SYMPOSIUM CC

Ferroelectric Thin Films IX

November 26 – 30, 2000

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TUTORIAL

FT CC: FERROELECTRIC THIN FILMS
Sunday, November 26, 2000
10:00 a.m. - 5:00 p.m.
Room 202 (Hynes)

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

- Introduction to material types, ferroelectric films, and a brief history of the field
- Applications, processing and properties of ferroelectric films, including recent commercial developments, and materials science issues. The section will be divided into the following categories:
  - Ferroelectric nonvolatile memories (device principles, material types, primary properties, processing methods)
  - Ferroelectric films for DRAMS and other capacitor applications (device principles, materials needs, material types, physical properties, impact on capacitor performance, processing and composition effects, obstacles to Gbit integration. 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 I. Kingon, North Carolina State University
Stephen Streiffer, Argonne National Laboratory
Paul Muralt, Swiss Federal Institute

SESSION CC1: FERROELECTRIC NON VOLATILE MEMORIES – TECHNOLOGY AND FUNDAMENTALS
Chairs: Paul C. McIntyre and Stephen R. Gilbert
Monday Morning, November 27, 2000
Room 312 (Hynes)

8:30 AM *CC1.1
AN OVERVIEW OF FeRAM TECHNOLOGY FOR HIGH DENSITY APPLICATIONS. Christine Dehm, Thomas Mikolajick, Nicolas Nagel, Carlos Mazuré, Infineon Technologies AG, Memory Products, Munich, GERMANY.

Ferroelectric random access memories (FeRAMs) are new types of memories especially suitable for mobile applications due to their unique properties like non-volatility, small DRAM-like cell size, fast read and write as well as low voltage/low power behavior. Although standard CMOS processes can be used for frontend and backend/metallization processes, FeRAM technology development has to overcome major challenges due to new materials used for capacitor formation. In this talk, advantages and disadvantages of different ferroelectric materials and major development issues for further scaling are discussed. Also, results of a 0.5m ferroelectric process using $SrBi_2Ta_2O_9$(SBT) as ferroelectric layer, Pt as electrode material as well as 2-layer tungsten/aluminum metallization are given.

9:00 AM CC1.2
INTEGRATED TiO_2/Pt/PLZT/IrOx FERROELECTRIC CAPACITOR WITH EXCELLENT FATIGUE AND IMPRINT PERFORMANCE FOR FRAM APPLICATIONS. Fan Chu, Glen Fox, Ramtron International Corporation, Colorado Springs, CO; Yoshimasa Horii, Tatsuya Yamazaki, Fujitsu Limited, Iwate, JAPAN.

Doped PLZT [(Pb, La)(Zr, Ti)O_3] thin film is the key component in current FRAM® products such as 64k and 256k memories. The same materials will be applied in 1 Meg memories that will be available in the market soon. When PZT or doped PZT thin films are applied or discussed for devices, a phenomenon called fatigue, which is defined as the loss of switchable polarization during continuous ferroelectric switching, is often addressed. There have been opinions that the fatigue problem will hinder the utilization of PZT materials in FRAM applications. However the attractive merits of PZT or doped PZT thin films, such as high switchable charge, better control of crystallographic texture which facilitate scaling, low temperature processing and the multi-functionality still make it the best choice of materials for FRAM devices. Good fatigue performance can be obtained on PZT or doped PZT thin films if proper electrodes and thin film processing are employed. This paper will present the excellent fatigue and imprint performance of doped PZT thin films. The ferroelectric capacitor stack investigated in this study was composed of TiOx sticking layer, Pt bottom electrode, doped (Ca and Sr) PLZT thin film and IrOx top electrode. The ferroelectric performance, such as switching (Q_{SW} and $V_{90}\%$), fatigue and aging performance, was collected after the integration of PZT capacitors (after local inter-connect process). The doped PLZT capacitor stack showed no fatigue at 5V 10^{11} fatigue cycles. Since the capacitor stack was designed for 3V FRAM devices, it is believed (based on the voltage acceleration model for fatigue performance) that the capacitor should be fatigue free up to at least 10^{12} fatigue cycles at 3V (167kV/cm). The excellent imprint performance of this integrated PZT capacitor structure will also be presented.

9:15 AM CC1.3
TWO TYPES OF LOCAL DEGRADATION IN FATIGUED PZT CAPACITORS FOR FRAM. Kimihiko Ito, Yasunori Mochizuki, Toru Tatsumi, Takashi Hase, Hiromitsu Hada, Naoya Inoue, Yoshihiro Hayashi and Yoichi Miyasaka, NEC Corporation, JAPAN.

Domain imaging in fatigued PZT capacitors using AFM is reported, which reveals two types of microscopic mechanisms causing apparent loss of switchable polarization. One is the pinning of ferroelectric polarization, similar to previous reports, and the other is a local loss of ferroelectricity. These signatures are distinguishable from DC-bias dependence of phase images of piezoelectric response. In the latter type of region, a local phase reversal in the piezo-response (under both bias polarities) is observed, which stems from a passive biaxial-strain effect caused by the piezoelectric vibration of surrounding ferroelectric regions. Indeed, such a region also showed a decreased vibration amplitude. An important finding is a strong dependence of dominant degradation mode on the film growth method. In particular, low-temperature-grown MOCVD-PZT films show no pinning of domains but only the local loss of ferroelectricity, which first appears in the near- boundary regions and then extends to the interior of grains. On the contrary the pinning of domains is clearly observed in sol-gel PZT films, and in fact both types of regions are found to coexist as fatigue proceeds. We attribute this difference to the different spatial configurations of grain boundaries, which should greatly affect the redistribution process of oxygen vacancies: the MOCVD films consist of columnar grains standing perpendicular to the substrate, whereas granular grains are stacked in sol-gel-PZT films. The apparent loss of ferroelectricity is explained either by an in-plane polarization pinning due to charged defects accumulated at vertical grain boundaries, or by material deterioration in the close vicinity of such boundaries. On the other hand, the polarization-pinned ferroelectric domains are likely to be correlated with in-plane grain boundaries, which are totally absent in MOCVD-PZT. Results of detailed AFM study at incremental fatigue steps will be also presented which further support our model.

9:30 AM CC1.4
DOMAIN PINNING SITES IN PZT. Grady S. White, John E. Blendell and Edwin R. Fuller, Jr., Ceramics Division, National Institute of Standards and Technology, Gaithersburg, MD.

Real-time AFM imaging of domains in Lead Zirconate Titanate (PZT) shows that select grain boundaries appear to act as domain pinning sites. Relative to the rest of the film, these regions require higher fields to switch and exhibit unusually large displacements normal to the film surface. The films are highly textured (<111> normal to the film surface) and thus the magnitude of the surface displacement is expected to be almost uniform across the film. However, the in-plane component of the polarization vectors in the various grains is expected to be random, giving rise to regions of high compressive and tensile stresses at grain boundaries. We propose that the presence of pinning sites localized on these grain boundaries is due to the degree of grain-to-grain misorientation at these sites. To explore this proposition, we have modeled the surface displacements at grain boundaries for different misorientations and compared these results to the observed displacements. Finite element analysis (OOF) is used to calculate the residual stresses resulting from these misorientations.

9:45 AM CC1.5
SCALING OF PROPERTIES IN FERROELECTRIC THIN FILMS. C.S. Ganpule, A. Stanishevsky, V. Nagarajan, S.P. Alpay, S. Aggarwal, J. Melngailis, E.D. Williams and R. Ramesh, MS&E Center, Univ. of Maryland, College Park, MD; P. De Wolf, Digital Instruments, Santa Barbara, CA; S. Tiedke, aixACCT Systems GmbH, Aachen, GERMANY; V. Joshi and Carlos Paz de Araujo, Symetrix Corporation, Colorado Springs, CO.

Scaling of the ferroelectric and piezoelectric properties in $Pb_{1.0}(Nb_{0.04}Zr_{0.28}Ti_{0.68})O_3$ (PNZT) and $Pt/SrBi_2Ta_2O_9/Pt$ thin films was studied. Focused ion beam milling was used to fabricate submicron devices (1x1, 0.5x0.5, 0.25x0.25, 0.09x0.09 and $0.07x0.07\mu^2$). Three complimentary atomic force microscope (AFM) based techniques were used to characterize these nanoscale devices. Piezoelectric, electrical polarization and capacitance spectroscopy measurements were done on the same set of FIB milled devices and the study of the correlation between the respective properties studied by these methods has been done. It was found that capacitors as small as $0.5x0.5\mu^2$ exhibit good piezoelectric/ferroelectric properties and that the sub-micron capacitors show resistance to bipolar fatigue with up to at least 10^9 cycles.
This work is supported by National Science Foundation - Materials Research Science and Engineering Center (NSF-MRSEC).

10:30 AM *CC1.6
ISSUES FOR INTEGRATION OF HIGH DENSITY FRAM WITH QUARTER MICRON DESIGN RULE. Soon Oh Park, Samsung Electronics Co., Semiconductor R&D Center, Seoul, KOREA.

The most critical issues in developing high density FRAM with 32Mbit density are integration of the ferroelectric capacitor with plugged buried contact (BC), making fine pattern of capacitor and backend processing without hydrogen/plasma damages. To avoid the oxidation of poly-Si plug, it is required to reduce the total thermal budget after BC formation. To make ferroelectric PZT film by sol-gel process, 650°-700°C, which is the highest temperature after the BC formation, is required to suppress the pyrochlore formation and to have the best crystallographic orientation. However, this temperature is too high to obtain the stable BC resistance. Therefore, we are developing MOCVD PZT process of which deposition temperature is about 550°C. Even with this low temperature, the ferroelectric properties are good enough for the device application. To make a fine pattern of ferroelectric capacitor stack, it is required to reduce the thickness of the ferroelectric and electrode layers and to have a high etching slope. For the case of MOCVD PZT, the film thickness can be reduced down to 100nm. A high temperature etching process is very effective in obtaining etch slope over 85 degree. However, it is important to avoid the etching damage at the side wall of PZT film during the capacitor etching process. In the case of small capacitor area, hydrogen damage induced by ILD/IMD process is a very serious issue because of the large side wall area. Very thin Al_2O_3 layer grown by atomic layer deposition is an effective hydrogen barrier. Furthermore, the step coverage of the Al_2O_3 layer was good enough to fully cover the side wall area of the PZT capacitors. It has to be confirmed that the capacitor should not be degraded during the Al reflow process which is for the filling of Al metal in the via contact, because the high temperature vacuum anneal can degrade the PZT capacitor. In summary, we successfully developed the high density FRAM device having quarter micron design rule with COB structure and PZT ferroelectric capacitor.

11:00 AM CC1.7
PRECURSOR AND THICKNESS EFFECTS OF PZT ULTRA THIN FILMS. Yong Kyun Lee, June Key Lee, Chang Jung Kim, In Sook Yi, Il Sub Chung, Electronic Materials Lab., Material and Device Sector, Samsung Advanced Institute of Technology, Suwon, KOREA.

Various thickness from 70 nm to 200 nm PZT thin films were fabricated on $Pt/Ti/SiO_2/Si$ substrates using different methods. First approach we taken was changing spin coating parameters like RPM or concentration. Then we attempted to achieve thin PZT film using etchback and cleaning process. Finally, modifying solution approach was done by adding additive in acetate based PZT solution. In addition, to enhance the crystallization, the effect of PTO seed layer was also examined by combining aforementioned methods. All PZT films were annealed at 650°C in nitrogen atmosphere after baking 300°C. The additive added solution with PTO seed layer shows the best properties in terms of coercive voltage and leakage current. We could obtain 70 nm PZT film with excellent hesteretic properties with smaller leakage current.

11:15 AM CC1.8
IN-SITU OBSERVATION OF 90° -DOMAIN SWITCHING IN EPITAXIAL $Pb(Zr,Ti)O_3$ THIN FILMS BY SYNCHROTRON XRD. Kyeong Seok Lee, Yong Kwan Kim, Sunggi Baik, Pohang Univ of Science and Technology, Dept of Materials Science and Engineering, Pohang, KOREA; Jung Kim, Il Sub Jung, Samsung Advanced Institute of Technology, Microelectronics Lab, Materials Device Sector, Yong-in, KOREA.

Switching behavior of 90° domains in epitaxial $Pb(Zr,Ti)O_3$ thin films under applied bias voltage was investigated in-situ using synchrotron X-ray diffraction, and contribution of the switching to ferroelectric P-E hysteresis curve could be estimated. The electric field in illuminated region was made confined exactly normal to the film/substrate interface by patterning an isolated cap (1.2×1.2 mm^2) and etching off the remainder in order to eliminate mechanical constraint from non-switching region. The portion of polarization taken up by 90° domain reversal was separated from 180° domain switching after measuring the changes in relative intensity ratio of PZT (001) and (100) rocking curves, which exhibited hysteresis behavior depending on applied voltage. At saturation field of 30 kV/mm, in the case of PZT (32/68) film, 25 % of 90° domains were reoriented, which corresponds to approximately 3 % contribution to total polarization.

11:30 AM CC1.9
CHARACTERIZATION OF FERROELECTRIC PROPERTY OF C-AXIS AND NON-C-AXIS ORIENTED EPITAXIALLY GROWN BISMUTH LAYER-STRUCTURED FERROELECTRIC THIN FILMS WITH DIFFERENT M-NUMBERS PREPARED BY MOCVD. Takayuki Watanabe, Tomohiro Sakai and Hiroshi Funakubo, Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Kanagawa, JAPAN; Atsushi Saiki, Research Cooperation Section, Tokyo Institute of Technology, Tokyo, JAPAN; Keisuke Saito, Application Laboratory, Analytical Department, Philips Japan, Ltd. Kanagawa, JAPAN.

