SYMPOSIUM C

Ferroelectric Thin Films X

November 25 – 29, 2001

Chairs

Stephen R. Gilbert
Electronic Research Laboratory
Agilent Laboratories
MS 26M-7
Palo Alto, CA 94304
650-485-5359

Yoichi Miyasaka
ULSI Device Development Div
NEC Corp
NEC Electron Devices
Sagamihara, 229-1198 JAPAN
81-42-771-0725

Susan Trolier-McKinstry
Materials Research Inst
Pennsylvania State Univ
151 Materials Research Lab
University Park, PA 16802
814-863-8348

Dirk J. Wouters
Division STDI/FE
IMEC
Leuven, B-3001 BELGIUM
32-16-281301

Stephen K. Streiffer
Argonne Natl Lab
Bldg 212 / C212
Argonne, IL 60439-4838
630-252-5832

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TUTORIAL

FT C: FERROELECTRIC THIN FILMS

Sunday, November 25, 2001
10:00 a.m. - 5:00 p.m.
Room 202 (Hynes)

There continues to be extensive research and development activities in the field of ferroelectric thin films, and significant progress towards commercial products. This tutorial provides an overview of the field, covering the following topics:

- Introduction to material types, ferroelectric films, and a brief history of the field.
- Applications, processing and properties of ferroelectric films, including recent commercial developments, and materials science issues. The section will be divided into the following application-based categories:
  - Ferroelectric nonvolatile memories
    - (Device principles; material types; primary properties, processing methods; status of low density devices in commercial production, and issues for high density devices)
  - Ferroelectric films for capacitor applications
    - (Device principles; materials needs; material types; physical properties; impact on capacitor performance; processing and composition effects; and obstacles to Gbit integration. A separate section will be devoted to high frequency properties and applications)
  - Piezoelectric and pyroelectric applications
    - (Device principles, material types, device properties, processing issues)
- Outlook

Instructors:
Angus Kingon, North Carolina State University
Paul Muralt, EPFL Lausanne

SESSION C1: PROCESSING OF Pb-BASED FERROELECTRICS

Chair: Scott R. Summerfelt
Monday Morning, November 26, 2001
Room 210 (Hynes)

8:30 AM *C1.1
LOW TEMPERATURE PREPARATION OF HIGH QUALITY $Pb(Zr,Ti)O_3$ FILMS BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION WITH HIGH REPRODUCIBILITY.
Hiroshi Funakubo, Kuniharu Nakashima, Masanori Aratani, Kouji Tokita, Takahiro Oikawa, Tomohiko Ozeki, Gouji Asano, Tokyo Institute of Technology, Interdisciplinary Graduate School of Science and Engineering, Department of Innovative and Engineered Materials, Kanagawa, JAPAN; Keisuke Saito, Philips Japan Ltd, Analytical Division, Kanagawa, JAPAN.

$Pb(Zr,Ti)O_3$[PZT] is one of the most promising materials for application to ferroelectric random access memory (FeRAM). Among the various preparation methods, metalorganic chemical vapor deposition (MOCVD) has been recognized as a most important to realize high density FeRAM because of its potential of high step coverage and the large-area-uniformity of the film quality. In the present study, the pulsed-MOCVD[1-3] were developed in which a mixture of the source gases was pulse introduced to the reaction chamber for 10 s with 5 s interval. By using this deposition technique, simultaneous improvements of the crystallinity, surface smoothness and electrical property have been reached by comparing to conventional continuous gas-supplied MOCVD. Moreover, this film had larger remanent polarization (Pr) and lower leakage current density. This is owing to the reevaporation of excess Pb element from the film and the increase of the migration time on the surface of the substrate during interval time. This process is also very effective to decrease the deposition temperature of the film having high quality. In fact, the Pr and the leakage current density of $Pb(Zr0.35Ti_{0.65})O_3$ film deposited at 415°C were 41.4 $\mu C/cm^2$ and on the order of 10^{-7} A/cm^2 at 200 kV/cm. This Pr value was almost the same as that of epitaxially grown film with the same composition corrected for the orientation difference[3]. This suggests that the polycrystalline PZT film prepared by pulsed-MOCVD had epitaxial-grade ferroelectric properties even through the deposition temperature was as low as 415°C C. [1] K. Nagashima et al., Jpn. J. Appl. Phys., 39 (2000) L996. [2] M. Aratani et al., Jpn. J. Appl. Phys., 40 (2001) L343. [3] M. Aratani et al., Appl. Phys. Lett., submitted for publication.

9:00 AM C1.2
ROLE OF FLUORITE FORMATION IN ORIENTATION SELECTION IN SOL-GEL DERIVED PZT FILMS ON PT ELECTRODE LAYERS.
Laura Fe, D.J. Wouters, G.J. Norga, IMEC, Leuven, BELGIUM; F.D. Vasiliu, National Institute of Materials Physics, Bucharest-Magurele, ROMANIA; O. Van der Biest, MTM-KU Leuven, Leuven, BELGIUM.

While the sol-gel method has been shown to be suitable for the production of high quality, oriented PZT films, the basic mechanisms governing orientation selection on different electrode layers remain still under debate. Many authors have attributed the observed dependence of film orientation on pyrolysis conditions to transient interfacial compounds, which could seed the nucleation of grains with fixed out-of-plane orientation during thermal treatment. In this paper, we present evidence that the microstructure of the metastable fluorite phase, which forms during pyrolysis by homogeneous nucleation throughout the film, has a larger impact on orientation selection than has previously been realized. Extensive TEM studies demonstrate that varying the pyrolysis time, temperature and duration greatly influences the crystallinity of the fluorite. For instance, a 10 s pyrolysis at 350C leads to a relatively well crystallized fluorite phase, as reflected in a large (>10) number of rings in the SAED patterns. Meanwhile, after a 2min, 450C pyrolysis step, the fluorite remains quasi-amorphous, demonstrating that fluorite formation is largely controlled by chemical factors, rather than being thermally activated. A nucleation model, which explains the combined effects of chemical structure (M-OH, residual organics content) and fluorite crystallinity in the pyrolysed film, on orientation selection during the crystallization step, is presented.

9:15 AM C1.3
PRECISE CONTROL OF NUCLEATION AND GROWTH IN LEAD ZIRCONATE TITANATE THIN FILMS BY SCANNING RAPID THERMAL ANNEALING.
Jang-Sik Lee, Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA

We previously reported the selectively nucleated lateral crystallization (SNLC) of PZT thin films and their electrical characteristics. [1-3] The SNLC was based on the selective nucleation and growth between the template layer and the perovskite seed. However, the selective growth was very difficult, because the annealing temperature should be low enough not to nucleate at other regions and thus, growth rate was too low due to low annealing temperature. In this work, we report a novel-type annealing method, that scanning rapid thermal annealing. SNLC annealing was carried out by scan RTA with tungsten-halogen lamps. A line-shaped light, which was focused with an elliptical reflector, was scanned over the specimen that had been preheated by bottom lamps. We used partially nucleated PZT thin films annealed at 680°C for 1 min with average grain size of 7 μm. Then, lamp-scan RTA process was carried out. The preheating temperature was 500°C and the speed of lamp was 1 mm/s. The peak temperature was 657°C. It was found that the grain growth occurred only at the pre-nucleated regions. The lateral growth was 3-4 μm. The lateral growth increased with lowering scan speed even at the same peak temperature. When the scan speed was reduced to 0.5 mm/s, the lateral growth was more than 20 μm. This scan-RTA process has many advantages over conventional furnace annealing or the RTA in selective growth, growth rate, as well as continuous process. In this work, the effects of preheating temperature, scan-lamp power and scan speed on the crystallization and microstructure of PZT thin films will be discussed in detail. [1] Jang-Sik Lee and Seung-Ki Joo, Jpn. J. Appl. Phys., 39(11), 6343. [2] Jang-Sik Lee and Seung-Ki Joo, Jpn. J. Appl. Phys., 40(1), 229. [3] Jang-Sik Lee and Seung-Ki Joo, Appl. Phys. Lett., to be published.

9:30 AM C1.4
LOW-TEMPERATURE CRYSTALLIZATION OF Pb(Zr0.4,Ti0.6)O3 THIN FILMS BY CHEMICAL SOLUTION DEPOSITION.
Kazunari Maki, Nobuyuki Soyama, Kaoru Nagamine, Satoru Mori, Katsumi Ogi, Mitsubishi Materials Corporation, Hyogo, JAPAN.

PZT films are attractive for application in nonvolatile memories, decoupling capacitors, infrared sensors, and microactuators. The PZT films need to be deposited on top of underlying semiconductor circuits or substrates with low heat-resistance for many proposed devices. In these cases, it is necessary to lower crystallization temperature of PZT films. We had studied crystallization of sol-gel derived PZT(40/60) thin films at 450 to 420°C on $Pt/SiO_2/Si$ substrates before [1, 2]. We reported that diol-based solutions and modified film

preparation processes, which were thinning of an annealed film (thin-film annealing) and piling of annealed layers (multi-annealing), were effective in lowering crystallization temperature. And we also reported that the PZT films had good ferroelectric properties by combination of the solutions and the preparation processes [1, 2]. In this study, further decreasing of crystallization temperature of PZT films were investigated and annealing temperature dependence of PZT films were evaluated. Firstly, we have studied crystallization of sol-gel derived PZT(40/60) thin films at 400 down to 390°C on $Pt/SiO_2/Si$ substrates and evaluated various properties of the PZT films such as microstructures, crystal orientation, and electric properties. It was found that PZT films could be crystallized at 390°C by diol-based solutions and multi-annealing. PZT films crystallized at 400°C had good electric characteristics such as 2Pr of about 20 uC/cm^2 and relative permittivity of more than 700. Secondly, we have evaluated annealing temperature dependence between 435 to 390°C of PZT(40/60) thin films. The results indicated that crystal orientation of PZT films changed from (111) to (100) and sizes of perovskite grains increased as annealing temperature decreased. [1] K. Maki, N. Soyama, S. Mori and K. Ogi: Integr. Ferroelectr. 30 (2000) pp. 193. [2] K. Maki, N. Soyama, K. Nagamine, S. Mori and K. Ogi: submitted to Jpn. J. Appl. Phys.

9:45 AM C1.5
FERROELECTRIC LEAD ZIRCONATE TITANATE THIN FILMS PREPARED BY HIGH-PRESSURE CRYSTALLIZATION (HPC) PROCESS. Chung-Hsin Lu and Yu-Chang Sun, Department of Chemical Engineering, National Taiwan University, Taipei, TAIWAN ROC.

Ferroelectric thin films to the application of the nonvolatile ferroelectric random access memories (FeRAM) have attracted considerable interests worldwide in the past decade. Because of their high read/write speed, nonvolatility, low operating power, and radiation hardness, they are considered to be the potential candidates for substituting the silicon-based electrically erasable, programmable read-only memories and flash EEPROMs. Lead zirconate titanate (PZT) with the perovskite structure is one of the major potential ferroelectric materials for the application to FeRAM. During the last decade, many studies have been devoted to investigate the preparation of thin films and their properties. Since this material is difficult to be crystallized, either in-situ heating or post-annealing at high temperatures for complete crystallization is necessary. In order to reduce the crystallization temperature of PZT, a novel high-pressure crystallization (HPC) process has been developed. The crystallization temperature of PZT thin films can be decreased to be lower than 400°. It is found that the crystallization process of PZT is significantly enhanced by high-pressure processing. In addition, the interaction between PZT films and substrates is substantially reduced. The formation process and the development of the microstructure have been investigated by XRD and SEM. The effects of this high-pressure crystallization (HPC) process on lowering the crystallization temperatures of other electronic ceramic thin films will be also discussed in this study.

SESSION C2: PROCESSING OF Bi-BASED FERROELECTRICS
Chair: Hiroshi Funakubo
Monday Morning, November 26, 2001
Room 210 (Hynes)

10:30 AM C2.1
GROWTH OF (103) FIBER-TEXTURED $SrBi_2Nb_2O_9$ AND $SrBi_2Ta_2O_9$ FILMS ON Pt-COATED Si SUBSTRATES. G. Asayama, J. Lettieri, M.A. Zurbuchen, S. Trolier-McKinstry, and D.G. Schlom, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA; S.K. Streiffer, Materials Science Division, Argonne National Laboratory, IL; J-P. Maria, Materials Science and Engineering, North Carolina State University, Raleigh, NC; S.D. Bu and C.B. Eom, Department of Materials Science & Engineering, University of Wisconsin-Madison, Madison, WI.

Since the discovery of high fatigue resistance in bismuth-based layered ferroelectrics, in particular $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$, these materials have been extensively investigated for ferroelectric random-access memory (FRAM) applications. To achieve high storage density with continued feature size reduction, it is desired to have high and uniform remanent polarization (P_r) in the ferroelectric materials used in FRAMs. Optimally one would like to prepare ferroelectric films in which the P_r is not only high, but also equal for every capacitor in the memory structure. Previously we reported the growth of $SrBi_2Nb_2O_9$ thin films with a P_r of 15.7 μC/cm^2 (which is more than 25% higher than the highest value reported for polycrystalline $SrBi_2Nb_2O_9$ thin films). These films were (103)-oriented $SrBi_2Nb_2O_9$ epitaxially grown on (111) $SrTiO_3$ substrates coated with a (111)-oriented $SrRuO_3$ epitaxial bottom electrode. However, preparation of films with these desired ferroelectric properties has required the use of single crystal substrates. In this study we show that high P_r (and the concomitant uniformity in P_r) can be achieved on Pt-coated silicon substrates using local epitaxy to impart the (111) fiber texture of a platinum film into a fiber-textured (103) $SrBi_2Nb_2O_9$ film. These fiber-textured (103) $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ films were grown by pulsed laser deposition (PLD). Four-circle x-ray diffraction analysis, transmission electron microscopy characterization, and electric characterization will be presented.

10:45 AM C2.2
HETERO-EPITAXIAL GROWTH OF (1, 0, m 1) ONE AXIS-ORIENTED BLSF THIN FILMS DIRECTLY CRYSTALLIZED BY MOCVD. Norimasa Nukaga, Takayuki Watanabe, Hiroshi Funakubo, Dept Innov Eng Mat, Interdisciplinary Grad School Science and Eng, Tokyo Inst Tech, Kanagawa, JAPAN; Toshimasa Suzuki, Yuji Nishi, Masayuki Fujimoto, Taiyo Yuden Ltd., Gunma, JAPAN.

Bismuth layer-structured ferroelectrics (BLSFs) thin films have been extensively investigated for a nonvolatile ferroelectric random access memory (FeRAM) application due to their fatigue-free property. The orientation control of BLSF films, especially one-axis preferred orientation, is essential to obtain the large ferroelectricity because it strongly depends on the film orientation. However, the control method of preferred orientation has been hardly reported on polycrystalline substrate. In the present study, we prepared BLSF thin films with different number of octahedron number (m-number) by MOCVD and directly crystallized on the substrates. From the X-ray reciprocal space mapping, $SrBi_2Ta_2O_9$ film directly crystallized had a strong (103) one-axis-orientation while that one crystallized with the anneal process from fluorite phase showed a random orientation. This result suggests that the crystallization mechanism strongly depend on the preparation method. In the case of the film directly crystallized from the gas phase, the crystallization and the orientation of the SBT phase are considered to be strongly influenced by those of the substrate. From the TEM observation, moreover, the (103)-oriented SBT grains were ascertained to be grew hetero-epitaxially on the (111)Pt grains. Therefore, this hetero-epitaxial crystallization mechanism of SBT phase is effect for lowering the crystallization temperature of SBT phase because of the low crystallization energy of SBT phase using hetero-epitaxial nucleation. Indeed, we succeeded in preparing SBT film with large ferroelectricity below 650°C. On the other hand, directly crystallized $Bi_2VO_{5.5}$ (m=1) and $Bi_4Ti_3O_{12}$ (m=3) showed (102) and (104) one-axis preferred orientation on (111)Pt substrates. These are basically the equal orientation because the tilting angle of c-axis from the substrate surface is 55°. Consequently, the direct crystallization is one of the important key techniques for lowering the crystallization temperature and also obtaining uniform ferroelectricity, which is essential to realize the high density FeRAM.

11:00 AM C2.3
ENHANCED CRYSTALLIZATION EFFECT IN Pb- AND Bi-BASED FERROELECTRIC THIN FILMS BY ADDITION OF DIELECTRIC MATERIAL. Takeshi Kijima, R&D Association for Future Electron Devices, Tokyo, JAPAN; Hiroshi Ishiwara, Tokyo Institute of Technology, Frontier Collaborative Research Center, Yokohama, JAPAN.

Recently, variety of ferroelectric materials have been examined for use in FeRAM, however each of them has weak points to be improved. Generally a long annealing process is necessary at higher temperature from 600°C to 800°C. It is difficult to make a film thinner than 100nm, because of the surface roughness and the low film density. The ferroelectric properties deteriorates greatly below that thickness. We succeeded in lowering the crystallized temperature drastically using a unique method of mixing the dielectric materials. The new materials based on $Bi_4Ti_3O_{12}$ (BIT), $SrBi_2Ta_2O_9$ (SBT) and $Pb(Zr,Ti)O_3$ (PZT) are examined, and they are mentioned here after as K1, K2 and K3, respectively. The sol-gel solutions are prepared by admixing the sol-gel solution of the dielectric material with that of BIT, SBT and PZT. The lowest temperatures required for the highly crystallized films were 500°C, 550°C and 450°C for 13-nm K1, 25-nm K2 and 25-nm K3, respectively. They were crystallized at temperatures lower than the conventional ferroelectric films by about 150°C to 200°C. Then, P-E hysteresis measurement showed that the switching polarization was saturated at 0.5V. Next, we formed their films on 6-inch wafers, and obtained good ferroelectric properties of 25μm×25μm stacked capacitors. Pr=16μC/cm^2 was confirmed steadily in the whole area of 6-inch wafer. As for our novel ferroelectrics, a large area preparation and an ultra thin film are possible enough. We will show the details of a dielectric material and a film formation at the meeting. This work was performed under the auspices of the R&D Projects in Cooperation with Academic Institutions (Next-Generation Ferroelectric Memory) supported by NEDO (New Energy and Industrial Technology Development

Organization in Japan) and managed by FED (R&D Association for Future Electron Devices).

11:15 AM C2.4
CRYSTAL AND ELECTRONIC STRUCTURES OF $Bi_{4-x}La_xTi_3O_{12}$ FERROELECTRIC MATERIALS.
Yuichi Shimakawa and Yoshimi Kubo, Fund. Res. Labs., NEC Corporation, Tsukuba, JAPAN; Yuuki Tauchi and Hajime Asano, Inst. Mat. Sci., Univ. of Tsukuba, Tsukuba, JAPAN; Takashi Kamiyama, Inst. Mat. Str. Sci., KEK, Tsukuba, JAPAN; Fujio Izumi, Adv. Mat. Lab., NIMS, Tsukuba, JAPAN.

La-substituted $Bi_4Ti_3O_{12}$ ferroelectric thin films have attracted considerable attention because of their use in non-volatile memory applications due to their fatigue-free nature and low deposition temperature. We investigated the crystal and electronic structures of $Bi_4Ti_3O_{12}$ (BTO) and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLTO) and the relationships between their structural features and ferroelectric properties. Large structural distortions of BTO and BLTO were revealed from the crystal structure analysis by neutron diffraction and such distortions produce polarizations along the *a* and *c* axes. Large atomic displacements of ions in perovskite-type units along the *a* axis cause the large polarizations of the materials. The polarizations along the *c* axis, on the other hand, are quite small. In $Bi_{3.25}La_{0.75}Ti_3O_{12}$, La atoms substitute for Bi atoms in the perovskite-type unit only, and the substitution causes less distortion of the structure, resulting in smaller spontaneous polarization and lower ferroelectric Curie temperature. Electronic-structure calculations revealed that covalent interaction, which originates from the strong hybridization between Ti-3*d* and O-2*p* orbitals, plays an important role in the structural distortion and ferroelectricity of the materials. We also discuss the synthesis temperature of B(L)TO materials. Although our solid-state reaction process is different from other processes for preparing thin films, changes in ceramic-sample density with sintering temperature give information concerning device fabrication temperature. The sintering temperatures necessary to produce BLTO samples are lower than those for SBT samples, but substituting La for Bi atoms appears to "increase" the synthesis temperature of the BTO and BLTO material systems.

11:30 AM C2.5
MOLECULAR ENGINEERING FOR FERROELECTRIC THIN FILMS OF BISMUTH-BASED LAYER-STRUCTURED PEROVSKITE. Kazumi Kato[a,b], Kazuyuki Suzuki[a], Kaori Nishizawa[a], Takeshi Miki[a], [a]National Inst of Advanced Industrial Science and Technology, Nagoya, JAPAN; [b]Frontier Collaborative Research Center, Tokyo Inst of Technology, Yokohama, JAPAN.

Electrical properties of Bi-based layer-structured perovskite compounds strongly depend on their anisotropic crystal structure. Because of the dependence, the properties are expected to design or control through two kinds of crystallographic approaches; choice of cations in both A and B sites and adjustment of a number, n, of oxygen octahedra along c-axis of perovskite layers between Bi-O layers. Chemical solution deposition is superior to other deposition techniques in precise compositional control and low processing temperature for synthesis of multi-component oxide thin films. Especially, it is a promising technique for control of crystal structure when molecules in the solutions are designed to have optimized structures for transformation to the functional oxides. In our previous study, thin films of Bi-based layer-structured perovskite compounds, such as $CaBi_2Ta_2O_9$ (n=2), $CaBi_3Ti_3O_{12-X}$ (n=3), and $CaBi_4Ti_4O_{15}$ (n=4), have been deposited using precursor solutions which were designed and synthesized through chemical reactions of metallorganic compounds such as metal alkoxides on the basis of the original concept. And their properties were primarily estimated [ref. 1-3]. This paper will focus on the molecular structure of the precursor solution, crystallization behaviors and electrical properties of $Ca_2Bi_4Ti_5O_{18}$ thin films (n=5), and then address the importance of molecular engineering by comparison with results obtained in the previous study. [1] K. Kato, K. Suzuki, K. Nishizawa, T. Miki, J. Appl. Phys., 88, 3779-3389 (2000). [2] K. Kato, et al., Appl. Phys. Lett., 78, 1119-1121 (2001). [3] K. Kato, et al., Appl. Phys. Lett, in print.

11:45 AM C2.6
ELECTRICAL CHARACTERISTICS OF $(Bi,Ce)_4Ti_3O_{12}$ (BCT) THIN FILMS FOR FERROELECTRIC RANDOM ACCESS MEMORY (FRAM) CAPACITOR PREPARED BY LIQUID SOURCE MISTED CHEMICAL DEPOSITION (LSMCD). Hyun Jin Chung, Memory TG-2 process Team, R&D Division, Hynix Semiconductor Inc., Cheongju, KOREA; Seong Ihl Woo, Dept of Chemical Engineering, KAIST, Taejon, KOREA.

For the first time, the physical and electrical properties of $(Bi,Ce)_4Ti_3O_{12}$ (BCT) thin films were prepared by liquid source misted chemical deposition (LSMCD), and are reported. BCT thin films were deposited on a platinum (Pt)-coated Si wafer. Bi(III) 2-ethylhexanoate, Ce nitrate 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 crystallization of BCT thin film was achieved by heat treatment above 600°C using rapid thermal process (RTA) and furnace annealing. The composition and depth profile of BCT thin film, measured by wavelength dispersive spectroscopy and auger electron spectroscopy, were uniform and reproducible. The electrical property of BCT thin film was strongly dependent on the condition of heat treatment such as baking, annealing and ambient gas during annealing. The remnant polarization ($2P_r$) and coercive field (E_c) of the 400nm thick $(Bi_{3.40},Ce_{0.50})Ti_3O_{12}$ films annealed at 650°C for 1hr in an O_2 ambient furnace were 9.2 ($\mu C/cm^2$) and 87(kV/cm) when the sweeping range was -10~10V, respectively. The leakage current density was $2.78x10^{-7}(A/cm^2)$ at 5V. Also, this film showed a good fatigue resistance without the decrease of remnant polarization to $3x10^{10}$ (cycle). The BCT thin film shows that the good electrical property for FRAM can be obtained at the lower annealing temperature compared with another candidates such as $SrBi_2Ta_2O_9$ and $Bi_4Ti_3O_{12}$. From this result, it is concluded that BCT is a promising material as a capacitor for ferroelectric random access memory (FRAM).

SESSION C3: FERROELECTRIC NONVOLATILE MEMORIES—TECHNOLOGY, FUNDAMENTALS, AND INTEGRATION

Chairs: Stephen R. Gilbert and Masaru Shimizu
Monday Afternoon, November 26, 2001
Room 210 (Hynes)

1:30 PM *C3.1
Abstract Withdrawn.

2:00 PM C3.2
LOW TEMPERATURE INTEGRATION OF LEAD BASED FERROELECTRIC CAPACITORS ON Si USING DIFFUSION BARRIER LAYER. B.T. Liu, Y. Wang, B. Nagaraj, and R. Ramesh Department of Materials and Nuclear Engineering Center for Superconducivity Research, Department of Physics University of Maryland, College Park, MD; K. Maki, Mitsubishi Materials Corporation.

Currently, great efforts are being devoted to integrate ferroelectric capacitors on Si wafers for the realization of high-density nonvolatile ferroelectric random access memories. Two important factors, at least, need to be considered during the integration. One is the processing temperature, which is related to the problems of diffusion or potential interaction between different layers; another is the success of selecting a conducting barrier layer between the polycrystalline Si plug and the ferroelectric capacitors.In the present work, we report results of PZT capacitors fabricated by the sol-gel technique at temperatures between 400°C and 600°C. Novel PZT precursors have proved to be very attractive for realization of low processing temperature of PZT capacitors with good physical properties. PZT thin films have been processed on several conducting perovskite electrodes including LSCO, SRO and LNO. We have integrated these capacitors on polycrystalline-Si/Si substrates using the Ti-Al intermetallic material system as a conducting diffusion barrier. Structural characterization was performed to confirm the integrity of the diffusion barrier after the growth of the ferroelectric capacitor. For potential application as nonvolatile ferroelectric random access memories, capacitors were investigated by the measurements of fatigue, imprint, pulse width dependence and retention to characterize their high speed and long term reliability. This work is supported by the NSF-MRSEC and by Telcordia Technologies.

2:15 PM *C3.3
THE STUDY OF FATIGUE ANISOTROPY IN $Pb(B_1B_2)O_3$-$PbTiO_3$ FERROELECTRIC SINGLE CRYSTALS AND THIN FILMS.
Clive Randall, Metin Ozgul, and Susan Trolier-McKinstry, Center for Dielectric Studies, Materials Research Institute, The Pennsylvania State University, University Park, PA; Veronique Bornand, University of Montpellier, FRANCE; Koichi Takemura, NEC Corporation, Kawasaki, JAPAN.

$Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) single crystal ferroelectrics have been studied to determine the relative rates of polarization fatigue. It was recently found that ferroelectrics with the rhombohedral phase in the PZN-PT solid solution have essentially no polarization fatigue in the $[001]_C$ directions (orientations will be given in terms of the prototype cubic (m3m) axes and denoted by the subscript C). In this study, we expand upon this observation to correlate fatigue rates more completely with respect to composition, orientation, temperature, and electric field strength. It is inferred that

an engineered domain state in a relaxor based ferroelectric crystal with the spontaneous polarization inclined to the normal of the electrode is associated with negligible or no fatigue at room temperature. However, if thermal history, temperature, or field strength induces a phase transition that produces a polarization parallel to the normal of electrode, these orientations fatigue. These observations are also explored in relaxor-ferroelectric thin films with compositions $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$. The fatigue behavior correlates strongly to the degree of epitaxy of the thin films. Films with incomplete $[001]_C$ orientations demonstrate partial fatigue in these thin films.

3:15 PM *C3.4
IMPRINT IN FERROELECTRIC THIN FILMS: THE INTERFACE SCREENING MODEL. M. Grossmann, O. Lohse, D. Bolten, U. Boettger, T. Schneller, Institut für Werkstoffe der Elektrotechnik, RWTH Aachen, Aachen, GERMANY; R. Waser, Institut für Festkörperforschung, Research Center Jülich, Jülich, GERMANY.

Comprehensive imprint measurements on $PbZr_xTi_{1-x}O_3$ (PZT) thin films were carried out. Different models which were proposed in literature to explain imprint in ferroelectric thin films or a similar aging effect (internal bias) in ferroelectric bulk material are discussed. Discrepancies between the experimental results obtained on the PZT films in this work and the prediction of the proposed literature models indicate that these models do not describe the dominant imprint mechanism. Hence, in this work a modified model is introduced which suggests imprint to be caused by a strong electric field within a thin surface layer at the ferroelectric-electrode-interface in which the ferroelectric polarization is smaller or even absent compared to that in the bulk of the film. In the course of aging the field at the interface is screened by a Frenkel-Poole type charge separation within the surface layer and the subsequent trapping of these charges at the ferroelectric-surface-layer-interface. The model is supported by numerical simulations which can explain a variety of experimental observations such as thickness and temperature dependence as well as the improvement of the imprint behavior due to the use of oxide electrodes.

3:45 PM C3.5
Abstract Withdrawn.

4:00 PM C3.6
POINT DEFECT DISTRIBUTION IN FERROELECTRIC PEROVSKITE THIN FILMS. Ruey-Ven Wang, Paul C. McIntyre, Stanford University, Dept of MS&E, Stanford, CA.

The distributions of charged defects, such as oxygen vacancies and hydrogen/deuterium interstitials, across perovskite thin films were investigated by both experimental and modeling procedures. (Ba, Sr) TiO_3 /Pt samples were annealed in different ambients (D_2/N_2 forming gas and D_2O carried by N_2). After long time annealing, the deuterium distribution appeared to reach equilibrium and was analyzed by SIMS depth profiling. Based on the final deuterium profiles obtained for different annealing conditions, and a previously developed model for point defect equilibrium in titanate thin films, the electrical potential variation across the films can be calculated and the distributions of charged defects other than deuterium can also be estimated. Similar methodology was also applied to PZT. In addition, the effect of the defect distribution on the ferroelectric properties of PZT thin films was quantitatively studied by both electrical characterization and SIMS analysis.

4:15 PM C3.7
PROPERTIES OF PZT CAPACITORS WITH Ir ELECTRODES FABRICATED ONLY BY MOCVD. Masaru Shimizu, Kentaro Kita, Hironori Fujisawa and Hirohiko Niu, Himeji Inst. Tech., Dept. of Electronics, Himeji, Hyogo, JAPAN.

Structural and electrical properties of PZT capacitors with top and bottom Ir electrodes fabricated only by MOCVD were investigated. Low temperature fabrication of capacitors at 395°C was performed. Ir thin films as both top and bottom electrodes were prepared at 300°C by MOCVD using $Ir(C_2H_5C_5H_4)(1,5\text{-}C_8H_{12})$ (Ir(EtCp)(cod)) as an Ir precursor. Ir films as a bottom electrode prepared on SiO_2/Si showed a high (111)-orientation and were highly reflecting. Resistivities were 23-44$\mu\Omega$·cm. PZT films were then deposited on MOCVD-Ir bottom electrodes at 395-540°C by MOCVD using $(C_2H_5)_3PbOCH_2C(CH_3)_3$, $Zr(O\text{-}t\text{-}C_4H_9)_4$ and $Ti(O\text{-}i\text{-}C_3H_7)_4$ as precursors. In order to obtain PZT films at a low growth temperature, two step MOCVD growth process using a $PbTiO_3$ seed was carried out. PZT thin films obtained at 395-540°C showed random orientations. Ir top electrodes were deposited on PZT at 300°C. Step coverages of Ir and PZT were 70-80%. The PZT capacitor prepared at 395°C showed 2Pr of 20μC/cm^2 and 2Ec of 180kV/cm. 2Pr of 40-50μC/cm^2 and 2Ec of 130-160kV/cm were obtained for PZT capacitors fabricated at 445-540°C. PZT capacitors fabricated with two step growth process using $PbTiO_3$ seed showed better electrical properties and step coverage characteristics than those of capacitors without two step growth process.

