BST) thin films for applications such as capacitors for resonant circuits and high-frequency phase-shifters. BST thin films have been deposited at 650°C on platinized silicon with good thickness and composition uniformity using a large area vertical metal organic chemical vapor deposition (MOCVD) system. A computer-controlled liquid delivery system was used to inject precursors into the deposition chamber to control the films composition and ensure good reproducibility. The Ti content of the BST films was varied from 50 - 53%, and the Ba/Sr ratio was 70/30 . The composition of the BST films has been analyzed using x-ray fluorescence (XRF) and Rutherford backscattering spectrometry (RBS). Patterned Pt top electrodes were deposited onto the BST films at 350°C through a shadow mask using electron beam evaporation. Annealing the BST films at 500°C in 1 mTorr of oxygen prior to Pt deposition was found to reduce the dielectric loss. A dielectric constant of approximately 900 was measured at room temperature, zero field and 1 kHz for 120nm thick films. Dielectric tunability as high as 3.5:1 was measured for an electric field of 400 kV/cm. We will report on a systematic study of the electrical properties as a function of BST growth conditions and annealing conditions of the entire capacitor structure. Work supported by the U.S. Department of Energy, BES-Material Sciences, under Contract W-31-109-ENG-38, and by DARPA, contract number 978040.

Y15.9/KK5.9

IDENTIFICATION OF TE MORPHOTROPIC PHASE BOUNDARIES IN LEAD PEROVSKITE TERNARY SYSTEMS WITH THE COMPOSITION SPREAD METHOD. Hauyee Chang, Ichiro Takeuchi, Tsuyoshi Ohnishi, XiaoDong Xiang, Lawrence Berkeley National Laboratory, Materials Sciences Division, Berkeley, CA.

Lead containing pervoskites such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ have been shown to have morphotropic phase boundaries (MPB), where the dielectric constants and tunabilities are extremely large. These compositions are promising candidates for a large variety of applications in areas including piezoelectric, electro-optic and frequency agile microwave devices. The existence of MPB at different compositions for mixtures of different lead compounds is also of great theoretical interest. Thus, there is a large impetus for identification and improvement of such compositions. The combinatorial and composition spread approaches that allow the simultaneous fabrication and analysis of a large number of different compositions are well suited for the task. We have fabricated the entire ternary composition spread of PMN-PT-PZ ($PbZrO_3$) and found peaks in the dielectric constants at the known MPB compositions. Thin film ternary composition spreads of $Pb(A,Nb)O_3$ - $PbTiO_3$ - $PbZrO_3$, where A = Ni, and Fe, are also investigated. Most compositions within the composition spreads form epitaxial thin films on $LaAlO_3$ with the layer by layer precursor method of synthesis. Entire phase boundaries within each ternary system have been identified using the scanning evanescent microwave microscope, which measures the dielectric constants and loss of thin films. Issues concerning the synthesis of these lead-containing films will be discussed.

Y15.10/KK5.10

DIELECTRIC PROPERTIES OF $Ba_{1-x}Sr_xTiO_3$. Y. Gim, Y. Fan and Q.X. Jia, Materials Science and Technology, Los Alamos National Laboratory, Los Alamos, NM.

We report on the dielectric properties of $Ba_{1-x}Sr_xTiO_3$ (BSTO) films at a frequency of 1 MHz. We have used targets with different Ba concentrations, x = 0.1 to 0.9 at an increment of 0.1, and deposited

the films by using pulsed laser deposition at 800 degrees and in an oxygen pressure of 200 mTorr. X-ray Θ-2Θ scans show that the all the films are c-axis oriented and the c-axis lattice constant decreases with x, as expected from the bulk values. To measure the dielectric properties of the BSTO film, we have deposited 2000 $\AA$ thick Au and defined 2 mm long electrodes with a separation of 10 μm. The dielectric constant increases slowly with x, becomes a maximum of 3200 at x=0.4, and then decreases rapidly when x is larger than 0.5. To test the tunability of our films, we have also performed the capacitance vs applied voltage (C-V) measurement. The tunability ratio, $\Delta C/C_{film}$, reaches a maximum of 80% for x = 0.3 - 0.4. From the C-V curves, we have found that the peak voltage which produces a maximum capacitance monotonically decreases with x.

Y15.11/KK5.11

MICROSTRUCTURAL ARCHITECTURE OF (Ba,Sr)TiO_3 THIN FILMS FOR TUNABLE MICROWAVE APPLICATIONS. Wontae Chang[1], James S. Horwitz[2], Won-Jeong Kim[3], Jeffrey M. Pond[2], Steven W. Kirchoefer[2] and Douglas B. Chrisey[2]; [1]Institute for Materials Science, School of Engineering and Applied Science, George Washington University, NW, Washington, DC, [2]Naval Research Laboratory, Washington, DC, [3]SFA Inc., Largo, MD.