Thin film of bismuth layer-structured ferroelectrics (BLSF) have been investigated for a ferroelectric random access memory (FeRAM) application because of its good ferroelectric properties, especially high fatigue resistance. We prepared epitaxially grown BLSF thin films with different m-number, i.e., $Bi_2VO_{5.5}$ (BVO) (m=1), $SrBi_2Ta_2O_9$ (SBT) (m=2), $Bi_4Ti_3O_{12}$ (BIT) (m=3), by MOCVD and compared the ferroelectric properties. BVO, SBT and BIT films prepared on $(110)SrRuO_3//(110)SrTiO_3$ substrates were epitaxially grown with (114)-, (116)- and (118)-orientations respectively. These orientations have almost the same tilting angle, 45°, from the c-axis of the BLSF. On the other hands, those films deposited on $(100)SrRuO_3//(100)SrTiO_3$ substrates showed (00l)-orientation. In the case of SBT film, (00l)-oriented SBT did not show ferroelectricity, but (116)-oriented one showed ferroelectricity with spontaneous polarization (Ps) of $11.4\mu C/cm^2$. From these results, Ps value along a-axis of SBT can be calculated to be $22\mu C/cm^2$ and this value almost agreed with the estimated one from SBT powder. On the other hand, in the case of BIT film, both of (00l)- and (118)-oriented epitaxially grown films showed ferroelectricity with Ps of 4 and $27.0\mu C/cm^2$, respectively. From the results of the above two different oriented films the estimated Ps values of BIT along c- and a-axes were 4.0 and $48.4\mu C/cm^2$, respectively. These values were almost agreed with the reported values for BIT single crystal by S.E. Cummins et al. As a result, the Ps value of BLSF film almost agreed with those of powder and single crystal. This suggests there is no effect of strain in the film. In fact, the lattice constant of the epitaxial SBT film was found to be almost the same as that of powder. This is strongly related to the existence of large number of lattice displacement along c-axis observed by HR-TEM in SBT film. This is the common feature of BLSF film. Therefore, these strain-free structures of BLSF film are suitable for a multi-stack structure in FeRAM devices.

11:45 AM CC1.10
MOCVD OF Ir AND IrO_2 THIN FILMS FOR PZT CAPACITORS. Masaru Shimizu, Kentarou Kita, Hironori Fujisawa and Hirohiko Niu, Himeji Institute of Technology, Dept of Electronics, Himeji, Hyogo, JAPAN.

Highly oriented Ir and IrO_2 thin films were successfully prepared on SiO_2/Si at 300-400°C by MOCVD using a new Ir precursor, $Ir(C_5H_4C_2H_5)(1,5\text{-}C_8H_{12})$, and O_2. This precursor was first used in our experiments. It is a liquid at room temperature and has a higher vapor pressure (85°C/0.1Torr) compared with that of conventional Ir solid precursors. Ir thin films obtained at 300-400°C were highly reflecting, and had a smooth surfaces (rms roughness : 1.4-3.4nm) and low resistivities of $23\text{-}44\mu\Omega\cdot cm$. Values of rms roughness and resistivity were nearly the same as those of sputtered-Ir films prepared at 530°C. MOCVD-Ir films showed good step coverage of 70-80%, which was higher than that of sputtered-Ir films, 20-30%. In order to clarify the effectiveness of Ir films as a bottom electrode, PZT films were deposited on MOCVD-Ir bottom electrodes at 600°C by MOCVD. PZT capacitors with evaporated Au top electrodes showed good ferroelectric D-E hysteresis loops. Auger analysis for $PZT/Ir/SiO_2/Si$ interface indicated that MOCVD-Ir bottom electrode was a good diffusion barrier for PZT components (Pb,Zr,Ti). Fabrication of PZT capacitors with both top and bottom Ir-based electrodes using all MOCVD process will also be reported.

SESSION CC2: INTEGRATION AND ELECTRODES
Chairs: Yoichi Miyasaka and Scott R. Summerfelt
Monday Afternoon, November 27, 2000
Room 312 (Hynes)

1:30 PM *CC2.1
ELECTRODES AND BARRIERS FOR DRAM AND FERAM: PROCESSING, INTEGRATION, AND FUNDAMENTALS.
Katherine L. Saenger[1], S.D. Athavale[2], J. Baniecki[2], C. Cabral, Jr.[1], G. Costrini[2], R.B. Laibowitz[1], J.J. Lian[3], Y. Limb[3], D.A. Neumayer[1], M.L. Wise[3]. [1]IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY. [2]IBM Microelectronics, Hopewell Junction, NY. [3]Infineon, Hopewell Junction, NY.

The conditions used for the deposition and processing of high-k dielectric and ferroelectric (FE) materials in high density DRAM and FERAM devices place severe demands on the electrode and barrier materials. Materials requirements for electrodes and barriers will be reviewed, along with recent results on promising electrode/barrier combinations. Process flows will be described for some alternative device geometries allowing bypass of contact oxidation problems. Electrode/barrier topics to be covered in more detail will include electrode deposition/patterning issues, TaSiN optimization for barrier applications, the stability of oxygen-containing electrodes (e.g., IrO_2 and PtO_x) in various processing ambients, plug resistance in 3-D devices as a function of electrode structure and annealing treatments, and our new application of a Bragg-Brentano x-ray diffraction technique to quantitatively probe etch-induced damage of noble metal electrode layers and Ir electrode consumption due to oxidation during FE deposition.

2:00 PM CC2.2
OXIDATION RESISTANCE OF TaSiN DIFFUSION BARRIERS FOR STACKED CAPACITORS.
F. Letendu,[1], M.C. Hugon[1], F. Bridou[1], J.M. Desvignes[1], B. Agius[1], I. Vickridge[2], D.J. Kim[3] and A.I. Kingon[3]. [1]Laboratoire Charles Fabry, Groupe Physique des Films Minces, Université Paris Sud, Orsay, FRANCE. [2]GPS, Université Paris 6, Paris, FRANCE. [3]Dept. of MS&E, North Carolina State University, Raleigh, NC.

The integration of high permittivity perovskite oxides such as $(Ba,Sr)TiO_3$ (BST) in advanced memory devices requires high temperature processing an O_2 containing atmosphere. To prevent plug oxidation and electrode/plug reactions a conductive barrier material is required between electrode and plug. The oxidation characteristics of the common barrier, TiN, is not sufficient for the process used to deposit optimized BST: it oxidizes quickly at temperatures above 500°C, accompanied by a large volume expansion. Therefore new materials have to be developed. In this paper we compare new results for the TaSiN system with earlier results for the TiAlN system. We report on the properties and the resistance to oxidation of TaSiN thin films deposited by reactive sputtering using a $TaSi_2$ target. The sheet resistance and the thickness of the as-deposited films were obtained by four point probe and X-ray reflectometry respectively. RBS (Rutherford Backscattering Spectroscopy) and NRA (Nuclear Reaction Analysis) allowed us to determine their compositions. The important role of the pressure will be emphasized (films density, oxygen contamination). Films were then processed by rapid thermal annealing (RTA) in $^{18}O_2$ at different temperatures (550, 650 and 750°C C) to simulate deposition conditions. The modifications brought by the RTA in terms of microstructure and compositions were determined by XRD, RBS and NRA. The concentration depth profiles of ^{18}O was measured after the RTA treatments via the narrow resonances $^{18}O(p,\alpha)^{15}N$ at 151 keV (fwhm=100eV). The relationship between the depth profiles and the excitation curves were deduced with the aid of the SPACES simulation program. Oxide thicknesses after oxidation were measured by X-ray reflectometry. Significant differences were observed between the TaSiN and TiAlN systems in terms of oxidation rates, crystallinity, N loss during oxidation and conductivity.

2:15 PM CC2.3
HIGHLY STABLE Ir-Ta-O ELECTRODE FOR FERROELECTRIC MATERIAL DEPOSITION.
Fengyan Zhang, Sheng Teng Hsu, Jer-shen Maa, Yoshi Ono, Hong Ying, Weiwei Zhuang, Sharp Laboratories of America, Inc, Camas, WA; Shigeo Ohnishi, Wendong Zhen, Norito Fujiwara, Sharp Corporation, Tenri-City, Nara, JAPAN.

Ir-Ta-O composite bottom electrode has been found to have extraordinary high temperature stability. This film showed good conductivity and integrity even after 5 min annealing at 1000 °C in oxygen ambient. SBT thin film has been successfully deposited on Ir-Ta-O bottom electrode and annealed at 800 °C for accumulated 50 min. Excellent ferroelectric properties were achieved. No any hillock and peelings of the bottom electrode were observed. This electrode was also used as electrode for other ferroelectric materials deposition for FeRAM and DRAMs devices. After depositing PGO on top of Ir-Ta-O bottom electrode at 550 °C, extremely smooth c-axis PGO can be obtained with well saturated hysteresis loop. SEM, TEM, XRD, AES, and XPS have been used to characterize the Ir-Ta-O film and the interfaces between the ferroelectric material, Ir-Ta-O bottom electrode, and Si substrate. The composition and conductivity changes of the electrode during oxygen ambient annealing, the contact resistance of the electrode with Si substrate, the interdiffusion issue, and the effect of this electrode on the ferroelectric properties of SBT and PGO will be presented. Finally, the mechanism of the highly stability of this electrode will be discussed.

2:30 PM CC2.4
STUDIES OF CONDUCTING DIFFUSION BARRIER THIN FILM GROWTH AND PROPERTIES VIA IN SITU SURFACE SENSITIVE ANALYTICAL TECHNIQUES*.
A.M. Dhote[1,2], O. Auciello[3], A.R. Krauss[1], D.M. Gruen[1], S. Aggarwal[2] and R. Ramesh[2]. [1]Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL. [2]Materials and Nuclear Engineering Department, University of Maryland, College Park, MD. [3]Materials Science Division, Argonne National Laboratory, Argonne, IL.

Low-density non volatile ferroelectric random access memories (NVFRAMs) have been introduced into the market for various applications. The next major effort is the development of high-density memories. In this case, conducting diffusion barrier layers will play a critical role since the ferroelectric capacitors will be fabricated directly on top of CMOS transistors. Therefore, it is relevant to study the growth, processing and interaction of diffusion barrier and bottom electrode layers used for integration of ferroelectric capacitors with CMOS devices. For PZT film-based capacitors, conductive oxide electrodes are necessary to minimize fatigue. We had previously demonstrated that $La_{0.5}Sr_{0.5}CoO_3$/Ti-Al alloy heterostructure can be used as bottom electrodes for PZT capacitors. The Ti-Al layer can provide the double functionality of diffusion barrier and bottom electrode. The LSCO/Ti-Al layer exibited a good ohmic behavior when the Ti-Al layer had an amorphous microstructure. We are exploring the possibility of implementing Ti-Al and TiAlN as a conducting diffusion barrier for integration of FRAMs with CMOS. Therefore, it is critical to study the growth and free surface oxidation of barrier layer to determine the processing conditions that will prove these materials to be implemented as a potential diffusion barriers for high density integration. We have studied ion-beam sputter deposited Ti-Al and TiAlN barriers. These layers were investigated using in situ mass spectroscopy of recoil ions (MSRI) and X-ray photoelectron spectroscopy (XPS). The MSRI analysis revealed that the amorphous Ti-Al layer does not get oxidized during free surface oxygen annealing up to 600°C. XPS also revealed the existence of metallic Ti peak in Ti-Al layer. The studies on TiAlN also show no oxidation upto 600°C. In the case of TiAlN, XPS revealed the formation of TiO_2 at 650-700°C by removal of Nitrogen chemically bonded to Ti. This work will discuss the situ diagnosis of these barrier layers and their potential applications in integration of memories.
*This work was supported by US-DOE, BES Material Sciences, under contract W-13-109-ENG-38; NSF-MRSEC under Grant #DMR-96-32521; the NSF/ONR under contract N00014-89-J-1178.

2:45 PM CC2.5
ETCHING CHARACTERISTICS OF NOBLE METAL ELECTRODE.
St. Schneider, H. Kohlstedt, R. Waser, Research Center Jülich, Institut für Festkörperforschung, Jülich, GERMANY .

A reactive etch process to pattern noble metal electrodes is considered necessary for DRAM integration and desirable for FRAM application in near terms. However, few information has been released on such processes to the public literature so far. 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. Furthermore those process regimes are characterized by process drifts and a low MTBC (mean time between clean) due to chamber contamination problems as non volatile etch products dominate. To systematically investigate possible reactive etch process regions, characterized by volatile etch products, we used a reactive ion beam etching (RIBE) tool with a filament free ICP source, that gives us exact control over the beam energy and the current density, and allows to use reactive gases. An energy dispersive quadrupole mass spectrometer is fitted to the chamber for in situ monitoring. We study the influence of the beam energy and the beam current impinging on the wafer surface as well as its angular dependence. Several additives to the chlorinated process chemistry are investigated and characterized in terms of their role to help to increase the etch rate, maintain a vertical profile, or to enhance process selectivity. Though the main focus of the study is on platinum, we compare its etch characteristics with those of iridium films. Blanket as well as patterned (hardmask) samples were used to describe the influence of the mask material. XPS measurements and SEM analysis were carried out to characterize the process in terms of etch rate, profile angle, residues, and selectivity.

3:30 PM *CC2.6
PROCESS DEGRADATION OF A FERROELECTRIC CAPACITOR.
Seigen Otani, Fujitsu Laboratories LTD., F Project, Atsugi, JAPAN.

Ferroelectrics used in a memory device such as (Pb,La)(Zr,Ti)O3 (PLZT) are vulnerable to reducing atmosphere and lose remanent polarization easily. In the PLZT capacitors, the hysteresis loop variations depend on the polarization states during baking. The hysteresis loop showed voltage shifts when the capacitor was polarized before baking, whereas it became a cramped shape when the baking was carried out on a virgin capacitor. Although remanent polarization diminished in all cases, saturation polarization was not suppressed. The clamped hysteresis loop can be described as an average of two loops shifted to positive and negative voltages. The results indicate that the loss of remanent polarization is not due to the suppression of switching, but due to the shift of the hysteresis of each domain larger than the coercive voltage. In the semiconductor processes, hydrogen gas is generated both from deposition gas of interlayer dielectric and from reaction between metals and moisture in the dielectric. Improvement of reduction endurance is required for the planarization and multi-layer interconnection for the future devices. Reduction of remanent polarization is related to the imprint properties of the capacitor and can be improved by controlling the deposition condition of sol-gel PLZT and annealing IrOx electrode in oxygen.