4:30 PM C3.8
IRIDIUM BASED ELECTRODES FOR FERROELECTRIC CAPACITOR FABRICATION. J.A. Johnson, J.G. Lisoni, D.J. Wouters, IMEC vzw, Leuven, BELGIUM.

Ir and its conductive oxide, IrO_2, are candidates to replace Pt as the electrodes in ferroelectric capacitors (FECAPs), because of improved endurance (since e.g. Pt/PZT/Pt shows strong fatigue) and also because of the oxygen barrier properties of Ir/IrO_2 stacks that enable the fabrication of stacked FECAPs on top of contact plugs. Two important issues related to these electrodes are the control of the ferroelectric layer orientation on top of these materials, as well as material stability (e.g. oxidation and possible growth of large IrO_2 crystallites). In this work, it will be discussed how Ir and IrO_2 bottom electrodes affect the crystallization of sol-gel deposited PZT. While PZT films deposited on (111) Pt show a strong (111) preferential orientation, (111) Ir and polycrystalline IrO_2 electrodes nucleate strongly differently oriented PZT. Controlling and changing the microstructure of the bottom electrode allows tuning of these PZT orientations and the resulting grain morphology, and, consequently, their FECAP polarization hysteresis properties. The effect of different thermal treatments on the stability of the of different bottom electrode stacks will be discussed. Results on IrO_2 are also compared to RuO_2.

4:45 PM C3.9
EVALUATION OF PLZT THIN FILM SPUTTERED ON Pt/IrOx/Ir BOTTOM ELECTRODE FOR FERROELECTRIC MEMORY APPLICATION. Yusuke Miyaguchi, Takehito Jimbo, Shin Kikuchi, Koukou Suu, Michio Ishikawa, ULVAC Inc., Shizuoka, JAPAN.

To realize high-density ferroelectric memory over 16Mbit, 1T1C cell architecture with ferroelectric capacitor stacked on plug structure (Stacked Type Capacitor, STC) is considered to be necessarily introduced. The ferroelectric capacitor structures with Pt/Ti or IrOx/Ti bottom electrodes (BEs) which is being used in current planer type capacitor will not suitable for STC directly contacting to the plug because capacitor-forming high-temperature oxidation process will cause oxygen diffusion in to bottom electrode layer and plug and finally their oxidation destroying the necessary conductive properties of plug and bottom electrode materials and their interface. So an anti-oxidation barrier is needed in between ferroelectric capacitor and plug. In this study, we chose Ir as oxygen barrier to form PLZT/Pt/IrOx/Ir structure for the above-mentioned STC application. PLZT thin films were deposited on Pt/IrOx/Ir BEs using RF sputtering technique. The PLZT capacitors were evaluated in terms of orientation, PLZT film composition and capacitor performance. Good ferroelectric properties were obtained by optimizing sputtering conditions and PLZT film composition.

SESSION C4: POSTER SESSION
Chairs: Michael Grossmann and Takeshi Shioga
Monday Evening, November 26, 2001
8:00 PM
Exhibition Hall D (Hynes)

C4.1
FERROELECTRIC-GATE STRUCTURES AND FETS USING $(Bi,La)_4Ti_3O_{12}$ FILMS. E. Tokumitsu, T. Suzuki, N. Sugita, Precision & Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

Recently, $(Bi,La)_4Ti_3O_{12}$ (BLT) has attracted much attention for nonvolatile ferroelectric memory applications. In this work, we fabricated and characterized metal-ferroelectric-metal-insulator-semiconductor (MFMIS) structures using BLT films for ferroelectric-gate FET applications. 9-nm-SiO_2 and 150-nm-BLT were used as buffer (I) and ferroelectric (F) layers. BLT films were fabricated by the MOD method at 750°C. Bi and La contents in the source solution were 3.35 and 0.75, respectively. The remanent polarization (Pr) and coercive field (E_C) were 15 μC/cm^2 and 100 kV/cm, respectively. It is shown that a memory window in capacitance-voltage (C-V) characteristics of the fabricated MFMIS structures increases with an area ratio S_{MIS}/S_{MFM}. A memory window as large as 3V can be obtained for a voltage sweep of ±5V, when the area ratio S_{MIS}/S_{MFM} is 15. It is also demonstrated that the MFMIS structures with an area ratio S_{MIS}/S_{MFM} of 15 exhibit good data retention characteristics. Next, we fabricated MFMIS-FETs using Pt/BLT(150nm)/Pt/SiO_2(9nm)/Si structures. Hysteresis loops due to the ferroelectric BLT film were observed in the drain

current-gate voltage (I_D-V_G) characteristics. Observed threshold voltage shift is 3V, which agrees with a memory window obtained in the C-V characteristics for the MFMIS diodes. This work was performed under the auspices of the R&D Projects in Cooperation with Academic Institutions (Next-Generation Ferroelectric Memory) supported by NEDO (New Energy and Industrial Technology Development Organization in Japan) and managed by FED (R&D Association for Future Electron Devices).

C4.2
CRYSTALLIZATION BEHAVIORS AND FERROELECTRIC PROPERTIES OF $YMnO_3$ THIN FILMS ON Si (100) SUBSTRATE.
Dong Chul Yoo, Jeong Yong Lee, Dept of MS&E, Daejeon, KAIST, KOREA; Ik Soo Kim, Yong Tae Kim, Semiconductor Materials Lab., KIST, Seoul, KOREA.

Ferroelectric $YMnO_3$ thin films have attracted much attention for use in metal-ferroelectric-semiconductor field effect transistors (MFSFETs). We investigated the crystallization behaviors and ferroelectric properties of $YMnO_3$ thin films on Si (100) substrate. $YMnO_3$ thin films were deposited on Si (100) substrate by rf-sputtering under different ambient. For the crystallization, the $YMnO_3$ films were annealed in RTA for 3 min at 850°C. The $YMnO_3$ films and the $YMnO_3$/Si interface were investigated using a high-resolution transmission electron microscopy (HRTEM). After post-annealing process, the $YMnO_3$ films deposited in Ar ambient had random orientations. The $YMnO_3$ films deposited in Ar O_2 ambient had two layers, i.e., a c-axis oriented layer in top region and a random oriented layer in bottom region in the $YMnO_3$ film. In C-V measurements, $YMnO_3$ films deposited in Ar O_2 ambient showed a large memory window and a high dielectric constant, which is due to the partial c-axis orientation in the $YMnO_3$ films. However, $YMnO_3$ films deposited in Ar O_2 ambient showed a high leakage current density. As the leakage current density is influenced by the interfacial microstructure, we investigated the microstructure of $YMnO_3$/Si interface using HRTEM. The role of amorphous $YMnO_3$ layer as buffer layer at the $YMnO_3$/Si interface is also discussed.

C4.3
CHARACTERISTICS OF MEMORY WINDOW AND RETENTION PROPERTIES OF ONE TRANSISTOR MEMORY DEVICE.
Tingkai Li, Sheng Teng Hsu, J.J. Lee, Bruce Ulrich, Lisa Stecker, Sharp Laboratories of America, Camas, WA.

One-transistor ferroelectric memory devices with PGO MFMOS and MFOS memory cells have been fabricated. The memory windows and retention properties of one-transistor memory device can be measured using different methods. For memory windows, one method is to measure the C-V curves of MFMOS or MFOS capacitor. The memory windows can be obtained from the hysteresis of the CV curves. Another method is to measure the threshold voltages from the one-transistor devices. The difference of the threshold voltages between "on" state and "off" state is the memory windows. For retention properties of one-transistor devices, one method is to measure the changes of the capacitance of MFMOS of MFOS capacitors "on" state and "off" state with time. Another method is to measure the changes of drain current of one-transistor devices "on" state and "off" state with time. In this paper, various methods have been used to measure the memory windows and retention properties of one-transistor memory devices with MFMOS and MFOS memory cells. The difference between methods and device structures have been found and discussed.

C4.4
IMPACT OF PROCESSING CONDITIONS ON THE MICRO-STRUCTURAL AND PHYSICAL CHARACTERISTICS OF FERROELECTRIC-GATE MEMORY CAPACITORS.
C. C.-Broadbridge, D.L. Pechkis, Southern Connecticut State Univ., New Haven, CT; J.-P. Han, C.J. Xie, W. Tong, K.-H. Kim, W. Zhu, Z. Luo and T.P. Ma, Yale University, New Haven, CT; A.H. Lehman, K.L. Klein, Trinity College, Hartford, CT; B.L. Laube, United Technologies Research Center, East Hartford, CT.

Ferroelectric (FE) thin films have great potential for nonvolatile memory and DRAM applications, the FE-gate transistor structure is one such device with many advantages. However, the successful fabrication of a ferroelectric-gate transistor structure is largely dependent on the ability to form a high-quality buffer layer between the ferroelectric film and the underlying silicon substrate. The behaviour of the FE/buffer/silicon system with respect to subsequent processing is of additional importance. We report the results of an ongoing study of the microstructural and physical properties of ferroelectric capacitors formed from $SrBi_2Ta_2O_9$ (SBT) layers on silicon buffered by a variety of dielectric materials. Specifically, we have examined silicon nitride, zirconium oxide, hafnium oxide, and zirconium aluminate as potential buffer materials. Additionally, to examine the impact of post-deposition processing, selected samples received oxygen annealing at temperatures ranging from 765-915°C. Characterization results were obtained with the use of Cross-sectional Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Non-contact (cross-sectional and planview) Atomic Force Microscopy (nc-AFM). These data, when coupled with capacitance-voltage (C-V) and Current-Voltage (I-V) data, indicate that the physical, microstructural and micromechanical properties of SBT films depend on the buffer layer material employed as well as the post deposition annealing temperature. Preliminary data will be presented to explain some of these dependencies.

C4.5
EPITAXIAL $LaVO_3$/BST/PLZT/LSCO HETEROSTRUCTURES FOR NON-DESTRUCTIVE READOUT FERROELECTRIC FIELD EFFECT MEMORY DEVICES.
Woong Choi and Tim Sands, University of California, Dept of Materials Science & Engineering, Berkeley, CA.

The ferroelectric field effect transistor (FET) configuration permits a nonvolatile memory element with nondestructive readout. However, the reliable performance of ferroelectric field effect transistors based on silicon has yet to be demonstrated, mainly because of the screening of the field effect by the interface states between the ferroelectric thin film and the silicon. The use of epitaxial oxide heterostructures has been suggested as a way of circumventing this problem. Epitaxial thin films of several semiconducting oxides such as $(La,Sr)_2CuO_4$ and $(La,Ca)MnO_3$ have been used by previous researchers to build epitaxial heterostructures in a ferroelectric FET configuration. In contrast to these heavily doped or degenerate semiconducting oxides, $LaVO_3$ can be synthesized with a relatively low ionized hole concentration ($\sim 10^{18}$ /cm^3) that could make the ferroelectric field effect more pronounced. Earlier work showed that epitaxial thin films of $LaVO_3$ could be grown on a perovskite substrate in vacuum at 500°C. But, since the properties of Pb-based ferroelectrics such as $(Pb,La)(Zr,Ti)O_3$ (PLZT) deteriorate in vacuum at 500°C, a ferroelectric interlayer that is not only stable to vacuum exposure but also structurally compatible with PLZT may improve resistance to degradation. In this study, therefore, $Ba_{0.75}Sr_{0.25}TiO_3$ (BST) has been grown between PLZT and $LaVO_3$ layers in epitaxial LaVO3/BST/PLZT/$(La,Sr)CoO_3$ (LSCO) heterostructures. (Semiconductor $LaVO_3$ layer is between 10 to 25nm thick. Ferroelectric PLZT layer and electrode LSCO layer are 400nm and 50nm in thickness, respectively.) With a 25nm layer of BST, the heterostructure shows optimal ferroelectric properties. The capacitance measurement as a function of the applied gate voltage showed the modulation of the depletion layer in $LaVO_3$ layer.

C4.6
FERROELECTRIC PROPERTIES OF THIN FILM RARE EARTH OXIDE FOR NON-VOLATILE MEMORY APPLICATIONS.
Joseph D. Cuchiaro, Gary S. Tompa, Lloyd G. Provost, Structured Materials Industries, Inc. (SMI), Piscataway, NJ.

The demand for thin film ferroelectric oxides for use in high density non-volatile memories, pyroelectric detectors, MEMS/MOEMs devices, photonics, and waveguides, among other applications is growing rapidly. For advanced devices the corresponding materials technology must be scaled and integrated to ultra-thin film form to meet these needs. However, peroviskite films are difficult to grow directly on silicon and usually result in mixed phase silicides when deposited directly on silicon. Further, regardless of substrate the desired bulk properties have been difficult to obtain with scaling as the overall film thickness approaches the intrinsic microstructure limit of common peroviskite ferroelectric materials. As an alternative to peroviskites, we have investigated rare earth $CeMnO_3$ thin films using Metal Organic Chemical Vapor Deposition (MOCVD) for direct deposition on silicon as a 1T non-volatile transistor gate material. We report material and electrical properties of $CeMnO_3$ films in MOS and MFM capacitor structures obtained by SMI's SpinCVD(TM)Rotating Disk Reactor (RDR)MOCVD.

C4.7
STRUCTURAL INHOMOGENEITY AND SWITCHING PROPERTIES OF $SrBi_2Ta_2O_9$ THIN FILMS PREPARED BY LAYER-BY-LAYER ANNEALING TECHNIQUE.
J.B. Xu, G.D. Hu, Department of Electronic Engineering and Materials Science & Technology Research Center, The Chinese University of Hong Kong, Shatin NT, HONG KONG.

Grazing incidence x-ray diffraction has been used to analyze the depth-profile of $SrBi_2Ta_2O_9$ (SBT) thin films with different preferential orientations. For the polycrystalline SBT thin film, is is found that the change in structural orientation occurs only within the 15-nm-thick top layer, which is associated with the formation of the (200)-predominant SBT thin film prepared by the layer-by-layer annealing process. The inhomogeneity of structural orientation is

more significant in the full film thickness for the (200)-predominant SBT thin film. (0010) peak can only be observed for the grazing angle larger than 0.6°. A layer with the highest ratio of I(200)/I(115) is found in the top surface layer (i.e., the latest layer during deposition) of the (200)-predominant SBT thin film. Studies of the microscopic switching properties of the thin films reveal that the (200)-predominant SBT film has a significant improvement in the polarization roughness.

C4.8
PROCESSING AND PROPERTIES OF SOL-GEL DERIVED SEEDED STRONTIUM BISMUTH TANTALATE ($Sr_{0.7}Bi_{2.4}Ta_2O_9$) THIN FILMS AND POWDERS. Gopinathan M. Anilkumar, Se-Yon Jung, Woo-Chul Kwack, Seung-Joon Hwang and Yun-Mo Sung, Dept of Materials Science & Engineering, Daejin University, Pochun-koon, Kyunggi-do, KOREA (SOUTH).

Submicron size $Sr_{0.7}Bi_{2.4}Ta_2O_9$ (SBT) seed particles were prepared from the powder obtained by pyrolyzing the SBT amorphous gel at 750°C. The SBT sol obtained from the alkoxide precursors has been seeded with 2-5 percentage by weight of the seed particles. The phase formation characteristics were studied using differential thermal analysis (DTA) and x-ray diffraction (XRD). A low temperature Aurivillius phase formation is observed for the seeded precursor compared to the unseeded one. The presence of seeds with Aurivillius phase provides nucleation sites in the form of low energy epitaxial interfaces and thereby increasing the nucleation frequency. This enhances the nucleation rate leading to enhanced transformation kinetics. Thin films were also made by spin coating the seeded/unseeded precursor sol on $Pt/Ti/SiO_2/Si$ substrates. Seed particles also affected the microstructural development of the thin films. The ferroelectric properties of the thin films were measured and the results of the investigation are presented and discussed.

C4.9
ORIGIN OF LOWERED CRYSTALLIZATION TEMPERATURE IN SBT-BTT(N) FERROELECTRIC THIN FILMS. Woo-Chul Kwack, Se-Yon Jung, Gopinathan M. Anilkumar, Seung-Joon Hwang and Yun-Mo Sung, Department of MS&E, Daejin University, Pochun-koon, Kyunggi-do, KOREA (SOUTH).

The fluorite and Aurivillius phase formation characteristics in $SrBi_2Ta_2O_9$-$Bi_3TiTa(Nb)O_9$ (SBT-BTT(N)) thin films, fabricated using sol-gel and spin coating method, was investigated in detail using x-ray diffraction (XRD) and differential thermal analysis (DTA). Activation energy for phase formation and Avrami exponent were determined for each phase formation reaction using isothermal and nonisothermal kinetics analysis. This kinetics analysis result was compared to that of $SrBi_2Ta_2O_9$ (SBT) thin films and different phase formation mechanisms were identified for the SBT and SBT-BTT(N) thin films. The origin of reduced Aurivillius phase formation temperature in SBT-BTT(N) solid-solution thin films was elucidated using a theory of bond strength between cations and oxygen ions.

C4.10
CATIONIC MODIFICATIONS OF $Bi_4Ti_3O_{12}$ FERROELECTRICS AND PROPERTY DESIGN BY RAMAN SPECTROSCOPY. Minoru Osada, Masato Kakihana, Materials & Structures Lab, Tokyo Inst of Tech, Yokohama, JAPAN; Takayuki Watanabe, Hiroshi Funakubo, Dep. Innov. Eng. Mater., Tokyo Inst of Tech, Yokohama, JAPAN.

We discuss some aspects of solid state chemistry in $Bi_4Ti_3O_{12}$ with the aim of understanding its ferroelectric properties and designing improved materials. Thin films of $Bi_{4-x}A_xTi_{3-y}B_yO_{12}$ ($A=La^{+3}$ and other lanthanides; $B=V^{+5}$, W^{+6}) have been prepared by metal organic chemical vapor deposition. We utilize Raman scattering to probe cation distribution and lattice instability related to ferroelectric properties of $Bi_4Ti_3O_{12}$. The distribution of lanthanide ions within two Bi sites has been analyzed using vibrations involving each site. A comparison of our Raman data with a simple mass consideration allows a precise picture of the cation distribution, which indicates a pronounced site selectivity of lanthanide ions for the A site for $x < \sim 1$. By studying series of compositions with the same doping level x and the mean A-site cation radius, we also find that T_C decreases with increasing A-site disorder, as quantified by the variance in the distribution A-site cation radii. In $Bi_{4-x}A_xTi_3O_{12}$, the composition-induced phase transition is directly associated with the softening of the lowest frequency mode, a behavior resembles the temperature dependence in the non-doped material (at constant composition). A remarkable correlation is found between the soft-mode frequency and T_C for $Bi_{4-x}A_xTi_{3-y}B_yO_{12}$. We suggest that this correlation as well as the soft-mode frequency for substituted materials offer useful guidelines toward designing properties in a controlled manner.

C4.11
EFFECT OF BOTTOM ELECTRODES ON STRUCTURAL AND ELECTRICAL PROPERTIES OF LASER ABLATED $SrBi_2Ta_2O_9$ THIN FILMS. Rasmi R. Das, W. Pérez, P. Bhattacharya and Ram. S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR.

Bismuth-layered ferroelectric thin films, particularly of $SrBi_2Ta_2O_9$ (SBT), is well known material for memory devices. In this study we have grown SBT thin films on various bottom electrodes such as $La_{0.5}Sr_{0.5}CoO_3/LaAlO_3$ (100), $LaNiO_3/LaAlO_3$ (100) and on commercial platinized silicon substrates. Both the oxide electrodes were grown using pulsed laser deposition technique at substrate temperature of 700°C and oxygen pressure of 100 mTorr with a pulse energy density of ~2 J/cm^2. The substrate temperature for SBT film was maintained at 500°C, with variation of oxygen pressure at 100-300 mTorr. As-grown films were post-annealed at different temperatures ranging from 700-800°C. X-ray diffraction results show that the films grown at lower temperature 500°C and annealed at 750 and 800°C has preferential orientation along polarization axis. Composition of the films were analyzed by using x-ray photoelectron spectroscopy. Although XRD results showed phase formation at lower temperature, micro Raman study confirmed the formation of SBT layered compound at growth temperature 750°C or above. The maximum value of dielectric constant was estimated to be about 320 with a dissipation factor of 0.02 at frequency of 100 kHz. Films grown on platinized silicon at 500°C substrate temperature, 100 mTorr oxygen pressure and annealed at 800°C showed maximum value of remanent polarization ($2P_r$ ~20 μC/cm^2) with coercive field of E_c (~60 kV/cm). The leakage current density of the films were found to be about ~10^{-9} A/cm^2. Micro Raman study has been done to understand the detailed behavior of various phonon modes of SBT on different electrodes. The difficulty of obtaining lowest Raman modes (28 cm^{-1}) of SBT on platinized silicon substrate was overcome by using oxide electrodes. Process optimization and detailed correlation of structural and electrical properties of as-grown and annealed SBT films on metallic oxide electrodes and platinized silicon substrates will be presented.

C4.12
AC CONDUCTION MECHANISMS OF $SrBi_2Ta_2O_9$ FERROELECTRIC THIN FILMS BELOW ROOM TEMPERATURE. Pingxiong Yang, David L. Carroll, Dept. of Physics, Clemson Univ., Clemson, SC.

The AC conductivity of $SrBi_2Ta_2O_9$ (SBT) thin films was measured for frequencies ranging from 100 Hz to 15 MHz in a temperature range of 10 to 300 K. For frequency ranges of 100 Hz to 1.5 MHz and 1.5 MHz to 8.3 MHz, well known conduction models can be used to describe the observed behavior. Above 8.3 MHz, we suggest a model in which the transport of polarons through the perovskite octahedron layers sandwiched between $(Bi_2O_2)^{2+}$ sheets is the primary conduction mechanism.

C4.13
PREPARATION OF $SrBi_2Ta_2O_9$ FERROELECTRIC THIN FILMS BY RF MAGNETRON SPUTTERING. Yutaka Nishioka, R&D Association for Future Electron Devices, Yokohama, JAPAN; Hiroshi Ishiwara, Frontier Collaborative Research Center Tokyo Institute of Technology, Yokohama, JAPAN.

$SrBi_2Ta_2O_9$ (SBT) thin films is superior to PZT in such viewpoints as fatigue-free switching characteristics and low-voltage operation. In this work, we prepared SBT ferroelectric thin films by RF magnetron sputtering using a Φ106 mm ceramic $Sr_{0.84}Bi_{2.80}Ta_{2.00}O_x$ target. Good film composition stability and large remanent polarization (P_r) were achieved by controlling a sputtering and annealing conditions. 200 nm-thick SBT films were formed by RF magnetron sputtering on $Pt/Ti/SiO_2/Si$ substrates. The substrate were cooled below 100°C for preventing Bi evaporation. Sputtering power and Ar pressure were varied from 50 W to 200 W and from 0.5 Pa to 4.0 Pa, respectively, which resulted in the change of the deposition rate and Bi composition from 7.5 nm/min to 55.4 nm/min and from 0.97 to 1.44. $Sr_{0.84}Bi_{2.34}Ta_{2.00}O_x$ films were crystallized at 800°C for 30 min in air. Pt top electrodes were formed by electron-beam evaporation via a shadow mask with Φ200 μm dots. After the crystallization annealing, (115) and (220) XRD peaks were observed and a remanent polarization value ($2P_r$) of 15 μC/cm^2 was obtained at 5 V. This work was performed under the auspices of the R&D Projects in Cooperation with Academic Institutions (Next-Generation Ferroelectric Memory) supported by NEDO (New Energy and Industrial Technology Development Organization in Japan) and managed by FED (R&D Association for Future Electron Devices).

C4.14
SYNTHESIS AND FERROELECTRIC PROPERTIES OF Sr- AND Nb-CODOPED $Bi_{4-x}Sr_xTi_{3-y}Nb_yO_{12}$ THIN FILMS BY SOL-GEL METHOD. Hirofumi Matsuda, Takashi Iijima, AIST, Smart Struct. Res. Center, Tsukuba, JAPAN; Hiroshi Uchida, Isao Okada,

Sophia.Univ., Dept. of chemistry, Tokyo, JAPAN; Takayuki Watanabe, Hiroshi Funakubo, T.I.Tech., Yokohama, JAPAN.

For improving the properties of $Bi_4Ti_3O_{12}$ (BIT)-based ferroelectric materials, defect controls by substitution of Bi^{3+} with non-volatile La^{3+} ions and Ti^{4+} with other ions of higher charge valence (c.f. V^{5+} and W^{6+}) have been proposed. To obtain optimal composition, chemical solution techniques are advantageous in controlling composition, although preferred c-axis orientation have degraded ferroelectric properties. In this study, therefore, to synthesize defect- and orientation-controlled BIT-based ferroelectric thin films, the influences of Sr-substitution for Bi and Nb-substitution for Ti on crystallization behavior and the ferroelectric properties were evaluated. Sr- and Nb-codoped thin films were fabricated by sol-gel method. Starting materials of Bi-acetate and Ti-, Sr-, and Nb-alkoxides were dissolved in 2-methoxyethanol as a precursor solution. The solution was cast on a $Pt/Ti/SiO_2/Si$ substrate by the spin-cast technique, heat-treated for pyrolysis, and fired subsequently at higher temperatures in air for crystallization. The casting and pyrolysis were repeated several times before firing. In the XRD studies, unlike to the preceding results on BIT-based ferroelectric thin films that c-axis orientation was preferred with increasing crystallization temperature, random orientation was confirmed by strong reflection of (117) peak even after firing at 800°C. On the other hand, however, preliminary results of ferroelectric and dielectric properties through the film thickness were poor with increasing firing temperature, may be affected by the less insulating properties along the $(Bi_2O_2)^{2+}$ layers and/or the presence of conducting second phase. Further studies on the optimal composition of Sr- and Nb-ions for ferroelectric properties and the effect of substitution will be presented.

C4.15
FABRICATION OF VANADIUM-SUBSTITUTED $(Bi,M)_4Ti_3O_{12}$ [M = LANTHANOIDS] THIN FILMS BY CHEMICAL SOLUTION DEPOSITION METHOD. Hiroshi Uchida, Hiroki Yoshikawa, Kana Okamura, Isao Okada, Sophia Univ., Tokyo, JAPAN; Hirofumi Matsuda, Takashi Iijima, AIST, Tsukuba, JAPAN; Takayuki Watanabe, Hiroshi Funakubo, T.I.Tech., Yokohama, JAPAN.

$Bi_4Ti_3O_{12}$ (BIT) -based new ferroelectric materials are proposed from the view of "the Site-Engineering", where Bi-site ions are substituted by lanthanoid ions (*e.g.*, La^{3+}, Nd^{3+} Pr^{3+}, etc.) and Ti-site ions by other ions with higher charge valence (*e.g.*, V^{5+} and W^{6+}), respectively. Researches for the optimal composition of this BIT-based thin films are essential for not only improvement of the ferroelectric properties but also clarify the effect of the substituted ions. In this study, influence of vanadium (V) -substitution for $(Bi,M)_4Ti_3O_{12}$ [M = lanthanoid] thin films on the crystallization behavior and the ferroelectric properties were evaluated. V-substituted $(Bi,M)_4Ti_3O_{12}$ films were fabricated by chemical solution deposition method. Solutions for the spin-coating were prepared using lanthanoid nitrates, $Ti(O\cdot n\text{-}Bu)_4$, $V(Acac)_3$ and 2-methoxyethanol as starting materials. As-coated films were heat-treated at 400°C for 5 min (pyrolysis) and subsequently at 600-800°C for 5 min (crystallization). In the case of M = La, BIT-based films were fabricated from BLT (Bi/La/Ti/V=3.41/0.75/3.00/0.00) and BLTV (Bi/La/Ti/V=3.40/0.75/2.97/0.03) solutions. There was no significant difference on the XRD patterns between BLT and BLTV films, indicating that presence of the second phase and/or change of the crystallization behavior ascribed to the V-substitution was not observed. Remnant polarization (P_r) of BLTV films crystallized at 600 - 800°C were higher than those of BLT films; P_r of BLT and BLTV at 750°C were 8.8 and 11.5 $\mu C\cdot cm^{-2}$, respectively. Those results suggest that the polarization properties of BLT films are improved by the V-substitution. Further researches for the optimal contents of La^{3+} and V^{5+} ions, effect of the substitution by other lanthanoids (*e.g.*, M = Nd, Pr, etc.) are also discussed.

C4.16
INFLUENCES ON HYSTERESIS LOOP TRANSLATION KINETICS IN PO_2 SENSITIVE FERROELECTRIC $Pb(Zr,Ti)O_3$ THIN FILMS. Mark McCormick and Elliott Slamovich, Purdue University, Dept of Materials Sci and Eng, W. Lafayette, IN; Mike McElfresh, Lawrence Livermore National Lab, Materials Research Institute, Livermore, CA.

Ferroelectric hysteresis loop measurements made under controlled pO_2 conditions were performed on $Pb(Zr,Ti)O_3$ (PZT) thin films. The PZT films, obtained from Ramtron Corporation, were deposited on Pt-coated Si substrates by rf-magnetron sputtering. An array of circular Pt electrodes was sputter-deposited on the surface of the PZT films, and electrical contacts were made to the surface electrode and the back Pt layer (sandwich capacitors). Translation of ferroelectric hysteresis loops along the polarization axis was observed, the magnitude and direction of which was strongly dependent on the partial pressure of oxygen at room temperature. Several variables were found to influence the time required for hysteresis loop translations to occur, including the magnitude of the applied electric field, duration of time the electric field was applied, temperature, and area of the surface electrode. These factors will be discussed in detail, and a possible explanation for the mechanism responsible for this behavior will be given.

C4.17
QUANTITATIVE ANALYSIS OF THE TEMPERATURE GRADIENT EFFECTS ON THE GRAIN GROWTH IN LEAD ZIRCONATE TITANATE THIN FILMS. Jong-In Yun, Jang-Sik Lee, Jung-Ho Park, Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

All phase transformations, including thin-film formation, involve the processes of nucleation and growth. The growth kinetics of PZT thin films has been studied for a long time. In the case of PZT thin films, it is crucial to obtain well crystallized structure for ensuring the good ferroelectric properties, so pre- and/or post-deposition anneal should be carried out. Temperature gradient as well as fluctuation during post annealing process, especially in rapid thermal annealing, occurs frequently. However, little study was done on the temperature gradient effects on the grain growth in PZT thin films to date. As previously reported, the selectively nucleated lateral crystallization (SNLC) of PZT thin films was based on the selective nucleation and growth between the template layer and the perovskite seed, resulting in grain-location controlled PZT thin films. In this work, the effects of artificial temperature gradient on the SNLC of PZT thin films by using a line-heating source were investigated. We used partially nucleated PZT thin films annealed at 680°C for 1 min with average grain size of 6-7 μm. Heat source was located in the front of sample. The preheating temperature was 500°C. It was found that there was difference in the grain growth behavior according to the location of pre-nucleated region. The lateral growth from the pre-nucleated region toward the center of sample was longer than the grown length from the pre-nucleated region toward the edge of the sample. The latter was 10 μm and the former was 5 μ, when the temperature of the heating source was 660°C. It was noticed that grains grew in ellipsoidal shape when there was temperature gradient across the sample. In this work, growth kinetics and the effects of preheating temperature and line heating power on the grain growth of PZT thin films will be discussed in detail.