$Ba_xSr_{1-x}TiO_3$ (BST, x=0.5 and 0.6) thin films have been deposited onto (100) MgO single crystal substrates by pulsed laser deposition (PLD). The room temperature capacitance and dielectric quality factor (Q=1/tanδ) have been measured as a function of electric field ($\leq$ 200 kV/cm) at microwave frequencies (1 to 20 GHz) using silver interdigitated electrodes deposited on top of the BST film. It has been observed that the dielectric constant of the film and its change with electric field are closely related to film crystallinity and strain which affects the ionic polarization of the film. Amorphous BST films show high dielectric Q (> 100) with low dielectric constant (~30-200) and low dielectric tuning (< 1%), presumably due to small ionic polarization. Crystalline films have a higher dielectric constant (~1000) and a higher dielectric tuning (~65%) but a lower dielectric Q (~20). As an optimal microstructure of the film for tunable microwave applications, strain-relieved large-grained (~5000 $\AA$) polycrystalline films were deposited using a thin amorphous buffer layer of BST (~50 $\AA$). To increase grain size (up to a few microns), BST films were prepared by the deposition of a series of a thin amorphous layers ($\leq$ 1000 $\AA$) deposited at room temperature followed by an encapsulated anneal at temperatures $\leq$ 900°C. We will present results of the film strain and grain size on the dielectric properties of BST films and show how careful control of microstructure can lead to films with optimal properties for the tunable microwave devices.

Y15.12/KK5.12

HELIUM-IMPLANTATION INDUCED LAYER DETACHMENT AND ELECTRICAL PROPERTIES OF SINGLE-CRYSTAL POTASSIUM TANTALATE FILMS. M. Levy, R.M. Osgood, Jr., Columbia University, Applied Physics Dept, New York, NY; R. Guo, A. Bhalla, L.E. Cross, Materials Research Laboratory, Pennsylvania State University, University Park, PA; A. Kumar, H. Bakhru, SUNY at Albany, Dept of Physics, Albany, NY.

Current interest in the development of tunable microwave systems for phased array radar and wireless communication applications has led to significant progress in ferrite and ferroelectric fabrication technologies. Various film deposition approaches are being investigated for the preparation of low-loss frequency-agile materials for integrated microwave applications. Single-crystal ferroelectric films are particularly attractive because of their low-loss and high-bandwidth. Here we report on the fabrication of mesoscopic (5-10μm-thick) single-crystal films of potasium tantalate ($KTaO_3$) by energetic helium ion implantation and subsequent thermal treatment and wet etching. A highly stressed sacrificial layer forms below the film upon implantation at dosages near 1 X 10^{16} cm^{-2} and energies of 3.8 MeV. Exfoliation occurs spontaneously by implantation above this threshold dosage or can be induced by wet etching or thermal treatment at lower dosages. 8μm-thick free-standing films up to 1 mm^2 in size have been fabricated and their capacitances measured. Low-temperature dielectric measurements show enhancement in the susceptibility, as expected for Curie-Weiss behavior, with a Curie temperature near 20K. The temperature evolution of the capacitance indicates incipient ferroelectric characteristics. Rutherford backscattering (RBS) and x-ray crystallographic measurements are used to study the evolution of strain leading to exfoliation with implantation dosage. Direct wafer bonding of implanted single-crystal KTa_3 onto semiconductor platforms will also be presented. M.L. and R.M.O. acknowledge support by DARPA/FAME under Contract No. N00173-98-1-G014.

Y15.13/KK5.13

ROLE OF $SrRuO_3$ BUFFER LAYERS IN ENHANCING DIELECTRIC PROPERTIES OF $Ba_{0.5}Sr_{0.5}TiO_3$ TUNABLE CAPACITORS. S.J. Park, J.H. Sok and E.H. Lee, Electronic Materials Laboratory, Samsung advanced Institute of Technology, Suwon, KOREA; J.S. Lee Analytic Engineering Laboratory, Samsung advanced Institute of Technology, Suwon, KOREA.

$Ba_{0.5}Sr_{0.5}TiO_3$ (BST) is a first candidate material for the development of voltage-tunable microwave devices, for example, filter, phase-shifter and VCO. In this work, the crystal structures and dielectric properties of BST film are investigated with and without $SrRuO_3$ (SRO) buffer layers. BST and SRO thin films are sequentially prepared by PLD and Au/Ti metal electrodes are ex-situ fabricated by a DC magnetron sputtering system. The capacitance and dielectric loss of the capacitors have been measured as a function of bias voltages at room temperature using a low frequency LCR meter. For the high frequency characteristics (~2GHz), a microstrip resonator with ~2GHz resonance frequency and the center coupling design is fabricated. Using flip-chip attached BST capacitor at the position of the center coupling on the microstrip resonator, we obtained its dielectric loss and tunability. The microwave loss probably due to the interfacial reaction, oxygen deficiency in the surface of the BST film was obviously enhanced by the SRO buffer layer.

SESSION Y16: FUNDAMENTAL PROPERTIES OF THIN-FILM FERROELECTRICS AND FERROELECTRIC GATE MATERIALS
Chairs: Thomas M. Shaw and Rainer Waser
Thursday Morning, December 2, 1999
Room 304 (H)

8:30 AM *Y16.1

STRUCTURE-PROPERTY RELATIONSHIPS OF EPITAXIAL FERROELECTRIC THIN FILMS OF VARIOUS BISMUTH-LAYERED PEROVSKITES WITH EVEN AND ODD AURIVILLIUS PARAMETERS. A. Pignolet, A.R. James, C. Spaeth, C. Harnagea, C. Schaefer, N.D. Zakharov, and D. Hesse, Max-Planck-Institut für Mikrostrukturphysik, Halle/Saale, GERMANY.