4:00 PM CC2.7
DEGRADATION OF FERROELECTRIC $Pb(Zr,Ti)O_3$ UNDER REDUCING CONDITIONS. Yuichi Shimakawa and Yoshimi Kubo, Fundamental Research Laboratories, NEC Corporation, Tsukuba, JAPAN.

Solid-state chemistry analysis of $Pb(Zr,Ti)O_3$ (PZT) ceramics helps us better understand the degradation mechanisms of materials during device fabrication processes under reducing conditions. In contrast to significant decreases in the sample weight of $SrBi_2Ta_2O_9$ (SBT) due to decomposition, the weight of PZT samples changes little during H_2-annealing at typical process temperatures. Although no apparent changes are seen from the results of thermogravimetric and x-ray diffraction measurements after annealing, *the PZT material is changed*: The sample appearance changes from white to black. A small amount of PZT (less than 0.03% even after 4%-H_2-annealing at 550°C) decomposes into Pb in the reducing atmosphere. This, however, is too little to cause all of the change in the sample appearance. Systematic changes in the lattice constants and the black color of the sample strongly suggest that oxygen defects are introduced into PZT during H_2-annealing. The oxygen defects produce a donor level within the PZT band gap, which would account for the change in color, and would increase leakage current in capacitors. We have also found interesting differences in material endurance against reducing conditions. $PbZrO_3$ decomposes through oxygen dissociation more easily than $PbTiO_3$. Regarding the use of the PZT material in capacitor devices, this result implies that a Zr-rich material would have inferior material endurance against the reducing conditions. A comparison between the degradation mechanisms of PZT and SBT ferroelectric materials is also discussed in terms of the results of experiments and electronic structure calculation.

4:15 PM CC2.8
DEGRADATION OF FERROELECTRIC CAPACITORS DURING METAL ETCHING AND ASHING PROCESSES. Chanro Park, O. Sung Kwon, Yeo Song Seol, Jin Woong Kim, and Hee Koo Yoon, Hyundai Electronics Industries, Memory R&D Div, Ichon, KOREA.

Damage induced by metal etching and photoresist(PR) strip processes has been investigated for Pt/SBT/Pt ferroelectric capacitors. Interconnect metal line consisting of TiN/Al/Ti/TiN/Ti layers was patterned by Cl_2/BCl_3 gas chemistry and PR was stripped by O_2/N_2 plasma. Etch parameter, etcher and stripper split were conducted to study the source of etch damage to ferroelectric capacitors. Damage to the capacitors was evaluated by measuring switching and non-switching polarization of the ferroelectric capacitors. Neither etch machine nor etch parameters including over-etch, bias power and gas chemistry played an important role for determining polarization of the ferroelectric capacitors. PR strip process, however, significantly affected the polarization characteristics of the capacitors. PR strip by microwave plasma source did not cause decrease of polarization of the ferroelectric capacitors. PR strip by helicon plasma source, however, resulted in significant decrease of polarization of the capacitors. The decrease of polarization during PR strip process in helicon source is attributed to the charging of ferroelectric capacitors due to high density of plasma. In comparison to microwave downstream plasma, helicon source plasma has very high plasma density. In this study, we correlated plasma density and charging of ferroelectric capacitors, and discussed charging process of the ferroelectric capacitors during plasma processing.

4:30 PM CC2.9
EFFECT OF INTER-LEVEL DIELECTRIC OXIDES ON THE ELECTRICAL PROPERTIES OF INTEGRATED $Pt/SrBi_2 Ta_2O_9/Pt$ CAPACITORS FOR FERROELECTRIC MEMORY. Suk-Kyoung Hong, B. Yang, Young Min Kang, Seok Won Lee, Chang Goo Lee, Chung Won Suh, Nam Soo Kang and H.K. Yoon, FeRAM Technology, Memory R&D Division, Hyundai Electronics Industries Co., Ltd., KOREA.

The effect of inter-level dielectrics (ILD) on the electrical properties of integrated $Pt/SrBi_2Ta_2O_9$(SBT)/Pt capacitors was investigated. The electrical performance of the fine-patterned SBT capacitors (2x2 100x100 mm^2) as measured after Al-based metallization strongly depended on the ILD oxide types. Tetraethylorthosilicate (TEOS)-based undoped silicon oxide (USG) (500 nm thick) as a ILD resulted in significantly reduced remanent polarization and highly increased leakage current and that even shorted capacitors in especially top Pt electrode area less than 10x10 mm^2. While the ILD oxide of O_3-TEOS-based borophosphosilicate glass (BPSG) exhibited little degradation for the whole test capacitor size. Stress measurements of the USG, BPSG, and combination of USG/BPSG films on Si wafer carried out over the temperature range of 20-800 and Transmission Electron Microscopy analysis indicate that the degradation of the USG-covered Pt/SBT/Pt capacitors was caused by pointed, small Pt hillocks developed mainly on the bottom Pt electrodes during recovery anneal processes performed at 700 or 800. Improvement in the electrical properties was achieved through the stress control in the ILD layer using double layers consisting of USG and BPSG. The 2x2 mm^2 array capacitors with optimized ILD of USG/BPSG (50/500 nm) resulted in high enough remanent polarization and low leakage current for ferroelectric memory after metallization.

4:45 PM CC2.10
200°C PREPARATION OF SiN_x PASSIVATION FILMS FOR PZT FERROELECTRIC CAPACITORS BY CATALYTIC CVD. Toshiharu Minamikawa[1,2], Yasuto Yonezawa[2], Yoshikazu Fujimori[1,3], Takashi Nakamura[3], Atsushi Masuda[1], Hideki Matsumura[1], [1]Japan Advanced Inst. of Science and Technology, Ishikawa, JAPAN. [2]Industrial Research Inst. of Ishikawa, Ishikawa, JAPAN. [3]Rohm Co., Ltd., Kyoto, JAPAN.

Feasibility of SiN_x passivation films at low substrate temperatures prepared by catalytic chemical vapor deposition (Cat-CVD), often called hot-wire CVD, is studied for ferroelectric nonvolatile random access memories (FRAMs). It has been reported that device-quality SiN_x films are prepared by Cat-CVD. However, deoxidization on the substrate surface due to active hydrogen in Cat-CVD processes may occur, since SiH_4 and NH_3 gases are decomposed by catalytic cracking reaction with a heated catalyzer. Sample temperature is elevated, since the sample is heated by thermal radiation from the catalyzer around 1700°C. However, it has been found that no degradation for ferroelectric $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) capacitors occurs by exposure to active ammonia gas cracked on catalyzer, when the sample temperature is lowered below 200°C by controlling the heat flow from the catalyzer. Therefore, SiN_x films were prepared at low substrate temperatures of 170°C and 200°C using Cat-CVD. Adjusting on flow rate ratio of SiH_4/NH_3, the refractive index of SiN_x film measured by ellipsometry can be controlled from 1.8 to 2.1. So far, the followings are found: 1) The film, with the refractive index about 2.03, deposited at 170°C was oxidized during air exposure for 10 days after the deposition. 2) No oxidation during air exposure for 10 days was observed for the film, with the refractive index of 2.07, deposited at 200°C. The dense SiN_x film, which is resistive for oxidation in air exposure, is prepared at 200°C. It is concluded that the SiN_x films prepared at 200°C by Cat-CVD inducing no degradation for ferroelectricity, are expected as the passivation film on ferroelectric devices.
This work is in part supported by NEDO.

SESSION CC3: POSTER SESSION
BST, GATE MATERIALS, AND DRAM: FUNDAMENTALS AND TECHNOLOGY
Chairs: Jamal Ramdani and John David Baniecki
Monday Evening, November 27, 2000
8:00 PM
Exhibition Hall D (Hynes)

CC3.1
INDUCTIVE-COUPLED RF MAGNETRON PLASMA PHYSICAL VAPOR DEPOSITION OF (Ba,Sr)TiO3. T. Kikkawa, N. Fujiwara, S. Miyazaki, F. Nishiyama, and M. Hirose, Hiroshima University, Higashi-Hiroshima, JAPAN.

An inductive-coupled plasma (ICP) in conjunction with a radio frequency (RF) magnetron plasma was applied to physical vapor deposition (PVD) of Barium Strontium Titanium Oxide (Bax,Sr1-x)TiO_3 (BST) films to control crystallinity and stoichiometry. The properties of BST films deposited by ICP-RF

magnetron plasma PVD were investigated. It is found that the ICP plasma enhances the crystallinity of the BST film. XRD spectra of BST films which were deposited by ICP-RF magnetron plasma in Ar O2 mixture gas (Ar:O2=4:1) ambient at 2.0 Pa at 680C indicated (200), (100), and (110) peaks. It is found that the ratio of Ba to Sr was not changed by the pressure but the ratio of Ti to (Ba Sr) was changed. More Ti atoms were incorporated in the BST film when the BST target was sputtered at 0.5 Pa. It is found that the band gap of the BST film deposited by ICP-RF magnetron plasma PVD was 4.30 eV. The valence band offsets at BST/Si and BST/SiO_2 interfaces were determined to be 3.55 eV and 1.86 eV, respectively. The work function of Ru was obtained to be 4.99 eV by photoelectron yield spectroscopy. An energy band diagram of Ru/BST/SiO2/Si(100) system is determined.

CC3.2
THICKNESS DEPENDENCE OF THE DIELECTRIC CONSTANT IN $SrRuO_3/Ba_{0.5}Sr_{0.5}TiO_3$/Au CAPACITORS AND THE EFFECT OF TOP ELECTRODE MATERIAL. Lesley Sinnamon, Robert Bowman, Marty Gregg, Queen's University of Belfast, Department of Pure and Applied Physics, Belfast, Northern Ireland, UNITED KINGDOM.

Thin film capacitor structures of $MgO/SrRuO_3/Ba_{0.5}Sr_{0.5}TiO_3$/Au were prepared by Pulsed Laser Deposition. XRD showed perovskite $SrRuO_3$ (SRO) and $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) layers with good crystallinity and respective orientations of $(00l)/(hh0)$ and $h00$. A nanocrystalline BST structure was observed from bright field TEM. The capacitors exhibited low frequency dispersion and loss tangents: typically $\epsilon(10\text{kHz})/\epsilon(100\text{Hz}) \approx 0.93$ and tan $\delta < 0.05$. The dielectric constant was mapped for BST thicknesses from 15 to 950nm and found to be consistent with the series capacitor model. Parameters from the model yielded information on the quality of the film-electrode interfaces. The effect on the dielectric properties of different top electrode materials deposited on the *same* films was then studied in an attempt to understand the role of the interfaces in the thickness dependence of the dielectric constant.

CC3.3
ULTRA-THIN BST FILMS FABRICATED BY METALORGANIC DEPOSITION. D.L. Kaiser, J.J. Ritter, I. Levin, P.K. Schenck, J.E. Blendell, C. Bouldin, Ceramics Division, NIST, Gaithersburg MD; R.B. Marinenko, J. Armstrong, Surface and Microanalysis Science Division, NIST, Gaithersburg MD; H. Beratan, Raytheon Systems, TX.

$Ba_{1-x}Sr_xTiO_3$ (BST) films with thicknesses down to 2 nm have been deposited on 5 cm diameter silicon wafers by spin coating. The coating solution was composed of a barium strontium titanium acetate lactate solution [(Ba Sr)/Ti = 1.00 0.01], glacial acetic acid, isopropanol, and either ethylene glycol methyl ether (EGME) or propylene glycol methyl ether. Various drying and annealing heat treatments involving temperatures up to 700°C were employed. The composition of the films as determined by electron microprobe analysis with wavelength dispersive spectrometry was x = 0.29 0.01 and (Ba Sr)/Ti = 1.00 0.05. The films were continuous, with RMS surface roughnesses of less than 1 nm as measured by atomic force microscopy. Film thicknesses were measured by high resolution transmission electron microscopy (HRTEM), reflectance mode spectrophotometry, and x-ray reflectivity. HRTEM examination also revealed a 2 nm to 7 nm thick amorphous interlayer between the BST film and the substrate. Films that were less than 5 nm thick were amorphous, even after annealing at 700°C.

CC3.4
INTERFACE STUDIES OF Nb- $SrTiO_3$/ $SrTiO_3$/LaSrCuO AND LaSrMnO HETEROSTRUCTURES. B. Nagaraj, T. Wu, S.B. Ogale, T. Venkatesan and R. Ramesh, Center for Superconductivity Research and Materials Research Science and Engineering Center, University of Maryland, College Park, MD.

Currently there is a considerable interest in the use of semiconducting oxides as candidate materials for next-generation MOSFETS, in conjunction with high-k dielectrics such as $SrTiO_3$ and ferroelectrics such as PZT. We have examined the interface electrical properties of epitaxially grown $SrTiO_3$ (STO) / $La_{1.85}Sr_{0.15}CuO$ (LSCO) and $La_{0.7}Sr_{0.3}MnO$ (LSMO) (MOS) heterostructures on Nb-$SrTiO_3$ (Nb-STO) substrates using C-V and I-V techniques. C-V studies indicate that the structures show field effect corresponding to that of a p-type semiconductor. No noticeable injection effects were observed indicating a "good" interface between STO and the semiconducting oxides. Majority carrier concentrations in the semiconductor materials were estimated from C-V data at various temperatures. For example, the room temperature carrier concentration in LSCO is estimated to be $\sim 10^{20}/cm^3$ and is seen to increase with increasing temperature. I-V studies show that the leakage current levels of these structures are as low as $\sim 10^{-9}$ A/cm^2 at 100°C and 5V. Analysis of the leakage current data shows that the mechanism of conduction is most likely bulk limited Poole-Frenkel conduction indicating that the interface between STO and the semiconductor is non-blocking. We will report the details of our structural, microstructural and electrical studies on these two heterostructures in our presentation.
This work is supported by the Center for Superconductivity Research and the NSF-MRSEC under contract No. DMR-96-32521.