C4.18
GROWTH OF LEAD BARIUM TITANATE THIN FILMS BY MOCVD: STRUCTURAL AND ELECTRICAL CHARACTERIZATION. S. Hoffmann-Eifert, S. Ritter, and R. Waser[a], IFF/EKM, Forschungszentrum Jülich GmbH, GERMANY; [a]also IWE II, RWTH Aachen University of Technology, GERMANY.

We report on the structural and electrical properties of thin films of the solid solution series $PbTiO_3$ - $BaTiO_3$. The films were grown by means of metal organic chemical vapor deposition in an AIXTRON AIX-200 horizontal reactor equipped with an aerosol-assisted liquid delivery system. The precursor solution is atomized before it is injected into a hot gas stream for vaporization. The metal-organic precursors used were $Pb(thd)_2$, $Ba(thd)_2$*diethylene-triamine, and $Ti(OiPr)_2thd_2$ (thd_2= tetramethylheptodionate $C_{11}H_{19}O_2$) dissolved in diglyme as a single source solution. Oxygen and nitrous oxide were used as process gases. In order to analyze the substrate influence on the growth, texture and stress in the films, we compared films which were grown on platinum coated Si and MgO substrates.
The structural characterization was performed by X-ray diffraction. The film stoichiometry was determined by X-ray fluorescence analysis, using different calibration standards prepared by chemical solution deposition. Additionally performed Rutherford backscattering analysis gave information about the film composition, film thickness and crystal quality. The morphology and surface topology were investigated by scanning electron microscopy and by scanning force microscopy, respectively.
The ferroelectric properties especially the hysteresis behavior are discussed with respect to the Pb/Ba-ratio of the films as well as to the microstructural properties.

C4.19
Transferred to C5.7

C4.20
EFFECT OF ETCH GASES ON BISMUTH LANTHANUM TITANATE THIN FILMS USING INDUCTIVELY COUPLED PLASMA. Chang Jung Kim and Suk Pil Kim.

Bismuth lanthanum titanate ($Bi_{3.25}La_{0.75}Ti_3O_{12}$) ferroelectrics thin film has been expected as a novel material for a ferroelectric random access memory (FRAM) device since it has a large polarization, fatigue free, and crystallized at low temperature compared to $SrBi_2Ta_2O_9$ material. Therefore, we etched BLT thin films for the fabrication of FRAM device. The BLT thin films were etched in Cl_2/Ar, $SiCl_4/Ar$, C_2F_6/Ar and HBr/Ar inductively coupled plasmas

as a function of each gases % in Ar gas. The etch rates increase with gas pressure and coil RF power, and go through a maximum point and then decrease in C_2F_6(10%)/Ar etching gas. Under our conditions, C_2F_6/Ar provided the best etching results such as etched profile, etching residue and etching rate.

C4.21
FABRICATION AND CHARACTERIZATION OF 1T2C-TYPE FERROELECTRIC MEMORY CELL WITH LOCAL INTERCONNECTIONS. Satoru Ogasawara, R&D Association for Future Electron Devices, Yokohama, JAPAN; Hiroshi Ishiwara, Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN.

A 1T2C-type ferroelectric memory cell was fabricated and characterized, in which the effect of depolarization field is expected to be much reduced. The fabricated cell was planar structure with local interconnections between two ferroelectric capacitors on the interlayer-dielectrics and a polysilicon gate of an usual n-type MOSFET with the gate length of 5 μm. The platinum top and bottom electrodes were deposited by sputtering method, and $SrBi_2Ta_2O_9$ (SBT) was formed by liquid source misted chemical deposition or sol-gel method as the ferroelectric film. This structure has such an advantage superior to the stacked gate Pt/SBT/Pt/Ti/SiO_2/Si structure we previously fabricated, as low damage to the MOSFET while the process like an electrode formation and a crystallization annealing. Ferroelectric capacitors had good saturated hysteresis loops with remanent polarization $2P_r$ of 11 $\mu C/cm^2$. And the counterclockwise hysteresis loops were observed in the drain current vs. gate voltage characteristics of an MFMOS-FET. These results indicate that ferroelectric capacitors and MOS transistor were successfully fabricated. After the data were written in the cell, the read-out operations were investigated. Nonvolatile memory operation was confirmed, and the on/off ratio of output current of 4-order-of magnitude was attained in the read-out operation at 1.5V. It was about one-order-of magnitude larger than that of the stacked gate structure, and it was found that for realizing the large operation margin it is effective to reduce the process damage by separating the ferroelectric capacitors from the gate of the MOSFET. This work was performed under the auspices of R&D Projects in Cooperation with Academic Institutions (Next-generation Ferroelectric Memories), supported by NEDO (New Energy and Industrial Technology Development Organization in Japan) and managed by FED (R&D Association for Future Electron Devices).

C4.22
BIAXIAL TEXTURE DEVELOPMENT OF MgO FILMS DURING GROWTH ON AMORPHOUS SUBSTRATES BY ION BEAM-ASSISTED DEPOSITION. Rhett Brewer and Harry A. Atwater, California Institute of Technology, Dept of Applied Physics, Pasadena, CA.

Ferroelectric-based actuator devices require development of a highly textured or single-crystal ferroelectric thin film fabrication process compatible with silicon integrated circuit fabrication technology. Biaxially textured MgO films in which both the crystallographic out-of-plane texture and in-plane orientation are highly controlled can be used as templates for epitaxy of pseudo-single crystalline oxides such as YBCO. Previous work has established that high-quality, biaxially textured MgO can be grown on amorphous Si_3N_4 using ion beam-assisted deposition (IBAD)[1]. We describe a ferroelectric-silicon integration strategy using a thin layer of IBAD MgO as a heteroepitaxial template for $BaTiO_3$ or $PbTiO_3$. This strategy eliminates stringent single crystal substrate requirements (e.g. high quality Si (001) surfaces) and permits heteroepitaxy of ferroelectrics on top of amorphous insulators during backend processing, after all integrated circuits have been fabricated. We report strategies to optimize the biaxial texture of IBAD MgO using electron beam evaporation of MgO onto amorphous Si_3N_4 with a simultaneous Ar^+ ion bombardment at 45° incidence angle. *In situ* RHEED measurements[2,3] of biaxial texture, grain size, and surface roughness were made during film growth, while varying the Ar^+ energy from 300 to 1000 eV, the substrate temperature from 25° to 600°C, and the ion/MgO molecule flux ratio from 0.2 to 0.6. The effects of ion bombardment energy, ion/MgO molecule flux ratio, temperature, and nucleation density on biaxial texture development will be explored and the IBAD biaxial texturing mechanisms will be discussed. We will also discuss the quality of heteroepitaxial $BaTiO_3$ grown on biaxially-textured IBAD MgO. 1. C.P. Wang, K.B. Do, M.R. Beasley, T.H. Geballe, and R.H. Hammond, Appl. Phys. Lett. **71**, 2955 (1997). 2. R.T. Brewer, J.W. Hartman, and H.A. Atwater, Mat. Res. Soc. Symp. Proc. **585**, 75 (2000). 3. R.T. Brewer, J.W. Hartman, J.R. Groves, P.N. Arendt, P.C. Yashar, H.A. Atwater, Appl. Surf. Scie. **175 – 176**, 691 (2001).

C4.23
Abstract Withdrawn.

C4.24
IMPROVEMENT OF SURFACE CRYSTALLINE QULAITY OF AN EPITAXIAL (100) ZrN FILM AS A BOTTOM ELECTRODE FOR FERROELECTRIC CAPACITOR. Sadayoshi Horii[a], Takeo Toda, Susumu Horita, Japan Advanced Inst of Science and Technology, School of Materials Science, Ishikawa, JAPAN; [a]Delegated from Kokusai Electric Co., Ltd, Toyama, JAPAN.

In order to fabricate 1T-1C ferroelectric memory with an epitaxial ferroelectric film, the epitaxial bottom electrode must be prepared on Si directly. As a bottom electrode, we have proposed the double layer structure of Ir on barrier metal ZrN for PZT, using reactive sputtering. However, we have two problems on fabrication of the epitaxial Ir film on the epitaxial ZrN film. One is easy oxidation of the ZrN film surface due to exposure to the air after its preparation. The other is generation of twin crystal in the ZrN film probably because of the film stress due to the difference of the deposition temperature, 850°C, form the room one. The former problem can be solved as follows; The exposed ZrN film was dipped into the 0.5% buffered HF solution to remove the surface oxide layer for less than 30 seconds and thereafter it was dipped into the hydrazine (N_2H_4) monohydrate solution immediately for suppressing surface oxidation. The X-ray photoelectron spectroscopy (XPS) spectrum of the treated ZrN film showed decreasing and increasing of the oxide and nitride signals of Zr, respectively. Also, we observed a clear RHEED pattern indicating the epitaxial growth film from the treated film, but a hallo pattern from the non-treated film. Although the generation of the twin structure can be suppressed by decreasing the deposition temperature less than 700°C, the crystalline quality become much poorer than that of high temperature. For example, the FWHM of XRD rocking curve at ZrN (200) of the 100-nm ZrN film deposited at 850°C is 1.7° but that at 600°C is about 3.8°. The film quality can be improved by changing the deposition temperature from 850° for 10 min to 600°C for 30 min during the deposition. The FWHM of the ZrN film prepared by this method was improved to be 2.3°.

C4.25
CHARACTERIZATION OF (Ba,Sr)RuO_3 FILMS DEPOSITED BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION. Duck-Kyun Choi, Joong-Seo Kang, Young-Bae Kim, Duck-Hwa Hong and Hyun-Chul Kim, Department of Ceramic Engineering, Hanyang University, Seoul, KOREA.

(Ba,Sr)RuO_3 [BSR] film was adopted as an electrode to improve the electrical properties of (Ba,Sr)TiO_3 [BST] film by minimizing the interfacial layer formation and by an epitaxial growth since BSR film has a chemical and structural similarity to BST. In this study, BSR thin films were deposited on a 4-inch p-type Si wafer by metal organic chemical vapor deposition(MOCVD) for the practical device application using new single cocktail source. Source materials for MOCVD BSR film were Ba(methd)2 [bis(methoxyethoxytetramethyl-heptanedionate)], Sr(methd)2 and Ru(methd)3 and these were dissolved in n-butylacetate. The source-feeding rate was precisely controlled by liquid mass flow controller(LMFC). In order to identify the crystalline structure of deposited film, X-ray diffraction analysis was carried out and the compositions of the films were measured by an X-ray fluorescence. As-deposited BSR films resulted in (110)-oriented structure and demonstrated good uniformity and adherence. The phase formation was strongly affected by source flow rate. As oxygen flow rate increased, the composition ratio of Ru/(Ba Sr) in film decreased while Ba/(Ba Sr) was almost insensitive to the oxygen flow rate. Rutherford backscattering spectroscopy revealed that as-deposited BSR films contain carbon impurities as expected. Rapid thermal annealing of the BSR films under oxygen ambient decreased the carbon impurity concentration and improved the crystalline quality, resistivity and surface roughness.

SESSION C5: INTEGRATION AND ELECTRODES
Chairs: Dirk J. Wouters and Paul C. McIntyre
Tuesday Morning, November 27, 2001
Room 210 (Hynes)

8:30 AM *C5.1
INTEGRATION ISSUES OF HIGH DENSITY EMBEDDED FERROELECTRIC MEMORY. Scott R. Summerfelt, Ted S. Moise, K. Udayakumar, Tomoyuki Sakoda, Sanjeev Aggarwal, Kelly Taylor, Scott Martin, Francis Celii, J.R. Rodriguez, and Trace Hurd, Si Technology Development, Texas Instruments Inc., Dallas, TX; Stephen R. Gilbert, David Taylor and Jun Amano, Agilent Laboratories, Agilent Technologies, Palo Alto, CA.

Embedded ferroelectric memory (eFRAM) has the potential to be the "universal" embedded memory for system-on-chip devices if eFRAM can demonstrate nearly infinite reads (~1E14) and a cell area comparable to embedded DRAM. This presentation will focus on the primary integration issues. In summary, the ferroelectric capacitors

needs to be added with near zero disruption to logic process using a small eFRAM cell and hence capacitor size. The basic concept to achieve this goal is to insert a FRAM module between contacts and metal one composed of ferroelectric capacitors and an additional via layer. The principal integration approaches necessary to achieve these goals are the following. Capacitors directly over W plugs for small cell size. MOCVD PZT can achieve thin films (<70nm) with low operating voltage (<1.2V) at a low thermal budget (<600°C). Oxide electrodes combined with appropriate PZT allow near infinite reads. One mask capacitor etch at high temperatures achieves steep sidewall profiles (~82 degress) and small capacitor size (<0.2um^2) with narrow spaces (0.18um). Diffusion barriers (hydrogen and Pb) are necessary to integrate ferroelectric into logic process with minimal degradation of ferroelectric or logic. Using this approach submicron IrOx/ MOCVD PZT/ IrOx capacitors were fabricated on W plugs with a maximum process temperature of 600°C and integrated with an SiO_2 interlayer dielectric and Cu metallization. The electrical properties of these submicron (<0.2 um^2) capacitors will be discussed in detail.

9:00 AM C5.2
PROPERTIES OF TaSiN DIFFUSION BARRIER FOR HIGH DENSITY MEMORY DEVICES. Franck Letendu, Marie Christine Hugon, Bernard Agius, LPGP, Universite Paris Sud, Orsay, FRANCE; Ian Vickridge, GPS, Université Paris 6 et 7, FRANCE; Angus Kingon, Dept. of MS&E, North Carolina University, Raleigh, NC.

Preparation of high dielectric constant perovskite materials for high density memory devices requires high temperature (550-750°C) processing in oxidising environments, providing strong limitations on the choice of electrode materials. To minimise interdiffusion and oxidation reactions, a diffusion barrier is needed below the electrode material (Pt, IrO_2, RuO_2). Amorphous ternary systems such as TaSiN films are more effective barriers than the crystalline $Ti_{1-x}Al_xN$ barriers. In this work, TaSiN films with thickness ranging from 80 to 120 nm have been deposited by reactive rf magnetron sputtering from a $TaSi_2$ target in N_2-Ar plasma. By investigating the effect of power density, N_2 to Ar flow ratio and pressure on the properties of TaSiN (mainly morphology, sheet resistance, electrical resistivity and elemental composition by RBS and NRA), optimum parameters have been identified for the growth of high quality film. Films deposited at 0.5Pa and 1Pa exhibit better properties for technological application (resistivity, roughness) than those made at 3Pa. We observe that high deposition pressures and power densities are correlated with increased oxygen contamination in the films. The reason for this is under investigation. The thermal stability of TaSiN thin films, as an oxygen diffusion barrier, has been investigated under typical conditions for crystallisation of perovskyte dielectrics. Oxygen movement during RTA was studied via stable isotopic tracing and profiling with the narrow resonance at 151 keV in $^{18}O(p,\alpha)^{15}N$ (fwhm=100eV). Power density and pressure have a crucial effect on oxidation resistance: films made at low pressure (0.5Pa) and a power density of 2.65W/cm^2 present high oxidation resistance. Initial XPS measurements subject the presence of SiO_2. Whatever the annealing temperature, TaSiN thin films seem to be more stable than TiAlN ones.

9:15 AM C5.3
STUDY ON OXIDATION RESISTANCE OF TiAiN/W-PLUG CONTACTS FOR HIGH-K CAPACITORS. Yasutoshi Okuno, Akihiko Tsuzumitani, Hisashi Ogawa, Matsushita Electric Ind Co, Ltd, Semiconductor Company, ULSI Process Tech Dev Ctr, Kyoto, JAPAN; Akie Yutani, Tomonori Okudaira, Keiichiro Kashihara, Yoshikazu Tsunemine, Mitsubishi Electric Corp, ULSI Develop Ctr, Hyogo, JAPAN.

TiAlN is one of the candidates for the oxidation barrier material for High-k capacitors, and its oxidation has been studied mostly with the sheet resistance change of the planar films after oxidation and a few with on the Poly-Si plug structure. However, it is very important to study the oxidation resistance of TiAlN with a metal plug such as W to establish the process integration of the embedded memory with high-k capacitors. The metal plug on silicide contact has been required to simplify the complex merged processes for embedded memory to the reasonable level. We had fabricated fully integrated test structure having STI isolation, I/I, Cobalt siliside contact and CVD-W plug covered with stack of TiAlN barrier metal layer and Pt bottom electrode layer. TiAlN barrier layer thickness, oxidation temperature and via-size dependence had been evaluated. After forming the W-plug with CMP, TiAlN barrier layer was deposited by reactive DC-sputtering with TiAl cast target in the thickness range of 20 nm to 50 nm. Then Pt bottom electrode was also deposited by DC-sputtering prior to the pattern and dry-etch process of the stack. The Pt bottom electrode was also used for the probing pads. Oxidation resistance evaluated the annealing temperature range from 400 degC to 600 degC. As a result of electrical measurement of Kelvin-patterns and contact-chain patterns, it was found that the plug resistance of the 0.24 um diameter via after oxidation anneal was several kiro-ohm/node that was an acceptable value for the device design. No structural degradation was observed with cross-sectional SEM up to 600 degC anneal even the structure with the 10 nm-thick TiAlN barrier layer. We have successfully demonstrated the oxidation-resistant metal plug with TiAlN as a barrier metal.

9:30 AM C5.4
INVESTIGATION OF ALUMINA BARRIER LAYER FOR FeRAM PREPARED BY RF MAGNETRON SPUTTERING. Takehito Jimbo, Yuusuke Miyaguchi, Shin Kikuchi, Koukou Suu and Michio Ishikawa, ULVAC Inc., Institute for Semiconductor Technologies, Shizuoka, JAPAN.

Alumina (Al_2O_3) thin films expected to be a hydrogen barrier layer for FeRAM for its high chemical stability were prepared by rf magnetron sputtering using a ceramic target and then investigated. CERAUS ZX-1000 PVD (ULVAC Inc.) was used as an rf sputtering appratus. RF power, sputtering pressure, oxygen partial pressure, substrate temperature and so on were varied as experimental conditions. Fundamental properties of alumina thin films such as refractive index were primarily investigated. Ferroelectric capacitors coated by alumina films were annealed in 3% H_2 forming gas and characterized in term of refractive index and electrical properties. Refractive index of 100-nm-thick alumina film deposited on Si substrate under the sputtering conditions as RF power of 2.0 kW, sputtering pressure of 1.0 Pa and substrate temperature of 500°C was around 1.66 for example, and the refractive index decreasing was as substrate temperature decreased and oxygen partial pressure increased. This result can be considered representing that the amount of oxygen existing in alumina was increasing, which is satisfying the requirement of sufficiently oxidized alumina which is supposed to be one of necessary conditions for alumina thin film as a hydrogen barrier layer. The results of electrical properties of alumina coated PZT capacitor before and after forming gas anneal will be presented and discussed in the meeting.

10:15 AM *C5.5
FeRAM DEVICE TECHNOLOGIES FULLY COMPATIBLE ADVANCED CMOS PROCESS. T. Tashiro and H. Toyoshima, ULSI Device Development Division, NEC Corporation, Sagamihara, Kanagawa, JAPAN.

Recent progress in FeRAM device technologies that are fully compatible with advanced logic CMOS and reliability results, such as fatigue, imprint and retention for FeRAM, are described. Embedding FeRAM memory cells in advanced logic CMOS will face some serious problems that are, for example, contamination of LSI wiring lines with ferroelectric and electrode materials and deterioration of ferroelectric capacitor properties by exposure of hydrogen-containing atmosphere during multilevel metallization process. To solve these problems, we have developed a ferroelectric capacitor of a CMVP (capacitor-on-Metal/Via-stacked-Plug) memory cell that is fabricated after the completion of multilevel metallization. A 0.35-um 2T/2C FeRAM macro based on the CMVP memory cell has been fabricated for smart card applications. The chip features a wide operation voltage range from 2.7V to 5.5V, high write/read endurance of more than 1E8 cycles, low consumption current of 0.3mA, and a flexible memory size from 32-Kbit to 128-Kbit. The CMVP technology also enables a 0.25-um ASIC SRAM 512-byte macro to be nonvolatile (NV-SRAM: nonvolatile SRAM). The NV-SRAM cell consists of a six-transistor SRAM(6T-SRAM) cell and two stacked back-up ferroelectric capacitors, and also achieves virtually negligible read/write fatigue using a Vdd/2 plate line architecture. This NV-SRAM cell with forth-metal layers is the same size of the 6T-SRAM cell. We finally discuss an overall scenario to embed a 2T/2C FeRAM and an NV-SRAM in a 0.25-um or even further miniaturized CMOS and show that ferroelectric -based-memories promise to open up new application fields.

10:45 AM C5.6
THE ROLE OF CARBONYLCHEMISTRY TO PATTERN PLATINUM ELECTRODES. Stefan Schneider, Hermann Kohlstedt, and Rainer Waser, IFF, Forschungszentrum Juelich, Juelich, GERMANY.

Noble metals like Platinum or Irdium are used as electrode materials in DRAM or FRAM devices. Their etch process is a challenge as conventional, sputter driven etch processes, either yield in redeposition problems (fences) or in a severe sloping (CD loss) and are not acceptable for high density integration architectures. The high temperature etch regime offers a solution by increasing the chemical etch component and thus the volatility of the etch products. As previously reported, the Platinum etch rate increases exponentially for a Chlorine etch process with increasing wafer temperature. In this study we investigate the particular role of Carbonmonoxide in a Cl_2/CO etch process. We observe Carbonmonixide additions to a Chlorine process chemistry to boost the chemical component of the

Platinum etch rate very significantly, exceeding the effects in the Chlorine only process regime by far. Additionally we compare these results with a Cl_2/O_2 process chemistry, which shows to be not that beneficial. To better understand the etch process we use an energy dispersive quadrupole mass spectrometer for in situ monitoring, attached to the chamber at two different locations. We are able to positioned the probe orifice at the place of the wafer electrode, to record ion energy and ion mass spectra of species impinging on the wafer plane. A second off axis position allows for etch product monitoring. We show the results of the process chemistry variation on Platinum wafers with a SiO_2 hardmask having a minimum feature size of 0.15 nm.

11:00 AM C5.7
THERMAL STABILITY AND ELECTRICAL PROPERTY OF RhO_2 THIN FILMS. Yoshio Abe, Kiyohiko Kato, Midori Kawamura and Katsutaka Sasaki, Kitami Institute of Technology, Dept of Materials Science, Kitami, JAPAN.

The family of conducting metal oxides with a rutile structure, such as RuO_2 and IrO_2, has attracted attention as capacitor electrode materials for dynamic random access memories (DRAMs) and ferroelectric RAMs (FeRAMs). RhO_2 belongs to the family and was reported to exhibit metallic behavior; however, thin films of RhO_2 have scarcely been investigated. In this study RhO_2 thin films were prepared on SiO_2/Si substrates by sputtering a Rh target in oxygen atmosphere. In order to clarify the applicability of the RhO_2 films to the capacitor electrodes, their thermal stability was studied by heat treatment at 200-800°C in oxygen partial pressures from 0.5 mTorr to 1 atm for 1 hour. The RhO_2 films were found to be stable up to 700°C and decomposed to Rh_2O_3 at 750°C in an oxygen pressure of 1 atm. However, the RhO_2 films began decomposition at 500°C in an oxygen partial pressure of 0.5 mTorr. Metallic conduction properties with a minimum resistivity of 80 $\mu\Omega$cm was obtained for the RhO_2 films after heat treatment at 600-700°C in oxygen atmosphere of 1 atm. The Rh_2O_3 films formed by the decomposition of RhO_2 indicated semiconducting property. Though the decomposition temperatures of the RhO_2 films are a little lower than those of RuO_2 and IrO_2 films, it seems possible to use the RhO_2 films as capacitor electrodes of DRAMs and FeRAMs if oxygen partial pressure and heat treatment temperature are controlled appropriately.

11:15 AM C5.8
METAL ORGANIC CHEMICAL VAPOR DEPOSITED PLATINUM, RUTHENIUM AND RUTHENIUM DIOXIDE ELECTRODES FOR OXIDE APPLICATIONS. P.K. Baumann[a], K. Frohlich[b], P. Doppelt[c], V. Cambel[b], D. Machajdik[b], F. Schienle[a], M. Schumacher[a], J. Lindner[a], G. Strauch[a], H. Juergensen[a]; [a]AIXTRON AG, Aachen, GERMANY; [b]Slovak Academy of Sciences, Bratislava, SLOVAK REPUBLIC; [c]ESPCI-CNRS University, Paris, FRANCE.

Platinum (Pt), ruthenium (Ru), and ruthenium dioxide (RuO_2) are possible candidates as electrodes for high permittivity and ferroelectric oxides. Increasing levels of device integration require good conformal deposition, decreased defect density, high deposition rates, precise large area uniformity control, and low cost of ownership. Metal organic vapor deposition (MOCVD) is the method of choice to achieve these requirements. In this study Pt, Ru and RuO_2 thin film electrodes have been deposited by MOCVD and their structural and electrical properties have been characterized. These electrodes have been developed to facilitate the integration of electrodes and oxide layers thru an all MOCVD process. A variety of deposition conditions was used to deposit high purity platinum films with near bulk resistivities (11 $\mu\Omega$ cm). The temperature dependent electrical conductivity of the Ru and RuO_2 films was metallic type. Room temperature resistivities as low as 18 and 30 $\mu\Omega$ cm were determined for Ru and RuO_2, respectively. The Pt, Ru and RuO_2 films were found to be continuous and smooth and exhibited excellent adhesion properties on the underlying substrates. Typical thicknesses of 50 to 100 nm have been determined. Conformal deposition on structured substrates has been achieved. Furthermore barium strontium titanate (BST) capacitor structures based on the Pt, Ru and RuO_2 electrodes have been fabricated and characterized.

11:30 AM C5.9
Abstract Withdrawn.

11:45 AM C5.10
Ru FILM STRIPPING AND CLEANING TECHNOLOGY ON THE BEVEL AND BACKSIDE OF WAFERS. Motoyuki Sato, Hiroshi Tomita and Soichi Nadahara, Toshiba Corporation Semiconductor Company Process & Manufacturing Center, Kanagawa, JAPAN.

Ru has been required for capacitor electrode of next-generation DRAM with MIM capacitors using Ta_2O_5, $BaSrTiO_3$ etc. Ru contamination may affect on the device characteristic. In terms of that, batch type CVD is more serious than single slice type. So, Ru cleaning technology on the bevel and backside of wafers is seriously required. At Ru-CVD process, Oxygen gases are supplied with organic metal gas, because they help decomposition of MO gases. Those Oxygen atoms are enclosed into CVD-Ru films on the bevel and backside of wafers. The ratio of Oxygen was about 17% in them, though CVD Ru films on the Ru seed layer (front side of wafers) hardly contains Oxygen. Ammonium Cerium Nitrate (ACN) solution is known as Ru etchant. But etching rates of Ru films depend on the Oxygen ratio in them. The Etching rate of Ru on backside is below 0.5nm/min. with 20% ACN at RT, that was 1/600 smaller than that of pure Ru. High temperature ACN is effective for such CVD-Ru film etching. Etching rate of that was 30nm/min with 20% ACN at 80°C. In the etching reaction, Ru changes RuO_4 due to high oxidation-reduction potential of Ce(IV) ions. The state of RuO_4 is gas but it easily decomposes to RuO_2 in the solution. The states of RuO_2 is solid below 80°C. And RuO_2 particles stick to wafers. Etchant of RuO_2 isn't well known. Roll sponge cleaning using alkaline water was found to be effective to remove those RuO_2 particles. However, 3.5E11 atoms/cm^2 of Ru atoms still remains on the wafer after roll cleaning. They are diffusion atoms into wafers in CVD process. After slight etching of ground layer, Ru contamination level was reduced to 3.3E9 atoms/cm^2.

SESSION C6/O5: JOINT SESSION
EPITAXIAL FERROELECTRIC FILMS
Chairs: Darrell G. Schlom and Stephen K. Streiffer
Tuesday Afternoon, November 27, 2001
Room 210 (Hynes)

1:30 PM C6.1/O5.1
FERROELECTRIC DOMAIN STRUCTURE OF $SrBi_2Nb_2O_9$ AND $SrBi_2Ta_2O_9$ EPITAXIAL FILMS. M.A. Zurbuchen, G. Asayama, J. Lettieri, Y. Jia, L.Q. Chen, and D.G. Schlom, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA; S.K. Streiffer, Materials Science Division, Argonne National Laboratory, IL; X.Q. Pan, Dept of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI.

Using two different techniques, dark field transmission electron microscopy (TEM) and FFT analysis of high-resolution TEM images, we have for the first time analyzed the ferroelectric domain structure of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ epitaxial thin films, grown on both (001) and (111) $SrTiO_3$ substrates. Ferroelectric domains are non-laminar, with an average diameter of 50 nm. Unlike the domain walls in many other ferroelectrics, the domain walls in $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ are often highly curved, particularly in $SrBi_2Nb_2O_9$. This is believed to arise due their extremely low ferroelastic distortion; $SrBi_2Nb_2O_9$ has a ferroelastic distortion three orders of magnitude less than that of PZT. This results in a much weaker role of preferred crystallographic orientation for domain walls. A brief overview of the techniques, which can be applied in a straightforward manner to many types of low-distortion ferroelectric films, will also be given. The resolution using the dark field TEM technique is anisotropic and is limited by drift and specimen thickness; however, with the high-resolution TEM technique it is possible to resolve ferroelectric domain structure detail of 2.5 nm.

1:45 PM C6.2/O5.2
PREPARATION AND CHARACTERIZATION OF a- AND b-AXES-ORIENTED EPITAXIALLY GROWN $Bi_4Ti_3O_{12}$-BASED THIN FILMS WITH LONG-RANGE LATTICE MATCHING. Takayuki Watanabe and Hiroshi Funakubo, Dept of Innovative and Engineered Materials, Tokyo Institute of Technology, Kanagawa, JAPAN; Keisuke Saito, Application Laboratory, Analytical Department, Philips Japan, Ltd., Kanagawa, JAPAN.