Thin films of Bismuth-layered perovskites $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2-}$ with n varying from 2 to 5, viz. $SrBi_2Ta_2O_9$, $Bi_4Ti_3O_{12}$, $BaBi_4Ti_4O_{15}$, and $Ba_2Bi_4Ti_5O_{18}$, have been grown by pulsed laser deposition on epitaxial conducting $LaNiO_3$ electrodes, either on single crystalline (100) $SrTiO_3$ or on epitaxial buffer layers on (100) silicon. The films consist of c-oriented regions with a smooth surface and regions with a high surface roughness and a mixed orientation. The regions with mixed orientation feature "rectangular-shaped" (110)-oriented grains with their long axis along two mutually perpendicular orientations on the substrate plane as well as (100)-oriented "spherical grains" protruding out of a smooth c-oriented background. Cross-sectional TEM reveals that the regions with mixed orientation actually consist of a c-oriented sublayer on top of which the growth of either (110)-oriented or (100)-oriented grains takes place. Macroscopic ferroelectric measurements as well as nanoscale investigations via AFM in the piezoresponse mode show a clear relationship between the ferroelectric properties and the morphology and orientation of the regions. The regions with mixed orientation exhibit saturated ferroelectric hysteresis loops with well-defined remnant polarization P_r and coercive field E_c. The c-oriented regions in contrast exhibit a linear P-E curve with no hysteretic behavior for Bi-layered perovskites with even n and a weak ferroelectric behavior for those with odd n. This clearly shows that the ferroelectric properties of Bi-layered ferroelectric oxides depend on the crystalline orientation of the film and that the observed ferroelectric hysteresis loops in $SrBi_2Ta_2O_9$ (n = 2) and $BaBi_4Ti_4O_{15}$ (n= 4) films are solely due to the (110)- and (100)-oriented grains. The results are relevant for the use of Bi-layered ferroelectric oxides in the fabrication of non-volatile FeRAMs memories.

9:00 AM Y16.2

DEGRADATION PERFORMANCE OF ASSYMMETRICAL OXIDE/(Pb,La)(Zr,Ti)O_3/Pt SYSTEM: EFFECT OF CHARGE INJECTION FROM THE OXIDE AND Pt ELECTRODES. Igor Stolichnov, Alexander Tagantsev, Nava Setter, Swiss Federal Institute of Technology (EPFL), Ceramic Laboratory, Lausanne, SWITZERLAND; Jeffrey S. Cross, Mineharu Tsukada, Fujitsu Laboratories, Atsugi, JAPAN.

A study of polarization fatigue endurance in relation to the leakage conduction of (Pb,La)(Zr,Ti)O_3 (PLZT) film capacitors grown on Pt electrodes with Pt, $SrRuO_3$ (SRO) and IrO_2 top electrodes shows that a trade off between these two important parameters is not necessary. On the contrary, fatigue performance and leakage conduction can be controlled independently. We show that the degradation properties of PLZT capacitors are related to the charge local injection into the near-by-electrode layer rather than due to leakage conduction through the capacitor. We study charge injection and subsequent entrapment by analyzing the coercive field

dependence of the maximal polarization and ferroelectric film thickness. According to our results, there is a direct relation between the efficiency of the entrapped charge relaxation and the polarization fatigue performance. Based on our results we conclude that the degradation performance of the PLZT capacitors can be substantially improved by enhancement of the relaxation of charge entrapped at the ferroelectric film interfaces. We demonstrate that this relaxation can be enhanced without increase of leakage conduction throughout the capacitor. The effect of the charge relaxation on the polarization imprint and time-dependent breakdown is discussed.

9:15 AM Y16.3
EFFECT OF COMPRESSIVE STRESSES ON THE DIELECTRIC BEHAVIOR OF EPITAXIAL LEAD MAGNESIUM NIOBATE(90%)-LEAD TITANATE(10%) THIN FILMS.
V. Nagarajan, B. Nagaraj, Y .Li, C.S. Ganpule, S. Aggarwal, S.P. Alpay, A.L. Roytburd and R. Ramesh, Univ of Maryland, Dept of Materials amd Nuclear Engineering, College Park, MD.

Recently we have shown the effect of compressive stresses on the electrical properties viz. the spontaneous polarization, the activation field and the coercive field, in epitaxial ferroelectric lead zirconate titanate thin films. We have further extended this to relaxor ferroelectrics, to systematically study the effects of lattice mismatch strain on the dielectric responses. Relaxor lead magnesium niobate-lead titanate epitaxial thin films with oxide electrodes was grown by pulsed laser deposition on $< 100 >$ lanthanum aluminate (LAO) substrates. We have systematically increased the thickness of the relaxor layer from 100 nm to 400 nm while keeping the thickness of the electrodes constant at 25 nm. We observe a systematic decrease in the phase transition temperature, from around 250°C to around 60°C as the relaxor film thickness is increased from 100 nm to 400 nm, accompanied by a systematic increase in the relative dielectric constant (ϵ_r) from 300 to 3600 respectively. This suggests that the compressive stress has two principle effects. It increases the phase transition temperature (by more than 150°C when compared to the bulk value) and secondly, constrains the film mechanically to drastically lower the value of relative dielectric constant. This effect is analogous to conventional ferroelectric thin films where we have shown that in plane compressive stresses in pseudomorphically constrained thin films can alter electrical properties by an order, when compared to very thick, relaxed films. In this presentation we will describe in detail these results as well results of EFM and HRTEM studies of these films. This work is supported by the National Science Foundation under Grant No. DMR-9633638 and by the NSF-MRSEC under Grant No. DMR-9632521.