CC3.5
PREPARATION AND CHARACTERIZATION OF MFM AND MFIS STRUCTURES USING $Sr_2(Ta_{1-x}, Nb_x)_2O_7$ THIN FILM BY PULSED LASER DEPOSITION. Masanori Okuyama, Toshiyuki Nakaiso and Minoru Noda, Graduate School of Engineering Science, Osaka Univ, Osaka, JAPAN.

$Sr_2(Ta_{1-x}, Nb_x)_2O_7$ (STN) ferroelectric thin films have been prepared on Pt/Ti/SiO_2/Si and SiO_2/Si(100) substrates by pulsed laser deposition (PLD) method. (151)-oriented STN thin films were deposited at a low temperature of 600°C in N_2O ambient gas of 0.08 Torr for composition ratio of x=0.2, 0.3 and 0.4. A symmetrical D-E hysteresis loop of the STN film for composition ratio of x=0.3 was observed, where the coercive force was 30 kV/cm. The remanent polarization was 0.4 μC/cm^2, which is enough from theoretical analysis to control Si surface potential. A dielectric constant at room temperature is as low as 55. The remanent polarization of post-annealed films was not changed after 10^{10} cycles of polarization reversal. A counterclockwise C-V hysteresis was observed in Metal-Ferroelectric-Insulator-Semiconductor (MFIS) structure using $Sr_2(Ta_{0.7}, Nb_{0.3})_2O_7$ on SiO_2/Si at deposition temperature of 600°C, where a memory window of 1.3 V was obtained with measuring frequency, sweep voltage rate and width were 1 MHz, 0.5 V/sec and 10 V, respectively. The C-V curve spreads symmetrically toward both positive and negative directions from flat-band voltage in the control MIS structure when applied voltage is increased, and the window did not change for the sweep rate ranging from 0.1 to 5.0 V/sec. These results indicate that the hysteresis is originated from the ferroelectric property in the STN film. The gate retention time was about 2e3 sec when the voltages and time of write pulse were /- 10V and 1 sec, respectively, and hold bias was -0.5 V. The time is in the same order as that in $SrBi_2Ta_2O_9$ previously we reported, although leakage in the STN is larger by about an order than that in the SBT. We therefore consider that the STN is more adequately polarized in the MFIS structure than the SBT because ε in the STN is lower by 3 to 4 times than that in the SBT. Then it is advantageous to use the STN with low ε to MFIS-FET memory, compared to using the other high-ε ferroelectrics.

CC3.6
NEW Pt/(Bi,La)$_4Ti_3O_{12}/Si_3N_4$/Si MFIS STRUCTURE FOR FET-TYPE FERROELECTRIC MEMORIES BY THE SOL-GEL METHOD. Takeshi Kijima, Yoshihisa Fujisaki, Research and Development Association for Future Electron Devices, Tokyo Institute of Technology, Frontier Collaborative Res. Center, Yokohama, JAPAN; Takeaki Isobe, Eisuke Tokumitsu, Tokyo Institute of Technology, Precision & Intelligence Lab., Yokohama, JAPAN; Hiroshi Ishiwara, Frontier Collaborative Res. Center, Tokyo Institute of Technology, Yokohama, JAPAN.

For FET-type ferroelectric memories, c-axis oriented (Bi,La) $_4Ti_3O_{12}$ (BLT) film with small remanent polarization Pr of 4μC/cm^2 has been investigated. BLT films were fabricated by the sol-gel method on a Si_3N_4 amorphous film formed by atomic nitrogen radicals. Using stoichiometric sol-gel solution, BLT crystallization couldn't be confirmed at temperatures lower than 800°C. Therefore, a 2.5-7.5% Bi-excess solution was used and the deposition conditions of the pre-bake temperature and the thickness of BLT nucleation layer for crystallization were optimized, the c-axis-oriented BLT film with a good crystallinity and a good interface was confirmed at temperatures higher than 650°C. Our new Pt/150nm-BLT/3nm-Si_3N_4/Si (Metal/Feroelectric/Insulator/ Semiconductor) structure showed a C-V hysteresis property with the memory window of about 1V, which corresponded to the coercive voltage of a Pt/BLT/Pt capacitor.
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).

CC3.7
FERROELECTRIC PROPERTIES OF La-DOPED $Bi_4Ti_3O_{12}$ THIN FILMS DEPOSITED DIRECTLY ON Si BY PULSE INJECTION MOCVD. Joon Hyeong Kim, Jin Yong Kim, and Hyeong Joon Kim, School of Materials Science and Engineering, Seoul National University, KOREA.

$Bi_4Ti_3O_{12}$ (BIT) is a promising gate dielectric material for a ferroelectric field effect memory because it can offer considerable value of remnant polarization and low coercive force with good fatigue

endurance. However, BIT thin films deposited on Si have been reported to have quite small polarization value for this application as well as to have poor fatigue endurance. Recently, La-substituted BIT (BLT) thin film in MFM capacitor structure was reported to have larger value of P_r than that of BIT thin film as well as to have very high fatigue endurance. However, there has been no systematic report about BLT film deposited directly on Si by MOCVD technique, which is advantageous to process integration. In this study, La-doped bismuth titanate, $(Bi,La)_4Ti_3O_{12}$ (BLT), thin films were prepared on p-type (100) silicon substrate by MOCVD. Because of the great difference in formation kinetics of Bi_2O_3, La_2O_3 and TiO_2, it was very difficult to control the film composition as well as to obtain a good interface between the film and Si substrate. Hence, the pulse injection method was used to deposit the film, in which the vapor of titanium and lanthanum precursors were allowed to flow periodically into the reaction chamber for compensating the deficient bismuth content in the film. We investigated the effect of pulse injection of the precursors on the structural and electrical properties of BLT thin films. In addition, we investigated the La doping effect on the ferroelectric properties in comparison with a $Bi_4Ti_3O_{12}$ thin film. The BLT thin films obtained by pulse injection showed a good interface and stoichiometric composition. The MFS capacitors exhibited clockwise hysteresis, which indicates the switching of the ferroelectric polarization, in the C-V characteristics. Memory windows were in the range of 0.3∼ 2 V when the sweeping voltages varied from 3 to 9V. The properties of $(Bi,La)_4Ti_3O_{12}$ thin films were strongly dependent on pulse injection conditions.

CC3.8

LOW TEMPERATURE PROCESSING OF LEAD BASED FERROELECTRIC CAPACITORS INTEGRATED ON Si USING DIFFUSION BARRIERS. B.T. Liu, S. Aggarwal, A.P. Monga, Y. Wang, R. Ramesh, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD.

$Pb(Zr,Ti)O_3$ based ferroelectric random access memories (FeRAMs) have received great attention because of its low operation voltage, large remanent polarization and fast switching speed. However, integration into the high-density CMOS architecture, is restricted by high processing temperatures (typically 650°C) and the identification of electrically conducting diffusion barrier layers between the polycrystalline Si plug and the ferroelectric capacitor. Lowering the processing temperatures to 500°C will drastically reduce the materials challenge for both the diffusion barrier and the potential interaction between materials. In the present work, we report results on PZT capacitors fabricated by the sol-gel technique at temperatures between 500°C and 600°C. Further, we have integrated these capacitor structures on polycrystalline-Si/Si substrates using the Ti-Al intermetallic material system as a conducting diffusion barrier. Electrical properties of the capacitors were measured in the vertical transport mode through the polycrystalline Si. Structural characterization was performed to confirm the integrity of the diffusion barrier after the growth of the ferroelectric capacitor. This work has been supported by the NSF-MRSEC grant DMR96-32521 and Bellcore.

CC3.9

A PROPOSAL OF METAL-INSULATOR-FERROELECTRIC-INSULATOR-SEMICONDUCTOR (MIFIS) STRUCTURE FOR LONG RETENTION OF FERROELECTRIC FET MEMORY DEVICE. Minoru Noda, Kazushi Kodama, Toshiyuki Nakaiso, Mitsue Takahashi and Masanori Okuyama, Graduate School of Engineering Science, Osaka Univ, Osaka, JAPAN.

In order to decrease drastically the leakage current in the ferroelectric layer in Metal-Ferroelectric-Insulator- Semiconductor (MFIS)-FET structure and finally to improve greatly its retention characteristics, we newly propose a Metal-Insulator-Ferroelectric-Insulator-Semiconductor (MIFIS) structure, where an insulator with a large band-offset against the ferroelectric is inserted in between the metal and ferroelectric layers. In this work, we used MgO as the insulator because the band-offset at the conduction band edge is roughly estimated to be about 1.5 eV. From our numerical calculation, a slight increase in Schottky barrier height in the insulator layer ($\Delta\Phi_b$) provides sufficiently long retention time. When $\Delta\Phi_b$=0.08eV is assumed, the retention time over 10 years is theoretically exhibited. The MgO film of 10 nm thickness was prepared by Pulsed Laser Deposition (PLD) on SBT(400nm)/ SiO_2(27nm)/n-Si stacked structure, thereafter Al and AuSb were evaporated as upper and lower electrodes, respectively. The gate retention time was observed to be more than 1e4 sec when the voltages and time of write pulse were /-15V and 1 sec, respectively, and hold bias was 0.2 V. The time was found to be larger by about one order than that in the above SBT(400nm)/SiO_2(27nm)/n-Si (MFIS) stacked gate structure. Also, we have no evidence until now that the insertion of MgO in between the upper electrode and SBT film degrades some MFIS memory characteristics. Finally, we expect that the MIFIS structure is very effective to realize a ferroelectric FET memory with a practically long enough retention time.

CC3.10

THE PROPERTIES OF MFMOS CAPACITORS WITH HIGH k DIELECTRICS FOR ONE TRANSISTOR MEMORY APPLICATION. Tingkai Li, Sheng Teng Hsu, Hong Ying, Bruce Ulrich and Yanjun Ma, Sharp Laboratory of America, Camas, WA.

MFMOS (Metal/Ferroelectrics/Metal/Oxide/Silicon) capacitors with high k dielectrics have been proposed for one transistor memory applications. P type Si wafers were used as the substrates of MFMOS capacitors. In the first, 3.5 - 15 nm thermal Si)$_2$, Zr)$_2$, Hf)$_2$, Y$_2$)$_3$, $La_2 0_3$ and etc. thin films were formed on the Si substrates. Then barrier layer Ti (20 nm thick) was deposited on the oxide layer by sputtering. After that, bottom electrodes (150 nm thick Ir) were deposited by electrical beam evaporation techniques. An oxide MOCVD reactor was further used for the growth of 200-300 nm thick c-axis oriented $Pb_5Ge_3)_{11}$ thin films on the Ir electrodes. Finally, the top electrodes (100 nm thick Pt) were deposited by electrical beam evaporation techniques to form the MFMOS capacitors. The MFM capacitors with c-oriented $Pb_5Ge_30_{11}$ thin films showed a good ferroelectric and electrical properties. 2Pr and 2Ec values were measured from 2 to 3.8 $\mu C/cm^2$, and from 30 to 93 KV/cm at an applied voltage 5V respectively. The leakage current of 3.6 - 7.5 x10^{-7} A/cm^2 at 100KV/cm and dielectric constants of 45 - 55 were obtained. The operation voltages of MFMOS capacitors reduced with decreasing the thickness of oxide thin films or using high k dielectrics. The memory windows of 2 - 3.8 V were measured from MFMOS capacitors. It was found that the memory windows increased with increasing 2Pr values of MFM capacitors, which was consistent with the calculation formula of the memory windows of MFMOS capacitors. The basic mechanism were also investigated and discussed.

CC3.11

IMPROVEMENT OF RETENTION PROPERTY OF $YMnO_3$/ Y_2O_3/Si MFIS CAPACITOR. Norifumi Fujimura, Daisuke Ito, Kosuke Kakuno and Taichiro Ito.

We have been proposing $YMnO_3$ with low remanent polarization and permittivity as a transistor type FeRAM, and reported that c-oriented $YMnO_3$ films are obtained on (111)Si with Y_2O_3 buffer layer. Ferroelectric nature was confirmed by plused C-V mesurement.[1] However, the memory tetention properties was not satisfied because of the poor crystallinity (FWHM of $YMnO_3$ film on Y_2O_3/Si was 2.2°). We attempted to fabricate epitaxial $YMnO_3$ films on epitaxial Y_2O_3/Si structure in order to obtain highly oriented $YMnO_3/Y_2O_3$/Si capacitor. Highly oriented epitaxial films have been obtained by optimizing the growth process in the initial stage. The retention properties are also discussed.
[1] T. Yoshimura et al, APL 73, 3 (1998) 414-416 T. Yoshimura et al, J. Appl. Phys., 87 (2000) 3444.

SESSION CC4: POSTER SESSION
INTEGRATION AND ELECTRODES
Chairs: Katherine L. Saenger and Sanjeev Aggarwal
Monday Evening, November 27, 2000
8:00 PM
Exhibition Hall D (Hynes)

CC4.1

OXIDATION AND CONTACT RESISTANCE OF (Ti,Al)N AND TaSiN BARRIERS. Francisco Ayguavives, Sungjin Kim and Angus I. Kingon, NCSU, Dept of MS&E, Raleigh, NC.

The preparation of ferroelectrics and high-permittivity perovskite materials, which is performed at high temperatures in oxidizing environments, imposes strong limitations on the choice of suitable conductive barriers which can be used for integration of these materials with semiconductor devices. These barriers must prevent plug oxidation and electrode/plug reaction and must remain conductive after the deposition and processing of the perovskite dielectric. In this work we report a direct comparison of the oxidation resistance properties of two promising materials: (Ti,Al)N and TaSiN. The barrier effect for oxygen diffusion and oxidation kinetics in these conductive materials have been studied using Auger electron spectroscopy analysis, X-ray diffraction and TEM. Results will be also correlated with O-18 depth profiling measurements undertaken at the University of Paris Sud. Determination of diffusion coefficient and activation energy, as well as electrical properties measurements reveal that the choice for such a barrier is a compromise between electrical and oxidation resistance which depend strongly on respectively Al and Si composition. The effect of microstructure (crystallization, grain boundary formation) on the oxidation diffusion mechanism is also discussed. Finally, in this paper, the effect of the oxidation treatment

on resistance contact is studied for both (Ti,Al)N and TaSiN layers. It reveals that, in the case of (Ti,Al)N, resistance contact increases dramatically due to the formation of a thin oxide component at the surface of the film.