Thin films of bismuth layer-structured ferroelectrics (BLSFs) have been investigated for a ferroelectric random access memory (FeRAM) application because of its good ferroelectric properties, especially high fatigue endurance. We have systematically investigated the dependence of the ferroelectricity on the film orientation and the m-number using various kinds of epitaxially grown BLSFs films. However, the characterization of the ferroelectricity along [100] direction, polar axis, is limited only for bulk single crystals. Especially there is no reports on the characterization of epitaxially grown films. This is due to the difficulty of the long range lattice matching between the long c-axis of BLSFs and the substrates. In the present study, we focused on an epitaxially grown conductive oxide films with rutile-type structure as bottom electrodes for the preparation of a- and b-axes-oriented BLSFs. We prepared Nd- and V- substituted $Bi_4Ti_3O_{12}$ [$(Bi,Nd)_4(Ti,V)_3O_{12}$] film with c-axis lattice constant of approximately 3.3nm. a- and b-axes-oriented epitaxial $(Bi,Nd)_4(Ti,V)_3O_{12}$ films were successfully deposited on $(101)RuO_2//(012)Al_2O_3$ and $(101)IrO_2//(012)Al_2O_3$ substrates at 600°C by metalorganic chemical vapor deposition. By X-ray pole

figure measurement with a fixed 2Theta angle corresponding to (117)BNTV peak, fourfold dense poles located around psi angle = 56° indicating the epitaxial growth of a- and b-axes-oriented BNTV films on each substrates;
$(100)(010)(Bi,Nd)_4(Ti,V)_3O_{12}//(101)RuO_2//(012)Al_2O_3$ and
$(100)(010)(Bi,Nd)_4(Ti,V)_3O_{12}//(101)IrO_2//(012)Al_2O_3$. Finally, a large remanent polarization above $20\mu C/cm^2$ was observed.

2:00 PM C6.3/O5.3
GROWTH AND CHARACTERIZATION OF FERROELECTRIC La-SUBSTITUTED $Bi_4Ti_3O_{12}$ EPITAXIAL THIN FILMS BY PULSED LASER DEPOSITION. Ho Nyung Lee, Dmitri N. Zakharov, and Dietrich Hesse, Max-Planck-Institut für Mikrostrukturphysik, Halle/Saale, GERMANY.

La-substituted $Bi_4Ti_3O_{12}$ (BLT) thin films have been received much attention due to their good ferroelectric properties and high fatigue endurance as well. Like $SrBi_2Ta_2O_9$ (SBT), BLT has an anisotropic crystallographic structure and anisotropic ferroelectric properties. There are several reports on either polycrystalline or randomly oriented BLT films. However, few works on the epitaxial growth of $Bi_4Ti_3O_{12}$ films are reported to date and these are mostly concerned only with the growth of *c*-axis-oriented films. Ferroelectric epitaxial BLT thin films having (001), (118), and (104) orientations (in orthorhombic indices) have been grown by pulsed laser deposition on conducting $SrRuO_3$-covered (001)-, (011)-, and (111)-oriented $SrTiO_3$ or Nb-doped $SrTiO_3$ substrates, and on buffered Si substrates. Due to the crystallographic anisotropy of BLT, epitaxial films of different crystallographic orientations display different properties along the direction normal to the film plane. This anisotropy is being investigated by x-ray diffraction, transmission electron microscopy, and electrical measurements, using epitaxially grown films of (001), (118), and (104) orientations. Heteroepitaxial films of BLT(118)/ $SrRuO_3$(110)/YSZ(100) and BLT(104)/$SrRuO_3$(111)/MgO(111)/ YSZ(100) are grown *in situ* on Si(100) substrates. Investigations of crystallographic orientation relationships and structural and electrical properties will be presented. The results will be compared to those obtained from non-doped $Bi_4Ti_3O_{12}$ epitaxial thin films having the same orientations, to characterize the effect of La substitution on the ferroelectric properties.

2:15 PM *C6.4/O5.4
SURFACE, THICKNESS, AND STRAIN EFFECTS ON STRUCTURAL INSTABILITIES IN EPITAXIAL $PbTiO_3$ FILMS. Brian Stephenson, Stephen Streiffer, Jeffrey Eastman, Orlando Auciello, Anneli Munkholm, Materials Science Div, Argonne National Laboratory, Argonne, IL; Carol Thompson, Marian Aanerud, Dept of Physics, Northern Illinois University, DeKalb, IL.

As in many perovskites, competing ferroelectric and antiferrodistortive instabilities are present in $PbTiO_3$. In the bulk, the ferroelectric instability is stronger. However, surface, strain, and film thickness effects can either augment or suppress such structural instabilities and the associated property enhancements. We present results from *in situ* x-ray scattering studies during and after organo-metallic vapor phase epitaxy of $PbTiO_3$ on $SrTiO_3$, carried out at the Advanced Photon Source. We find that, under an equilibrium vapor pressure of PbO, the $PbTiO_3$ (001) surface reconstructs to a $c(2\times 2)$ structure consisting of a single antiferrodistortive layer with oxygen cages counter-rotated 10 degrees about the Ti ions. We have also investigated the ferroelectric phase transition in thin (< 400 Å), coherently-strained films. We find that not only is T_C elevated above the bulk value, as predicted, but in addition the ferroelectric phase forms as 180-degree stripe domains in these films, with a thickness-dependent T_C. This results from a fascinating competition between strain, polarization, and electric field that determines the minimum free energy configuration. This work is supported by the State of Illinois under HECA, and the U.S. Department of Energy, BES-DMS under contract W-31-109-ENG-38.

3:15 PM *C6.5/O5.5
SIZE EFFECTS ON POLARIZATION IN EPITAXIAL FERROELECTRIC THIN FILMS. H. Kohlstedt, N.A. Pertsev, R. Waser, Forschungszentrum Jülich, Institut für Festkörperforschung, Jülich, GERMANY; A.G. Zembilgotov, State Technical Univ of St. Petersburg, St. Petersburg, RUSSIA.

Extrinsic and intrinsic size effects on the spontaneous polarization of epitaxial single-domain ferroelectric films are discussed. The former includes the dead-layer effect and the misfit-strain one, while the latter is due to spatial correlations of the ferroelectric polarization. The competition between different effects may lead to a nonmonotonic scaling of polarization with the film thickness. The dead-layer effect is known to be associated with the presence of nonferroelectric subsurface layers. It is supposed that in perovskite ferroelectrics the depolarizing-field effect on the static properties may be neglected due to their finite conductivity. Experimental data suggest that the structure of subsurface layers depends on the electrode material. The use of electrodes with a perovskite structure is expected to reduce the dead-layer effect. The extrinsic size effect is also attributed to the thickness dependence of the film in-plane lattice strain S. This dependence appears via the strain relaxation caused by the generation of misfit dislocations. A nonlinear thermodynamic theory, which allows for the mechanical film/substrate interaction, is used to describe the variation of the film polarization with the misfit strain S in the heterostructure. The intrinsic effect of the film surfaces is taken into account via the concept of extrapolation length L. Thermodynamic calculations are performed for lead titanate and barium titanate (BTO) films grown on compressive substrates ($S < 0$). The negative intrinsic size effect ($L > 0$) is found to be reduced in strained films. It is shown that, well below the transition temperature, the film mean polarization may be larger than the bulk polarization even in an ultrathin epitaxial layer. This increase is caused by the in-plane compression the film lattice, which overlaps the negative surface effect. The theory explains the increase of polarization in very thin (10-20 nm) BTO films grown on strontium titanate.

3:45 PM C6.6/O5.6
NANOSCALE CONTROL AND SWITCHING DYNAMICS IN EPITAXIAL $Pb(Zr_{0.2}Ti_{0.8})O_3$ THIN FILMS. P. Paruch, T. Tybell and J.-M. Triscone, University of Geneva, DPMC, Geneva, SWITZERLAND.

Atomic force microscopy (AFM) was used to precisely manipulate and study individual ferroelectric domains in high quality $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films. Nanoscale control of domain size was achieved by varying the strength and duration of the voltage pulses used to polarize the material, permitting the creation of sub-20nm width lines and ultra-high density arrays reaching ~30 Gbit/cm^2. The domains were individually accessible, fully reversible, and all, including those written with ~100ns pulses, remained completely stable for the 7-day duration of the experiment. Understanding the relation between domain size and writing parameters, and the resulting local control, are potentially important for applications such as random access ferroelectric memories and ultra-high density storage. The AFM approach developed also allowed us to investigate the fundamental physics of domain interactions and switching behaviour in ferroelectrics. For sub ~20μs writing times, domain size was observed to saturate at ~40nm diameter, limited, we believe, by the size of the AFM tip itself. For longer writing times, domain size was found to depend linearly upon the writing voltage and logarithmically upon the writing time. This indicates a field activated domain growth mechanism, via nucleation-assisted domain wall motion. The activation field increases with decreasing film thickness. For the thinnest films investigated, 200Å, the value is ~200 times larger than the experimentally measured coercive field in thick films. P. Paruch, T. Tybell, J.-M Triscone, to appear in Appl. Phys. Lett. July 23, 2001. "Nanoscale control of ferroelectric polarization and domain size in epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films"; T. Tybell, C.H. Ahn, J.-M. Triscone, Appl. Phys. Lett. 75, 856 (1999). "Ferroelectricity in thin perovskite films"; T. Tybell, C.H. Ahn, J.-M. Triscone, Appl. Phys. Lett 72, 1454 (1998). "Control and imaging of ferroelectric domains over large areas with nanometer resolution in atomically smooth epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films".

4:00 PM C6.7/O5.7
FUNCTIONAL BEHAVIOUR OF THIN FILM DIELECTRIC SUPERLATTICES. J.M. Gregg, M.H. Corbett, D. O'Neill, G. Catalan, R.M. Bowman, Queens University Belfast, Department of Pure and Applied Physics, Belfast, N. Ireland, UNITED KINGDOM.

Pulsed laser deposition has been used to fabricate thin-film capacitor structures in which the dielectric layer is a superlattice. The properties of two superlattice systems were investigated as a function of superlattice wavelength (λ) - one based on barium strontium titanate and the other on lead-based relaxor electroceramics. In both systems the dielectric constant was significantly enhanced at stacking wavelengths of a few unit cells. However, the dielectric enhancement seen in the barium strontium titanate superlattices was found to be due to Maxwell-Wagner effects, whereas in the relaxor superlattices Maxwell-Wagner behaviour was not evident; rather, in relaxors, the dielectric enhancement was associated with the onset of polar coupling around λ - 10nm.

4:15 PM C6.8/O5.8
STRUCTURAL AND FERROELECTRIC PROPERTIES OF $BaTiO_3$ AND $Ba_xSr_{1-x}TiO_3$ THIN FILMS. J. Schubert, O. Trithaveesak, Ch. Buchal, Institut für Schichten und Grenzflächen, Forschungszentrum Jülich GmbH, Jülich, GERMANY; J. Rodríguez Contreras, K. Szot, H. Kohlstedt, Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, Jülich, GERMANY.

The ferroelectric properties of $BaTiO_3$ and $Ba_xSr_{1-x}TiO_3$ thin films are of current interest for future electronic devices. We have prepared

epitaxial $BaTiO_3$ (BTO) and $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films using pulsed laser deposition. Films of thicknesses between 10 nm and 200 nm were grown on epitaxial $SrRuO_3$ (SRO) films on $SrTiO_3(100)$ substrates (STO) or directly on STO. The SRO was prepared ex-situ by high-pressure on-axis sputtering. The structure of the films was characterized by X-ray diffraction, Rutherford backscattering spectrometry/channeling and atomic force microscopy (AFM) measurements. X-ray diffraction indicates that the BTO and BST thin films grow c-axis oriented on STO and on SRO/STO. The c-axis is elongated in the thinner films. A small mosaicity of $\Delta\omega<0.2^\circ$ is observed. Minimum yield values of less than 2% are typical for BST thin films down to a thickness of 10 nm. AFM measurements reveal very smooth surfaces of order 0.3 nm RMS roughness for a 60 nm thick BST-film on STO as well as on SRO/STO. Pt/BST/SRO and SRO/BTO/SRO trilayers were patterned to capacitors. Ferroelectric hysteresis loops have been obtained for BST film thicknesses ranging from 200 nm down to 50 nm and for BTO down to 10 nm. A 12 nm thick BTO film on SRO bottom electrode using SRO top electrode shows a remanent polarization of 26 $\mu C/cm^2$ ($2P_r$) and an coercitive field of 720 kV/cm ($2E_c$) (measured at f=40 kHz). Generally the remanent polarization P_r decreases while the coercitive field E_c increases towards thinner BTO film thickness. 100 nm thick BTO films showed no fatigue for 10^8 cycles.

4:30 PM C6.9/O5.9
IN-SITU GROWTH OF COMPOSITIONALLY GRADED OXIDE FILMS BY PLD. H.M. Christen, H.Y. Zhai, and D.H. Lowndes, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

Rapid sequential deposition of sub-monolayer amounts of different materials is an effective way to form alloys between multiple constituents without requiring a post-annealing process to promote interdiffusion. This technique is readily implemented in pulsed laser deposition, where the firing of the laser can be synchronized with the exchange of multiple targets, and where a small set of targets is sufficient to obtain films with various stoichiometries. Using appropriate automation techniques, any arbitrary composition profile perpendicular to the substrate surface can be obtained, including continuously graded profiles and periodic structures with smooth or abrupt composition variations. Differently graded materials can exhibit interesting of strain profiles that may prove useful for the stabilization of metastable phases. Results will be shown for the case of alloys between dissimilar ferroelectrics as well as between conducting and insulating perovskites. Applications to oxide electronics, mode-discriminating optical waveguides, and buffer layers for the integration of dissimilar materials will be discussed, including the development of compositionally graded buffer layers for the growth of high-Tc superconductors on metal tapes. Research sponsored by the US Department of Energy under contract DE-AC05-00OR22735 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, and by the DOE Office of Energy Efficiency and Renewable Energy, Office of Power Technologies Superconductivity Program.

4:45 PM C6.10/O5.10
PULSED LASER DEPOSITION OF $Ba_{1-x}Sr_xTiO_3$, (x = 0.4) THIN FILMS ON $LiNbO_3$ X-CUT AND Z-CUT SUBSTRATES: STABILIZATION OF THE RHOMBOHEDRAL PHASE AT ROOM TEMPERATURE. Daniel M. Bubb, J.S. Horwitz, S.B. Qadri, R.M. Stroud, W. Chang, S. Kirchoefer, and D.B. Chrisey, Naval Research Laboratory, Washington, DC.

Single phase, epitaxial thin films of $Ba_{1-x}Sr_xTiO_3$, (x = 0.4) have been grown on x-cut and z-cut $LiNbO_3$ substrates by pulsed laser deposition. X-ray diffraction studies show that the films are epitaxial and assume the rhombohedral symmetry of the substrate. To our knowledge, this is the first such observation of rhombohedral $Ba_{1-x}Sr_xTiO_3$ thin films at room temperature. Rutherford Backscattering measurements have been performed on the films and demonstrate that the films have the correct stoichiometry. Transmission electron microscopy (TEM) images of the film/substrate interface will be presented as an aid in understanding the stabilization of the rhombohedral phase. Interdigitated capacitors have been placed on the films and the microwave dielectric response has been extensively investigated. We will compare these results with earlier structure/property studies of cubic/tetragonal $Ba_{1-x}Sr_xTiO_3$ thin films on MgO and $LaAlO_3$ substrates.

SESSION C7: POSTER SESSION
Chairs: Susanne Hoffmann-Eifert and Nava Setter
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hynes)

C7.1
THICKNESS DEPENDENCE OF LONGITUDINAL PIEZOELECTRIC COEFFICIENTS IN SUBMICRON TETRAGONAL $Pb(Zr_{0.3}Ti_{0.7})O_3$. Dong-Joo Kim, Jon-Paul Maria, Angus I. Kingon, Dept of Materials Science and Engineering, Raleigh, NC; Seung-Hyun Kim, Inostek, Seoul, KOREA.

The piezoelectric coefficients of PZT thin films have been measured to be much smaller than those of bulk PZT. It has been proposed that the reduced piezoelectric effect in thin films can be attributed to limited extrinsic contribution and the clamping effect of the substrate. In addition, such effects were reported to be predominant when the film thickness is below 1 μm. However, there is lack of information to explain the decrease of piezoelectric coefficients through the submicron thickness range. It is found that the effective piezoelectric coefficients (d_{33}) of tetragonal PZT films decreased with decreasing film thickness from 35 $\sim$ 48 pm/V between 150 nm and 600 nm. However, the investigation of nonlinearity in d_{33} measured as a function of electric field indicates that the extrinsic contribution is quite negligible. One possible explanation for this increase of d_{33} is based upon a decrease of the intrinsic dielectric constant, which is supported by measuring C-V and temperature dependent permittivity. In addition, possible factors such as effectiveness of poling, the influence of an interface, and residual stress are discussed here.

C7.2
PZT AND PMN-PT THIN FILM CANTILEVERS: COMPARISON BETWEEN MONOMORPH AND BIMORPH STRUCTURES. M. Hoffmann, U. Böttger, and R. Waser, IWE II, RWTH Aachen, GERMANY.

Piezoelectric and electrostrictive materials are potential candidates for integrated microsystems. They can be used in cantilever laminated structures for different applications, e.g. active vibration control or agile transducers. Due to the necessity of miniaturization of MEMS devices and the possibility of reducing process costs and time, the use of chemical solution deposition (CSD) technique with micro-lithography and reactive ion etching (RIE) are essential. Within this work we used these techniques in combination with silicon bulk micro machining technique to fabricate piezoelectric PZT and electrostrictive PMN-PT coated micro-cantilevers with different lengths for e.g. microswitch or micromirror applications. In general PMN shows no elastic hysteresis and a better aging behavior than PZT ceramics. Since the electrostrictive effect is obviously smaller than the piezoelectric effect the tip deflection of PMN-PT coated beams is much lower. Therefore, cantilevers with two ceramic thin film layers and an internal electrode (bimorph) were designed and compared to such with single ceramic thin film layers (monomorph). For fabrication control and electrical characterizations microscopy, SEM, hysteresis-, CV-, and SE-measurements were performed. Laser interferometry and resonance frequency measurements were used to characterize the electromechanic performance of the cantilevers.

C7.3
FABRICATION AND CHARACTERIZATION OF A PZT THIN FILM ACTUATOR FOR A MICRO ELECTROMECHANICAL SWITCH APPLICATION. M. Hoffmann, H. Küppers, U. Böttger, U. Schnakenberg, W. Mokwa, and R. Waser, IWE I & II, RWTH-Aachen, GERMANY.

Micromachined silicon cantilever beams actuated by the converse piezoelectric effect are of great interest for actuator applications, e.g. microrelays or micromirrors. For the miniaturization and cost saving aspects the combination of silicon bulk micromachining in combination with chemical solution deposition (CSD) technique for the cermamic thin films is very promising. In this context the paper presents a fabrication process for a PZT thin film micro actuator for a switch application. The process handles the occurring problems of the combination of both mentioned techniques. For a tip deflection of 10μm a finite element method simulation (FEM) was carried out to obtain the optimum cantilever length. Hence, the actuator was designed with lengths of 190-1000μm. The bending beams were characterized by laser interferometry measurements and resonance frequency measurements. The measured values are compared to the calculated ones. Influences of different temperatures, voltages and frequencies to the deflection are demonstrated and opposed to the electric characteristics of the PZT thin films.

C7.4
HIGH TEMPERATURE DIELECTRIC PROPERTIES OF SOL-GEL DERIVED THICK PZT THIN FILMS WITH DIFFERENT Zr/Ti ATOM RATIOS. Jinrong Cheng, Wenyi Zhu, Nan Li and L. Eric Cross, The Pennsylvania State University, Materials Research Laboratory, University Park, PA.

Thick PZT thin films are of great interest in applications of Microelectromechanical Systems (MEMS). Composition changes of PZT thin films are expected in different devices. More than 3.5 μm thick PZT thin films with different Zr/Ti atom ratios of 60/40, 52/48

and 45/55 were coated onto platinized silicon substrates by using 2-MOE based sol-gel spin-on techniques and rapid thermal annealing (RTA) process. XRD analysis revealed that PZT thin films had (100) preferred orientation independent on different Zr/Ti atom ratios. The dielectric constants and dissipation of PZT thin films were measured at different temperatures and frequencies. Curie points of PZT thin films shifted from 350 to 432°C with decreasing Zr/Ti ratios, which were coincide with bulk PZT ceramics with corresponding compositions. The Zr-rich 60/40 PZT thin films had the highest dielectric constants compared with the 52/48 and 45/55 PZT thin films from the room temperature to Curie point, and the remnant polarization of more than 40 $\mu C/cm^2$. The composition dependent piezoelectric properties were also measured.

C7.5
RELAXOR FERROELECTRIC (1-x)Pb[(Mg1/3Nb2/3)-xPbTiO3 THICK FILMS: PROCESSING AND THEIR ELECTRO-MECHANICAL PROPERTIES. Sandrine Gentil, Dragan Damjanovic, Nava Setter, Ceramics Laboratory, Materials Department, Swiss Federal Institute of Technology-EPFL, Lausanne, SWITZERLAND.

The lead magnesium niobate, PMN, and its solid solutions with lead titanate, PT, are of great interest from technological and fundamental point of view. At large PMN content, materials are relaxors with large electrostrictive strains and a large permittivity, while compositions near the morphotropic phase boundary present very interesting piezoelectric properties. So far, properties of these materials in ceramic, thin film and single-crystal form have been investigated. In this paper we report properties of PMN-PT thick films. Pyrochlore free PMN and (1-x)PMN-(x)PT thick films (thickness = 10-30 microns) were prepared from ethyl cellulose ink by the screen printing technology on alumina substrate. The influence of various parameters, such as powder characteristics, inks formulation and films sintering process, on film densification is discussed for x=0, 0.1, 0.3, 0.35, and 0.4 The dielectric and electromechanical properties of the films were examined. Relaxor-like behavior was clearly demonstrated in films with x <= 0.3. The relative permittivity at the temperature where permittivity reaches maximum was 11000 for pure PMN, which is lower than in bulk ceramics (18000) prepared under the same conditions. For PMN-PT with x=0.35 the relative permittivity was around 17000 against 24000 in the bulk. Several parameters, which might be responsible for the lower permittivity, are suggested. Poled 0.65PMN-0.35PT thick films exhibit large piezoelectric response (d33= 200 pm/V) and unipolar strains up to 0.1%.

C7.6
INTERDIGITAL $Ag(Ta,Nb)O_3$ THIN FILM CAPACITORS ON THE SAPPHIRE AND Si SUBSTRATES. Max Lindstedt[a], Peter Eriksson[a], Akira Shibuya[a,b], Jung-Hyuk Koh[a], Alex Grishin[a], Masanori Okuyama[b], [a]Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN; [b]Department of Physical Science, Graduate School of Engineering Science, Osaka University, JAPAN.

Thin films of $Ag(Ta,Nb)O_3$ (ATN) were grown on a sapphire (Al_2O_3, r-cut) substrate, high and low resistive silicon wafers by pulsed 248nm KrF excimer laser deposition technique. X-ray diffraction indicates slight (001) preferential orientation of ATN films. Interdigital capacitors consisting of 5 pairs of 1 mm long fingers with 2 and 4 um gap were defined on the ATN film surface by photolithography. $Au/Cr/ATN(0.4\mu m)/Al_2O_3$ film structures exhibit superior dielectric performance. In frequency range 1 kHz to 1 MHz dielectric permittivity shows dispersion as low as 3.5%, loss tan delta $\sim$ 0.0035, K-factor (tunability/loss tan delta) is about 20.2 @ 200 kV/cm, and resistivity as high as 1.7×10^{11} Ωcm kV/cm. Recording of the instantaneous C-V and I-V characteristics enable to study the relaxation of polarization. Spectral density of electrical noise has been recorded in "true leakage" and resistance degradation regimes. Low frequency dispersion and loss, high tunability and low noise in biased state promise ATN films for microwave applications.

C7.7
RF-MAGNETRON SPUTTERED $Au/Na_{0.5}K_{0.5}NbO_3/SiO_2/Si$ MFIS-DIODE STRUCTURES. Akira Shibuya[a], Jung-Hyuk Koh[a], Veronika Kugler[b], Denis Music[b], Ulf Helmersson[b], Alex Grishin[a], [a]Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN; [b]Thin Film Physics Division, Department of Physics, Linköping University, Linköping, SWEDEN.

Recently we proposed new ferroelectric sodium potassium niobate oxide ($Na_{0.5}K_{0.5}NbO_3$, NKN) films as a candidate for applications in nonvolatile memories and electrically tunable devices [1-3]. In this paper we report on processing and characterization of metal-ferroelectric-insulator-semiconductor (MFIS) diode structures based on rf-magnetron sputtered NKN films. 0.7 μm thick NKN films have been deposited on the thermally grown 470 nm thick SiO_2 layer on the Si(001) wafers at temperature 650°C. Stoichiometric $Na_{0.5}K_{0.5}NbO_3$ ceramic target was sputtered in O_2-Ar plasma with the total pressure of 5 mTorr. Films deposition was followed by oxygen post annealing at 400°C for 1 hour. Fabricated NKN films exhibit strong (001) preferential orientation, resistivity as high as 3.9 $\times 10^{11}$ Ohm cm @160 kV/cm, and memory window of 17 V at the programmable voltage of 40 V. I-V measurements have been performed in the time domain to distinguish the relaxation of polarization, "true leakage" current regime and degradation of the resistance in ferroelectric NKN film. [1]Xin Wang, U. Helmersson, S. Olafsson, S. Rudner, L.D. Wernlund, and S. Gevorgian, Appl. Phys. Lett. 73, 927 (1998). [2]Choong-Rae Cho, Jung-Hyuk Koh, and Alex Grishin, Appl. Phys. Lett. 76, 1761 (2000). [3]Choong-Rae Cho, Alex Grishin, J. Appl. Phys. 87, 4439 (2000).

C7.8
PROCESS INDUCED MODIFICATION OF THE HIGH FREQUENCY DIELECTRIC BEHAVIOR OF (100) TEXTURED $Ba_xSr_{1-x}TiO_3$ (x = 0.5 AND 0.6) THIN FILMS. S.B. Majumder, M. Jain, A. Martinez, R.S. Katiyar, E.R. Fachini[a], Department of Physics; [a]Department of Chemistry, University of Puerto Rico, San Juan, PR; F.W. Van Keuls, F.A. Miranda, National Aeronautics and Space Administration, Glenn Research Center, Communications Technology Division, Cleveland, OH; P.K. Sahoo, and V.N. Kulkarni, Department of Physics, Indian Institute of Technology, INDIA.

Paraelectric $Ba_xSr_{1-x}TiO_3$ (x = 0.5 and 0.6) thin films are attractive candidates for the fabrication of various microwave dielectric devices such as phase shifters, resonators, oscillators etc. In the present work we have studied the effect of annealing temperature and ambient on the epitaxial quality, surface morphology and phase shifter characteristics of $Ba_{0.5}Sr_{0.5}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$ thin films. The epitaxial quality was markedly improved as the annealing temperature was increased from 1000 to 1100°C. The degree of phase shift increased from 221 to 328° (measured at 20 V/μm electric field) with the improvement of epitaxial quality of the film. The insertion loss was also increased with the increase in annelaing temperature and therefore the effective κ factor (defined by the ratio of degree of phase shift with insertion loss) was not significantly improved. Annealing these films in N_2 ambient significantly reduced the insertion loss, however in these films dielectric breakdown was observed at relatively lower operative voltage as compared to air and oxygen annealed films. The observed electrical behavior was correlated with the film composition, chemical state of the constituent elements and epitaxial quality of the films prepared under different annealing conditions. This work is supported in part by NASA-NCC5-518, NSF-DMR and DEPSCOR grants.

C7.9
REACTIVE COEVAPORATION OF $SrTiO_3$ THIN FILMS FOR TUNABLE MICROWAVE DEVICES. Luke S.-J. Peng, Nina F. Heinig, and Brian H. Moeckly, Conductus, Inc., Sunnyvale, CA.

Electric-field tunable dielectric thin films such as $SrTiO_3$ (STO) have potentially important applications in advanced wireless communications. We have successfully grown STO films on $LaAlO_3$ and MgO substrates up to 2'' in diameter using the deposition technique of reactive coevaporation. Our deposition system incorporates an oxygen pocket heater, which has proven invaluable in facilitating growth of multiple large-area complex oxide thin films such as $YBa_2Cu_3O_7$. We have explored a range of deposition rate, substrate temperature, and oxygen pocket pressure in order to determine the optimal process window. X-ray diffraction analyses demonstrate that samples prepared within this window are single phase and highly epitaxial. We will discuss the low- and high-frequency dielectric properties of these films as a function of growth conditions, stoichiometry, and film thickness.

C7.10
Abstract Withdrawn.

C7.11
Abstract Withdrawn.

C7.12
PROPERTIES OF STRONTIUM BARIUM NIOBATE THIN FILMS GROWN BY PULSED LASER DEPOSITION. Víctor Rodrguez, Yelitza González, and Félix E. Fernández, Univ of Puerto Rico, Dept of Physics, Mayagüez, PR; Carl H. Mueller, Fred W. Van Keuls, and Félix A. Miranda, NASA Glenn Research Center, Communications Technology Division, Cleveland, OH.

Strontium barium niobate ($Sr_xBa_{1-x}Nb_2O_6$ - SBN) with composition $0.25 \leq x \leq 0.75$ is the solid solution of the $SrNb_2O_6$ - $BaNb_2O_6$ binary system. SBN is a promising material for diverse optoelectronic applications such as electro-optic modulators, real-time holography, and information storage. Dielectric properties of bulk SBN crystals were studied over 30 years ago for a range of

compositions and at frequencies up to 20 MHz. It is known that SBN is a relaxor ferroelectric with peak ϵ_r values in the 10^4 range but dropping steadily in the kHz and MHz ranges, while ϵ" appears to peak in the MHz range. However, little work has been done in relation to dielectric properties of SBN thin films, and we are not aware of published results for these properties at higher frequencies. For this work, SBN thin films with x = 0.61 were grown by PLD and characterized as to their structure, composition, optical properties, and dielectric properties up to the GHz range. Films were deposited on MgO and $LaAlO_3$ substrates. A detailed structural study with x-ray diffraction and ellipsometric techniques was performed. Surface morphology was studied with optical, atomic force, and scanning electron microscopy. Composition was determined by Rutherford Backscattering Spectroscopy. Films with excellent texture, thickness of ~500 nm, an area of 1 cm^2, and oriented with the c-axis normal to the substrate surface were obtained. Metal composition was the same as that of the target, within the experimental error of the RBS technique. Results for permittivity and dielectric losses, obtained by fabricating interdigitated planar capacitors with the films, are given as a function of frequency.

C7.13
PYROELECTRIC PROPERTIES OF ALANINE DOPPED TGS SINGLE CRYSTALLINE THICK FILMS UNDER CONSTANT ELECTRIC STRESS. Lucian Pintilie, Ion Matei, Ioana Pintilie, National Institute of Materials Physics, Bucharest, ROMANIA; Horia V. Alexandru, Ciceron Berbecaru, Dept. Of Physics, Bucharest University, ROMANIA.

Triglycine sulfate (TGS) is a ferroelectric material used for pyroelectric detector applications. Previous dielectric and pyroelectric measurements of pure TGS have shown unstable and non-reproducible data in the ferroelectric phase crossing down the Curie point. L and D alanine doped material, we have used in this paper, show much more stable ferroelectric parameters. Internal bias field of 1-2 kV/cm, induced by the two dopants, stabilize the polarization in opposite direction. Pyroelectric current (under constant stress) was recorded with a computer controlled Keithley 6517 electrometer, crossing up and down the Curie point. Spontaneous polarization PS(T) was also recorded using the charge integration method. A reverse external electric field was applied on doped materials during heating, crossing up the Curie point. The spontaneous polarization restores in the same direction at cooling, if the external field is removed. If this field is maintained during cooling, the pyroelectric current shows peculiar behavior. It switches partially (near the Curie point) or totally its direction, depending on the field value in respect to the coercive field. A simple model is proposed to explain the behavior of pyroelectric current under constant electric stress. It is shown that higher values for pyroelectric coefficient can be obtained if a constant electric field is applied on the pyroelectric wafer during heating. Pyroelectric detectors with increased sensitivity can be obtained using this method.