9:30 AM Y16.4
OBSERVATION OF AMBIENT OXYGEN DEPENDENT VOLTAGE OFFSETS IN $Pb(Zr,Ti)O_3$ THIN FILMS.
M. Brazier, S. Mansour, and M. McElfresh, Purdue University, West Lafayette, IN.

Thin film $Pb(Zr,Ti)O_3$ (PZT) capacitors were observed to develop a dc voltage offset, similar to those previously reported in compositionally graded PZT films, when driven with an ac applied electric field and measured using a Sawyer-Tower circuit. This voltage offset displayed a strong dependence on the oxygen partial pressure, pO_2, of the atmosphere above the film, in addition to applied electric field and temperature dependencies. Furthermore, voltage offsets in compositionally graded films were also shown to display a strong pO_2 dependence. A scenario is proposed to explain the observations in conventional (non-graded) and graded PZT films involving redistribution of oxygen ions in reponse to a spatially varying chemical potential for oxygen species throughout the films.

9:45 AM Y16.5
DEFECT IDENTIFICATION IN PZT USING HIGH MOMENTUM SENSITIVE POSITRON ANNIHILATION SPECTROSCOPY.
T. Friessnegg, Univ. of Maryland, College Park, MD, D.J. Keeble, Univ. of Dundee, SCOTLAND; B. Nielsen and V.J. Ghosh, Brookhaven National Laboratory, Upton, NY; R. Godfrey, S. Aggarwal and R. Ramesh, Univ. of Maryland, College Park, MD; E.H. Poindexter, Army Research Laboratory, Adelphi, MD.

Positron Annihilation spectroscopy has been shown to be sensitive to vacancy-related defects in thin film ferroelectrics. Here we detail a variation of this technique, which further allows the direct identification of the chemical environment of the defect site. In Doppler-broadening spectroscopy the energy distribution of the annihilation gamma ray, centered at 511 keV, is measured. The chemical information of the annihilation site is contained in the high-energy part of the spectrum. In the annihilation process two photons are created and travel in nearly opposite directions. By using a coincidence technique to detect these photons a reduction in the background count rate of several orders of magnitude can be achieved. This allows a detailed measurement of annihilation events occurring with tightly bound electrons and therefore providing chemical information on the environment of the positron-trapping center. Coincidence Doppler-broadening spectroscopy measurements were performed on PZT and related materials. The results are compared to theoretical spectra simulated using an atomic superposition model. This work is supported by the Army Research Laboratory under contract No. DAAL01-95-2-3530, the US Army ERO contract N68171-98-M-5740 and DOE under contract No. DE-AC02-98CH10886.

10:30 AM Y16.6
DEPTH-RESOLVED ANALYSIS OF PZT FILMS BY RADIO FREQUENCY GLOW DISCHARGE ATOMIC EMISSION SPECTROSCOPY (RF-GD-AES).
R. Kenneth Marcus, Alwyn Anfone, Clemson University, Department of Chemistry, Clemson, SC; Robert W. Schwartz, Clemson University, Department of Ceramic and Materials Engineering, Clemson, SC.

Ferroelectric thin films are under development for a range of electronic, opto-electronic, and micromachine applications. The many uses of these devices dictate wide variations in chemical composition and physical structure of both the films and substrates. Film production may be pursued by a number of methods including both gas phase and solution phase deposition. As-deposited films are then typically annealed for pyrolysis of organic species and crystallization of the perovskite structure. Clearly, layer composition and thickness, interface integrity, and identification of impurities are key issues in film performance characteristics. As such, analytical methods used for characterization of these systems must have multielement (including C, H, O, etc.) capabilities and the ability to perform depth-resolved analyses across layer thickness of up to a few micrometers and resolving powers on the order of 10s of nanometers. $< p >$ We describe here the use of a relatively new analytical technique, radio frequency glow discharge atomic emission spectroscopy (rf-GD-AES), for the depth-resolved analysis of ferroelectric films, specifically lead zirconate titanate (PZT) layers on silicon. The rf-GD-AES technique is analogous to rf sputter deposition systems, except that low energy (<50 eV) argon sputtering is used to ablate the film and the resultant atoms are detected by their optical emission. The figures of merit for the method include limits of detection of ~50 ppb for most metals and 1 ppm for non-metals, sputtering rates of 0.01-5 micrometers/minute, and depth resolution on the order of 10 nm. The technique is applied here to profile PZT films fabricated via the sol-gel process. Depth-resolved elemental analysis provides both composition and film (interface) quality information. Of additional interest is the monitoring of residual non-metal species which may give insights into the production and annealing chemistries used in film fabrication.

10:45 AM *Y16.7
CURRENT STATUS OF FABRICATION AND INTEGRATION OF FERROELECTRIC-GATE FETs.
Hiroshi Ishiwara, Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN.