CC4.2
SUPRESSION OF OXIDATION OF AN EPITAXIAL (100)ZrN FILM ON Si DURING THE DEPOSITION OF THE Ir FILM. Sadayoshi Horii* and Susumu Horita, Japan Advance Institute of Science and Technology, School of Material Science, Ishikawa, JAPAN. *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. However, the ZrN film was oxidized by residual oxygen during the Ir film deposition. So, in this study, we tried to suppress the oxidation of ZrN film during the Ir film deposition. The ZrN film was deposited on (100)Si by rf sputtering with Ar and N_2 gas containing 4% H_2 at 850°C. At N_2/ArN_2 gas flow rate ratio of 5~50% we obtained an epitaxial (100)-oriented ZrN film on Si with a cube-on-cube relationship and at 20% the ZrN film had the lowest resistivity of 14.1 $\mu\Omega$·cm. The Ir film was deposited by rf sputtering with N_2 gas containing 4% H_2 instead of Ar at 600°C on the epitaxial (100)ZrN/(100)Si structure. Although the sputtering chamber was pumped down to a base pressure of less than 7×10^{-6} Pa, the ZrN film was fully oxidized at the deposition rate of 0.5 nm/min. Then, by increasing the deposition rate to 25 nm/min, about 73% of entire ZrN film was oxidized. In order to suppress the oxidation further, we placed 10 pieces of 10×10 mm^2 Zr metallic plates on the non-errosion area of the Ir target 4 inch in diameter, because the sputtered Zr particles can be expected to have high effect on gettering the residual oxygen. In fact, no oxidation of the ZrN film was occurred during the 200-nm-thick Ir film deposition. Also no contamination of Zr in the Ir film was observed by XPS measurement. Therefore, this method is very effective to suppress the oxidation of the barrier metal during the Ir film deposition.

CC4.3
THE PREVENTION OF HYDROGEN INDUCED DEGRADATION OF PZT FILM BY LEAD COATING. Hwan-Kuk Yuh, Euijoon Yoon, School of MS&E, Seoul National University, Seoul, KOREA; Sang In Lee, Semiconductor R&D Division, Samsung Electronics, Yongin, Kyungki, KOREA.

Recently, the ferroelectric random access memory (FRAM) has received much attention due to its non-volatility, high-speed and low-power operation. One of the problems in fabricating FRAM is the severe ferroelectric degradation of ferroelectric thin films caused by hydrogen-containing processes such as inter-level dielectric (ILD) deposition, passivation layer (Si_3N_4) deposition, and forming gas annealing, etc. It was reported that the degradation occurs rapidly at low temperatures below 400°C due to the catalytic reaction of hydrogen with the Pt electrode. Also, the oxygen deficiency by hydrogen-induced reduction and the incorporation of hydrogen atom in the lattice of ferroelectric material were possible mechanisms of ferroelectric degradation. In this report, PZT thin film capacitors with three different types of electrodes were fabricated and annealed in a hydrogen atmosphere at 400°C; PZT film with Pt top and bottom electrodes (Pt/PZT/Pt), PZT film with a Pt bottom electrode (PZT/Pt), and PZT film whose top electrode was Pb coated (Pb/Pt/PZT/Pt). After the hydrogen annealed, the remnant polarization of the Pt/PZT/Pt capacitor dropped to almost zero. On the other hand, the Pb/Pt/PZT/Pt capacitor survived the hydrogen annealing. In the Pt/PZT/Pt film, hydrogen molecules were dissociated by the exposed Pt surface, leading to the degradation of PZT capacitors at this low temperature. When the Pt film was coated with Pb thin film, the catalytic reaction by Pt film was effectively suppressed. This result clearly shows that Pt catalytic reaction is an important factor in hydrogen-induced degradation of ferroelectric films.

CC4.4
MICROSTRUCTURES OF $SrRuO_3$ THIN FILMS EPITAXIALLY GROWN BY PULSED LASER DEPOSITION. Sang Sub Kim, Byung Il Kim, Sunchon National University, Dept of Materials Science & Metallurgical Engineering, Sunchon, KOREA; Tae Soo Kang, Jung Ho Je, Pohang University of Science & Technology, Dept of Materials Science & Engineering, Pohang, KOREA; Tae Yeon Sung, Kwangju Institute of Science & Technology, Dept of Materials Science, Kwangju, KOREA.

As one of conducting oxides, $SrRuO_3$ has been receiving great attention due to its various useful properties. Along with its metallic conductivity, good campatibility in structure and chemistry with most of perovskite ferroelectric materials makes it very promising as a bottom electrode for growing films of perovskite materials in device applications. Epitaxial $SrRuO_3$ thin films have been successfully grown on different single crystal substrates by various deposition methods. However, understandings on the early stage growth behaviors and microstructures seem to be lacking. In this work, we prepared a series of ultrathin epitaxial $SrRuO_3$ thin films on $SrTiO_3$(001) using pulsed laser deposition. Then we ananlyzed their microscopic structures mainly using synchrotron x-ray scattering and transmission electron microscopy. We discuss the early stage growth behavior and domain evolution of $SrRuO_3$ thin films.

CC4.5
PROPERTIES OF REACTIVELY SPUTTERED IRIDIUM OXIDE THIN FILMS. F. Letendu, M.C. Hugon, F. Varniere, J.M. Desvignes, B. Agius, Laboratoire Charles Fabry, Groupe Physique des Films Minces, Université Paris Sud, Orsay, FRANCE; I. Vickridge, GPS, Universit Paris 6 et 7, Paris, FRANCE.

The preparation of ferroelectric and high dielectric perovskite materials, which is performed at high temperature (550-750°C) in oxidising environments, provides strong limitations on the choice of electrode materials which have to be used for integration with semiconductor devices. Due to its low resistivity and excellent thermal stability, IrO_2 has attracted attention as an alternative for electrode material in ferroelectric integrated circuit applications. In this work, IrO_2 thin films have been successfully deposited on Si(100) substrates by RF magnetron sputtering from a metal Ir target in an O_2-Ar plasma. By investigating the effects of the power density, the O_2/Ar flow ratio and the substrate temperature on the properties (mainly microstructure, surface roughness, composition, electrical resistivity) of IrO_2 films, optimum parameters have been identified for the growth of high quality IrO_2. It was found that the crystalline nature and morphology of IrO_2 films were strongly depended on O_2/Ar flow ratio and substrate temperature. The thermal stability of these films has been investigated at conditions typical for crystallization of perovskite dielectrics by RTA (rapid thermal annealing) in $^{18}O_2$ at 550-750°C. The as deposited and annealed samples were characterized using Rutherford backscattering spectroscopy (RBS) for Ti content and nuclear reaction analysis (NRA) $^{16}O(d,p)^{17}O$ and $^{18}O(p,\alpha)^{15}N$) for ^{16}O and ^{18}O contents respectively. The concentration depth profiles of ^{18}O was measured after the RTA treatments via the narrow resonances of $^{18}O(p,\alpha)^{15}N$ at 151 keV (fwhm=100eV). The relationship between the depth profiles and the measured excitation curves was deduced with the aid of the SPACES simulation program. However, an additional ohmic layer such TaSiN is required to prevent the formation of a SiO_2 layer between IrO_2 and Si.

CC4.6
LEAKAGE PROPERTY IMPROVEMENT OF PLZT CAPACITOR USING $CaRuO_3$ TOP ELECTRODE. Hiroshi Funakubo, Norikazu Okuda and Noriyuki Higashi, Tokyo Institute of Technology, Dept. Innov. Engr. Mater., Yokohama, JAPAN.

$SrRuO_3$ has been investigated as a top electrode of PZT based ferroelectric random access memory because of small degradation against ambient gas treatment and fatigue compared with Pt. However, the increase of the leakage has been pointed out . In the present study, we investigated $CaRuO_3$ as a top electrode. $CaRuO_3$ film was prepared at 650° by MOCVD from $Ca(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_x$ -$Ru(C_{11}H_{19}O_2)_3$ - O_2 system. It was deposited on sol-gel-PLZT/Pt/IrO_2/SiO_2/Si through a metal shadow mask. The leakage current density was below half when 100 nm -thick $CaRuO_3$ was used as a top electrode instead of same thickness $SrRuO_3$ prepared by same MOCVD. Moreover, the leakage of 50 nm -thick $CaRuO_3$ top electrode was smaller than that of 100 nm one. The leakage mechanism of $SrRuO_3$ was pointed out by the generation of conductive $SrPbO_3$ phase at the grain boundary of PLZT by the diffusion of Sr element of $SrRuO_3$ top electrode into PLZT. Therefore, the high resistively of $CaPbO_3$ compared with $SrPbO_3$ is the reason that the leakage current density decrease when $CaRuO_3$ is used as a top electrode instead of $SrRuO_3$. Moreover, the degradation of P-E hystsresis loops of PLZT capacitor was measured when it was heat treated at 270° for 15 min under the $H_2/(H_2\ N_2)$ ratio of 5 % atmosphere. It was almost the same when $CaRuO_3$ was used as a top electrode instead of $SrRuO_3$. However, it was smaller than that of a Pt top electrode. Moreover, it was perfectly recovered after 450° heat treatment for 30 min in O_2 atmosphere As a result, $CaRuO_3$ is the suitable materials as electrode of PLZT capacitor instead of $SrRuO_3$ for ferroelectric random access memory application.

CC4.7
CHARACTERIZATION OF CONDUCTIVE RuO_2 THIN FILMS FOR OXIDE BOTTOM ELECTRODES AND THEIR EFFECT ON FERROELECTRIC PROPERTIES OF PLT THIN FILMS.
S. Bhaskar, P.S. Dobal, S.B. Majumder and R.S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR.

Thin films of RuO_2 were prepared on silicon by solution chemistry

technique, using $RuCl_3.x.H_2O$ as a precursor material. X-ray characterization shows a rutile structure in these films. No intermetallic Ru reflections were observed. The films show good electrical properties with lowest resisitivity of 29 x 10^{-5} ohm-cm when annealed at 700°C. The presence of E_g, A_{1g} and B_{2g} , modes is consistent with the Raman spectrum of rutile. These modes as well as an additional unknown band at about 477cm^{-1} were investigated by temperature dependent Raman studies. Based on the results, the band at 477cm^{-1} that disappears above 370K is attributed to the hydrated RuO_2 present in the films. A detailed XPS analysis shows the stoichiometric rutile RuO_2 in the films. Small concentrations of $RuCl_3$, RuO_3 and hydrated RuO_2 were also detected. The presence of hydrated RuO_2 in the films by XPS analysis corroborates the Raman results. RuO_2 as a bottom electrode was found to enhance the ferroelectric properties of La modified lead titanate(PLT) films. Temperature dependent ferroelectric charcterization of these films will be presented in detail.
This work is supported in part by DAAG55-98-1-0012 and DE-FG02-91ER 75764 grants.

CC4.8
REACTIVE ION ETCHING OF SOL-GEL DEPOSITED LEAD ZIRCONATE TITANATE THIN FILMS IN SF_6 PLASMAS.
G. McLane, R. Polcawich, General Technical Services, Wall Township, NJ; J. Pulskamp, Univ. of Maryland, College Park, MD; B. Piekarski, M. Dubey, E. Zakar, J. Conrad, R. Piekarz, M. Ervin, M. Wood, Army Research Lab, Adelphi, MD.

Lead Zirconate Titanate (PZT) material has highly desirable ferroelectric properties, making it attractive for microelectromechanical (MEMS) applications such as sensor, actuator, electronic and optoelectronic devices. The sol-gel technique provides for rapid deposition of high quality PZT thin films in the micron thickness range. For fabrication of PZT devices with micron-sized structures, dry etch processes are required to provide anisotropic etching of patterned PZT. Reactive ion etching (RIE) with halogen plasmas has shown much promise for dry etching of PZT. This paper reports results obtained on RIE of PZT sol-gel films in a Plasma-Therm 720 RIE system with SF_6 etch gas, and compares them with results obtained in the past using HC_2ClF_4 (Freon 124) etch gas. $Pb(Zr_{0.52}Ti_{0.48})O_3$ was sol-gel deposited onto SiO_2/Si substrates, and patterned with a photoresist etch mask. Previously, RIE of PZT in Freon 124 plasmas has resulted in relatively low etch rates (<20 nm/min), and in the photoresist being coated with a carbon-type layer that made its subsequent removal difficult. Significant increases in etch rates were achieved with SF_6 plasmas, etch rate increasing with applied power up to 75 nm/min at 300 W. Etch rates decreased with pressure increase due to reduction in associated cathode bias voltages and ion bombardment energies, suggesting an etch process that is dependent on ion-induced mechanisms. In addition, photoresist masks could be removed subsequent to etching, demonstrating that PZT RIE with SF_6 plasmas is compatible with the common manufacturing technology of the silicon substrate. Scanning electron microscope measurements indicated that smooth etched surfaces with anisotropic profiles were achieved.

SESSION CC5: POSTER SESSION FERROELECTRIC NON-VOLATILE MEMORIES – FUNDAMENTALS AND TECHNOLOGY

Chairs: Christine F.E. Dehm and Seigen Otani
Monday Evening, November 27, 2000
8:00 PM
Exhibition Hall D (Hynes)

CC5.1
PROPERTIES OF Au/PZT/BIT/p-Si FERROELECTRIC MEMORY DIODES. Jun Yu, Hua Wang, Xiaomin Dong, Wenli Zhou, Yunbo Wang, Lili Zhu, Huazhong University of Science & Technology, Department of Electronic Science & Technology, Wuhan, CHINA.