C7.14
INFRARED SPECTROSCOPY OF EPITAXIAL ANTIMONY SULPHO IODIDE THIN FILMS. D. Donnelly, Southwest Texas State University, Dept of Physics, San Marcos, TX; S. Kotru, S.R. Surthi and R.K. Pandey, University of Alabama, Dept. of Electrical and Computer Engineering, Tuscaloosa, AL.

Infrared reflectance and transmittance measurements were done in the frequency range 500 - 5000 cm^{-1} (λ = 2 - 20 μm) on epitaxial antimony sulpho iodide (SbSI) thin films prepared by pulsed laser deposition. Dependence of the spectra on temperature was studied. In particular, the spectra were measured above and below the ferroelectric transition. The index of refraction for a (121) oriented film was determined to be 2.83 ± 0.35 at a temperature of 25.6°C, and 2.80 ± 0.35 at a temperature of 9.6°C. For a (002) oriented film, the index was 3.82 ± 0.48 at a temperature of 26.5°C, and 3.76 ± 0.48 at a temperature of 8.0°C. From these results, we get a pyro-optic coefficient of 1.5 x10^{-3} $°C^{-1}$ for the (121) oriented film, and 3.2 x 10^{-3} $°C^{-1}$ for the (002) oriented film. These results are consistent with other measurements done in the visible region, and demonstrate the potential of SbSI as an infrared detector material.

C7.15
SELF-ORGANIZATION DURING FATIGUE AND REJUVENATION IN PZT THIN FILMS. Vladimir Ya. Shur, Evgenii L. Rumyantsev, Ekaterina V. Nikolaeva, Eugene I. Shishkin, Ivan S. Baturin, Ural State Univ., Inst. of Phys. & Appl. Math., Ekaterinburg, RUSSIA; Dierk Bolten, Theodor Schneller, Rainer Waser, Inst. fuer Werkstoffe der Electrotechnik, RWTH Aachen, Aachen, GERMANY.

The fatigue and rejuvenation (increase of the switching charge) phenomena have been investigated in PZT thin films by recording of the switching current data and C-V characteristics during cycling. The self-organized evolution of bias field spatial distribution was extracted from the set of subsequent switching current and C-V data by original mathematical treatment based on our kinetic approach to the fatigue and rejuvenation phenomena. The investigated sol-gel PZT films (120-200-nm-thick) have been deposited on Pt bottom electrode. The rectangular and triangular pulses (U = 5-10V, f = 10Hz-1MHz) have been used for cycling. The hysteresis loops and switching currents have been measured in triangular pulses (f = 10-100Hz) by aixACCT TF Analyzer 2000. The C-V characteristics were carried out during switching (f = 10Hz). We have investigated in details two rejuvenation processes: first observed during cycling of the fresh spot and second started just after increasing of cycling field in fatigued spot. The analysis of the evolution of switching current at rejuvenation and fatigue stages allows us to extract the dependence of the internal bias field distribution function on cycle number. It was shown that the maximum value of the switching current is the most sensitive parameter for characterization of the fatigue and rejuvenation dynamics. All obtained results are in accordance with theory of self-organized evolution of the frozen domains during cyclic switching proposed by us recently. The research was made possible in part by Programs "Basic Research in Russian Universities" (Grant No. 563) and "Priority Research in High School. Electronics" (Grant No. 03-03-29), by Grant No. 01-02-17443 of RFBR, by Award No. REC-005 of CRDF.

C7.16
DIRECT SUB-MICRON OBSERVATION OF PZT CAPACITOR SIZE EFFECT ON POLARIZATION INSTABILITY BY AFM. Igor Stolichnov, Enrico Colla, Alexander Tagantsev, Seighbum Hong, Nava Setter, Swiss Federal Institute of Technology (EPFL), Lausanne, SWITZERLAND; Jeffrey S. Cross, Mineharu Tsukada, Fujitsu Laboratories, Atsugi, JAPAN.

Polarization distribution mapping of PZT ferroelectric capacitors (FeCAP) with sizes down to 0.5 x 0.5 um has been performed using an atomic force microscope (AFM), by measuring the piezoelectric response through the top electrode. A highly reproducible anomaly in polarization distribution namely elevated polarization at the capacitor edges and inverse polarization in the center has been observed for the FeCaps of several um size. This polarization pattern is found to be insensitive to the poling voltage polarity and voltage stress prehistory but strongly dependent on the FeCAP size. Specifically, the polarization anomaly tends to disappear as the FeCAP size scales down to submicron range. The observed effect may be responsible for improved switching polarization earlier reported (at ISIF 2001) for submicron PZT FeCAPs used for high density ferroelectric memories. Tentative interpretation of this effect in terms of different mechanisms is discussed.

C7.17
THICKNESS DEPENDENT STRUCTURAL EVOLUTION IN (001) TEXTURED MOCVD-GROWN PZT THIN FILMS. Maxim Kelman, Paul McIntyre, Department of Materials Science & Engineering, Stanford University, Stanford, CA; Bryan Hendrix, Steven Bilodeau, Jeff Roeder, ATMI, Danbury, CT.

We have investigated the structural evolution of MOCVD-grown polycrystalline $Pb(Zr_{0.35}Ti_{0.65})O_3$ thin films as a function of film thickness. We have studied PZT films varying in thickness from 70 to 400nm. X-ray diffraction and cross-section SEM showed that these films have a (001) textured columnar microstructure with grains extending through the thickness of the film. From high resolution x-ray diffraction measurements it is clear that, while the thickest films contain tetragonal PZT with mixed {100} and {001} out-of-plane texture, neither of these orientations is present for the films thinner than 150nm. Instead XRD reflections consistent with either cubic or rhombohedral PZT are detected from the thinnest films investigated. Electrical measurements show that the thinnest films are ferroelectric, suggesting that the non-tetragonal PZT is rhombohedral. We have performed electron backscatter diffraction experiments to investigate this possibility. We have also performed a variety of annealing treatments on these films. Wafer curvature measurements show that as the film is annealed, it is under increasing tensile stress. X-ray diffraction measurements also indicate that as the film is annealed, the volume fraction of the non-tetragonal PZT phase increases at the expense of the tetragonal phase.

C7.18
RELATIONSHIP BETWEEN ELECTRIC PROPERTIES OF PLZT THIN FILM AND FERROELECTRIC DOMAIN STRUCTURE. Koichiro Honda, and Takahiro Kimura, Fujitsu Laboratories Ltd., Atsugi, JAPAN.

To achieve the low voltage drive capability for FeRAM, we need to have ferroelectric thin films that satisfy both requirements of high polarization and low voltage saturation. These are both thought to depend on the grain size and grain orientation of thin films. So, in the ferroelectric thin film application of FeRAM, it is highly important to

evaluate and control the distribution of crystallographic orientation of the grains in order to develop films that provide high polarizability. The relationship between the orientation and the electric properties of polycrystalline Pb(La)ZrxTi1-xO3 (PLZT) has been investigated. PLZT films with different ratios of < 111 > and < 100 > orientation were prepared by RF magnetron sputtering on Pt/Ti/SiO2/Si substrates. After the deposition, these films were annealed in flowing O2 for crystallization. Orientation of each film was observed by XRD, and film crystallinity especially at the PLZT-Pt interface was precisely observed by TEM. Optical characterization using RAMAN scattering was also preformed to distinguish between [100] (a-axis) and [001] (c-axis). The results showed that: 1) the higher the PLZT < 111 > in the film, the higher the polarization (Qsw) is observed in the capacitor. In this, the PLZT < 111 > film had grown epitaxially on the Pt < 111 > film. There were no mismatching between PLZT and Pt bottom electrode. 2) The volume ratio of n[001] to n[100] was 0.35:0.65 for the lowest < 111 > (and the highest < 100 >) film and 0.50:0.50 for the medium. With respect to the highest < 100 > sample, the ratio is close to a value of 1:2 that would be expected for a random distribution of orientation in a cube. The medium sample contained more [001] oriented grains than we would expect for a random distribution. There were 90-degree domains at the PLZT-Pt or PLZT-PZT interfaces. There were also Pb-rich inclusions in the grains in sample A. 3) Poor electrical characteristics (higher leakage current as well as low Qsw) of the < 100 > film was caused by 90-degree domain pinning at the PLZT-Pt interface, lower n[001] component, and non-ferroelectric region in the films.

C7.19
GRAIN BOUNDARY ORIENTATION EFFECTS ON DOMAIN PINNING SITES IN PZT. Evan Pickett, John E. Blendell and Grady S. White, Ceramics Division, National Institute of Standards and Technology, Gaithersburg, MD.

Real-time AFM imaging of domains in Lead Zirconate Titanate (PZT) has shown that some of the grain boundaries appear to act as domain pinning sites. Observation of the domain behavior as the field is increased shows that regions of the grain boundary resist switching or serve as nucleation sites for switched areas. Simulations of the elastic behavior as a function of grain-to-grain misorientations in the plane of the film found regions of high compressive and tensile stresses at grain boundaries. It was proposed that these regions of high stress act as pinning sites. We report AFM results in which we have measured the vertical and lateral response of domains to applied electric fields. The PZT thin films are highly textured normal to the plane of the film, but the in-plane orientation of the various grains in the films is expected to be random. This in-plane orientation variation can be correlated with the lateral and vertical response, which will allow an estimate of the degree of misorientation across a grain boundary. The degree of pinning required to switch the domains at these pinning sites and the stability of the domains after switching will be correlated with the misorientation across the grain boundary.

C7.20
OBSERVATION OF SATURATED FERROELECTRIC HYSTERESIS LOOP AND ANOMALY IN DIELECTRIC BEHAVIOR IN MAGNETOELECTRIC $BeFeO_3$ THIN FILMS. V.R. Palkar, J. John and R. Pinto, Tata Institute of Fundamental Research, Mumbai, INDIA.

$BiFeO_3$ has drawn attention of many physicists and materials scientists due to coexistence of antiferromagnetic (T_N ~370°C) and ferroelectric (T_C ~830°C) ordering. The controversy over ferroelectric nature of $BiFeO_3$ was put to rest after the observation of ferroelectric/ferroelastic domains using polarized light microscopy. However, saturated hysteresia loop in $BiFeO_3$ bulk as well as thin film samples has not yet been observed due to low resistivity. In this paper we are reporting the growth of single phase, *c*-axis oriented thin films of $BiFeO_3$ on $Si/SiO_2/TiO_2/Pt$ substrate by pulsed laser deposition technique. By optimizing the process conditions, mainly oxygen pressure in the ablation chamber, we have been able to control oxygen stoichiometry in the films which helped to maintain Fe in Fe^{+3} state [1]. The films thus obtained were highly resistive and hence could give saturated ferroelectric hysteresis loop for the first time. Thy hysteresis loop observed by us is confirmed evidence about the presence of ferroelectric ordering in multiferroic magnetoelectric $BiFeO_3$ system. Measurement of dielectric response with temperature of $BiFeO_3$ thin films indicated anomalous behavior near 400°C. The temperature at which the anomaly has been observed coincides with the Néel temperature. This anomaly is ε(T) could be explained on the basis of abrupt change and recovery in lattice parameters of $BiFeO_3$ within the same rhombohedral modification occurring near Néel temperature [2].
[1] V.R. Palkar, J. John and R. Pinto, Patent Under Processes: 210/Mum/2001.
[2] Yu. E. Roginskaya, Yu. Ya Tomashpol'skii, Yu N. Venevtsev, V.M. Petrov and G.S. Zhdanov, Soviet Physics JETP, 23, 47 (1966).

C7.21
ANALYSIS OF ALTERNATING CURRENT CONDUCTION AND IMPEDANCE SPECTROSCOPY STUDY OF $BaBi_2Nb_2O_9$ THIN FILMS. Apurba Laha and S.B. Krupanidhi, Materials Research Centre, Indian Institute of Science, Bangalore, INDIA.

Alternating current conduction in $BaBi_2Nb_2O_9$ (BBN) thin films has been studied over a wide range of temperatures. A universal power law relation was brought into picture to explain the frequency dependent of ac conductivity. At higher frequency region ac conductivity of BBN thin films become temperature independent. The activation energy calculated from the arrheneous plot of ac conductivity was found to be around 0.25 eV. It was attributed to the shallow trap controlled space charge conduction in the bulk of the sample. The impedance analysis for BBN a thin film was also performed to get insight of the microscopic parameters, like grain, grain boundary, and film-electrode interface etc. The response of a single RC combination has been observed for our case. The effect to other components, such as the grain boundary interface and electrode/film interface was negligible. The imaginary component of impedance exhibited different peak maxima at different temperatures. Debye type mechanism was found to be appropriate to explain the polarization relaxation in BBN thin films.

C7.22
ELASTIC DEFORMATIONS IN THIN FREESTANDING FERROELECTRIC FILMS. Jaya P. Nair and Igor Lubomirsky, Weizmann Institute of Science, Rehovot, ISRAEL.

Thin $BaTiO_3$ ferroelectric films are important for a number of applications such as high charge density capacitors, ferroelectric memory, microwave and optoelectronic devices. The dielectric properties of a thin film, however, depend not only on the ferroelectric material itself, but also on the substrate material, film thickness and mechanical stress. The last one is one of the most influential factors and experimental data on the effect of mechanical stress on dielectric constant, Curie temperature and spontaneous polarization, are numerous. Most of the data on mechanical stress in thin $BaTiO_3$ films are based on measurements of the *substrate curvature with and without the film*. In contrast, we report on measurements of the *film with and without the substrate*, i.e., we investigate *freestanding films*. $BaTiO_3$ films were prepared on bare silicon and on silicon, covered by a 120 nm thick, randomly oriented Al_2O_3 buffer. Films prepared on bare silicon by RF sputtering are essentially stress-free. However, they disintegrate after substrate removal. In contrast, the films prepared on the Al_2O_3 buffer have tensile stress of 100-170 MPa but retain their structural integrity after separation from the substrate. Substrate removal is accompanied by film corrugation, indicating $\approx$ 1% linear expansion of the films. At the same time, the freestanding films resonate mechanically, indicating a tensile stress of 2.2 GPa. This seeming contradiction can be understood on the basis of a recently developed theory of 2D clamping in thin ferroelectric films.

C7.23
DETERMINATION OF RESIDUAL STRESSES IN $Pb(Zr_{0.53}Ti_{0.47})O_3$ THIN FILMS WITH RAMAN SPECTROSCOPY. Weihua Xu, Dexin Lu, Tong-Yi Zhang, Hong Kong University of Science and Technology, Department of Mechanical Engineering, Kowloon, HONG KONG.

The present work measures residual stresses in $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films with Raman spectra. The $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films with thicknesses of 172, 258 and 344 nm were deposited on Pt/Ti/Si (100) substrates by the sol-gel method, baked at 110°C for 3 minutes, pyrolyzed at 350°C for 10 minutes and finally annealed for 60 minutes at 600, 650 or 700°C. We calibrate the relationship between the Raman spectra shift with stress, by measuring the Raman spectra of stressed bulk $Pb(Zr_{0.53}Ti_{0.47})O_3$ samples. The bulk samples have the same composition as the deposited thin films and the stress is applied by four-point bending and monitored by a strain gauge. A linear relationship is found between the square of the Raman frequency and stress for each of the $A_1(TO_3)$ and $E(LO_3)$ modes. Then, we assess the residual stresses in the PZT thin films with different thicknesses and different annealing temperatures. The residual stresses extracted from the TO mode are consistent with those from the LO mode. The results show that the residual stresses decrease as the film thickness increases. The higher annealing temperature leads to a higher residual stress. A thermodynamic analysis is conducted to explain the observed experimental phenomenon.

C7.24
SIMULATION OF THE VARIABILITY IN NEXT-GENERATION MICROELECTRONIC CAPACITORS WITH POLYCRYSTALINE DIELECTRICS. Jesse L. Cousins, David E. Kotecki, University of Maine, Department of Electrical and Computer Engineering, Orono, ME.

Increasing circuit densities drive the search for microelectronic capacitors with smaller areas. One alternative to using large capacitors is to use a thin film such as Ta_2O_5, $SrTiO_3$ (STO), or (Ba,Sr)TiO_3 (BSTO), whose dielectric constants are much higher than those of currently used dielectrics. One drawback of these dielectric films is that they have a polycrystalline microstructure and the permittivity and leakage of a crystal depends on grain size and orientation. It is unknown how microstructure variations will affect the yield of devices incorporating these films. We have developed a Monte Carlo computer simulation in order to investigate variables that produce atypically high or low capacitance and/or leakage. Statistical distributions of crystal area, capacitance, and leakage were evaluated. The capacitance model was developed based on permittivity vs. grain size, and the leakage was based on the Schottky model of electron injection, taking into account barrier height vs grain size and barrier height lowering vs permittivity. The simulation results were examined to find the variability in capacitance and leakage. For one simulation, two grain size distributions were used, with mean grain areas of 100 nm^2 and 1000 nm^2. Capacitor area was set at a constant of 0.3μm^2, and 300,000 capacitors were generated. Results show that for the two grain size distributions, the larger-grained distribution's capacitance varied by 8.5%, while the smaller-grained distribution's capacitance varied by 2.2%. Two different leakage models were used for the smaller-grained distribution; the leakage of the capacitors was found to vary between 1 and 26%. For capacitors with amorphous dielectrics, these variations would not exist.

C7.25
ELECTRICAL PROPERTIES OF Pt/(Ba,Sr)TiO_3/Pt THIN FILM CAPACITORS EXPOSED TO H2 OR D2 CONTAINING AMBIENTS OVER THE TEMPERATURE RANGE OF 4.2 - 400K.
J.D. Baniecki, A. Akasegawa, T. Shioga, K. Kurihara, Fujitsu Laboratories, Atsugi, JAPAN.

Thin films of the high dielectric constant material (Ba,Sr)TiO_3 (BSTO) have attracted great interest in recent years for use in future high density dynamic random access memories (DRAMs), tunable microwave devices, and high frequency decoupling capacitors applications. However, unpassivated perovskite titanate thin film capacitors often exhibit severe degradation in electrical properties after exposure to a hydrogen containing ambient. In the case of Pt/(Ba,Sr)TiO_3/Pt capacitors, both steady state and relaxation currents are observed to increase while the capacitance density decreases after exposure to a hydrogen (H2) or deuterium (D2) containing ambient. Hydrogen containing atmospheres are often present at several points in the fabrication of metal-oxide-silicon devices and, thus, it is vital to understand the mechanisms for the degradation in electrical properties. In order to achieve a better understanding for the origin of the degradation in electrical properties, we have studied the capacitance-voltage characteristics (C-V), steady state leakage currents, and dielectric relaxation currents of as deposited polycrystalline BSTO thin films and thin film BSTO capacitors exposed to H2 or D2 containing ambients over a very wide range of temperatures (4.2 - 400 K). BSTO thin films (30 - 200 nm thick) were deposited by RF magnetron sputtering and chemical solution deposition. At cryogenic temperatures, the steady state leakage currents of both as deposited and samples exposed to H2 or D2 ambients could be successfully interpreted in terms of the tunnel emission of carriers through an interfacial Schottky barrier. The origin for the increase in the dielectric relaxation currents observed for Pt/(Ba,Sr)TiO_3/Pt capacitors after exposure to a H2 or D2 containing ambient was investigated using the technique of thermally stimulated dielectric relaxation currents. Based on the experimental results, mechanisms for the increase in leakage and dielectric relaxation currents of BSTO thin film capacitors exposed to H2 or D2 ambients will be presented.

C7.26
CHARACTERIZATION OF MOD $BaTiO_3$ THIN FILM CRYSTALLIZED BY HYDROTHERMAL TREATMENT AT 140°C.
Zhiqiang Wei, Minoru Noda and Masanori Okuyama, Graduate School of Engineering Science, Osaka Univ, Osaka, JAPAN.

MOD $BaTiO_3$ thin films have been successfully crystallized by hydrothermal treatment at low temperature of 140°C. MOD solution of $BaTiO_3$ was spin-coated on Pt/Ti/SiO_2/Si wafer. The films were successively dried in air at 120°C for 10 minutes, and pre-baked at 400°C for 10 minutes. Hydrothermal treatment was carried out in an autoclave by submerging the films in 30ml $Ba(OH)_2$. The thin films in autoclave were heated to 140°C and high pressure of 2.7atm in 10min, and the system was hold for 10min, 30min, 60min, and 180min. The samples were rinsed in boiling de-ionized water and dried at 120°C in air. XRD analysis shows that the $BaTiO_3$ thin film is amorphous structure before hydrothermal treatment, but the pure perovskite phase with (101) preferred orientation was clearly observed after the hydrothermal treatment. The diffraction peaks become stronger with increasing the treatment time. Raman spectra show that the $BaTiO_3$ characteristic peaks at 520cm^{-1} and 700 cm^{-1} were observed in the thin films after hydrothermal treated. SEM shows that the grain grows with the increasing the treatment time. Thickness of the $BaTiO_3$ thin films is about 230nm, which is not changed after hydrothermal treatment at various times. The pinhole-free and smooth surface was found in the case of 60min. AES and XPS depth profiles show that the composition ratio of Ba/Ti in thin film treated by hydrothermal method is almost the same with that before hydrothermal treatment. The P-E hysteresis loop was measured with Pt electrode at ±5V, and 66Hz. The polarization at E=0 and the field at P=0 are 9.2$\mu C/cm^2$ and 101kV/cm respectively. The leakage current density at ±1V is about 3.3× 10^{-7} A/cm^2.

C7.27
OPTIMIZATION AND CHARACTERISTICS OF FOIL BASED PLZT THIN FILMS FOR EMBEDDED CAPACITOR TECHNOLOGY.
T. Kim, D-J. Kim, A. I. Kingon, and J-P. Maria, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC; R. Croswell, Motorola Advanced Technology Center, Schaumburg, IL.

PLZT thin films have been prepared using methanol-based chemical solution deposition (CSD) on 17 micron Cu foils coated with electroless Ni. Reducing atmospheres were used to prevent excessive foil oxidation during the high temperature annealing steps. The PLZT composition was tailored to provide reduction resistance. The effects of chelating agents on the final film microstructure and the electrical properties were studied. In general, acetic acid showed improved properties when compared to other chelating agents for embedded components use. The property improvements were manifested in both microstructual and electrical aspects. Capacitance density and loss tangent measurements were performed as a function of voltage, frequency and temperature. Optimized values of capacitance density and loss tangent were 300 nF/cm^2 and 0.01 respectively over a frequency range spanning 500 Hz to 500 kHz. The low-field electrical properties were only modestly temperature dependent. Between -150°C and 300°C the permittivity changes by less than 10% even though a ferroelectric transition is evidenced by a permitivity maxima at approximately 250°C. This flat temperature dependence was reflected in the similarly modest voltage dependence. In general, the permittivity shows less than 5% voltage tunability over a range of voltages capable of causing electrical breakdown. These results will be discussed in terms of film crystallinity and processing conditions, and the embedded capacitor applications ultimately envisioned for this technology.

C7.28
STUDY OF RELAXOR BEHAVIOR IN $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ THIN FILMS GROWN USING PULSED EXCIMER LASER ABLATION TECHNIQUE.
Apurba Laha, S. Saha and S.B. Krupanidhi, Materials Research Centre, Indian Institute of Science, Bangalore, INDIA.

Polycrystalline thin films of $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-PT) were grown using pulsed excimer laser ablation technique on Pt/Ti/SiO_2/Si substrates.Thin films of Titanium Oxide (TiO_2) and Lead Titanate ($PbTiO_2$) were employed as a buffer layer to enhance the perovskite fractions in the crystalline structure of the PMN-PT thin films. We observed the influence of the buffer layers on the dielectric properties of the PMN-PT thin films. The ferroelectric properties of the grown films were studied from the hysteresis and capacitance voltage measurements. The relaxor nature of the films was examined from the frequency dispersion of the dielectric constant (ϵ_r) versus temperature behavior and also from the diffuse nature of the phase transition (DPT). Various models were used to identify the relaxor nature of the PMN-PT films and the characteristics showed a strong tendency to follow the Vogel-Fulcher model,which has been used to describe the behavior of relaxor ferroelectrics in conjunction with spin-glass systems.

C7.29
EFFECT OF LANTHANUM ON POLARIZATION REVERSIBLE MECHANISM IN ANTIFERROELECTRIC $PbZrO_3$ THIN FILMS.
S.S.N. Bharadwaja, S.B. Krupanidhi, Materials Research Centre, Indian Institute of Science, Bangalore, INDIA.

The ability of field enforced ferroelectric phase transition from antiferroelectric phase in antiferroelectric thin films, makes these compositions suitable for high charge storage and micro-electromechanical system applications. Pure $PbZrO_3$ thin films exhibited ferroelectric and paraelectric phases with the addition of La. The effect of La- addition to aniferroelectric $PbZrO_3$ thin films on field induced switching phenomenon has been investigated in terms of reversible and irreversible contributions to total polarization mechanism.

C7.30
STRUCTURAL DEVELOPMENT AND DIELECTRIC PROPERTIES OF BARIUM TITANATE GLASS-CERAMIC THIN FILMS. Kui Yao, Francis Eng Hock Tay, Institute of Materials Research and Engineering, SINGAPORE; Weiguang Zhu, Nanyang Technological University, School of EEE, SINGAPORE.

Perovskite barium titanate family ceramic thin films have received extensive investigation because of their great potentials as integrated high dielectric media and electric-field tunable elements for high frequency devices. However, no effort has been reported to study integrated barium titanate glass-ceramic thin films. In this presentation, barium titanate glass-ceramic thin films were deposited on silicon substrates by sol-gel method. The structural development and surface morphology of the films were investigated using thermal analysis, scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. The barium titanate grains were grown in the glass matrix with heat treatments. The resulted glass-ceramic films exhibited a mixed structure of glass phase and the barium titanate grains tens of nanometers in diameter. An interesting self-mending phenomenon for microcracks during the annealing process was observed in the films with increased thickness. Electrical measurements showed the glass-ceramic films had a high dielectric constant, low leakage current and dielectric loss. No ferroelectric hysteresis loop was observed for the films with a standard ferroelectric testing system. The experimental results demonstrated the potential value of barium titanate glass-ceramic thin films for integrated high dielectric media. The advantages of the chemical-route derived dielectric glass-ceramic films over ferroelectric ceramic films were discussed.

C7.31
ELECTRICAL PROPERTIES OF BST THIN FILM ON Pt AND Ru BOTTOM ELECTRODE UTILIZING 2-STEPS O_2 ANNEAL TECHNIQUE. Michio Tanimura, Isao Kimura, Koukou Suu, and Michio Isikawa, Institute for Semiconductor Technologies, ULVAC Inc., Susono, Shizuoka, JAPAN.

It is well known that high dielectric constant thin film such as BST should be utilized necessarily to realize the Gbit DRAM or on-chip backend decoupling capacitor. In our studies, RF magnetron sputtering technique was used for preparing BST thin films. BST thin film was deposited on the bottom electrode utilizing 2-steps O_2 anneal technique[1]. Electrical properties of BST capacitors investigated in cases of Pt bottom electrode and Ru bottom electrode respectively. BST capacitor with Ru bottom electrode shows larger k-value and smaller leakage current. Composition of BST thin film was investigated by AES analysis. The AES profiles indicate that Ti shows different behaviors at the interface of BST and electrodes between Pt bottom electrode and Ru bottom electrode. Furthermore, in case of BST capacitor using Ru bottom electrode, TFA (target factor analysis) method[2] revealed that Ti exists in a form of oxide state. Surface morphology by AFM and crystalinity by XRD will be reported in the meeting.
[1]M. Tanimura et al: Extend abstracts (The 61st Autumn Meeting, 2000); The Japan Society of Applied Physics, No.2, pp.423.
[2]T. Morohasi et al: Science of surface, Vol.18, 5, pp.304,1997.

C7.32
DIELECTRIC BEHAVIOR AND MICROSTRUCTURE OF PEROVSKITES MULTILAYER THIN FILM PREPARED BY SOFT CHEMICAL PROCESS. Edson R. Leite, F.M. Pontes, E.J.H. Lee, E. Longo, Department of Chemistry, Federal University of São Carlos-UFSCar, SP, BRAZIL; J.A. Varela, Institute of Chemistry, UNESP, Araraquara, SP, BRAZIL

Multilayer thin film of oxides with perovskites structures were fabricated by soft chemical process. Perovskites ($SrTiO_3/BaTiO_3$) multilayer were deposited on $Pt(111)/Ti/SiO_2/Si(100)$ substrate by spin-coating technique and heating in air at 700°C. The microstructure and crystalline phase of the multilayered thin film were examined by FE-SEM, TEM, HRTEM, AFM and X-ray diffraction. The perovskite multilayer thin film consists of grain structure with grain size of about 60 nm. The multilayered thin film has a very clear interface between the components and exhibited dielectric constants of about 527 and loss tangent of 0.03 at 100kHz. The dielectric constant of the multilayered films could be explained by the series connection of those films. The multilayer $SiTiO_3/BaTiO_3$ thin films also showed ferroelectric behavior with a remanent polarization of 2.5 $\mu C/cm^2$ and a coercive field of 30 kV/cm. The films exhibited good fatigue characteristics under bipolar stressing after application of 10^{th} switching cycles.

C7.33
PULSED LASER DEPOSITION (PLD) OF LEAD MAGNEZIUM NIOBATE (PMN) BASED HETEROSTRUCTURES: A PARAMETRIC STUDY. M. Dinescu, C. Grigoriu, G. Dinescu, R. Savu, I. Vrejoiu, IFA, NILPRP, Lasers Dept., Bucharest, ROMANIA; P. Verardi, F. Craciun, CNR - IDAC, Rome, ITALY; C. Galassi, IRTEC-CNR, Faenza, ITALY.

A multi-step PLD process was used for "in situ" growth on different substrates of lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) based heterostructures. PZT, LSCO or/and TiN films have been deposited by PLD in the same process in order to be used as intermediate layers and/or bottom electrodes. Other films have been grown directly on Pt/NiCr/Si and Au/Pt/NiCr/Glass substrates. Laser wavelength and fluence, substrate temperature and the buffer layer characteristics were found to strongly influence the heterostructures properties. Pyrochlore free PMN films have been obtained when an ultraviolet (UV) radiation (wavelength 265 nm) was used and a $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) film was deposited as template layer and/or bottom electrode. The use of $Pb(Zr_xTi_{1-x})O_3$ (PZT) template layer was found to strongly diminish the pyrochlore amount in films deposited using the infrared laser radiation (wavelength 1060nm) delivered by a Nd-YAG laser. Sharp interfaces and small interdiffusion were observed in UV laser deposited heterostructures. Electrical properties have also been tested.

C7.34
MICROSTRUCTURAL AND DIELECTRICAL PROPERTIES FOR CERAMICS AND THIN FILMS OF THE $xPbTiO_{0.3}$-(1-x)$SrTiO_{0.3}$ SOLID SOLUTION. E. Martínez, Centro de Investigacion Científica y Educacion Superior de Ensenada, CICESE, Ensenada, B.C., MEXICO; J.M. Siqueiros, Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, B.C., MEXICO; A. Fundora, Facultad de Física-IMRE, Universidad de la Habana, Vedado, La Habana, CUBA.