Current status of ferroelectric-gate FETs is reviewed. It is pointed out that an array of ferroelectric-gate FETs formed on an SOI(silicon-on-insulator) structure is important in such applications as a single-transistor-cell-type digital memory and synaptic connection for an artificial neural network. It is also shown that a PFM (pulse-frequency-modulation) type adaptive-learning neurochip can be fabricated using a ferroelectric-gate FET. Then, recent experimental studies on ferroelectric-gate FETs are presented, and it is described that insersion of a buffer layer between the ferroelectric film and Si substrate is essential in preventing interdiffusion of the constituent elements and in obtaining good electrical properties of the interface. It is also shown, however, that the buffer layer degrades the memory retention characteristic severely, and necessary conditions to solve the short retention time problem are discussed from viewpoints of materials, device structure, and circuit. Finally, our recent attempt based on the above considerations is introduced, in which a stacked layer of $Pt/SrTa_2O_6/SiON$ was used as a buffer layer between the ferroelectric $SrBi_2Ta_2O_9$ film and Si substrate and the area of the ferroelectric capacitor was made much smaller than that of the gate capacitor composed of $SrTa_2O_6/SiON$. It has been shown after optimization of the area ratio that the current on/off ratio larger than 10^3 can be retained for more than 10 hours. It is concluded from these results that optimization of both the buffer layer materials and device structure is important to improve the memory retention characteristic of ferroelectric-gate FETs.

11:15 AM Y16.8
GATE STACKS FOR LOW VOLTAGE FERROELECTRIC FIELD EFFECT DEVICES BASED ON $Pt/SBT/CeO_2/Si(100)$.
Thomas Haneder, Harald Bachhofer, Wolfgang Hoenlein, Infineon Technologies, Corporate Research, Munich, GERMANY; Marc Ullmann, University of the Federal Armed Forces, Institute of Electronics, Hamburg, GERMANY; Henning von Philipsborn, University of Regensburg, Physics Department, GERMANY; Rainer

Waser, IFF, Forschungszentrum Juelich and RWTH Aachen, GERMANY.

The interest in ferroelectric field effect devices like metal ferroelectric insulator semiconductor (MFIS) and metal ferroelectric metal insulator semiconductor (MFMIS) field effect transistors (FETs), respectively, is permanently increasing as they provide the possibility to fabricate unique memory devices combining characteristics such as high speed, non-volatility, and high density. Compared to ferroelectric 1T1C cells they allow a smaller cell size and, even more important, a non-destructive readout. One of the drawbacks of these devices up to now is their need for high write and erase voltages in the range of 5 to 7 volts. However, these devices will only be used in future memory cells if they can be operated at sufficiently low voltages comparable to other advanced memory devices. The MFMIS FET approach seems to be very promising in terms of a low programming voltage but suffers from rather poor data retention due to net charge flow through the ferroelectric layer to the bottom metal layer. Therefore, we focus our development on an MFIS FET that requires low programming voltage. Using chemical solution deposition (CSD) we fabricated gate stacks based on $Pt/SrBi_2Ta_2O_9/CeO_2$ on silicon substrate. Memory windows (i.e. shifts in C(V) curve) of more than 1.5 volts could be obtained using relatively small programming voltages of ± 3 volts. To achieve these results, special attention was paid to the drying and pyrolysis conditions of the samples. Interface state density is around $2x10^{11}$ /cm^2 eV and remanent polarization was found to be in the range of 0.3 μC/cm^2 which are suitable values for the considered application. The samples were comprehensively characterized by C(V), P(E), and I(V) measurements as well as X-ray diffraction and optical microscopy.

11:30 AM Y16.9
MFMOS CAPACITOR FOR ONE TRANSISTOR MEMORY APPLICATION. Tingkai Li, Fengyan Zhang, Sheng Teng Hsu, Sharp Laboratory of American, Camas, WA; Yufei Gao and Mark H. Engelhard, Pacific Northwest National Laboratory, Richland, WA.

The basic mechanism for one transistor memory device has been studied. Many ferroelectric materials such PZT, PLT, SBT, PGO etc. were analyzed for this applications. Finally, MFMOS (Metal/Ferroelectrics/Metal/Oxide/Silicon) capacitor for one transistor memory application was proposed. Because its low remanent polarization and dielectric constant, the C-oriented $Pb_5Ge_3O_{11}$ thin films was selected for one-transistor memory applications. In order to demonstrate the one-transistor memory applications, $Pb_5Ge_3O_{11}$ films have been prepared using MOCVD and RTP (Rapid Thermal Process) post-annealing. The lead bis-tetramethylheptadione [Pb(thd)$_2$] and germanium ethoxide [Ge(OC$_2$H$_5$)$_4$] were used as the precursors for lead and germanium source, respectively. The $Pb_5Ge_3O_{11}$ films were deposited onto $Ir/Ti/SiO_2/Si$ wafers to measure their composition, phase formation, microstructure and ferroelectric properties. The C-oriented $Pb_5Ge_3O_{11}$ thin films prepared by MOCVD and RTP post-annealing showed a good ferroelectric and electrical properties: 2Pr 3.8 μC/cm^2, 2Ec 93 KV/cm at an applied voltage 5V, leakage current $3.6x10^{-7}$ A/cm^2 at 100KV/cm, dielectric constant close to 45, and almost fatigue free. For integrated circuit processes, the barrier metal, etching damage, forming gas and activated, densification-annealing processes are critical issues for the one-transistor memory applications and have also been investigated.