A ferroelectric memory diode that consists of Au/PZT/BIT/p-Si multilayer configuration was fabricated by pulsed laser deposition (PLD) technique. The ferroelectric properties were investigated. The P-E curve of the PZT/BIT/ p-Si film system had an asymmetry hysteresis loop with Pr=20$\mu C/cm^2$ and Ec=48kV/cm, and the decay in remanent polarization was only 10% after 10^9 switching cycles. The C-V curve and I-V curve showed memory effects derived from the ferroelectric polarization of PZT/BIT films. The current density was $6.7\times10^{-8}$$A/cm^2$ at a voltage of 4V, and the conductivity behavior is discussed. The results suggest that the growth of the BIT ferroelectric layer is helpful to increase the memory windows and to reduce the current density by impairing the serious interaction and interdiffusion.

CC5.2
PREPARATION AND CHARACTERIZATION OF $SrBi_2Ta_2O_9$ THIN FILMS ON (100)-ORIENTED $LaNiO_3$ ELECTRODES.
J.B. Xu, G.D. Hu, I.H. Wilson, C.P. Li, and S.P. Wong, Department of Electronic Engineering and Materials Science and Technology Research Center, The Chinese University of Hong Kong, Shatin NT, Hong Kong, CHINA.

We have prepared $SrBi_2Ta_2O_9$ (SBT) thin films on (100)-oriented $LaNiO_3$ (LNO) electrodes at annealing temperatures of 600°C and 650°C on Pt/Ti/SiO_2/Si substrates. To fabricate high quality films, we have developed a sol-gel technique combined with a layer-by-layer annealing method. Using this technique, we have fabricated a (200)-predominant SBT thin film on $LaNiO_3$(100)/Pt/Ti/SiO_2/Si substrate at 600°C. We have studied the effects of the LNO oxide electrode on the structure, surface morphology, dielectric and ferroeletric properties of SBT thin films annealed at 600; and 650°C. Although the remanent polarization of the (200)-predominant SBT thin film is not as large as expected, the film can be uniformly polarized and imaged using an atomic force microscope in the piezoelectric mode.

CC5.3
DIRECT COMPARISON OF STRUCTURAL AND ELECTRICAL PROPERTIES OF EPITAXIAL (001)-, (116)-, AND (103)-ORIENTED $SrBi_2Ta_2O_9$ THIN FILMS. Ho Nyung Lee, Alina Visinoiu, Stephan Senz, Nikolai D. Zakharov, Alain Pignolet and Dietrich Hesse, Max-Planck-Institut für Mikrostrukturphysik, Halle/Saale, GERMANY.

Epitaxial $SrBi_2Ta_2O_9$ (SBT) thin films with well-defined (001)-, (116)-, and (103)-orientations have been grown by pulsed laser deposition on (001)-, (011)-, and (111)-oriented Nb-doped $SrTiO_3$ (STO) substrates. X-ray diffraction pole figure and ϕ-scan measurements revealed that the three-dimensional epitaxial orientation relation SBT(001)||STO(001) and SBT[$1\bar{1}0$]||STO[100] is valid for all cases of SBT thin films on STO substrates, irrespective of their orientations. The measured remanent polarization and coercive field of (116)-oriented SBT films were 4.8 $\mu C/cm^2$ and 84 kV/cm, respectively, at a maximum applied electric field of 320 kV/cm. A higher remanent polarization (5.2 $\mu C/cm^2$) and lower coercive field (52 kV/cm) than those of SBT(116) films were observed in (103)-oriented SBT thin films, and (001)-oriented SBT films revealed no ferroelectricity along the [001] axis. The dielectric constants of (001)-, (116), and (103)-oriented SBT films were 133, 155, and 189, respectively. The results of a comparative analysis of the crystallographic orientations and electrical properties will be presented.

CC5.4
FATIGUE-FREE La-SUBSTITUTED BISMUTH TITANATE THIN FILMS GROWN USING CHEMICAL SOLUTION DEPOSITION.
Uong Chon, Sun Hwa Lee, Gyu-Chul Yi, and Hyun Myung Jang, Dept of Materials Sci. and Eng., Pohang University of Science and Technology (POSTECH), Pohang, KOREA.

There has been much interest in fatigue-free ferroelectric thin films for developing nonvolatile memory devices. As one of the fatigue-free materials, La-substituted bismuth titanate (BLT) is so interesting since the material can be prepared at a lower temperature than strontium bismuth tantalate (SBT). Recently, fatigue-free BLT films have been successfully grown at low temperatures of 650°C by using pulsed laser deposition (PLD). However, large-scale processing in the integrated circuit industry requires high reproducibility and relative simplicity of all the processing steps. The chemical solution deposition employed in this research fulfills these requirements as they offer excellent composition control, short fabrication times as well as low-temperature processing at comparatively low cost. BLT thin films were grown on Pt/Si(100) substrates with intermediate layers using the chemical solution deposition. For the film growth, acetate-based precursors were employed. The films were crystallized during thermal annealing at temperatures above 500°C. As shown in x-ray diffraction measurements of the films, the BLT films were crystallized with a strong c-axis orientation. Furthermore, the XRD results show significant changes in the crystallographic orientation of the BLT films due to the addition of La. Electrical measurements of the BLT films were carried out after depositing top electrodes of Pt. From hysteresis measurements, a remanent polarization and a coercive field of the BLT films annealed at 650-700°C for 5-60 min ranged from 5 to 10 of $\mu C/cm^2$ and from 50 to 75 kV/cm, respectively. Furthermore, the films did not show any fatigue behavior after 10^{10} read/write cycles at a frequency of 1MHz. In addition, the effect of the La composition in the films on the electrical properties of the films will be presented.

CC5.5
MOCVD KINETICS OF PRECURSORS FOR FERROELECTRIC SBT FILM. A. Baeri, G.G. Condorelli, I.L. Fragalá, Dipartimento di Scienze Chimiche, Universitá di Catania, Catania, ITALY.

MOCVD fabrication of SBT ferroeletric films is of great interest for Fe-RAM application. It is well suited for highly conformal layers compared to other deposition techniques such as Sol-gel, MOD and Laser ablation deposition. In this contest kinetics and deposition mechanism posses a critical role as far as industrial scaling-up is concerned.
This paper reports on SBT deposition process adopting $Sr(hfa)_2(tet)$, $Bi(C_6H_5)_3$ and $Ta(C_2H_5O)_5$ precursors.
Experiments were performed in a reduced pressure, horizontal cold wall reactors for single and multi component depositions. Surface morphologies and film compositions were analysed by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS). The structural nature of the films has been investigated by x-ray diffraction techniques (XRD). Growth rates were estimated by EDX and SEM cross sections.
The deposition kinetics of single precursors have been studied upon varying operational deposition parameters namely temperatures and precursors partial pressures. Depending upon experimental conditions, deposition processes occur either in the reaction rate limited regime or in the mass transport regime. Kinetics controlled by reaction rates ($T_{deposition}$<350 °C) gives insights on the process mechanisms. The activation energies of single component deposition processes have been determined from the Arrhenius plots for the three precursors. Two and three component deposition experiments provide information on mutual interactions between precursors and their effects on the total growth rate.

CC5.6
PREPARATION AND CHARACTERIZATION OF Ba AND Nb SUBSTITUTED $SrBi_2Ta_2O_9$ THIN FILMS AND POWDERS.
R.R. Das, P.S. Dobal, A. Dixit, W. Peréz, R.S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR; R.E. Melgarejo and M.S. Tomar, Department of Physics, University of Puerto Rico, Mayaguez Campus, Mayaguez, PR.

Bi-layered ferroelectric compounds are considered most promising for non-volatile memory applications due to their high fatigue endurance. We have prepared $SrBi_2Ta_2O_9$ powders with Ba (A sites) and Nb (B sites) substitutions using a novel solution based route. These powders were then presses and sintered at 1050°C to obtain high quality targets. Thin films were prepared from these ceramic targets on Si(100) and $Pt/TiO_2/SiO_2/Si$ substrates by utilizing pulsed laser deposition technique. The effects of growth conditions on phase formation as well as the structural and electrical properties in films (and powders) are studied. Initial results on films show good hysteresis and fatigue characteristics. Though phase formation begins at much lower temperatures, these films crystallize in a complete layered perovskite phase when prepared at 700°C. Optical phonon modes in these materials exhibit systematic variations with changing compositions. The changes in the Raman spectra are explained in terms of Ba and Nb substitutions on A and B sites, respectively. The results of temperature dependent studies indicating substitution induced changes in transition temperatures of these materials will be presented.
This work is supported in parts by DAAG55-98-1-00112, DAAD19-99-1-0362, and NSF DMR 9801759 grants.

CC5.7
ROLE OF THE ELECTRODE MORPHOLOGY AND DOMAIN ORIENTATION ON THE FERROELECTRIC PERFORMANCE OF EPITAXIAL $Pb(Zr,Ti)O_3$ THIN FILMS NEAR THE MORPHOTROPIC PHASE BOUNDARY.
Cesar Guerrero, Florencio Sanchez, Jose Roldan, Maria V. Garcia-Cuenca, Cesar Ferrater, Manuel Varela, Universitat de Barcelona, Departament de Fisica Aplicada i Optica, Barcelona, SPAIN.

Epitaxial ferroelectric $Pb(Zr,Ti)O_3$ (PZT) thin films have been fabricated by pulsed laser ablation of a ceramic target with the composition of the tetragonal-rhombohedral morphotropic phase boundary (MPB). Lattice matched $LaAlO_3$ and $SrTiO_3$, as well as (100) Silicon substrates have been used for the preparation of epitaxial $SrRuO_3$ and $LaNiO_3$ bottom electrodes with room-temperature electrical resistivities in the range of 150 Ohm·cm for both materials. Square hysteresis loops with remanence exceeding 40 $\mu C/cm^2$ are obtained for the PZT films on $LaNiO_3$, which form in the tetragonal phase aided by the long-range biaxial stress due to lattice misfit and different thermal expansion coefficients. This long-range stress is lost when PZT is grown on $SrRuO_3$ due to orthorhombic domain pattern formation in the electrode, along with its slightly rougher surface morphology. As a result, the rhombohedral phase typically appears and slimmer hysteresis loops are observed. We show that the phase formation can be tuned by modifying the deposition parameters, e.g. tetragonal PZT can be obtained on $SrRuO_3$ when deposited at higher substrate temperature (750°C) than on $LaNiO_3$(600°C). On the contrary, little effect of the laser fluence has been observed, although recently it has been reported to affect the Zr/Ti ratio. The role of the electrode thickness, which affects its electrical transport properties and domain pattern formation is also studied. These results are discussed from the point of view of non-volatile memory applications, so imprint and fatigue measurements are also included. The role of the top electrode (Al, Au, $SrRuO_3$, $LaNiO_3$) is also studied; intrinsic and induced imprint is observed when aymmetric electrode configurations are used.

SESSION CC6: BST FOR DRAM AND GATE DIELECTRICS
Chairs: Orlando Auciello and Rainer Waser
Tuesday Morning, November 28, 2000
Room 312 (Hynes)

8:30 AM *CC6.1
THE EFFECT OF FORMING GAS ANNEALING ON METAL/$(Ba,Sr)TiO_3$/METAL THIN FILM CAPACITORS FOR FUTURE DRAM APPLICATIONS: ELECTRICAL PROPERTIES AND DEGRADATION MECHANISMS.
J.D. Baniecki, C. Parks, IBM Microelectronics Div, Hopewell Junction, NY; R.B. Laibowitz, T.M. Shaw, IBM Research Div, T.J. Watson Research Ctr, Yorktown Heights, NY; J. Lian, Infineon Technologies, Hopewell Junction, NY.

Perovskite-type titanate dielectrics, such as Barium Strontium Titanate (BSTO), are being actively considered as replacements for the conventional silicon oxynitride dielectrics in DRAM capacitors. However, before BSTO thin films can be successfully integrated into a CMOS process flow, many integration challenges still must be overcome. One important consideration is the effect of forming gas, which is commonly used to control SiO_2/Si interface states, on the electrical properties of Pt/BSTO/Pt thin film capacitors. In the talk I will present the results of studies we have made on the electrical properties of unpassivated Pt/BSTO/Pt thin film capacitors that have been annealed in forming gas (95% Ar 5% H_2 or D_2) at temperatures between 23 C - 400°C. The BSTO thin films (15-100 nm thick) were prepared by metal-organic chemical vapor deposition (MOCVD) and the nominal composition for the films was a Ba to Sr ratio of 70:30 and a Ti to (Ba Sr) ratio of 1.02 - 1.05. Deuterium SIMS depth profiles for metal/BSTO/metal capacitors with different electrode metals (catalytic (Pt) vs non catalytic (Au)) will also be presented. The talk will focus on investigating the mechanisms for hydrogen induced degradation of the electrical properties of Pt/BSTO/Pt thin film capacitors. Particular emphasis will be placed on understanding the current density - applied field (J-E) characteristics which exhibited features that could not be fully explained by either a simple thermionic emission or tunneling (Fowler-Nordeim) formalism. We show that the data can be successfully interpreted in terms of thermionically assisted tunneling of electrons through the interfacial Schottky barrier with the peak in energy distribution of the incident carriers depending on applied voltage. Based on the results, some strategies for minimizing the degradation in electrical properties of Pt/BSTO/Pt thin film capacitors after forming gas exposure will be discussed.

9:00 AM CC6.2
KINETICS AND MECHANISMS OF DEUTERIUM DOPING AND REMOVAL FROM PEROVSKITE DIELECTRIC THIN FILMS.
Ruey-Ven Wang, Joon-Hyung Ahn, Robert J. Becker and Paul C. McIntyre, Department of MS&E, Stanford University, Stanford, CA; Stephen R. Gilbert, Agilent Laboratories, Palo Alto, CA; Michelle Schulberg, Novellus Systems, San Jose, CA.