The effect of the mixing of the two $PbTiO_3$ and $SrTiO_3$ simple perovskites to form the $xPbTiO_3$-(1-x)$SrTiO_3$ ceramic system is studied for different compositions using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electronic Microscopy (TEM) to analyze its influence on the microstructural properties. Thermoelectric analysis for ceramics was used for the dielectric measurements and to analyze the dispersive behavior of the dielectric permittivity in the para-ferroelectric transition region. Measured values for dielectric constant k at the transition temperature increases with the $PbTiO_3$ content, for x>0.5, k becomes higher than 4000. Films of $0.5PbTiO_3$-$0.5SrTiO_3$ (PST50) have been obtained by RF ion sputtering on different substrates to investigate the relation between the crystalline structure and the dielectric properties of PST50 films deposited on Si(111) and the performance of different metallic films as diffusion barriers to prevent Si oxidation and the diffusion of the metal species to the dielectric PST50 film. Auger Electron Spectroscopy (AES) and Scanning Electron Microscopy (SEM) were used for the chemical analysis and structural studies of the interfaces of the PST50/Si, PST50/TiN/Si, PST50/RuO_2/Si and PST50/RuO_2/TiN/Si systems. A depth profile study allowed us to determine the degree of diffusion of each element in the system from one film to the other and their relation to the deposition conditions. The capacitive properties of the PST50 films were measured in Pt/PST50/Si, Pt/PST50/TiN/Si, Pt/PST50/RuO_2/Si and Pt/PST50/RuO_2/TiN/Si capacitors finding values for the dielectric constant between 150 and 350. These results were correlated to the structure and composition determined by SEM and AES. This work was partially supported by CONACyT, Mexico, Proj. 33586-E and DGAPA-UNAM, Proj. IN104000. Thanks are due to F. Ruiz, E. Aparicio, V. García and I. Gradilla for their technical support.

C7.35
COMPOSITIONAL DISORDER INDUCED RELAXOR BEHAVIOR OF (PbLa)TiO_3 THIN FILMS. S. Bhaskar, S.B. Majumder and R.S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR.

The characteristics of the diffuse phase transition and possible relaxor behavior of $PbTiO_3$ thin films doped with different amounts of La are investigated. Temperature dependent dielectric behavior of the sol-gel derived ferroelectric $Pb_{1-x}La_xTiO_3$ (PLT) (x = 0.05 to 0.30) thin films on Pt/Si substrates has been studied. Room temperature X-ray and micro Raman results indicate that the crystal structure of the PLT films was strongly influenced by the La contents. The softening of the E(1TO) mode with increasing La content indicates that the incorporation of La in PT lattice results in a structural disorder in the material. The dielectric permittivity and loss tangent of the PLT thin films were measured in the temperature range 80 - 700 K at a frequency of 1kHz - 1MHz. Transition temperatures (T_m) for PLT5, PLT20, and PLT30 are 640, 460, and 254 K respectively, was higher in comparison to reported values in bulk ceramics. The permittivity maximum broadened, showed relaxor- type frequency dependent permittivity characteristics for PLT30 films. Broadening parameter was significantly influenced by La doping and results indicate that PLT thin films undergo normal-to-relaxor ferroelectric transformation

for 30 at% La content in PLT films. The relaxor behavior in PLT30 films was evaluated in terms of deviation of Curie-Weiss behavior, diffuseness (γ) and Vogel-Fulcher relationship. This work is supported in parts by DAAG55-98-1-0012 and NASA NCC5-518 grants.

C7.36
PULSED LASER DEPOSITION OF BISMUTH PYROCHLORE THIN FILMS FOR DIELECTRIC APPLICATIONS. Lisa Edge, Ryan Thayer, and Susan Trolier-McKinstry, Materials Research Institute and MS&E Department, Pennsylvania State University, University Park, PA.

There is considerable interest in thin films with moderate, temperature-stable permittivities for on and off-chip capacitor applications. Towards this end, $Bi_{1.5}$ $Zn_{1.0}$ $Nb_{1.5}O_7$ pyrochlore thin films were prepared on platinum coated Si wafers using pulsed laser deposition. The laser fluence was varied between 1.5-2.5 J/cm^2 and the laser frequency was varied between 3 and 20 Hz. Films were grown using on-axis ablation geometry in a mixed oxygen/ozone atmosphere. The chamber pressure was varied between 50-400 mTorr. The films showed the cubic pyrochlore phase when deposited at temperatures of 500°C or higher. The crystalline films have dielectric constants between 150 to 300, a tan $\delta < 0.01$, and tunable dielectric constants. This combination of properties makes bismuth pyrochlore thin films candidate materials for applications for tunable rf components and decoupling capacitors. Support for this work was provided by the Semiconductor Research Corporation.

C7.37
MAGNETIC PHASE OF IRON-DOPED THIN-FILM $BaTiO_3$. R. Maier and J.L. Cohn, Dept. of Physics, Univ. of Miami, Coral Gables, FL; J.J. Neumeier, Dept. of Physics, Florida Atlantic Univ., Boca Raton, FL; L.A. Bendersky, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MA.

The structural and physical properties of cubic/tetragonal thin film $BaFe_xTi_{1-x}O_3$ ($0.5 \leq x \leq 0.75$) grown by pulsed-laser deposition are reported, and compared to pure barium titanate films made under the same conditions. The Fe-doped material is of interest because the corresponding bulk compounds have hexagonal structure for comparable x, and because the films are both ferroelectric and ferrimagnetic well above room temperature. A substantial increase of the ferroelectric transition temperature relative to that of bulk $BaTiO_3$ is attributed to lattice expansion induced by Fe doping. Temperature dependent measurements of lattice parameters (XRD), capacitance, resistivity and magnetism will be presented.

SESSION C8/O6: JOINT POSTER SESSION
EPITAXIAL FERROELECTRIC FILMS
Chairs: Masaru Shimizu and Sanjeev Aggarwal
Tuesday Evening, November 27, 2001
8:00 PM
Exhibition Hall D (Hynes)

C8.1/O6.1
FERROELECTRIC $BaTiO_3$ THIN FILM OPTICAL WAVEGUIDE MODULATORS. A. Petraru, M. Siegert, J. Schubert and Ch. Buchal, Institut für Schichten und Grenzflächen (ISG1-IT), Forschungszentrum Jülich, GERMANY.

High quality $BaTiO_3$ epitaxial thin films on MgO substrates have been grown by pulsed laser deposition. Both, c-axis and a-axis $BaTiO_3$ orientation were studied. For growing the c-axis films the substrate temperature was approx. 800°C and the laser energy 1100 mJ/pulse. In the case of the a-axis films the substrate temperature was 50°C higher and the laser energy 300 mJ/pulse. Mach-Zehnder optical waveguide modulators with a fork angle of 1.7 deg. have been fabricated by ion beam etching. The waveguides are of the ridge type, the $BaTiO_3$ thickness is 1 μm, the ridge step 50 nm, the width 2 μm. Light was coupled into the waveguides from optical fibers. The $BaTiO_3$ waveguide propagation losses are 1-2 dB/cm. Electrodes of 3 mm length were deposited besides the waveguides. Electro-optic modulation has been demonstrated with V_π= 6.3V @ 632nm wavelength and V_π = 9.5V @1550nm wavelength for the a-axis samples and with V_π= 7V @ 632nm wavelength and V_π= 15V @1550nm for the c-axis samples. Theoretical modelling of the Mach-Zehnder modulators for both crystalline orientations of the $BaTiO_3$ films gave the Pockels coefficients r_{51} =30 pm/V for the c-axis film and an effective Pockels coefficient r_{eff} = 734 pm/V for the a-axis films at 632 nm wavelength.

C8.2/O6.2
EQUIVALENT CIRCUIT INTERPRETATION OF DIELECTRIC DISPERSION IN FERROELECTRIC SUPERLATTICE CAPACITOR. Mufei Xiao, CCMC-UNAM, San Ysidro, CA.

We present an alternative explanation to the dielectric dispersion at low frequency in ferroelectric superlattice capacitors. The dispersions were recently observed and attributed to the Maxwell-Wagner effects in [D. O'Neill, R.M. Bowman, and J.M. Gregg, Appl. Phys. Lett. 77 (2000)1520]. We alternatively explain the observations based on an equivalent circuit. For small stack periodicities that are less than a few Angstroms, the model reaches similar conclusions that the Maxwell-Wagner effects contribute to the dielectric loss at low frequencies. For larger stack periodicities, the model interprets correctly the experimental observations. Finally, the model appears useful for understanding dielectric responses in relaxor ferroelectrics, and thus suggests that stacking various ferroelectric thin films may produce relaxor responses.

C8.3/O6.3
ELECTROMECHANICAL RESPONSES OF SUB-MICRON RELAXOR STRUCTURES. Robert Bowman, Carles Morros, Gustau Catalan, Niall Donnelly and Marty Gregg, School of Maths & Physics, Queen's University of Belfast, UNITED KINGDOM.

The large electromechanical response of relaxor compounds makes these materials interesting for numerous applications. Recent advances in film fabrication have lead to creation of high quality thin films and much work is underway to quantify and understand the relaxor behaviour in thin films. Dielectric and electromechanical measurements at a microscopic level and very small volumes are an additional aid. Using pulsed laser deposition we fabricate single layers of PMN and PMN-PT and superlattices of relaxor compositions such as PZN-BT/PMN. Piezoresponse microscopy using a modified AFM allows the mapping and quantification of electromechanical behaviour on the surface of the films. In PMN layers we measure an effective d_{33} of around 300pm/V in fields of 0.25MV/cm. In 90 x 6nm period superlattices of 0.2PZN-0.8BT/PMN strains of 0.4% in 0.25MV/cm are seen. In this paper we will describe the properties of such films and superlattices when they have been laterally confined by the creation of sub-micron ($\leq$500nm) features such as mesas and strips; in addition to the confinement by reducing thickness of the grown film. The relaxor films are fashioned using a focused ion beam microscope (FIB); a FEI Strata using a Ga^+ beam is used to define the elements. Detailed dielecric and electromechanical measurements are preformed on either bare surfaces of patterned films or metalised top layers, with either ex-situ noble metal coating or FIB deposited Pt. HRTEM is also used to correlate measurements with microstructure.

C8.4/O6.4
INITIAL GROWTH STAGES OF $BaTiO_3$ THIN FILMS ON Nb-DOPED $SrTiO_3$ SUBSTRATES. A. Visinoiu, M. Alexe, H.N. Lee, C. Harnagea, D.N. Zakharov, A. Pignolet and D. Hesse, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

The growth mechanism of epitaxial $BaTiO_3$ films on vicinal Nb-doped $SrTiO_3$ (Nb:$SrTiO_3$) substrates has been studied. (100)-oriented $BaTiO_3$ thin films and nanostructures have been grown on (100)-oriented Nb:$SrTiO_3$ substrates with well-defined terraces by pulsed laser deposition. As initial stages of film growth, self-organized $BaTiO_3$ nanostructures 5 to 10 nm in height and 100 nm in lateral size have been formed. Substrate surfaces consisting of TiO_2-terminated steps have been prepared by chemical etching in buffered HF solution and 10 min thermal annealing at 1200°C. Under our conditions, barium titanate preferred to grow with an island growth mechanism. The lattice mismatch of 2.28 % along the a direction between $BaTiO_3$ (a = 3.994 Å) and $SrTiO_3$ (a = 3.905 Å) strongly influences the epitaxial relationship between film and substrate. The size of the individual $BaTiO_3$ islands has been controlled by the variation of laser repetition rate and overall number of laser shots. X-ray diffraction and high-resolution transmission electron microscopy have been performed in order to check the orientation and crystallinity of the $BaTiO_3$ films and structures. Macroscopic measurements of dielectric properties of 500 nm thick films show a relative dielectric constant ϵ_r of 200, a remnant polarization P_r of 0.72 μC/cm^2, and a coercive field E_c of 27 kV/cm for a maximum applied field of 100 kV/cm. Local piezoelectric measurements confirmed the ferroelectric behavior, as well as the presence of an initial imprint in $BaTiO_3$ thin films on Nb:$SrTiO_3$ substrates.

C8.5/O6.5
ORIENTATION-CONTROLLED EPITAXIAL GROWTH OF $SrBi_2Ta_2O_9$ THIN FILMS. Ho Nyung Lee, Dmitri N. Zakharov, Stephan Senz, Alain Pignolet, and Dietrich Hesse, Max-Planck-Institut für Mikrostrukturphysik, Halle/Saale, GERMANY; Peter Reiche and Reinhard Uecker, Institut für Kristallzüchtung, Berlin, GERMANY.

$SrBi_2Ta_2O_9$ is a well known ferroelectric material due to its high fatigue endurance, which is related to its bismuth layered perovskite

structure. Moreover, the ferroelectric properties of $SrBi_2Ta_2O_9$ strongly depend on its crystallographic orientation because the spontaneous polarization is directed along the *a* axis of the highly anisotropic orthorhombic system. In order to study its basic ferroelectric properties, we have grown epitaxial thin films having different orientations on various single crystalline substrates of different orientations including silicon. Epitaxial $SrBi_2Ta_2O_9$ thin films having their *c* axis tilted 0°, 47°, 56°, and 90° from the normal to the film plane have been grown by pulsed laser deposition on complex oxide single crystal substrates. For the substrates, we have chosen lattice-matched substrates, such as (001)-, (011)-, and (111)-oriented $SrTiO_3$, (100)-oriented $SrPrGaO_4$, and (110)-oriented $SrLaGaO_4$, as well as non-lattice-matched Si(100) substrates. For the latter, heteroepitaxial buffer layers of $SrRuO_3$(110)/YSZ(100) and $SrRuO_3$(111)/MgO(111)/YSZ(100) have been deposited *in situ* on Si(100) substrates in order to grow (116)- and (103)-oriented $SrBi_2Ta_2O_9$ epitaxial thin films, respectively. A comparative analysis of the electrical properties for the various crystallographic orientations will be presented.

C8.6/O6.6

TEMPERATURE-DEPENDENT DIELECTRIC RESPONSE AND TUNABILITY OF $KTaO_3/KNbO_3$ SUPERLATTICES. Jennifer Sigman, David Norton, Rajiv Singh, and Josh Howard, Univ. of Florida, Dept. of Materials Science and Engineering, Gainesville, FL; Hans Christen, John Budai, Elliot Specht, Pam Fleming, and Lynn Boatner, Oak Ridge National Laboratory, Oak Ridge, TN.

In recent years, significant effort has focused on the manipulation of material properties through reduced dimensionality. Understanding size effects in ferroelectrics is useful in delineating local versus collective phenomenon in polarization behavior. In this talk, we will report on the temperature-dependent dielectric properties of $KTaO_3/KNbO_3$ superlattice structures grown by pulsed-laser deposition. This is an interesting system to consider as it provides a nearly lattice-matched perovskite multilayer structure in which the end compounds range from a paraelectric ($KTaO_3$) to a ferroelectric ($KNbO_3$) with T_c = 704 K. Previous work has shown that the structural transition associated with ferroelectricity is modified by strain and layer thickness in superlattice structures. In this talk, we will present temperature-dependent capacitance measurements using interdigitated capacitor structures fabricated on $KTaO_3/KNbO_3$ superlattice films. The peak in the dielectric response indicate the Curie temperature for a given superlattice structure. These measurements will then be compared with structural data obtained from temperature dependent x-ray diffraction. Comparison of superlattice dielectric response is also made with alloy thin film structures in which the composition corresponds to the average Ta/Nb ratio in the superlattices. We will also discuss relatively large voltage tunability of the dielectric response as a function of temperature both below and above the Curie temperature.

C8.7/O6.7

GROWTH MECHANISM OF PZT THIN FILMS EPITAXIALLY GROWN ON $SrRuO_3/SrTiO_3$ BY MOCVD. H. Nonomura, H. Fujisawa, M. Shimizu and H. Niu, Dept. of Electronics, Himeji Inst. Tech., Hyogo, JAPAN.

Investigation of the growth mechanism of PZT thin films is very important because very thin films with high quality are required for the realization of ferroelectric random access memories (FeRAMs) with high integration and low voltage operation. In this paper, the growth mechanism of MOCVD-PZT thin films epitaxailly grown on $SrRuO_3/SrTiO_3$ was investigated using scanning probe microscopy (SPM) and transmission electron microscopy (TEM). $SrRuO_3$ films were prepared at 550°C on $SrTiO_3$(100) by rf magnetron sputtering. Then PZT films were prepared on $SrRuO_3/SrTiO_3$ at 540°C by MOCVD using $(C_2H_5)_3PbOCH_2C(CH_3)_3$, $Zr(O\text{-}t\text{-}C_4H_9)_4$, $Ti(O\text{-}i\text{-}C_3H_7)_4$ and O_2. In order to observe the initial growth stage of PZT films, they were grown for various deposition time, 10-120 sec. From SPM observations, at early initial growth stage, two dimensional layer growth was observed. Afterward three dimensional islands were observed and these gradually grew until finally they covered the surface. Surface roughness measured by SPM drastically increased after the appearance of PZT islands. These results suggest that the growth mechanism of PZT on $SrRuO_3/SrTiO_3$ is the Stranski-Krastanov growth mode.

C8.8/O6.8

STRUCTURE AND DIELECTRIC PROPERTIES OF EPITAXIALLY GROWN PMN THIN FILMS ON (100)MAGNESIUM OXIDES. Y. Yamada, M. Shimoda, R. Suzuki, T. Matsuda, A. Unno, K. Wasa, Yokohama City Univ, Faculty of Science, Yokohama, JAPAN.

Thin films of [Pb(Mg1/3, Nb2/3)]O3 (PMN) were grown on the (100)MgO substrates by rf-magnetron sputtering. The crystal structure and the dielectric properties were studied.The substrate temperature during the sputtering deposition was 600°C. The sputtered thin films were rapidly cooled to a room temperature after the deposition. The thickness of the PMN thin films were 200 to 400nm. The XRD analyses showed that the crystalline (100)PMN thin films of perovskite strucure were epitaxially grown on the MgO substrates without a pyrochlore phase. The in-plane XRD analysis indicated that the PMN thin films showed 3-dimensional epitaxy. A cross sectional TEM (transmission electron microscopy) image suggested that the PMN thin films were continuous single crystal-like structure. The dielectric properties of the PMN thin films were evaluated in the sandwich structure, Au/PMN/(100)Pt/ (100)MgO,with epitaxial (100)Pt thin films as a base electrode and vacuum evaporated Au thin films as a top electrode. A typical room temperature dielectric constant was 600 to 800 at 100kHz with a loss factor D=0.01 and a small frequency dispersion. The dielectric constant increased with a decrease of the temperature as expected. The PMN thin films showed P-E hysteresis curve at a room temperature with Pr=4 micro-Coulomb/cm^2 and Hc=125kV/cm.The Pr increased with the decrease of the temperature and Pr=15 micro-Coulomb/cm^2 was observed at 0°C.

C8.9/O6.9

FABRICATION AND PROPERTIES OF EXPITAXIAL LITHIUM NIOBATE THIN FILMS BY COMBUSTION CHEMICAL VAPOR DEPOSITION (CCVD). Yong Dong Jiang, Jake McGee, Todd A. Polley, Robert E. Schwerzel, Andrew T. Hunt, MicroCoating Technologies, Chamblee, GA.

Lithium niobate has been widely investigated because it has a great number of useful physical properties: excellent ferroelectricity and piezoelectricity, high electrooptic coefficient, and large photorefractive effect. These characteristics make lithium niobate an attractive material for electrooptic and acousto-optical applications such as waveguides, modulators, second harmonic generators, and transducers. In addition, erbium-doped lithium niobate can be used as active material for waveguide lasers. In this study, expitaxial lithium niobate thin films were deposited on c-sapphire (α-Al_2O_3) by the low-cost, open-atmosphere CCVD technique developed by MicroCoating Technologies, Inc. It was found that the process parameters, such as solution concentration and deposition temperature, play a critical role in determining the growth behavior of the lithium niobate thin films. In order to improve the quality and performance of lithium niobate, the effects of dopants and seed layers were investigated as well. XRD 2-Theta scans and pole figure analysis were utilized to determine the identities and relative ratios of the orientations present in the deposited films. Film surface morphology was examined using optical microscopy and SEM. Surface roughness was measured using optical profilometry, and film thickness and index of refraction were determined by spectroscopic ellipsometry.

C8.10/O6.10

STRUCTURAL AND FERROELECTRIC PROPERTIES OF $PbZr_{0.52}Ti_{0.48}O_3/SrRuO_3$ THIN FILMS ON $SrTiO_3$ SUBSTRATES. J. Rodriguez Contreras, U. Poppe, K. Szot, C.L. Jia, H. Kohlstedt, R. Waser, Forschungszentrum Jülich, Institut für Festkörperforschung, Jülich, GERMANY; J. Schubert, Forschungszentrum Jülich, Institut für Schichten und Grenzflächen, Jülich, GERMANY.

Lead based ferroelectric materials are currently the most promising candidate for use in non-volatile ferroelectric random access memory (FeRAM). We have deposited $PbZr_{0.52}Ti_{0.48}O_3/SrRuO_3$ (PZT/SRO) heterostructures on $SrTiO_3$ (STO) substrates using high-pressure on-axis sputtering. X-ray diffraction indicates that both PZT and SRO layers are c-axis oriented and have exact parallel orientations with the STO (100) substrate. No secondary phase contribution, e.g. pyrochlore phase in PZT films, has been observed. The PZT films possess a small mosaicity ($\Delta\omega < 0.1°$, $\Delta\Phi < 1°$). Whereas in the case of SRO films these values are $\Delta\omega < 0.1°$ and $\Delta\Phi < 0.4°$. Atomic Force Microscopy reveals very smooth surfaces in the order of 0.25 nm and 0.65 nm (RMS roughness) for SRO and PZT films respectively. High Resolution Transmission Electron Microscopy shows very homogenous interfaces without defects in 10 nm and 4 nm thick PZT films on SRO. The stoichiometry has been verified by Rutherford Backscattering Spectrometry. As can be seen by channeling measurements the SRO bottom electrode improves significantly the crystalline quality of the PZT film on top. Pt/PZT/SRO as well as SRO/PZT/SRO trilayers were patterned to form capacitors. Ferroelectric hysteresis loops has been obtained for PZT film thickness ranging from 90 nm down to 12 nm. For example a 23 nm thick PZT film on SRO bottom electrode using Pt top electrode shows a remanent polarization of 105 μC/cm^2 ($2P_r$) and an coercitive field of 1024 kV/cm ($2E_c$) (at 10 kHz). Generally the remanent polarization P_r decreases while the coercitive field E_c increases towards thinner PZT film thickness.

C8.11/O6.11
EFFECT OF A-SITE SUBSTITUTION ON THE MAGNETIC AND DIELECTRIC BEHAVIORS OF FERROELECTRIC $RMnO_3$ (R:YTTRIUM OR RARE EARTH ION) THIN FILMS. N. Fujimura, H. Sakata, D. Ito, T. Yokota and T. Ito, Department of Applied Materials Science, College of Eng, University of Osaka Prefecture, Sakai, Osaka, JAPAN.

Ferroelectric materials with magnetic properties might have several advantages when the materials use for memory devices. Hexagonal yttrium and rare earth manganites form an interesting class of materials known as ferroelectro-magnet in which the ferroelectric and magnetic orders coexist at low temperatures. We have demonstrated that $YMnO_3$ thin films show ferroelectric and antiferromagnetic behaviors and demonstrate a relationship between carrier concentration and magnetic properties of $YMnO_3$ films. However, little interaction was observed between the magnetic spin and dipole moment. This paper describes that the effect of A-site substitution on the magnetic properties of $YMnO_3$ and also demonstrates that the relationship between magnetic ordering and ferroelectric or transport property.

C8.12/O6.12
STRUCTURAL VARIANT CONTROL IN EPITAXIAL $SrBi_2Nb_2O_9$ THIN FILMS THROUGH GROWTH ON VICINAL SUBSTRATES. J. Lettieri, G. Asayama, Y. Jia, and D.G. Schlom, Penn State University, Dept of Materials Science and Engineering, University Park, PA.

The inherent low symmetry common to many multicomponent oxides often results in complicated structural variants or growth twins during heteroepitaxial growth. A number of these materials also undergo phase transformations during cooling after growth that can contribute to a very complex domain structures. Given the anistropy of these low symmetry oxides and the defects associated with variant boundaries, variant control is an important part of isolating and maximizing properties of heteroepitaxial oxides. Such is the case with the ferroelectric $SrBi_2Nb_2O_9$ whose highly anisotropic polarization makes variant control in heteroepitaxial films crucial. In this study we show structural variant control of (103) oriented $SrBi_2Nb_2O_9$ films on through growth on vicinal (111) $SrTiO_3$ substrates. The orientation relationships and resultant growth based on x-ray diffraction data will be discussed.

C8.13/O6.13
INVESTIGATION OF NUCLEATION AND GROWTH OF EPITAXIAL BARIUM TITANATE THIN FILMS BY MOVPE. D.J. Towner, B.W. Wessels, Department of Materials Science and Engineering, Northwestern University, Evanston, IL; J. Ni, T.J. Marks, Department of Chemistry, Northwestern University, Evanston, IL.

$BaTiO_3$ is being considered for thin film light wave devices. Epitaxial thin films with atomically smooth surfaces and interfaces are required for these applications. We have been developing low pressure metal-organic vapor phase epitaxy to meet this need. A two dimensional nucleation and growth process is required to obtain the requisite surface roughness. The fluorinated MOVPE precursor $Ba(hfa)_2$:PEB has been utilized as the barium source due to its low melting point (71°C), high volatility, and long-term stability. Optimization of the film quality is achieved through a controlled nucleation process, with temperature and reactant partial pressure as the variable parameters. Near atomically smooth $BaTiO_3$ films (as low as 0.89 nm for 275 nm thick) with excellent crystalline quality (rocking curve FWHM as low as 0.29 degrees) have been grown on MgO (100) substrates.

C8.14/O6.14
GROWTH AND ELECTRICAL PROPERTIES OF Fe DOPED $(Ba,Sr)TiO_3$ THIN FILMS DEPOSITED BY PULSED LASER DEPOSITION. Yoshiyuki Yonezawa, Megumi Kato, Yoshinori Konishi, Nobuhiro Okuda, Hideaki Matsuyama, Shinji Ogino, Noboru Furusho, Fuji Electric Corporate Research and Development, Ltd. Yokosuka, JAPAN; Toyohiro Chikyow, National Institute for Materials Science (NIMS), Tsukuba, JAPAN; Masashi Kawasaki, Institute for Materials Research, Tohoku University, Sendai, JAPAN; Hideomi Koinuma, Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN.

$(Ba,Sr)TiO_3$ is a good candidate for gate oxides and integrated capacitors because of its high dielectric constant and absence of lead content. Consequently, direct epitaxial growths of BST on Si substrate have been studied extensively. However, there are problems with the formation of SiO_2 interlayer and leakage current due to stoichiometrical deviation. In particular, thin films deposited by Pulsed Laser Deposition require more than 100mtorr of oxygen partial pressure to get the required high break down voltage. To suppress the leakage current we tried to dope transition metals into the target, such as Mo, Mn, Cr, W and Fe. The target was prepared by sintering mixed powders of $SrTiO_3$, $BaTiO_3$ and 1mol% transition metal oxide. Nb-doped:$SrTiO_3$ was used for the substrate and the Pulsed Laser Deposition was used for the film fabrication. Substrate temperature was 600°C; oxygen partial pressure of 5mtorr and a post annealing process was performed under 1atm oxygen pressure. After the deposition film qualities were studied by atomic force microscopy(AFM), scanning electron microscopy (SEM) and x-ray diffraction (XRD). Pt upper electrodes were deposited on the films and the electrical properties were measured. Among the transition metals, the Fe-doped film had a significant effect on suppressing the leakage current. Subsequently, we changed the amount of Fe doping from 0.1mol% to 6%. Then we fabricate the film and compare the electrical properties. As a result, with post annealing, the sample with 4% Fe showed the lowest leakage current among those. While without post annealing, the sample with 6% Fe doped showed the lowest leakage current. As for the dielectric constants, it decreased as the doping increased. But at most only 20% of reduction was observed. XAFS results will be presented for estimating the local structure of the Fe ions.

C8.15/O6.15
FEMTOSECOND PULSED LASER DEPOSITION OF $BaTiO_3$ THIN FILMS. W. Tian[a], P.A. Van Rompay[b], Z.Y. Zhang[b], P.P. Pronko[b], J. Lettieri[c], D.G. Schlom[c], and X. Q. Pan[a]; [a]Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI; [b]Center for Ultrafast Optical Science and Department of Electrical Engineering and Computer Science, The University of Michigan, Ann Arbor, MI; [c]Department of Materials Science and Enginerring, Penn State University, University Park, PA.

Considerable attention has recently focused on the use of femtosecond pulsed lasers for the fabrication of oxide thin films. The high intensity pulse of a femtosecond laser ($\sim 10^6$ order of magnitude higher than nanosecond laser), regardless of wavelength, is thought to have advantages over nanosecond laser for fabricating oxide thin films at relatively lower substrate temperature. We employed a femtosecond pulsed laser, with wave-length centered at 780 nm and pulse width 100 - 150 fs, to deposit $BaTiO_3$ thin film on the (001) $SrTiO_3$ substrate. The repetition rate of the laser is 10Hz. Processing parameters including target composition, oxygen partial pressure, substrate temperature, substrate-target distance, and diameter of the focused laser beam were varied to optimize the growth conditions. X-ray diffraction, Rutherford backscattering spectroscopy (RBS), x-ray photoelectron spectroscopy (XPS), TEM, and AFM were used to characterize the structure, microstructure, surface morphology, and chemical composition of the films. At the nominally optimum growth condition, x-ray diffraction studies indicate the formation of nearly phase-pure and epitaxial $BaTiO_3$ thin films, however, RBS and XPS studies reveal an overall off-stoichiometry of the films from the desired $BaTiO_3$. Moreover, the thin films grown by femtosecond laser exhibit much rougher surface than that of the films grown by nanosecond Excimer laser under similar growth conditions, which is most likely due to the non-stoichiometry nature of the films. Thus, the applicability of infrared (IR) femtosecond laser into complex oxide thin film deposition needs further investigation.

SESSION C9: DOMAINS AND NANOSTRUCTURES
Chairs: Andreas Seifert and Yoichi Miyasaka
Wednesday Morning, November 28, 2001
Room 210 (Hynes)

8:30 AM *C9.1
SIZE EFFECTS IN FERROELECTRIC FILMS: ANOMALIES IN POLARIZATION DISTRIBUTION, DEPLETION, DEPOLARIZATION, AND GEOMETRICAL FACTORS IN SUBMICRON CAPACITORS. Igor Stolichnov, Enrico Colla, Alexander Tagantsev, Nava Setter.

Polarization switching of ferroelectric films as well as related phenomena show a marked size dependence characteristics whose features, when understood and controlled, can be used to enhance capacitor performance. We report on the study of these size effects using advanced characterization techniques such as polarization distribution mapping of submicron structures, and variable depth piezoresponse measurements, in combination with the traditional hysteresis measurements. Of particular importance is the analysis of anomalous polarization patterns observed in submicron ferroelectric capacitors. Our interpretation of the size effects takes into account depletion, depolarization, and mechanical phenomena. The results are discussed in relation with high density memories.

9:00 AM C9.2
FOCUSED ION BEAM ENGINEERED SUB-QUARTERMICRON

FERROELECTRIC STRUCTURES. A. Stanishevsky, V. Nagarajan, C. Ganpule, J. Melngailis, E. Williams, and R. Ramesh, Materials Research Science and Engineering Center, University of Maryland, College Park, MD.