11:45 AM Y16.10
EVALUATION OF FERROELECTRICITY IN MFIS TYPE CAPACITOR USING PULSED C-V MEASUREMENT. Norifumi Fujimura, Takeshi Yoshimura and Taichiro Ito, Osaka Prefecture Univ., College of Eng., Sakai, Osaka, JAPAN.

We have been proposing $YMnO_3$ or ZnO:X with low remanent polarization and dielectric permittivity as a transistor type FeRAM. Conventional C-V measurement is normally used to simply evaluate the ferroelectricity of the ferroelectric thin film on Si substrate. For these ferroelectric thin films with low polarization, however, there are some issues to understand the C-V hysteresis. Interfacial polarization and space charge affect the C-V hysteresis. To understand the effect of interfacial polarization, brief calculations have been done supposing the connection of ferroelectric and dielectric layer with different leakage current. If ferroelectric layer with the leakage current of $1x10^{-6}$ is connected to dielectric layer with the leakage current of $1x10^{-9}$, charge density of 10^{-9} C/cm^2 should be generated in the period of 0.2 sec. Space charge should have longer time constant for accumulating the charge. Pulsed C-V measurement must be effective to avoid these issues. This paper proposes simple evaluation method to have the real component of ferroelectricity in the C-V hysteresis using $YMnO_3$ or ZnO:X with very low remanent polarization.

SESSION Y17: PIEZOELECTRIC THIN FILMS AND THIN-FILM CAPACITOR MATERIALS
Chairs: L. Eric Cross and Stephen K. Streiffer
Thursday Afternoon, December 2, 1999
Room 304 (H)

1:30 PM *Y17.1
INTEGRATED THIN FILM CAPACITOR ARRAYS UTILIZING SOL-GEL DERIVED FERROELECTRICS. David Liu, Robert Heistand II, Steve Makl, Advanced Product and Technology Center, AVX Corporation, Myrtle Beach, SC.

In order to meet the continuing miniaturization of electronic systems, especially those in hand held and portable systems, further miniaturization of passive components is critical. The integration of these passive components, especially the capacitors, poses processing technology challenges. First, integrated capacitors need to be fabricated in much smaller dimensions while achieving the comparable capacitance required of discrete components. Therefore, the application of high dielectric constant materials in integrated capacitors is essential. Second, integrated capacitor array devices need to withstand fairly high rated voltages (~25V). Thicker dielectric layer (~1 micron)compared to integrated ferroelectric memory devices is thus a necessity. Third and most important, the technique must be low cost and exhibit good processing control for mass production. In this paper, we will describe a low cost technology to integrated ferroelectric PZT thin layer on silicon via a thick coating sol-gel route. Compared to the conventional process, the developed technique has at least four-fold processing time reduction in depositing micron thick PZT layers and yields components with improved electrical strength and better long term reliability. The technology has been adopted in fabrication of commercial thin film capacitor array devices with various rated voltages and capacitance. The technology is also a key for the further success of integration with other passives such as resistors and inductors.

2:00 PM Y17.2
PROCESSING AND CHARACTERIZATION OF FULLY EMBEDDED FOIL-BASED (Pb,La)$ZrTiO_3$ THIN FILMS WITH BASE METAL ELECTRODES. J.-P. Maria, K. Cheek, S.-H. Kim, G. Dunn[1], J. Sovic[1], M. Zhang[1], S.K. Streiffer[2] and A.I. Kingon, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC; [1]Motorola Materials Research Laboratory, Corporate Manufacturing Center, Schaumburg, IL; [2]Argonne National Laboratory, Materials Science Division, Argonne, IL.

Embedding capacitive and resistive layers into polymeric electronic packages for the replacement of surface-mounted components has been an attractive option for both processing expense and device size reduction. The major difficulty in realizing this goal has been the high temperature processing conditions typically required for traditional high permittivity dielectrics. One method of circumventing this problem is to process the capacitive layers separately, then laminate to complete the embedded stack. This approach has been investigated at NCSU by chemical solution deposition (CSD) of PLZT thin films on Ni-based foils. The PLZT composition used (~9% La substitution) is resistant to the inert crystallization anneals necessary to preserve the Ni-foil properties, and typically exhibits loss tangent values between 0.01 and 0.02 from 1 to 1000 kHz. Capacitance densities of the as-processed foils typically range between 300 and 400 nF/cm^2 over the same frequency range; this represents a 2 to 3 order of magnitude increase over existing embedded capacitor technologies for polymeric packages. Base-metal top electrodes (ion-beam sputtered Ni or Pd) were used to define capacitor structures. After all high temperature processing steps, the foils remain flexible. Foil samples were introduced into Motorola's board fabrication research facility in an attempt to produce fully embedded passive layers in FR4 polymeric printed wiring boards. Foils were laminated, top electrodes were patterned, and print, etch, and via cycles were applied. The resulting prototypes survived the standard fabrication routines and revealed electrical properties similar to those of as-deposited samples. Details of the entire process will be presented, as well as electrical and structural characterization for as-deposited and embedded devices.