Exposure to hydrogen-containing ambients may cause severe leakage current degradation and/or polarization degradation in high-k perovskite thin films. Charged hydrogen defects act as shallow donor dopants and, in the case of leakage current degradation, their contribution to the space distribution within the dielectric can lead to a pronounced lowering of the dielectric/electrode Schottky barrier height. Here we report a systematic study of the kinetics and mechanisms of deuterium doping and removal from BST and PZT dielectric thin films grown via MOCVD. Deuterium, used because it avoids interference with hydrogen present in the as-deposited films, was introduced during deuterated forming gas anneals. Its distribution in the films was probed by SIMS sputter-depth-profiling analysis. Post-forming gas recovery anneals in both inert and oxygen-containing ambients were used to remove the deuterium. Methods for modeling the deuterium doping/removal kinetics and the effects of film microstructure are described in detail. Observed deuterium concentration profiles are correlated with changes in the electrical properties of the films.

9:15 AM CC6.3
INVESTIGATION AND MODELING OF AC AND DC FAILURE MODES AND IMPLICATIONS FOR DEVICE RELIABILITY IN LS-MOCVD $(Ba,Sr)TiO_3$ THIN FILMS.
C.B. Parker, S.-J. Kim, and A.I. Kingon, North Carolina State University, Raleigh, NC.

(Ba0.7,Sr0.3)TiO3 thin films on Si are being investigated for use in DRAMs and other integrated capacitor applications. The types of lifetime limiting electrical failure observed in BST are resistance degradation, DC tDDB, AC tDDB, soft breakdown, and high temperature AC failure. Previous investigation of failure has focused on high temperature resistance degradation. It is important, however, that failure under low temperature and AC stressing conditions be understood, as this more closely approximates the real operating conditions of a BST capacitor. To understand the relationship between AC and DC modes, extensive characterization of failure under low temperature DC and AC conditions has been performed under varying fields and frequencies. These measurements were also performed as a function of temperature to determine if this additional stress produced additional failure modes or accelerated rates. This work has combined with previous work on resistance degradation and stress induced leakage currents in BST to arrive at a more general understanding of failure in BST. Zero Bias Thermally Stimulated Current measurements scanning a wide range of trap energies in the BST will be presented. These measurements are especially sensitive to effects resulting from non-stochiometry, point defect concentrations, and thus reliability. The TSC measurements will allow calculation of trap densities, thereby providing insight into the site occupancy of the excess Ti routinely added to achieve optimal electrical performance.

9:30 AM CC6.4
BST THIN FILM DIELECTRICS: LOW TEMPERATURE SPUTTER DEPOSITION, STRUCTURE/PROPERTY RELATIONS, AND RELIABILITY. R.J. Becker and P.C. McIntyre, Stanford University, MS&E, Stanford, CA.

Barium strontium titanate (BST) is being investigated as a high k dielectric material for application in high frequency decoupling capacitors and other backend applications. While systematic structure-property studies and some reliability data have been reported for BST thin film dielectrics grown by MOCVD at temperatures in excess of 600°C, much less is known about BST films deposited at temperatures of 450°C or less. Here we present an investigation of the compositional, microstructural, and electrical properties of BST thin films deposited by low-temperature RF magnetron sputtering. Also, we have investigated the effects of mobile charged defects, particularly oxygen vacancies, on BST properties by using isotopic exchange experiments, SIMS analysis, and electrical characterization. Migration of such charged defects within BST in response to an applied electric field is thought to be a key limiting factor in the reliability of BST thin films for dielectric applications.

9:45 AM CC6.5
IMPROVED DEPOSITION PROCESS OF CVD-(Ba,Sr)TiO_3 ON Ru. Masayoshi Tarutani, Takehiko Sato, Mikio Yamamuka, Takaaki Kawahara, Tsuyoshi Horikawa, Takashi Takenaga, Yoshikazu Yoneda, Takeharu Kuroiwa, Teruo Shibano, Mitsubishi Electric Corp., Advanced Technology R&D Center, Hyogo, JAPAN.

Metal/insulator/metal [MIM] (Ba,Sr)TiO_3 [BST] capacitor has attracted much attention for applications in future high density memories. Ruthenium is promising for the electrode material, because of its feasibility in micromachining via dry etching. To meet with severe design rules, the thickness of BST needs to be limited to less than ~ 30 nm. In the present paper, we will report on an improved formation process of CVD-BST on Ru electrodes including the planarization by Ru annealing, the optimization of CVD process, and the control of MO source flow-ratio, which enables thin BST films of high-permittivity with a good leakage property. BST films were deposited by the flush vaporization CVD method with a unique liquid delivery system. BST films were finely crystallized by a two-step deposition method. An inductively coupled plasma mass spectrometry [ICP-MS] analysis revealed the deviation of (Ba Sr)/Ti molar ratio of the 1st BST-layer on Ru. By readjusting the flow ratio of liquid sources, we obtained 30nm-thick BST films with uniform composition across the film, exhibiting good electrical properties. The leakage property, however, was severely deteriorated in BST films less than 25 nm thick. A SEM observation showed the presence of micro-roughness or micro-hillocks in these films, which were confirmed to be caused by Ru oxidation. Therefore, an annealing process of the Ru electrode was added for its planarization, and the CVD process was also improved. As a result, we obtained smooth and finely crystallized 20nm-thick BST films with good electrical properties of $t_{eq} \sim 0.45$ nm and leakage current $< 2 \times 10^{-7}$ A/cm^2. We also measured properties of BST films deposited on the 3-D Ru electrode. The results will be discussed.

10:30 AM *CC6.6
MANUFACTURABILITY STUDY FOR ETCHING HIGH-DENSITY BST/PT CAPACITORS. Jay Hwang, Applied Materials, Santa Clara, CA.

BST (Barium Strontium Titanate) has been widely regarded as the future dielectric material for use with Pt electrodes, especially in the manufacture of high-density capacitors for $\geq$4 Gb DRAM applications. It is well known that etching Pt electrode presents many difficulties. One of the technical challenges is the pattern etching of high-density BST/Pt capacitors for production. While etching Pt, the etch by-products tend to re-deposit on the etched Pt profile as well as on the inside surfaces of the etch chamber, both due to the low volatility of the etch by-products. This results in poor profile control and a high number of particles. This paper will detail how to form the Pt electrodes necessary for manufacturing high-density BST capacitors, as well as how to overcome re-deposition of non-volatile with the etch by-products, thus controlling CD and improving productivity. The feasibility of etching $\leq$0.13μm Pt electrodes in a Metal Etch DPS Centura chamber will be shown. Marathon data showing good process repeatability and low particle counts will be presented to demonstrate the manufacturability of etching Pt electrodes. BST defect prevention after etching will also be discussed.

11:00 AM CC6.7
HIGHLY C-AXIS ORIENTED Ru FILMS PREPARED BY CHEMICAL VAPOR DEPOSITION AND THEIR APPLICATION TO ELECTRODE OF Ru / $SrTiO_3$ / Ru CAPACITORS.
Mitsuaki Izuha, Tomonori Aoyama, Masahiro Kiyotoshi and Kazuhiro Eguchi, Toshiba Corporation, Semiconductor Company, Process & Manufacturing Engineering Center, Yokohama, JAPAN.

Ruthenium (Ru) is one of the most promising candidates for electrode materials of high dielectric constant capacitors. In the crystal structure of Ru, hexagonal system, c-axis surface is the most energetically stable. Takings into account post- thermal process in the LSI device, c-axis oriented Ru films are preferable for degradation of their electrical properties. However, c-axis oriented Ru films by CVD, which are required for electrodes of three-dimensional capacitor, have not been reported. In the present study, we successfully prepared highly c-axis oriented Ru films by CVD and applied them to the bottom electrode of Ru / $SrTiO_3$ / Ru capacitors. CVD-Ru films were deposited using Ar carried bis-(ethyl- cyclopentadieny)ruthenium [Ru(EtCp)$_2$] and O_2 in a hot-wall batch-type reactor. By lowering the deposition temperature to 300 °C, good step coverage (>90 %; 0.13 μm-hole, aspect ratio=5.4) were achieved. For 300°C deposition, lower partial pressure of O_2 tends to cause smoother surface morphology and lower resistivity (30 $\mu\Omega$cm). In order to obtain highly (002) orientation observed by XRD, in addition, the ratio between the partial pressure of Ru(EtCp)$_2$ and O_2 was found to be important. If the partial pressure of Ru(EtCp)$_2$ is close to that of O_2, Ru(EtCp)$_2$ probably dissociates to Ru and 2·(EtCp). So, the Ru film grows on c-axis orientation. In the case of excess O_2 circumstance, by-products of EtCp probably impede the growth of c-axis oriented Ru films. Furthermore, we fabricated Ru / $SrTiO_3$ / Ru capacitors using the highly c-axis oriented CVD-Ru films as a bottom electrode. Even after post-annealing at 650°C, the SiO_2 equivalent thickness was low (t_{eq}=0.38 nm) and the degradation of leakage current was small (J<1E-7 A/cm^2 at $\pm$0.7 V). As a result, highly c-axis oriented Ru films by CVD were suggested to be excellent electrodes for three-dimensional capacitors in next-generation DRAMs.

11:15 AM *CC6.8
PROPERTIES OF $Ba_xSr_{1-x}TiO_3$ THIN FILMS ON SILICON (100) SUBSTRATES GROWN BY MOLECULAR BEAM EPITAXY.
J. Ramdani, L.L. Hilt, Z. Yu J.A. Curless, C.D. Overgaard, J. Finder, K. Eisenbeiser, R. Droopad, W.J. Ooms, Physical Sciences Research Laboratories, Motorola Labs, Tempe, AZ; V. Kaushik, B.Y.Nguyen, DigitalDNA Laboratories, Semiconductor Product Sector, Motorola, Austin, TX.

High-K materials are of great importance in future ULSI devices. Among the long list of these high-K oxides, $SrTiO_3$ (STO) and $Ba_xSr_{1-x}TiO_3$ ($BSTO$) are excellent candidates for CMOS gate dielectric and ferro-gate materials. In the present work, we will report on the epitaxial growth of STO and BSTO on Si by Molecular Beam Epitaxy and on the material and electrical properties. RHEED was used in-situ to monitor the films at different growth stages and XRD, SE, XPS, AES, AFM, EELS and, HTEM were used to characterize the films. As grown, BSTO/Si is single crystal and 45° rotated with respect to the Si mesh as confirmed from RHEED, TEM and XRD. However, the material and electrical characteristics depend strongly on the initial nucleation stage and on the template preparation. Particularly, the generation of an amorphous layer at the crystalline oxide/ Si interface that can be as thick as 25$\AA$. The optimization of growth sequence has led to an amorphous layer as thin as 7$\AA$. The C-V characteristics shows an equivalent oxide thickness (EOT) of 0.9 nm for a 50$\AA$ thick STO and a leakage current as low as 0.2 mA/cm^2 at -1 Volt. We will discuss the origin of this amorphous layer its stability and impact on the material and electrical properties. BSTO with Ba composition ranging from 50 to 100% has been prepared on STO/Si and directly on Si with crystalline quality similar to STO. The ferroelectric tetragonal phase was obtained, however the

magnitude of the saturated polarization was much smaller for thin films (<120Å) than that of bulk crystals. We will report on the structural/electrical properties of these thin films.

11:45 AM CC6.9
INVESTIGATION OF INTERFACE STRUCTURE IN $SrTiO_3$/Si HETEROSTRUCTURES BY HRTEM. G.Y. Yang , R. Ramesh, University of Maryland, Materials Research Science and Engineering Center, College Park, MD; J. Finder, J. Wang, J. Yu, J. Ramdani, R. Droopad, K. Eisenbeiser, Motorola Inc., Physical Science Research Laboratories, Tempe, AZ; Z.L. Wang, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA.

Deposition of $SrTiO_3$ (STO) dielectric films on silicon substrates is of much interest since $SrTiO_3$ is one of the attractive perovskites for high-k gate dielectric applications. Due to the dramatic differences in crystal structure and crystal chemistry between Si and STO, the nature of the interface and structural defects becomes critical to the structural and chemical integrity and electrical performance of the device. We are studying the microstructure of epitaxial STO films grown on Si substrates by MBE using high-resolution transmission electron microscopy (HRTEM) in conjunction with detailed image simulations. The interface structure shows an orientation relationship of $(001)_{STO}//(001)_{Si}$ and $[100]_{STO}//[110]_{Si}$. It was established that, under appropriate processing conditions, the $SrTiO_3$/Si interface was abrupt to within one atomic plane and the interface most likely consists of Si bonded with O in $SrTiO_3$, forming 2x1 and 1x1 domains. Lattice rotation of $SrTiO_3$ on (001) surface of Si substrate by 45° efficiently minimizes the difference in crystallographic parameters and crystal chemistry between $SrTiO_3$ and Si substrate. Consequently, the effective mismatch of 1.7% is accommodated by the presence of interface dislocations at the Si substrate side. Structural defects in the STO thin film consist mainly of domain rotations and stacking faults. Mis-orientation is directly correlated with the Si substrate surface roughness. Stacking faults confined within the STO might be resulted from layer by layer deposition. In this paper, we will presents results of our HRTEM imaging and corresponding image simulation studies to carefully discern the structure and chemistry of the interface.
This work is partly supported by a NSF-MRSEC under grant No. DMR-96-32521.

SESSION CC7: FUNDAMENTAL PROPERTIES OF FERROELECTRIC THIN FILMS

Chairs: Robert W. Schwartz and Angus I. Kingon
Tuesday Afternoon, November 28, 2000
Room 312 (Hynes)

1:30 PM *CC7.1
DEFECTS IN FERROELECTRIC THIN FILMS. R. Ramesh, Materials Research Science and Engineering Center, University of Maryland, College Park, MD; S. Aggarwal, Texas Instruments, San Jose, CA.