Studies of the properties of ferroelectric materials scaled to submicron dimensions are important in understanding the fundamental issues relevant to high-density memories. One of the most intriguing questions is what is the smallest volume of a ferroelectric material that will still exhibit ferroelectric properties? We have demonstrated earlier that focused ion beam (FIB) patterned ferroelectric capacitor structures with both bottom and top electrodes exhibit ferroelectric properties even when scaled down to a lateral size of 70 nm. Ion induced damage of such structures required a post-annealing procedure to recover the ferroelectric properties. In this work, we present results of a novel approach to fabricate damage-free sub-100 nm ferroelectric structures using FIB. The approach consists of fabricating sub-100nm trenches in a titania dielectric layer, which is subsequently "filled" with ferroelectric PZT. We show that at least 50 nm discrete PZT structures can be fabricated. Electric force microscopy was used to examine the properties of these structures. The effects of pattern design and fabrication process induced damage on the physical properties of micromachined ferroelectric structures are discussed in detail. This work is supported by the University of Maryland - NSF - MRSEC under contract No. NSF-DMR-00-80008.

9:15 AM C9.3
NOVEL *IN – SITU* CHARACTERISATION OF THE NANO-METER SCALE FERROELECTRIC PROPERTIES OF PZT THIN FILMS AT MEGAHERTZ FREQUENCIES. Bryan D. Huey, Andrew Briggs, Oleg V. Kolosov, Oxford University, Department of Materials, Oxford, UNITED KINGDOM.

Variations of scanning probe microscopy (SPM) have been shown to be powerful tools for investigating the piezoelectric properties of ferroelectric thin films with nanometer scale spatial resolution. Thus far, however, these techniques could only be used to measure the characteristics of ferroelectric domains at kHz frequencies or less, whereas eventual industrial applications will require a better understanding of the ferroelectric response for higher frequency excitations. For this reason, a novel SPM-based technique has been developed that uniquely allows piezoelectric properties to be measured *in – situ* at MHz frequencies. This is achieved by heterodyning ultrasonic and electrostatic tip-sample interactions. By scanning the tip during the measurement, the orientation of poled domains can be mapped with nanometer resolution. For a fixed position, the response of domains to high frequency poling and/or access (to identify the polarization) can also be characterized. Finally, for a 5 MHz frequency excitation, the polarization loop has been determined.

9:30 AM C9.4
DEPOLARIZING-FIELD-INDUCED 180° SWITCHING OF A-DOMAINS IN POLYDOMAIN EPITAXIAL PZT THIN FILMS BY AFM. A. Roelofs, N.A. Pertsev and R. Waser, Institut für Werkstoffe der Elektrotechnik, RWTH Aachen, GERMANY; F. Schlaphof and L.M. Eng, Institut für angewandte Photophysik, Technische Universität Dresden, GERMANY; C. Ganpule, V. Nagarajan and R. Ramesh, Materials Science Research and Engineering Center, University of Maryland, College Park, MD.

The change of the domain structure in polydomain epitaxial $PbZr_{0.2}Ti_{0.8}O_{0.3}$ thin films after switching the out-of-plane (c-domain) and in-plane (a-domain) polarizations is studied. This is done using a modified AFM monitoring the inverse piezoresponse (three-dimensional piezoresponse force microscopy, PFM). Under an electric field applied between the PFM tip and the bottom electrode, the 180° switching is found in both c- and a-domains. Removing this field leads to the spontaneous reversal of the out-of-plane and in-plane polarizations back to their initial orientations, evolving via heterogeneous development of antiparallel c-domains. The switching of in-plane polarization inside a-domains and the preferential formation of reversing c-domains at 90° domain walls are explained by effects of the depolarizing fields caused by transient polarization charges appearing on these domain walls.

10:15 AM *C9.5
LOCAL POLARIZATION, CHARGE COMPENSATION, AND CHEMICAL INTERACTIONS ON FERROELECTRIC SURFACES: A ROUTE TOWARD NEW NANOSTRUCTURES. Dawn A. Bonnell and Sergei V. Kalinin, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA.

The local potential at domains on ferroelectric surfaces results from the interplay between atomic polarization and screening charge. The presence of mobile charge affects surface domain configuration, switching behavior, and surface chemical reactions. By measuring the temperature and time dependence of surface potential and piezo response with scanning probe microscopies, thermodynamic parameters associated with charge screening can be determined. This is illustrated for the case of $BaTiO_3$ (100) in air, for which the charge compensation mechanism is surface adsorption and enthalpy and entropy of adsorption are determined. The local electrostatic fields in the vicinity of the domains have a dominant effect on chemical reactivity. The specificity of physisorption and chemisorption of simple molecules (H_2, H_2O, CH_4, OH, etc.) on 'a' and 'c' domains will be demonstrated. The relative contributions of the site specific chemical interaction and the electrostatic attraction to adsorption will be discussed. Extensions to organic molecules will be illustrated. Finally, photo reduction of a large variety of metals can be localized to domains with the appropriate surface charge. It has been demonstrated that proximal probe tips can be used to switch polarization direction locally. Combining the ability to 'write' domains of local polarization with domain specific reactivity of metals, vapors of small molecules, and organic compounds leads to a new approach to fabricating complex nanostructures.

10:45 AM C9.6
BEYOND PIEZOELECTRIC IMAGING IN PIEZORESPONSE-AFM. C. Harnagea, A. Pignolet, M. Alexe, and D. Hesse, Max-Planck-Institut fuer Mikrostrukturphysik, Halle(Saale), GERMANY.

Although piezoresponse scanning force microscopy (PFM) is a widely used method for the characterization and study of the basic polarization phenomena in ferroelectric thin films, little effort has been put to understand the exact origin of the signals carrying the polarization information. Beside the simple scenario of the converse piezoelectric effect (detection of a local oscillation of the sample surface induced by an AC voltage applied to the tip), the electrostatic interaction may play an important role in certain circumstances. The Maxwell stress force between the conductive tip and the bottom electrode of the sample cannot be avoided and induces vibrations of the cantilever that may be easily confused with the pure piezoelectric vibration of the ferroelectric sample. Additionally, an analysis of the electric field distribution under the PFM tip shows that for sharp tips (apex radius smaller or comparable to the film thickness), there is a region in the ferroelectric where the electric field exceeds the local coercive field even under the small AC testing voltage. The polarization switching that occurs in this region may drastically influence the piezoresponse signals and therefore may lead to an erroneous interpretation of the measurements. An analysis of the balance between the piezoelectric and electrostatic signals in PFM was performed and the conditions needed to obtain the real piezoresponse signal will be presented. The influence of the probing parameters such as the amplitude of the testing AC voltage and contact force will also be shown.

11:00 AM C9.7
BEHAVIOR MAPS OF PIEZORESPONSE FORCE MICROSCOPY: SIMPLE RELATIONSHIPS FROM EXACT SOLUTIONS. Sergei V. Kalinin and Dawn A. Bonnell, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA.

Piezoresponse force microscopy (PFM) is a promising tool for characterization of ferroelectric surfaces on the nanometer level. To quantify local surface properties, a clear understanding of PFM imaging mechanism must be achieved. It is recognized that both electrostatic and electromechanical interactions contribute at the tip-surface junction. Here we present analytical solutions for the electrostatic sphere- anisotropic dielectric plane problem coupled to Hertzian contact and for the electromechanical piezoelectric indentation problem. In the electromechanical model, the limits of strong and weak indentation are established and the relative contributions of electroelastic constants are determined. These results are used to construct 'piezoresponse behavior maps' that correlate the imaging conditions with the image contrast mechanism. These maps are verified with experimental measurements. Under some conditions, i.e. those corresponding to relatively large indentation force and tip radius, the real piezo electric coefficient can be determined. This analysis reconciles existing discrepancies in the interpretation of PFM imaging contrast. The approach also provides a framework for the quantification of tip-induced polarization switching. The 'piezoresponse behavior maps' indicate regimes of experimental conditions in which quantification of the properties is problematic. Some of these difficulties can be overcome with a new variant of PFM in which the excitation bias is applied to the sample. Use of this lateral modulation scheme allows imaging excitation and switching biases to be decoupled.

11:15 AM C9.8
CHARACTERIZATION OF INHOMOGENEOUS FERROELECTRICS BY ANALYSIS OF THE SWITCHING CURRENT DATA. Vladimir Ya. Shur, Evgenii L. Rumyantsev,

Ekaterina V. Nikolaeva, Eugene I. Shishkin, Ivan S. Baturin, Marina V. Kalinina, Ural State Univ, Ekaterinburg, RUSSIA.

Switching of ferroelectric with spatially inhomogeneous coercive/ threshold field in slow increasing field was investigated by computer simulation under the assumption that the threshold field for arising of isolated nuclei is essentially higher than for nucleation at the existing wall. The obtained relation of the switching current data and the threshold field distribution functions differs significantly from the Preisach approximation. It was assumed during computer simulation that switching at each time-step occurs in two stages: formation of isolated nuclei and subsequent nucleation at the walls. The isolated nuclei appear in all points, where the external field exceeds the threshold one. Nuclei at the existing wall appear at lower field. Taking into consideration the input of domain growth in switching current leads to strong dependence of the current shape on the spatial correlation of the threshold field. Different types of the spatial correlation functions ranging from random to periodic have been investigated. We have shown how the information about the distribution function of the threshold fields and the spatial correlation function can be extracted from the switching current data measured in triangular pulses at low frequencies. The proposed approach has been applied for analysis of the experimental currents in PZT thin films. Our investigations revealed that the proposed method opens the possibilities for quantitative characterization of the ferroelectric films produced by different technologies and can be used for detail investigation of the fatigue effect. The research was made possible in part by Programs "Basic Research in Russian Universities" (Grant No.5563) and "Priority Research in High School. Electronics" (Grant No. 03-03-29), by Grant No. 01-02-17443 of RFBR, by Award No. REC-005 of CRDF.

11:30 AM C9.9
HIGHER ORDER NONLINEAR DIELECTRIC MICROSCOPY. Yasuo Cho, Koya Ohara, Tohoku Univ, Research Institute of Electrical Communication, Sendai, JAPAN.

Recently, we proposed a new, purely electrical technique for imaging the state of ferroelectric polarization and the local crystal anisotropy of dielectric materials. This technique involves the measurement of point-to-point variations of the nonlinear dielectric constant of a specimen and is called scanning nonlinear dielectric microscopy (SNDM). This is the first successful purely electrical method for observing ferroelectric polarization distributions that is unaffected by free-charge shielding. The resolution of the technique has thus far been improved down to the sub-nanometer scale. We have developed a new SNDM technique with a much higher resolution, capable of detecting a higher order nonlinear dielectric constant. In the conventional SNDM technique, we measure the lowest order nonlinear dielectric constant $\varepsilon(3)$, which is a 3rd rank tensor. To improve the performance and resolution of SNDM, we have modified the technique such that a two-order higher nonlinear dielectric constant $\varepsilon(5)$ (5th rank tensor) is detected. It is expected that higher order nonlinear dielectric imaging will provide higher lateral and depth resolution. We confirmed this improvement over conventional SNDM imaging experimentally, and used the technique to observe the growth of a surface paraelectric layer on periodically poled $LiNbO_3$. The thickness of this surface layer is one unit cell order. Therefore, we concluded this higher order nonlinear dielectric imaging is very useful for understanding an atomic scale polarization structure in ferroelectric materials.

11:45 AM C9.10
IN-SITU X-RAY DIFFRACTION STUDIES OF FERROELECTRIC 180° STRIPE DOMAIN FORMATION IN HETEROEPITAXIAL $PbTiO_3$ THIN FILMS. J.A. Eastman[a], G.B. Stephenson[a], Carol Thompson[b,a], S.K. Streiffer[a], O. Auciello[a], M.E.M. Aanerud[b], L.J. Thompson[a], and G.-R. Bai[a], [a]Materials Science Division, Argonne National Laboratory, Argonne, IL; [b]Department of Physics, Northern Illinois University, Dekalb, IL.

Using a unique *in-situ* film growth and processing facility at BESSRC Sector 12-ID of the Advanced Photon Source, we have experimentally demonstrated for the first time that heteroepitaxially-strained lead titanate ($PbTiO_3$) thin films grown on strontium titanate substrates exist in a non-centrosymmetric (ferroelectric) tetragonal phase as much as 235°C above the bulk ferroelectric-to-paraelectric phase transition temperature. This misfit-strain-induced increase in transition temperature, as well as the fact that the phase transition is observed to be second order, are consistent with theoretical predictions (Pertsev *et al.*, PRL, 84, 3722, 2000). Furthermore, we observe that the ferroelectric phase is partitioned into a highly-ordered nanoscale stripe structure that forms as the film is cooled through the phase transition temperature. This striped structure consists of periodically-arranged 180° domains that are believed to arise to minimize depolarization energies. The phase transition temperature depends on film thickness, decreasing from approximately 725°C for a 40 nm film thickness to near the bulk transition temperature of 490°C for a film thicknesses of 3.5 nm. Cooling samples to room temperature results in a second structural transition from the striped 180° domain structure to the commonly observed ferroelastically-distorted microstructure consisting of non-ordered c-axis oriented domains and a small volume fraction of 90° domains (twins). The effects of substrate electrical conductivity and substrate/film misfit on the phase transition behavior will be discussed.

SESSION C10: PIEZOELECTRICS AND PYROELECTRICS
Chairs: Paul Muralt and Susan Trolier-McKinstry
Wednesday Afternoon, November 28, 2001
Room 210 (Hynes)

1:30 PM *C10.1
OPTIMIZATION AND REPRODUCIBILITY ISSUES OF SOLUTION DERIVED THIN FILMS FOR DEVICE APPLICATIONS. Andreas Seifert, Zian Kighelman, Nicolas Ledermann, Paul Muralt, and Nava Setter, Ceramics Laboratory, Swiss Federal Institute of Technology Lausanne (EPFL), SWITZERLAND.

Conservation of the principle materials properties throughout the fabrication process of piezoelectric and pyroelectric devices, as well as good reproducibility of post-processing device performance, requires close control of the involved processing steps. Whereas parameter control during precursor synthesis, deposition, pyrolysis and crystallization is necessary, it was shown insufficient for certain systems. To achieve good film and device properties it was important to use purified starting-products, optimized precursor chemistries and adapted substrate/nucleation layer systems. Phase pure relaxor $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}(x)PbTiO_3$ thin films with reproducible properties could only be obtained after careful optimization of the precursor synthesis. For that purpose all synthesis steps were routinely performed under a dry argon atmosphere using Schlenk vacuum techniques. Solvents were distilled, dried and stored under argon with molecular sieves. Starting products were purified by vacuum distillation and reaction by-products were removed from the synthesized solutions by multiple distillations, resulting in stable PMN-PT precursors. The influence on microstructure and properties will be discussed. In the case of $PbZr_xTi_{1-x}O_3$ thin films for device applications, optimized processing allowed to establish the probably ultimate transverse piezoelectric coefficient that can be achieved with chemical solution deposition. Understanding film/electrode interactions was found to be crucial to fabricate single-phase $PbZr_xTi_{1-x}O_3$ thin films in the composition range of x=0.3-0.6, with controlled orientation and stress as well as identical grain size and thickness. Comparison between tetragonal and rhombohedral {100} or {111} oriented films allowed to establish reference values of the transverse piezoelectric coefficient e_{31}, and a maximum value of -12 C/m^2 was measured for {100} oriented PZT 53/47. In addition to processing control issues, it was shown that careful statistical examination of a relevant parameter-set can give important information on processing/property correlation, leading to increased reproducibility.

2:00 PM C10.2
DIELECTRIC AND ELECTROMECHANICAL BEHAVIOUR OF RELAXOR $[(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3]$ THIN FILMS. N.J. Donnelly, G. Catalan, R.M. Bowman, J.M. Gregg, Queens University Belfast, N. IRELAND.

Thin film capacitor structures were fabricated by pulsed laser deposition on MgO{100} substrates, using (La,Sr)CoO_3 (LSCO) as a bottom electrode and the relaxor $[(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3]$ (PMN-PT) as the dielectric. For several compositions [x = 0; 0.07; 0.1; 0.2; 0.3], the crystallography was verified by XRD and TEM analysis and was found to be 100% perovskite and highly oriented. Films showed excellent dielectric properties with peak dielectric constants of $\epsilon_r \approx 1800$ and losses of tan $\delta < 0.05$ (300K & 1kHz). Frequency dispersion was considerable below T_m and negligible above it, and the migration of T_m could be well fitted to Vogel-Fulcher functions yielding 'freezing' temperatures and mean relaxation times comparable to bulk single crystals. The electromechanical strain in the $< 100 >$ direction was measured for each composition by *in situ* x-ray diffraction and also by piezo-response atomic force microscopy. The maximum strain achieved was 0.34%. Though comparable to that of single crystal, such electromechanical strains required much higher electric field strengths than in bulk, resulting in a lower value of the field-dependent electrostrictive coefficient M_{11}. This deficiency is a manifestation of the lower dielectric permittivity inherent to thin films and is more apparent in polarisation measurements. Using an E-field of 300kV/cm, the polarisation was measured as $35\mu C/cm^2$, however comparable polarisation can be achieved in single crystal

using fields of the order of 100kV/cm. Despite reductions in dielectric permittivity and M_{11}, the polarisation-dependent electrostrictive coefficient Q_{11} is unaffected in thin films. Using the measurements of polarisation and absolute strain, Q_{11} has been determined for each member of the compositional series and was found to be typically between 1×10^{-2} and 2×10^{-2} m^4/C^2, which is of the same order of magnitude as found in bulk single crystal.

2:15 PM C10.3
ELECTROMECHANICAL PROPERTIES OF (1-x)PMN-xPT THIN FILMS (x=0,0.1, 1). Zian Kighelman, Dragan Damjanovic, Nava Setter, Ceramics Laboratory, Materials Department, Swiss Federal Institute of Technology - EPFL, Lausanne, SWITZERLAND.

Lead magnesium niobate-lead titanate (PMN-PT) solid solution, including the end members, is of a great interest from the fundamental and technological point of view. In form of thin films, this system is of interest for various microsystems. We report on the properties of PMN, PT, and 0.9PMN-0.1PT films prepared by chemical solution deposition on silicon and conducting strontium titanate substrates. PMN and 0.9PMN-0.1PT films are pyrochlore free, and show typical relaxor characteristics but with reduced dielectric permittivity (up to 5000 at the temperature of maximum permittivity). PMN films deposited on Nb-doped strontium titanate are epitaxial and have a larger permittivity (up to 8000). The reduction in the permittivity is partly due to the stresses in the film, but our present results suggest that this stress is not the only factor that reduces the permittivity. Electrostrictive and piezoelectric properties of the films were investigated in detail. The strain-field response is hysteresis free and the field induced longitudinal piezoelectric coefficient is comparable to the one reported for typical ferroelectric PZT thin films. Unusual self-polarization of PMN films is discussed. Ferroelectric lead titanate films exhibit well developed domain structure, and the piezoelectric coefficient comparable to the one in calcium modified material. The small but nonzero nonlinearity of the piezoelectric response suggests some contribution of the 90Å domain walls despite the high stresses and high spontaneous strain in the films.

2:30 PM C10.4
PIEZOELECTRIC PROPERTIES OF EPITAXIAL $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ FILMS. Takeshi Yoshimura, Susan Trolier-McKinstry, The Pennsylvania State University, Materials Research Institute, University Park, PA.

Microelectromechanical systems (MEMS) have shown significant promise for miniaturized devices. Piezoelectric thin films are one of the key elements to enhance the sensing and actuation function of such devices. Relaxor ferroelectric films are especially attractive, since relaxor based ferroelectric single crystals exhibit very large piezoelectric responses. In this study, the ferroelectric and piezoelectric properties of epitaxial (1-x)$Pb(Yb_{1/2}Nb_{1/2})O_3$ - x$PbTiO_3$ (PYbN-PT) films with compositions of x=0.5 and 0.4 were investigated. Since PYbN-PT has the highest Curie point ($\sim$360°C) near the morphotropic phase boundary (x$\sim$0.5) of the known relaxor ferroelectric-$PbTiO_3$ solid solutions, temperature stable MEMS devices can be expected. PYbN-PT films with $SrRuO_3$ bottom electrodes were deposited on (100)$LaAlO_3$, (100)$SrTiO_3$, and (111)$SrTiO_3$ single crystal substrates by pulsed laser deposition. PYbN-PT films with high phase purity (the estimated pyrochlore content <0.5%) were obtained on each substrate. Epitaxial growth of PYbN-PT films was confirmed by x-ray ϕ scan. In some cases, in addition to the cube-on-cube epitaxy of the perovskite, 45° rotations in plane were also observed. The remanent polarizations of (001) and (111)PYbN-PT films with the 50:50 composition were as high as 29 $\mu C/cm^2$ and 25 $\mu C/cm^2$, respectively. On (001)PYbN-PT films with compositions of 50:50 and 60:40, the $e_{31(eff)}$ coefficients of -10 C/m^2 and -8 C/m^2 were observed, respectively.

3:15 PM *C10.5
FERROELECTRIC AND DISPLACEMENT PROPERTIES OF LEAD ZIRCONATE TITANATE THICK FILMS PREPARED BY CHEMICAL SOLUTION DEPOSITION PROCESS. Takashi Iijima, Smart Structure Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, JAPAN; Yoshinori Hayashi, Jyun Onagawa, Faculty of Engineering, Tohoku Gakuin Univ., Tagajyo, JAPAN.

Lead zirconate titanate (PZT) films are in demand for applications in many fields like memories, sensors and actuators. Combination of the preparation technique for the ferroelectric films and for the micro machining of Si is considered to be effective way to fabricate piezoelectric micro devices like micro actuators. Therefore, various processes were investigated to fabricate thick PZT films varied from 5 to 100 μm. On the other hand, low process temperature of PZT thick films is required to keep the compatibility with the Si micro machining process. In the case of the thick films prepared by the powder sauce technique like a screen printing, the usual firing temperature was more than 800°C, and the density of the thick films are not so high because of imperfect sintering. We successfully fabricated 10 μm thick dense PZT films using a chemical solution process, and evaluated the ferroelectric and displacement properties. A 0.5 M precursor solution of $Pb_{1.1}(Zr_{0.53}Ti_{0.47})O_3$ were prepared from trihydrated lead acetate, titanium iso-propoxide and zirconium iso-propoxide as starting materials and 2-methoxyethanol as the solvent. The process of spin coating and pyrolysis at 500°C was repeated five times, and then the precursor films fired at 700°C for 5min. This sequence repeated 30 times, and finally the films fired at 700°C for 10min. The fabricated crack-free 10 μm thick PZT films showed flat surface and dense microstructure. Ferroelectric properties were comparable with the bulk PZT ceramics, because remnant polarization (Pr) was 50 $\mu C/cm^2$, which is the highest value of reported PZT thick films, and coercive field (Ec) was 30 kV/cm at a applied field of 175 kV/cm. The displacement property of the PZT thick film simultaneously measured with ferroelectric property exhibited a butterfly like hysteresis. The detail investigation of displacement properties is undertaken now.

3:45 PM C10.6
MEASUREMENT OF THE TEMPERATURE DEPENDENCE OF THE EFFECTIVE TRANSVERSE PIEZOELECTRIC COEFFICIENT ($e_{31,f}$) IN LEAD ZIRCONATE TITANATE FILMS. R.A. Wolf, P. Moses, S. Trolier-McKinstry, Materials Research Institute, The Pennsylvania State University, University Park, PA.

As a result of their superior piezoelectric properties, lead zirconate titanate (PZT) films are popular candidate materials for use in microelectromechanical systems (MEMS). Knowledge of the temperature dependence of the electromechanical properties of these films is required in sensor and actuator applications. A modified wafer flexure technique was developed to characterize the transverse piezoelectric coefficient ($e_{31,f}$) of films as a function of temperature between -55°C and 85°C. In this method, a coated substrate is cyclically flexed so that the film is subjected to an oscillating biaxial stress. The $e_{31,f}$ coefficient is determined by simultaneously monitoring strain and the generated surface charge. Several PZT films of different thickness (2 μ, 4 μ, and 6 μ) and different Zr/Ti ratios (40/60, 52/48, and 60/40) were prepared by chemical solution deposition and subsequently analyzed. $e_{31,f}$ was found to vary between 7% and 56% over the -55°C to 85°C range. Thinner films with higher Ti content exhibited the lowest temperature variability. Experimental results for films were compared both with phenomenological predictions and experimental data for bulk PZTs.

4:00 PM C10.7
THE COMPOSITIONAL EFFECTS OF CSD PZT THIN FILMS ON THE PIEZOELECTRIC AND FERROELECTRIC PROPERTIES. Dong-Joo Kim, Jon-Paul Maria, Angus I. Kingon, Dept of Materials Science and Engineering, Raleigh, NC; S.K. Streiffer, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Although the compositional dependence of piezoelectric and ferroelectric properties across the PZT phase diagram has been reported by many authors, simultaneous assessment of the results does not lead to a consistent conclusion regarding the importance or influence of the morphortropic composition. A consistent difficulty, especially in sub-micron films, is encountered when attempting to guarantee that the orientation, the film stoichiometry, and microstructure are of sufficient consistency that meaningful comparisons can be drawn. We present here the piezoelectric and ferroelectric properties of highly textured polycrystalline PZT films from Zr/Ti ratio from 80/20 to 15/85. These films are prepared by CSD (chemical solution deposition) on platinized substrates with the thickness of 200 nm. All films are consistently {111}-oriented and have dense microstructures with 80-100 nm grain diameters. The piezoelectric hysteresis loops (d_{33} - E) were measured using a highly sensitive double beam laser interferometer. It was found that tetragonal compositions show larger remanent d_{33} ($\sim$40 pm/V) and polarization P_r ($\sim$28 $\mu C/cm^2$) values. Squareness of polarization and piezoelectric hysteresis loops was optimized in tetragonal compositions. For comparison, the remanent d_{33} values were estimated by a modified phenomenological approach; the maximum d_{33} values did not depend strongly (35-45 pm/V) on composition. Temperature dependent measurements of ferroelectric and dielectric properties were also collected. This analysis suggests that most electrical behavior can be explained by the presence of intrinsic contributions alone. A peak of dielectric constant was observed near the MPB but a similar peak did not occur in d_{33}. This observation can be explained by the absence of non-180 degree domain wall motion. The results are discussed in the context of structural and texture analyses.

4:15 PM C10.8
PIEZOELECTRIC PHENOMENA IN Pb-BASED FERROELECTRIC THIN FILMS. Chandan Ganpule, V. Nagarajan, Yu Wang, Alexander Roytburd, Ramamoorthy Ramesh, University of Maryland, Dept of Materials Engineering, College Park, MD; Ellen

Williams, University of Maryland, MRSEC-Department of Physics, College Park, MD.

Piezoelectric properties of thin ferroelectric films has been a subject of intense research in the last few years. It is now understood that piezoelectric properties of thin films are often dramatically different compared to parent bulk or single crystal compositions. The most cited reason for this behavior has been substrate induced clamping and stress in these thin films. In this talk the various aspects thin film-substrate interaction will be outlines. Particularly for PZT based compositions the effect of substrate in terms of both crystal orientation and mechanical clamping will be presented. We show that as the film grain structure is changed from polycrystalline to epitaxial by choosing a suitable templete, the d33 response more than doubles. Secondly we have modeled via detailed theory the electromechanical interaction of the substrate-thin film system in terms of the materials compliances and we show that by changing the compliance of the substrate one can dramatically induce changes in the piezoresponse for the same composition and thickness. This has been verified experimentally. The details of this phenomenon and methods to release the substrate clamping will be presented in the talk. This work is supported by the NSF-MRSEC foundation.

4:30 PM C10.9
ENHANCED PYROELECTRIC RESPONSE IN ULTRA-THIN PZT FILMS. R.P. Godfrey and R. Ramesh, University of Maryland, Department of Physics, College Park, MD; C. Wesley Tipton, U.S Army Research Laboratory, Adelphi, MD.

We report a significant enhancement in the pyroelectric response in ultra-thin PZT thin films. We have utilized the tunablity of the metallic oxide electrode La-Sr-Co-O to induce enhanced pyroelectric response in ultra-thin, epitaxial Pb-La-Zr-Ti-O films on single crystal $LaAlO_3$ substrate. The defect chemistry of LSCO allows for modification of the intrinsic carrier concentration either electronically or ionically. In the case of this work we have systematically varied the oxygen defect concentration in LSCO by reduction during deposition. A capacitor grown with a reduced bottom electrode yields asymmetric electrical characteristics due to a large internal field. The space charge field effectively self-poles virgin devices which in turn show significantly enhanced pyroelectric coefficients without poling treatment. Positron annihilation data clearly reveal the location of oxygen vacancies in the bottom electrode as well as the vacancy concentration gradient within the capacitor stack. Pyroelectric and ferroelectric measurements indicate that film thickness and defect concentrations both play critical roles in determining the final structure and the pyroelectric response within the device. This work was supported, in part, by the U.S. Army Research Laboratory MRCP Agreement and by the NSF-MRSEC under contract No. DMR-00-80008.

4:45 PM C10.10
MICRO-MACHINED PYROELECTRIC INFRARED DETECTOR BASED ON SOL-GEL DERIVED $Pb(Zr_{0.3}Ti_{0.7})O_3/PbTiO_3$ MULTILAYER THIN FILM. Ling Ling Sun, Wei Guo Liu, Ooi Kiang Tan, Wei Guang Zhu, School of Electrical and Electronic Engineering, Nanyang Technological University, SINGAPORE.

Sol-gel derived $Pb(Zr_{0.3}Ti_{0.7})O_3/PbTiO_3$ (PZT/PT) multilayer thin film has been studied for the application of infrared detection. Compare to the pure $Pb(Zr_{0.3}Ti_{0.7})O_3$ (PZT) thin film deposited by the same process, the multilayer thin film shows lower dielectric constant and similar pyroelectric coefficient and dielectric loss. The detectivity figures of merit for the PZT/PT and PT thin films are 12.3×10^{-6} $Pa^{-1/2}$ and 10.2×10^{-6} $Pa^{-1/2}$, and values of voltage response figures of merit are 0.025 m^2/C and 0.017m^2/C, respectively. The results show the multilayer PZT/PT film is a better choice for the pyroelectric infrared detection. Pyroelectric infrared detectors have been successfully developed based on the multilayer PZT/PT thin film. Silicon bulk-machined thermal isolation structure has been applied to reduce the thermal loss from the sensing thin film to the Si substrate. To evaluate the detector performance and to aid in the thermal structure design, finite element analysis (FEA) of the detector in the terms of heat transfer has been carried out by using a software package ANSYS. The detector response has been characterized by a modified Chynoweth system. At 20 Hz, the dynamic pyroelectric voltage responsivity is measured to be 132V/W (in rms) with the sensing element size of 240×360 μm^2. The measured results are consistent with the simulated results.

SESSION C11: FERROELECTRIC GATES
Chair: Jon-Paul Maria
Thursday Morning, November 29, 2001
Room 210 (Hynes)

8:30 AM C11.1
GROWTH AND FERROELECTRIC PROPERTY OF EPITAXIAL $YMnO_3$ THIN FILMS. Daisuke Ito, Norifumi Fujimura and Taichiro Ito, Dept. of Applied Materials Science, Graduate School of Engineering Osaka Prefecture University, Osaka, JAPAN.