2:15 PM Y17.3
THIN FILM DECOUPLING CIRCUITS MAKING USE OF A THREE DIMENSIONAL INTEGRATION OF THIN FILM PASSIVE COMPONENTS. M. Klee, P. Locbl, R. Kiewitt, W. Brand, Philips GmbH Forschungslaboratorien Aachen, Aachen, GERMANY; P. van Oppen, Philips Advanced Ceramics and Modules, Roermond; P. Lok, Philips Discrete Semiconductors, Nijmegen.

In numerous electronic circuits such as power amplifier modules for mobile telecommunication, discrete passive components such as X7R capacitors, NP0 capacitors and discrete resistors are designed to filter ac signals out of the dc power lines and to guarantee a constant dc power supply. Usually a X7R capacitor and a NP0 capacitor are

designed in parallel. In series with the X7R capacitor a resistor is mounted. Especially in the telecommunication circuits, miniaturisation is a major issue. To reduce the circuit size, discrete surface mount passive components, a X7R capacitor, a NP0 capacitor and a resistor of the size 0.5mm * 1 mm (0402 products) for each product are designed in standard modules. We have realised a miniaturised decoupling filter, build-out of a thin film X7R capacitor with a thin film resistor in series and a thin film NP0 capacitor in parallel. A thin film technologies offers us the potential to grow the capacitors and the resistor in low temperature processes on top of each other. Extremely small sized three dimensionally integrated thin film decoupling circuits with a size of 0.5mm*1mm and high accuracy are achieved.

3:00 PM *Y17.4
DEVELOPMENT AND UTILIZATION OF PREFERRED POLARIZATION DIRECTIONS IN FERROELECTRIC FILMS FOR MEMS APPLICATIONS. S. Trolier-McKinstry, R. Polcawich, J-P. Maria,* W. Ren, R. Wolf, and F. Xu, Materials Research Laboratory, the Pennsylvania State University; *North Carolina State University.

Ferroelectric films must possess a net polarization to provide a useful piezoelectric response. However, several groups have now shown that lead zirconate titanate (PZT) films tend to depole rapidly, leading to unacceptably fast aging rates (often 5 - 10% per decade in sol-gel films). The aging can be markedly reduced (to 1 - 3%) if the films are stabilized into a preferred polarization direction via poling at elevated temperatures or during ultraviolet exposure to induce imprint. Similarly small aging rates can also be achieved in vapor-deposited films exposed to bombardment during growth. In addition, it has been found that even relatively modest levels of imprint stabilize the piezoelectric coefficients during ac excitation with a bipolar electric field. This is particularly important for films to be used in high strain MEMS applications or in pyroelectric arrays. This paper will describe the roles of defect dipoles, space charge fields, bombardment-induced imprint, and strain gradients in developing preferred polarization in perovskite ferroelectric films for MEMS applications.

3:30 PM Y17.5
RELAXOR $Pb(Mg_{1/3}\ Nb_{2/3})O_3$ THIN FILMS AND THEIR ELECTROMECHANICAL PROPERTIES. Zian Kighelman, Dragan Damjanovic, Andreas Seifert, Nava Setter, Ceramics Laboratory, Materials Department, Swiss Federal Institute of Technology, Lausanne, SWITZERLAND.

Relaxor properties in thin films are important from both, an application and a fundamental point of view. In this study we investigated if the interesting dielectric, electrostrictive and electric field-induced piezoelectric properties known for $Pb(Mg_{1/3}\ Nb_{2/3})O_3$ (PMN) and PMN-$PbTiO_3$ bulk ceramics and crystals could also be found in thin films. Thin films of pure PMN were prepared by spin coating from modified alkoxide solution precursors. Preparation of the films was found to be very sensitive to the synthesis conditions of the solutions and other processing parameters. Details of the precursor synthesis from purified starting compounds and the influence of different seeding layers on the resulting microstructures will be discussed. The dielectric properties of the PMN thin films were examined. Whereas relaxor-like behavior was clearly demonstrated, the relative permittivity of the layers was low compared to bulk ceramics and single crystals. Large electric dc bias fields (up to 120 kV/cm) can be applied to the films. This dc field reduces the permittivity, suppresses the frequency dispersion and flattens the permittivity peak. No anomaly in the temperature dependence of the permittivity associated with the field induced transition into a ferroelectric phase was observed. These phenomena and electromechanical characteristics (electrostrictive strain and electric dc bias induced piezoelectric properties) will be discussed

3:45 PM Y17.6
FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF MOCVD $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ EPITAXIAL THIN FILMS. P.K. Baumann, S.K. Streiffer, G.R. Bai, O. Auciello, Argonne National Laboratory, Materials Science Div, Argonne, IL; S.Stemmer, University of Illinois at Chicago, Dept of Physics, Chicago, IL; K. Gosh, Argonne National Laboratory, Materials Science Div, Argonne, IL; C. Thompson, Northern Illinois University, Dept. of Physics, DeKalb, IL.

Relaxor-based ferroelectrics such as lead magnesium niobate (PMN) and lead magnesium niobate titanate (PMN-PT) have excellent properties that could make them suitable candidates for dielectric and piezoelectric applications. We have grown epitaxial PMN and PMN-PT thin films by metalorganic chemical vapor deposition at 700°C on $SrRuO_3/SrTiO_3$ substrates. The zero-bias dielectric constant and loss measured at room temperature and 1 kHz for 350 nm thick pure PMN films were 1100 and 1.1%, respectively. For 300 to 350 nm thick PMN-PT films the small-signal permittivity ranged from 900 to 1300 depending on deposition conditions and Ti content; correspondingly low values for the dielectric loss between 1 and 3% were determined for all specimens. We will report on a systematic study of the dielectric and ferroelectric properties as a function of temperature and Ti content, and on initial piezoelectric measurements of these films.

4:00 PM Y17.7
CRYSTAL STRUCTURE AND TEXTURE EFFECTS ON PIEZOELECTRIC AND DIELECTRIC PROPERTIES OF PZT THIN FILMS. David V. Taylor and Dragan Damjanovic, Swiss Federal Institute of Technology-EPFL, Laboratory of Ceramics, Lausanne, SWITZERLAND.

A systematic investigation of the piezoelectric and dielectric properties of sol-gel derived $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) thin films was carried out for a rhombohedral (x= 0.4), tetragonal (x=0.55) and morphotropic (x=0.48) composition. Each composition was grown with three different crystallographic orientations (textures): random, (111) and (100). Nonlinearity (field dependence) of d_{33} piezoelectric coefficient and dielectric permittivity of the films was studied in detail under subswitching conditions to reveal extrinsic (mostly domain-wall related) contributions to the properties. After analyzing for each texture and composition the built-in stress, polarization and strain hysteresis loops, the intrinsic lattice properties, the domain-wall struucture, and contributions due to domain-wall displacements, a consistent interpretation of the electro-mechanical properties and nonlinear behavior was proposed. The (100) oriented rhombohedral films show largest piezoelectric coefficient (intrinsic effect) but limited nonlinearity (domain-wall structure effect) and should therefore be considered as potential candidates for piezoelectric devices.

4:15 PM *Y17.8
OPTIMIZATION, POLING, AND AGING STUDIES OF PZT THIN FILMS FOR PIEZOELECTRIC APPLICATIONS. Paul Muralt, Nicolas Ledermann, Andreas Seifert, Laboratoire de Cèramique, Swiss Federal Institute of Technology Lausanne (EPFL), SWITZERLAND.

For microactuators, piezoelectric actuation with $Pb(Zr,Ti)O_3$ thin films is a competitive method and has been demonstrated for a number of devices, such as ultrasonic micromotors, AFM cantilevers, Lamb wave pumps, and others more. Larger output forces and powers, and higher upper frequency limits are the main advantages over other techniques utilized in MEMS technology. Whereas bulk PZT has been optimized during the last 40 years, thin film materials are not as advanced yet. Thin film materials are different from bulk ceramics, because they often exhibit a texture, have smaller grains sizes, more defects (much lower growth temperature), and are clamped to the substrate. In this work, PZT thin films have been studied as a function of film texture and Zr to Ti concentration ratio. The in-plane piezoelectric coefficient $e_{31,f}$ has been measured by a cantilever bending method. (100) films exhibit superior properties as compared to (111) textured films. The peaking of $e_{31,f}$ occurs at different compositions. Important for applications are also coercive field and break-down field. Both are considerably higher in thin films than in bulk materials. This allows to drive thin films at much higher electric fields, and thus to achieve much higher energy densities. In ultrasonic applications, a permanent dc field, or a Ti-rich composition with large coercive and internal field are the options to chose when operating at high fields. Results on poling, on the decay of the piezoelectric coefficient during operation of cantilevers, and on strain effects of the poling onto the substrate will be presented.

4:45 PM Y17.9
MEASUREMENT AND CALCULATION OF THIN FILM $Pb(Zr,Ti)O_3$ PIEZOELECTRIC PROPERTIES. J.-P. Maria, D.-J. Kim, S.K. Streiffer†, S.-H. Kim and A.I. Kingon, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC; †Argonne National Laboratories, Materials Science Division, Argonne, IL.

Using the phenomenological relationship for the intrinsic piezoelectric response of ferroelectric materials, electrical property measurements for $Pb(Zr,Ti)O_3$ thin films, and derived electrostrictive constants, voltage-dependent effective piezoelectric coefficients ($d_{33}{}^E$)were calculated. Calculations were made for (111)-oriented samples with tetragonal, near-morphotropic, and rhombohedral symmetry. Specific efforts were made to separate the intrinsic and extrinsic contributions to the permittivity such that accurate estimations could be made. This was accomplished by extrapolation from high-field property measurements such that a single-domain state could be approached. In addition, derivations for the electromechanical coefficients were compensated for symmetry, film texture, and the presence of a residual thermal expansion mismatch induced strain. The calculated values were compared to values measured using double-beam interferometry. In general, agreement was observed in both d_{33}-loop shape and magnitude. The results are presented with regard to the

film orientation and the expected domain orientation and geometry. The results strongly support the premise that non-180° domain wall motion does not contribute strongly to the electromechanical response. Moreover, it appears that in the absence of a strong extrinsic contribution, (111)-oriented tetragonal compositions may offer the optimal piezoelectric properties.