We have been proposing the use of $YMnO_3$ film for an MFIS-type ferroelectric gate transistor. Epitaxial grown $YMnO_3$ exhibits better ferroelectric properties compared to the (0001) oriented films. However, the detailed ferroelectric properties of $YMnO_3$ film has not been reported. This paper describes the detailed analysis of ferroelectric properties of epitaxially grown $YMnO_3$ films and the potential for the applying a ferroelectric gate transistor. $YMnO_3$ film was obtained on (111)Pt/(0001)sapphire by a pulsed laser deposition (PLD) method. By RHEED measurement, the films were epitaxially grown on (111)Pt/(0001)sapphire. The ferroelectric P-E hysteresis was observed and the remanemt polarization, coercive field and the ratio of Pr/Ps were recognized as 1.7 $\mu C/cm^2$, 80 kV/cm and 0.7 respectively. The endurance property was over 10^{10} cycle at the frequency of 100 kHz, at which was observed polarization saturation. Using these values, the potential for the MFIS transistor with Y_2O_3 buffer layer is also demonstrated.

8:45 AM C11.2
INTEGRATION PROCESSES AND PROPERTIES OF Pb5Ge3O11 MFOS ONE TRANSISTOR MEMORY DEVICES. Tingkai Li, Sheng Teng Hsu, Bruce Ulrich, Lisa Stecker Sharp Laboratory of America, Inc., Camas, WA.

The basic mechanism for one transistor memory device has been studied. Because its low remanent polarization and dielectric constant, the c-oriented Pb5Ge3O11 thin films was selected for one-transistor memory applications. In order to demonstrate the one-transistor memory applications, Pb5Ge3O11 (PGO) MFOS (M: Metal, F: Ferroelectrics, O: oxide, S: silicon) for one transistor memory application was prepared. Processing of one-transistor memory devices was dealt with the following issues: decomposition of ferroelectric materials, the etching damage of ferroelectric materials, the forming gas annealing damage of ferroelectric materials, the selective deposition of ferroelectric materials, the alignment for device making processes. The integration processes for one transistor memory device have been optimized to reduce process-induced damages. High k gate oxide such as ZrO2, HfO2 were used for one-transistor memory device applications. Extremely high c-axis oriented Pb5Ge3O11 thin films were successfully deposited on high k gate oxide. One-transistor ferroelectric memory devices with MOCVD PGO MFOS memory cells have been fabricated. The working 1T-memory devices with the size of 0.6, 3 and 10 x 10 μm showed memory windows around 1 - 2V. The memory windows were almost saturated from operation voltage of 4V. After programming to -5V (on "off" state), the drain current (ID) at VD of 1V and VG of 2.5 V was measured about 1.13 x10-10A. After programming to 5 V (on "on" state) the drain current (ID) at VD of 1V and VG of 2.5 V was measured about 1.03 x10-8 A, which was 100 times high than that of "off" state. The drain current differences between "on" and "off" states were large enough to identify the "on" or "off" states. The imprint and fatigue properties of the 1 T memory devices were also measured.

9:00 AM C11.3
EFFECT OF ULTRA THIN SiON BUFFER LAYERS ON ELECTRICAL PROPERTIES OF $Bi_4Ti_3O_{12}$ THIN FILMS ON Si(100) SUBSTRATES. Eiji Rokuta, Yasuhi Hotta, Hitoshi Tabata, Hikaru Kobayashi, Tomoji Kawai, Osaka University, Ibaraki, JAPAN.

Electrical properties of ferroelectric $Bi_4Ti_3O_{12}$ (BIT) films on Si(100) using a 1 nm thick silicon oxynitride (SiON) buffer were investigated. The ultra thin layer (1 nm) of SiON films is quite effective to terminate oxidization of Si surface. The capacitance-voltage (C-V) characteristics of Au/BiT/SiON/Si(100) exhibited hysteresis loops with a memory window of 2 V due to the ferroelectricity, and did not show large carrier injections. The effects of the ultra thin films of SiON buffer were demonstrated in a current voltage characteristics: In the reverse bias region, a leakage current density of the specimen without the SiON buffer was much larger than that of the specimen with the buffer. Apart from these electrical measurements, anomalous features appeared in C-V characteristics of the illuminated specimen, which were likely to be due to the ac response of the optically generated electrons in some trap states at the interface.

9:15 AM C11.4
Al_2O_3/Si_3N_4 BUFFER LAYER FOR HIGH PERFORMANCE MFIS TRANSISTORS. Yoshihisa Fujisaki, Hiroshi Ishiwara, Tokyo Institute of Technology, Frontier Collaborative Research Center, Research and Development Association of Future Electron Devices, Yokohama, JAPAN.

To realize MFIS (Metal Ferroelectric Insulator Semiconductor)

transistors with long retention characteristics under low voltage operations, we have to develop a high performance I-layer that satisfies the following features; 1) The film should be a good diffusion barrier between Si and ferroelectric oxide film, 2) The film should have a high permittivity and resistivity, 3) The interface state density between Si and I-layer should be as low as the value realized in the conventional Si-MOS (Metal Oxide Semiconductor) structure. We have already reported a high performance MFIS with Si_3N_4 made by direct nitridation of a Si substrate using nitrogen radicals.[1] Different from the conventional Si_3N_4 films, the radical-Si_3N_4 is perfectly hydrogen-free and damage-free that makes the film highly resistive against the oxidation process higher than 900C.[2] To improve the insulating property, we combined radical-Si_3N_4 and Al_2O_3 thin film. Thin Al_2O_3 films were formed by oxidizing metal-Al films that was deposited by evaporation method. The 2.2nm-thick Al_2O_3 film in this stacked Al_2O_3/Si_3N_4 structure was proved to have the permittivity of 9.76 which is similar to the value of the bulk Al_2O_3 ceramics. It was confirmed by TEM (Transmission Electron Microscope) and XPS (X-ray Photoelectron Spectroscopy) analysis that the Si_3N_4/Si interface showed no degradation during the Al_2O_3 formation anneal at 750C in pure oxygen. This is why the high permittivity value was realized in such a thin film. The MIS (Metal Insulator Semiconductor) diode with Al_2O_3/Si_3N_4 realized the 10^5 times smaller leakage current compared to the MIS diode with Si_3N_4. We found that the stacked Al_2O_3/Si_3N_4 insulator has enough stability as a buffer layer in MFIS devices. [1] Y. Fujisaki et al., Appl. Phys. Lett. 78, 1285 (2001). [2] Y. Fujisaki et al., Jpn. J. Appl. Phys. 39 L1075 (2000).

9:30 AM C11.5
A STUDY OF CHARGE CONTROL AND GATE TUNNELING IN A FERROELECTRIC-OXIDE-SILICON FIELD EFFECT TRANSISTOR. Yih-Yin Lin, Jasprit Singh, Univ of Michigan, Dept of Electrical Engineering and Computer Science, Ann Arbor, MI; Yifei Zhang, Integrated Device Technology, Duluth, GA.

It is known that conventional MOS devices will have gate tunneling related problems at very thin oxide thicknesses ($d_{ox} \leq 20$ Å). In this paper we discuss the potential of polar and non-polar high-dielectric films for gate tunneling suppression and charge control. We also examine ferroelectric thickness effects in ferroelectric-oxide-silicon field effect transistors (MFISFETs). Our formalism is based on a blocking-layer model for the ferroelectric film and a self-consistent solution of the Poisson and Schrödinger equations. We show that the polarization effects of ferroelectrics can allow greater controllability of the silicon interface (mobile) charge density and also the high dielectric constant effectively suppresses gate tunneling probability. In addition, the effects of ferroelectric film thickness are quite important in a MFISFET device and allow a small control of the threshold voltage. Results will be presented for the capacitance-voltage (C-V) curve, tunneling probability, and leakage currents. As an example, we find for a sheet charge of 10^{13} cm^{-2}, the gate tunneling probability in a MOS structure is 10^{-6} (d_{ox} = 13 Å), while that in a MFISFET is 10^{-14} with the same equivalent oxide thickness. Our studies also show that details of the blocking layer model (dead layer thickness, coercive field, and polar charge) can be estimated from C-V measurements.

SESSION C12: THIN FILMS FOR RF APPLICATIONS
Chair: Angus I. Kingon
Thursday Morning, November 29, 2001
Room 210 (Hynes)

10:15 AM *C12.1
BST THIN FILMS FOR HIGH FREQUENCY APPLICATIONS; MATERIAL PROPERTIES AND DEVICE DESIGN. J-P. Maria, F. Ayguavives, C.B. Parker, B. Boyette, and A.I. Kingon, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC; A. Tombak, Z. Jin, and A. Mortazawi, North Carolina State University, Department of Electrical and Computer Engineering, Raleigh, NC; G. Stauf, C. Ragaglia, D. Vestyk, and J. Roeder, Advanced Technology Materials Inc., Danbury, CT; M. Brand, Raytheon Systems Company, El Segundo, CA.

The incorporation of barium strontium titanate thin films into high frequency devices has been investigated. Results will be presented which correspond to both material properties and high frequency (RF and μwave) design and operation. It is well known that the properties of BST and other paraelectric materials are a sensitive function of temperature, thickness and electric field. For the first time, a comprehensive set of data will be presented covering all variables simultaneously. In this manner, the utility of BST in high frequency circuits can be practically assessed, as the temperature dependence of the tunability and permittivity is now known. Implications of expected temperature and electric field variations and their determination of the ideal BST composition and thickness will be discussed. In addition, comments will be made regarding the ongoing development of a phenomenological model for BST. The second half of this investigation will focus on high frequency device design and characterization. The frequency ranges of interest for devices targeted in this program span MHz to GHz values. An example VHF element developed in this program is a 135 pF tunable BST band pass filter with a Q of 26 and an insertion loss of 3 dB at 150 MHz. Combining low ESR metallization and low loss BST provided for these high frequency characteristics, which compare favorably with similarly large capacitive components. Results will be presented for higher frequency devices fabricated on low loss substrates using two approaches: low capacitance MIM structures fabricated on inexpensive flat-panel display glass, and low capacitance MIM structures deposited on ultra-thick thermal oxides. A discussion of the integration challenges and device characteristics will be given.

10:45 AM C12.2
DIRECT WRITE DEPOSITION OF BST FILMS FROM LIQUID METALORGANIC PRECURSORS. T.V. Rivkin, C.J. Curtis, A. Miedaner, J. Alleman, J.D. Perkins, P.A. Parilla and D.S. Ginley, National Renewable Energy Laboratory, Golden, CO; A. Kozyrev, M. Gaidukov, V. Keis, O. Soldatenkov, Electrotechnical University, St. Petersburg, RUSSIA.

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) tunable dielectric films are under investigation for a new generation of room temperature microwave devices including tunable filters, phase shifters, oscillators, etc. Thin film technology is an important means to integrate the tunable dielectrics into multilayer microwave circuits. Liquid precursor based deposition techniques such as Metal Organic Decomposition (MOD) or Sol Gel processing are potentially inexpensive atmospheric processes that easily scale to large area production. Ink based liquid precursors can also be used in direct write deposition systems to provide a unique means for circuit integration. Direct write deposition such as inkjet printing also eliminates undesirable photolithography and etching steps and minimizes materials usage making this a cost effective way to produce BST films for tunable circuit elements. Combined with deposition of high quality silver and copper coatings from metal-organic inks, potentially the entire tunable device/circuit may be directly written via inkjet printing. We report on the structural and dielectric properties of the inkjet printed BST films from metal-organic precursors. Also we present initial results on the BST tunable capacitors with contact metallization and dielectric films produced via ink jet printing. Initial results show that phase pure crystalline materials can be obtained by writing Strontium and Barium Neodecanoate in combination with Titanium 2-ethylhexoxide based precursors at 100°C followed by a 900°C anneal. Subsequent measurement of the microwave properties indicates that the tuning of 60% with a loss of 0.05 can be attained at 2GHz.

11:00 AM C12.3
EFFECTS OF MICROSTRUCTURE ON THE DIELECTRIC PROPERTIES OF $Ba_{0.6}Sr_{0.4}TiO_3$ FILMS. B.H. Park, Luke A. Emmert, J. Randy Groves, Paul N. Arendt, Q.X. Jia, Los Alamos National Laboratory, Superconductivity Technology Center, Los Alamos, NM; K.H. Ahn, A. Saxena, Los Alamos National Laboratory, Theoretical Division, Los Alamos, NM.

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) films have many useful properties, such as low dielectric loss, high dielectric permittivity, and high tunability defined by the electric field dependence of dielectric permittivity. We have systematically investigated the effects of microstructure on the dielectric properties of BST films deposited using pulsed laser deposition. By inserting a very thin strain layer between the BST film and the substrate, we can control the strain states of the BST film. Measured dielectric properties showed a strong dependence on the strain states. In particular, both the dielectric permittivity and the tunability decreased rapidly as the strain increasesd. The strain effect, theoretically analyzed by a thermodynamic potential with proper boundary conditions, will be discussed in this paper. We will also discuss the relationship between crystalline and dielectric properties using epitaxial, highly-oriented, and polycrystalline BST films.

11:15 AM C12.4
EFFECTS OF MICROSTRUCTURES ON THE DIELECTRIC PROPERTIES OF SPUTTERED BARIUM-STRONTIUM-TITANATE THIN FILMS IN THE MICROWAVE-FREQUENCY RANGE. Tae-Gon Kim, Yongjo Kim, Jeongmin Oh, Taeho Moon, and Byungwoo Park, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA.

Polycrystalline $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films were deposited on the $Pt/TiO_2/SiO_2/Si$ substrate by RF magnetron sputtering. To obtain various microstructures of BST thin films, deposition temperature and working pressure were controlled. Dielectric constants (ϵ) and losses ($\tan\delta$) were measured up to ~10 GHz with the circular-patch capacitors by the vector network analyzer, and the parasitic (stray)

effect is effectively removed with equivalent-circuit model. As the deposition temperature and working pressure increased, the degree of non-uniform local strain and dilation were reduced, that is, the crystallinity of the BST thin films was enhanced. The microwave dielectric constants and losses correlated very well with the level of crystallinity or strain. The effect of off-stoichiometry was also investigated for the quality factors in the microwave-frequency range. Ref. Y. Kim, J. Oh, T.-G. Kim, and B. Park, "Effect of Microstructures on the Microwave Dielectric Properties of $ZrTiO_4$ Thin Films," Appl. Phys. Lett. **78**, 2363 (2001).

11:30 AM C12.5
RAMAN STUDIES OF THE SOFT PHONON MODES IN $Ba_xSr_{1-x}TiO_3$ THIN FILMS. D.A. Tenne, A.M. Clark, A. James, K. Chen, and X.X. Xi, Department of Physics, The Pennsylvania State University, University Park, PA.

The vibrational properties of barium strontium titanate thin films were studied by Raman spectroscopy in the temperature range from 5 to 300 K. The films were grown by pulsed laser deposition on $SrTiO_3$ and $LaAlO_3$ substrates with $SrRuO_3$ buffer layers. Soft phonons are observed in Raman spectra of $Ba_xSr_{1-x}TiO_3$ films with Ba contents x = 0.05, 0.1, 0.2 and 0.5. Temperature dependence of the soft mode frequency shows evidence of the ferroelectric phase transition in the films. The soft mode is overdamped in the temperature range close to the ferroelectric phase transition, with the exception of the $Ba_{0.05}Sr_{0.95}TiO_3$ film, where no overdamping is observed over the entire temperature range. At temperatures away from the phase transition the soft mode peak is clearly seen in the spectra of all films studied. The relative Raman intensity of hard phonon modes in $Ba_xSr_{1-x}TiO_3$ films decreases in the temperature range of the ferroelectric phase transition, while remaining nearly constant away from that range. The temperature dependence of the soft mode frequency and the intensity of hard modes shows the ferroelectric phase transition occurs over a broad range of temperatures in thin films, which is different from bulk behavior. Comparison of Raman spectra for films grown on $SrTiO_3$ and $LaAlO_3$ substrates shows the influence of strain on the temperature of the ferroelectric phase transition. Raman spectroscopy results are correlated to the temperature dependence of dielectric constant.

11:45 AM C12.6
LOCAL FERROELECTRICITY IN $SrTiO_3$ FILMS OBSERVED BY CONFOCAL SCANNING OPTICAL MICROSCOPY. Oleg Tikhomirov, Jeremy Levy, Univ of Pittsburgh, Dept of Physics and Astronomy, Pittsburgh, PA; Hua Jiang, Corning Applied Technologies, Woburn, MA.

The physical properties of ferroelectric thin films differ dramatically compared to bulk samples of similar composition. A broad distribution of local stresses and strong elastic interaction with the substrate are the most likely factors of this discrepancy. Examination of local electrooptic properties of films in $(Ba,Sr)TiO_3$ (BST) films show that the local phase transition temperature can be significantly higher than the corresponding bulk value. Here we report observations of local ferroelectric response in nominally pure $SrTiO_3$ (STO) films at liquid nitrogen temperatures. Bulk STO is non-ferroelectric due to quantum fluctuations and the antiferrodistortive phase transition. We measure the electrooptic response of STO films as a function of bias electric field, position and temperature. The behavior is qualitatively similar to that observed in BST films, though no traces of ferroelectricity exist at room temperature. The results are discussed on the basis of recent theory by Pertsev *et al.* This work is supported by the DARPA FAME program (ONR N00173-98-1-G011).

SESSION C13: HIGH-PERMITTIVITY MATERIALS
Chairs: Clive A. Randall and David Y. Kaufman
Thursday Afternoon, November 29, 2001
Room 210 (Hynes)

1:30 PM *C13.1
POINT DEFECTS IN PEROVSKITE-STRUCTURE TITANATE THIN FILMS AND THEIR EFFECTS ON FERROELECTRIC PROPERTIES. Paul C. McIntyre, Stanford University, Department of MS&E, Stanford, CA.

This presentation will review recent progress in characterizing the point defect chemistry of titanate thin films, including both experimental and theoretical approaches. Experimental results obtained by several groups using SIMS tracer depth profiling, positron annihilation spectroscopy, STEM/EELS, and electrical characterization will be discussed. A theoretical model for defect equilibrium in titanate films will also be described briefly. The effects of acceptor impurities, non-stoichiometry and hydrogen doping on the properties and reliability of BST and PZT thin films will be emphasized.

2:00 PM C13.2
HIGH TEMPERATURE CONDUCTION BEHAVIOR AND SEGREGATION PHENOMENA IN $SrTiO_3$ AND $BaTiO_3$ THIN FILMS. S. Hoffmann-Eifert, Ch. Ohly, K. Szot, and R. Waser[a]; IFF/EKM, Forschungszentrum Jülich GmbH, GERMANY; [a]also IWE II, RWTH Aachen University of Technology, GERMANY.

The integration of functional electroceramic materials into semiconductor devices opens a broad spectrum of new applications like for example non-volatile ferroelectric memories (FeRAMs) or voltage tunable high frequency devices. Typically, the materials are deposited as polycrystalline thin films at temperatures far below the sintering temperature of bulk ceramics. Thus, the thin films, which show a significantly different microstructure compared to bulk ceramics, are also expected to exhibit a different defect structure. In order to elucidate basic charge transport properties we performed high temperature conductivity measurements on $SrTiO_3$ and $BaTiO_3$ thin films, varying the temperature between 700 and 1000°C and the oxygen partial pressure between 10^{-20} bar and 1 bar. It was found that the conduction behavior of $SrTiO_3$ and $BaTiO_3$ thin films exhibits quite different characteristics and portrays a far more complex and not yet understood defect chemistry compared to bulk materials. The most remarkable facts are a sharp drop and a broad plateau region in log-conductivity vs. log - pO_2 plots. The results were accompanied by certain segregation phenomena, which implied to look at thin films from a surface point of view.
The present paper will address to a discussion of the different phenomena observed during high temperature treatment of $SrTiO_3$ and $BaTiO_3$ thin films.

2:15 PM C13.3
DC BIAS STRESSING OF BST THIN FILMS: OXYGEN TRACER STUDIES. Robert J. Becker, Paul McIntyre, Stanford University, Materials Science and Engineering, Stanford, CA.

We have observed the motion of ^{18}O tracer atoms in MOCVD grown thin films of $(Ba,Sr)TiO_3$ and used these measurements to study the mobility of oxygen vacancies under an applied electric field. Pt/BST/Pt capacitors were fabricated, ^{18}O atoms were introduced by a thermal exchange anneal, and the initial tracer concentration versus depth profiles were measured using SIMS. The devices were then held under a constant voltage stress for various lengths of time at temperatures ranging from 60 to 200°C. SIMS measuremnts made post-stressing were compared to the original profiles, and a finite difference model was used to calculate the tracer mobility of oxygen and of oxygen vacancies in the BST lattice. Capacitance-voltage and current-voltage data were also collected as a function of bias stressing conditions, and the results compared to the SIMS tracer motion data.

3:00 PM *C13.4
ELECTRICAL PROPERTIES OF LOW-INDUCTANCE THIN FILM CAPACITORS FOR DECOUPLING APPLICATIONS. Takeshi Shioga, John D. Baniecki, Yoshihiko Imanaka, and Kazuaki Kurihara, Fujitsu Laboratories Ltd., Materials and Material Engineering Laboratories, Kanagawa, JAPAN.

In recent years, there have been increasing demands of operating with high frequency in the field of high-speed LSI digital circuits for decoupling capacitors. In order to suppress voltage fluctuations around power supply buses in digital circuits, it is important to minimize the internal inductance and equivalent series resistance of the capacitors. This is a key element in the design for the future decoupling capacitors. The electrical requirements for the capacitors are an inductance less than 100 pH, a resistance less than 100 mΩ, and a capacitance more than 1,000 nF/cm^2. Multi-layer bulk ceramic capacitors which have relative high-inductance of over 100 pH are not suitable for low-inductance decoupling capacitor applications. The talk will focus on the design considerations of the high frequency decoupling capacitors having low-inductance, which are fabricated using Barium Strontium Titanate (BSTO) thin films. The BSTO films were prepared by chemical solution deposition (CSD) and RF magnetron sputtering deposition. We will present the results of studies we have made on the electrical properties of BSTO thin film capacitors.

3:30 PM C13.5
NUCLEATION AND GROWTH OF ULTRA THIN $(Ba,Sr)TiO_3$ FILMS IN A MOCVD REACTOR. S. Regnery[a,b], F. Fitsilis[a], P. Ehrhart[a], R. Waser[a], F. Schienle[b], M. Schumacher[b], H. Juergensen[b], [a]IFF-Forschungszentrum Jülich, GERMANY; [b]AIXTRON AG Aachen, GERMANY.

BST thin films were deposited in a planetary multi-wafer MOCVD reactor combined with a liquid delivery system using 0.35 molar

solutions of $Ba(thd)_2$ and $Sr(thd)_2$ and a 0.4 molar solution of $Ti(O\text{-}i\text{-}Pr)_2(thd)_2$. Film growth on Pt-(111) is discussed within a wide parameter field, e.g., the deposition temperature was varied between 500°C and 650°C and the stoichiometry, Group-II / Ti content, from 0.9 to 1.1. Hence, nucleation and growth is investigated for films of different microstructures ranging form amorphous layers over micro-crystalline layers to perfectly (100)-oriented columnar structures. The microstructure was routinely investigated by X-ray diffraction and the composition of the films by X-ray fluorescence analysis. Details of the microstructure were investigated by scanning electron microscopy, SEM, and by transmission electron microscopy, TEM. The surface topology was investigated by scanning force microscopy, SFM, and the chemistry of the interface by SIMS. The nominal thickness of the BST films was varied between 0.3 and 100 nm and the variation of the nucleus sizes, the surface morphology and the film properties are discussed in detail. Pore free films with no shortcuts after deposition of Pt top electrodes are observed for a thickness above 7 nm. The finally achieved electrical properties, e.g., permittivity and leakage current, are discussed with special emphasis on the dependencies on film thickness and microstructural properties.

3:45 PM C13.6
Ba/Sr RATIO DEPENDENCE OF THE DIELECTRIC RESPONSE OF POLYCRYSTALLINE MOCVD $(Ba_xSr_{1-x})Ti_{1+y}O_{3+z}$ THIN FILMS. S.K. Streiffer, J. Im, S. Saha, O. Auciello, Materials Science Division, Argonne National Laboratory, Argonne, IL; D.Y. Kaufman, R.A. Erck, Energy Technology Division, Argonne National Laboratory, Argonne, IL.

The dielectric response of polycrystalline $(Ba_xSr_{1-x})Ti_{1+y}O_{3+z}$ thin films has been measured by many groups. However, deviations from ideal bulk behavior are still not fully understood. Here, we examine the role of the Ba/Sr ratio in determining properties for BST films deposited by MOCVD. Clear deviations from Curie-Weiss behavior occur at approximately the same temperature of 370K for 25/75, 45/55, and 70/30 samples. In contrast, 0/100 samples display Curie-Weiss behavior down to approximately 200K. This implies that Ba clustering may strongly impact properties. Possible models incorporating strain in addition to clustering will be compared to help explain the observed dielectric response.

4:00 PM C13.7
THE ROLE OF ANTIPHASE DOMAIN BOUNDARIES ON THE FERROELECTRIC PROPERTIES OF $Ba_xSr_{1-x}TiO_3$ FILMS GROWN ON MgO BY PLD. L. Salamanca-Riba, Hao Li, and R. Ramesh, Materials and Nuclear Engineering Department.

Bulk $Ba_xSr_{1-x}TiO_3$ (BST) exhibits a large permittivity that can be as great as 10,000 near the ferroelectric-paraelectric transition temperature (T_c) which can in turn be tuned significantly with an applied electric field. Compared to bulk BST samples, however, the dielectric constant and its nonlinearity in epitaxial thin films are markedly lower. Strain and defects are considered to be two primary causes for the degradation of the dielectric properties of BST thin films. Annealing at or above the growth temperature leads to partial recovery in the dielectric properties of BST films. We have observed antiphase domain boundaries in BST films grown on MgO which we believe are partially responsible for the reduction of the dielectric constant of BST films compared to bulk. We attribute the formation of ADBs to the different crystal symmetry of the film and the substrate. This difference in symmetry allows only the nucleation of TiO_2 as the first layer deposited on the MgO substrate. Furthermore, there are two possible nucleation sites for the TiO_2 which give rise to two possible domains being nucleated at the same time. The ADBs are thin layers of either (Ba,Sr)O or TiO_2 that act as low dielectric interfaces in BST films and cause the lowering of the effective in plane dielectric constant. Upon annealing the average size of the domains increases and the density of ADBs decreases giving rise to a higher value of the dielectric constant. This work was supported by the University of Maryland NSF-MRSEC, grant #DMR 00-80008.

4:15 PM C13.8
PROBING THE DEAD-LAYER IN ULTRATHIN STRONTIUM TITANATE (BST) CAPACITORS MADE BY PULSED-LASER DEPOSITION. L.J. Sinnamon, R.M. Bowman, J.M. Gregg, Queens University Belfast, Department of Pure and Applied Physics, Belfast, Northern Ireland, UNITED KINGDOM.

It is widely accepted that the dramatic collapse in dielectric constant that occurs on decreasing film thickness is a result of a so-called "dead-layer" at the dielectric-electrode interface; yet, there is very little known about the nature, dielectric structure or even the existence of such dead-layers. In order to probe the dead-layer, the authors present experimental results from both direct (high-resolution TEM) and indirect (implications from dielectric response) characterisation of the electrode-dielectric interfaces in the $Au/BST/SrRuO_3$ capacitor system, grown by pulsed-laser deposition. Dielectric characterisation of a capacitor series with BST layers between ~7.5 and 950 nm in thickness revealed a large interfacial d_i/ϵ_i ratio of 0.40 ± 0.05 nm, implying a highly visible parasitic dead-layer within the capacitor structure. Despite this, none of the expected anomalies in the dielectric constant behaviour with thickness were observed, implying that either (i) 7.5 nm is an upper limit for the total dead layer thickness in the SRO/BST/Au system; or (ii) dielectric collapse is not associated with a distinct interfacial dead layer, and is instead due to a through-film effect [1]. This study has been extended down to BST films ~1nm in thickness, and the results of dielectric behaviour and implications for the physical extent of the dead-layer will be presented. Results from direct imaging, microstructural, and nanoprobe chemical analysis performed on cross-sectional specimens on HRTEM will also be presented, and related to the dielectric observations. [1] L.J. Sinnamon, R.M. Bowman & J.M. Gregg, "Investigation of dead layer thickness in $SrRuO_3/Ba_{0.5}Sr_{0.5}TiO_3/Au$ thin film capacitors", Applied Physics Letters, 78, 1724 (2001)

4:30 PM C13.9
MICROSTRUCTURAL EFFECTS ON THICKNESS DEPENDENCE OF LEAKAGE CURRENT BEHAVIOR IN (Ba,Sr)TiO_3 THIN FILMS. Kun Ho Ahn and Sunggi Baik, Pohang Univ of Science and Technology, Dept of Materials Science and Engineering, KOREA; Sangsub Kim, Sunchon National Univ, Dept of Materials Science and Metallurgical Engineering, KOREA.

We have recently reported the effects of microstructure on the leakage current behavior of BST thin films by comparing the films having different microstructures but the same interface states on bottom electrodes [1]. Schottky emission was dominating in the films composed of granular polycrystalline grains while the epi-like single crystalline films showed higher leakage current following Fowler-Nordheim tunneling mechanism. In this study, thickness dependence of the leakage current behavior was investigated for the BST thin films with two different microstructures but maintaining identical interface state on epitaxial Pt(001)/MgO(001). The results will be discussed based on the prevailing conduction mechanism that is critically dependent on the microstructure of BST thin films. [1] K.H. Ahn, S. Kim and S. Baik, to be published in Integrated Ferroelectrics (2001).

4:45 PM C13.10
BISMUTH PYROCHLORE DIELECTRIC FILMS. Ryan Thayer, Clive A. Randall, Thomas R. Shrout, Susan Trolier-McKinstry, Materials Research Inst, Pennsylvania State Univ, University Park, PA.

Bismuth pyrochlore ceramics have modest temperature coefficients of capacitance (TCC) (-400 to -150 ppm/°C), good microwave properties, and can be sintered at <1000°C. This work focuses on the preparation and characterization of thin films in this family. A chemical solution deposition procedure was used to prepare $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$, $Bi_{1.5}Zn_{0.5}Nb_{1.5}O_{6.5}$, and $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ films. In all three cases, crystallization occurs by 550°C into the cubic pyrochlore structure. At 750°C and above, $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ adopts a monoclinic zirconolite structure. $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ films show a permittivity of 150 when fired at 750°C, $\tan\delta$ <0.005, and a TCC of -400 ppm/°C. In addition, this composition has leakage of $2.0{\cdot}10^{-10}$ A/cm^2 at low field, $1.4{\cdot}10^{-8}$ A/cm^2 at 500 kV/cm, and shows thickness independent permittivity and leakage down to 500 Å. $Bi_{1.5}Zn_{0.5}Nb_{1.5}O_{6.5}$ films have a permittivity of 180, $\tan\delta$ <0.005, and TCC = -225 ppm/°C. The maximum permittivity occurs at a crystallization temperature of 600°C. Monoclinic films show a permittivity of 80 when fired at 750°C, $\tan\delta$ <0.005, and TCC = 150 ppm/°C. All three compositions studied have field tunable permittivity, with tunabilities up to 40%.