Over the past six years, we have focused considerable effort on understanding the growth and characterization of ferroelectric thin films and heterostructures. Using both epitaxial and polycrystalline capacitors on a variety of substrates as test vehicles, we have been carrying out systematic studies on the effect of composition, point defect chemistry, strain and other processing variables on the structural and ferroelectric properties. A novel aspect of our work is the use of scanning electric force microscopy, microwave microscopy and Raman scattering techniques to understand the microscopic influence of film microstructure on the ferroelectric properties. The role of point defects, both interstitial (such as hydrogen) and substitutional (cationic and anionic vacancies, isovalent and aliovalent substituents), at doping level concentrations, has not been well understood. In this talk, we will present results of our studies of hydrogen (for example in forming gas) and cationic defects (specifically lead vacancies and excess lead) on the properties of ferroelectric PZT thin films. We have focused on aspects where fundamental measurements in conjunction with theoretical studies and modeling are likely to enable better understanding of the complex phenomena involved in these materials. Specifically, we will focus on the following topics: (i) polarization switching and relaxation dynamics in ferroelectric thin films; (ii) microscopic observations of ferroelectric properties and time dependent changes; (iii) interaction of defects with polarization switching.
This work is supported by the NSF-MRSEC.

2:00 PM CC7.2
IMAGING MECHANISM AND QUANTIFICATION OF SCANNING PROBE MICROSCOPIES OF FERROELECTRIC SURFACES. Sergei V. Kalinin, Dawn A. Bonnell, Dept. Mat. Sci. Eng., University of Pennsylvania, Philadelphia, PA.

In the last few years a wide spectrum of non-contact, intermittent contact and contact scanning probe microscopies have been applied to imaging ferroelectric surfaces. The imaging mechanism in non-contact SPM is ultimately related to the total charge distribution on the ferroelectric surface, including both polarization and screening charges. Contact voltage modulation (piezoresponse) imaging (PRI) is sensitive to both local polarization via electromechanical coupling and surface charge via capacitive interactions. Quantification of surface properties from SPM data represents a largely unresolved problem. In the present research we analyze the contrast formation mechanism in PRI using an analytical solution for the piezoelectric indentation problem[1,2,3]. The influence of modulation frequency and bias on image contrast was analyzed. The distance dependence of amplitude and phase of the voltage modulation response is quantified. The contribution of electrostatic forces to the image is estimated. A simplified model for the interpretation of local hysteresis loops (PRI spectroscopy) in terms of effective material properties is proposed. Variable-temperature PRI imaging of domain structures in $BaTiO_3$ is performed and the temperature dependence of the piezoresponse is compared with the Ginzburg - Devonshire theory. To simultaneously study surface potential and polarization distribution a novel dual scan-line modification of PRI was implemented. Relevant theory, existing difficulties and experimental results are discussed.
[1]V.Z. Parton and B.A. Kudryavtsev, Electromagnetoelasticity, Gordon and Breach publishers (1988).
[2]S.A. Melkumyan and A.F. Ulitko, Prikladnaya mechanika 23, 44 (1987).
[3]A.E. Giannakopoulos and S. Suresh, Acta mater. 47, 2153 (1999).

2:15 PM CC7.3
NANOMETER-SCALE ELECTRICAL CHARACTERIZATION AND MANIPULATION OF FERRO-ELECTRIC FILMS USING SCANNING CAPACITANCE MICROSCOPY AND TUNNELING-AFM. P. De Wolf, A. Erickson, E. Brazel, M. Lefevre, N. Pangon, Digital Instruments, Santa Barbara, CA.

Two scanning probe microscopy modes have been used for the characterization and manipulation of ferro-electric (FE) films: Tunneling-AFM (TUNA) and Scanning Capacitance Microscopy (SCM). In TUNA a conductive probe is scanned across the sample surface in contact mode while applying a DC bias between the probe and the sample. The current flow through the probe is measured using a linear ultra low current amplifier, which has a range of 80 fA to 100 pA. Conductivity data is collected simultaneously with topography and with a lateral resolution of 10-20 nm. The resulting 2-D current maps reveal variations in film thickness, thin areas, electrically weak spots or local degradation. This technique has been applied here to the investigation of dielectric properties in polycrystalline FE thin films of Barium Titanate and Lead Zirconate Titanate (PZT). Enhanced leakage currents at grain boundaries as well as in individual grains were observed. Broad areas separated by high current boundaries, which may be a result of stress in the films, were also seen in the Barium Titanate sample. A second technique, SCM has been used to manipulate and image the domain polarization in different FE films, including PZT and SBT, with nanometer spatial resolution. The SCM is used in its normal operation to image differences in the polarization of the FE films. The sensitivity and spatial resolution are compared to other AFM-based methods: Electric Field Microscopy and Piezo-response imaging. It is also demonstrated how the SCM can be used to control and alter (and check) the polarization state with nanometer spatial resolution. In addition, using SCM, capacitance-voltage curves have been measured for the first time on sub-quarter micron sized FE capacitors. These results demonstrate the potential value of AFM based techniques for the nanometer scale manipulation and electrical characterization of FE thin films.

2:30 PM CC7.4
NANOMETER SCALE DOMAIN MEASUREMENT ON FERRO-ELECTRIC THIN FILMS USING SCANNING NONLINEAR DIELECTRIC MICROSCOPY. Hiroyuki Odagawa, Yasuo Cho, Research Institute of Electrical Communication, Tohoku University, Sendai, JAPAN.

Recently, we have proposed and developed a new purely electrical technique for imaging the state of ferroelectric polarization and local crystal anisotropy of dielectric materials, and is termed “scanning nonlinear dielectric microscopy” (SNDM).[1] Using this system we observed a ferroelectric polarization distribution on several ferroelectric materials with nanometer resolution, and reported the results.[2] In this paper, a new type of scanning nonlinear dielectric microscope (SNDM), with an additional function of simultaneous observation of surface morphology, is developed. This is achieved by using an electrically conducting atomic force microscope cantilever as a probe needle. Using this new SNDM, simultaneous measurements of extremely small ferroelectric domains pattern and surface morphology on ferroelectric thin films are performed. Topographic and domain images, which are simultaneously taken from the same location of the

materials, are successfully obtained. The experimental result shows that nano-sized 180° c-c ferroelectric domain with the width of 1.5 nm for PZT thin film having a good correlation with a topographic image are observed. The result also shows that the resolution of the microscope is less than 0.5 nm for PZT thin film. Thus the SNDM system with the function of simultaneous observation of surface morphology is very useful for understanding domain structures and domain dynamics of ferroelectric thin film.

1) Y. Cho, A. Kirihara and T. Saeki: Rev. Sci. Instrum. **67** (1996) 2297.
2) Y. Cho, S. Kazuta and K. Matsuura: Appl. Phys. Lett. **72** (1999) 2833.

2:45 PM CC7.5
LATTICE VIBRATIONAL PROPERTIES OF $SrBi_2Ta_2O_9$. Ran Liu, Motorola, Materials and Structures Labs, Mesa, AZ; Peir Chu, Motorola, Materials and Structures Labs, Austin, TX; Xinliang Lu, Pengdi Han, University of Illinois at Urbana-Champaign, Depertment of Materials Science, Urbana, IL.

$SrBi_2Ta_2O_9$ is one of the layered perovskite ferroelectrics with excellent fatigue resistance and thus has gained great interest of semiconductor industries recently in non-volatile ferroelectric random access memory (FERAM) applications. The understanding of the lattice vibrational properties of this material can provide crucial information on its structure and dielectric behaviors. In this work, we carried out Raman spectroscopy study of thin film, powder and single crystal $SrBi_2Ta_2O_9$. At temperature above the Curie temperature, all 12 Raman modes expected from the tetragonal (I4/mmm) structure have been observed and assigned to the 4 A_{1g}, 6 E_g and 2 B_{1g} modes based the polarized Raman spectra from the single crystal samples. At lower temperature, the Raman spectra have revealed all 22 A_1 modes, but only 3 out of the 20 A_2 modes and 5 out of the 42 B_1/B_2 modes were observed in the ferroelectric phase ($A2_1am$). The soft mode was found to be of A_1 symmetry and appearing only when light polarization lay in the ab-plan.

3:30 PM *CC7.6
TRANSIENT BEHAVIOR OF THE POLARIZATION IN FERRO-ELECTRIC THIN FILM CAPACITORS. Rainer Waser, IFF, Research Center Juelich, GERMANY; Oliver Lohse, Michael Grossmann, Dierk Bolten, Ulrich Böttger, Institut für Werkstoffe der Elektrotechnik, University of Aachen, GERMANY.

The understanding of the polarization switching process of ferroelectric capacitors is highly relevant for the development and optimization of FeRAM devices. We report on the characterization of $Pb(Zr,Ti)O_3$ thin films which have been studied by means of hysteresis measurements extended into the MHz regime and by dedicated rectangle pulse measurements. Decreasing the voltage level of the excitation pulses decelerates the polarization switching significantly to the range of milliseconds and reduces the switchable polarization of high frequency hysteresis measurements. It is found that the switching behavior is further deteriorated with decreasing temperature. In this work the influence of the composition and process conditions of CSD prepared PZT thin films on the switching properties are investigated to reach the aspired conditions of low voltage operation, read and write access pulses in the range of nanoseconds, and low temperatures down to -40°C. For the implementation of the transient behavior of ferroelectric capacitors in circuit design and simulation tools it is necessary to develop a model which describes the polarization hysteresis and the pulse switching behavior correctly as well as the small signal capacitance. This model is presented, based on an ideal ferroelectric capacitor, taken into account the Curie-von Schweidler behavior, which can be observed in non-ferroelectric high-K materials as well as in ferroelectric thin films.

4:00 PM CC7.7
SELF-POLARIZATION OF TEXTURED PZT THIN FILMS FORCED BY ELECTRODE-PZT INTERACTION. G. Suchaneck, G. Gerlach, Dresden University of Technology, Institute for Solid State Electronics, GERMANY; P. Poplavko, National Technical University of Ukraine, UKRAINE.

The self-polarization effect is extremely important for integrated pyroelectric sensor array fabrication, where a large number of small elements should be poled uniformly in an easy way and high electric fields must be prevented to avoid damage of nearby elements of the read-out integrated circuit. In this work, a self-polarization mechanism is proposed based on film microstructure investigations, profiling of optical properties by ellipsometry and of polarization by pyroelectric spectroscopy of thermal wave distribution (laser intensity modulation method - LIMM). The reducing interaction of the metal electrodes with PZT during film deposition and cooling down leads to the formation of an oxygen deficient n-type region near the interface. An asymmetric n^p junction forms with a space charge distribution consisting of the positive space charge of the n-region formed by oxygen vacancies and the space charge of the bulk p-region caused probably by lead vacancies. As a result, the Fermi level is pinned near the interface by donor states such as oxygen vacancies and Ti^3 states and downward band bending results. The generated electric field causes a drift of oxygen vacancies and an overcompensation of the negative space charge of p-type PZT occurs. Ti^3 ion formation is then favored by electron injection barrier lowering due to image forces (Schottky effect) and a thin negative space charge layer at the interface formed by Ti^3 ions. Injected electrons are easily distributed within a n-type layer by polaronic conduction due to electron hopping between Ti^4 and Ti^3 ions. By this way, stable against annealing even above the Curie temperature Ti^3-V_O^2 dipole complexes are formed which nucleate domain formation and determine domain orientation during cooling down below the Curie temperature.

4:15 PM CC7.8
STRESS-INDUCED ELEVATION OF THE SPONTANEOUS POLARIZATION IN $BaTiO_3$ THIN FILMS. W. Tian and X.Q. Pan, Dept. of Materials Science and Engineering, The Univ. of Michigan, Ann Arbor, MI; J.H. Haeni and D.G. Schlom, Dept. of Materials Science and Engineering, Penn State University, University Park, PA.

Stress effect has been considered to be responsible for many of the dielectric and electrical anomalies observed in the thin film heterostructures and small particles, in most of cases involving $BaTiO_3$. However, separating the stress effect from other factors such as size effect remains a challenge. In this paper, we present our experimental work on the highly strained superlattice structures. The $BaTiO_3/SrTiO_3$ superlattice with a bilayer period of ten monolayers was synthesized by reactive molecular beam epitaxy (MBE) on (001) $SrTiO_3$ substrate. Atomically-abrupt interfaces between two constituents were achieved. Despite the large lattice mismatch between $BaTiO_3$ and $SrTiO_3$ (~3.0%), the high-resolution transmission electron microscopy (HRTEM) examination demonstrated that the substrate/film interfaces are fully coherent, e.g. no misfit dislocation was found at the interfaces. This leaves a homogeneous biaxial strain in the a-b plane of the $BaTiO_3$ layers because the in-plane lattice constant of the entire superlattice is the same as that of the $SrTiO_3$ substrate. This strain is calculated to be ~5.0 GPa. Quantitative HRTEM studies revealed an elevated displacement of Ti cations with respect to oxygen octahedra in the $BaTiO_3$ layers. Based on the newly developed atomic model, the spontaneous polarization of the strained $BaTiO_3$ is determined to be about three times of that of the bulk $BaTiO_3$, which agrees well with the prediction using the modified Laudau-Ginsburg-Devonshire theory.

4:30 PM CC7.9
FATIGUE DEGRADATION MODEL BASED ON FOWLER-NORDHEIM ELECTRON INJECTION. Susumu Shuto, Toshiba Co, Memory LSI Research and Development Center, Yokohama, JAPAN; Paul C. McIntyre, Stanford University, Dept of MS&E, Stanford, CA.

A quantitative fatigue model is proposed as one of possible mechanism of fatigue degradation. In this model, we assume that there is a thin transition region between a metal electrode and a bulk ferroelectric film. Electric field is applied to the transition region as well as the bulk ferroelectric film during switching cycles. Due to this electric field, electrons are injected from the cathode to a ferroelectric film by Fowler-Nordheim tunneling, and are trapped at domain boundaries (and/or transition region-ferroelectric film interfaces). These electrons cause a loss of the polarization by pinning domain. Differential equations are derived in accordance with this model and are solved numerically to get the dependence of the switching charge on the number of switching cycle. These calculated results show good agreement with the experimental data in a wide range of applied voltage. Moreover, the model can well explain the small temperature dependence of fatigue characteristics and 1/V dependence of fatigue characteristics on external stress voltage.

4:45 PM CC7.10
EASY COLLECTIVE POLARIZATION SWITCHING IN FERROELECTRICS. A.M. Bratkovsky, A.P. Levanyuk, Hewlett-Packard Laboratories, Palo Alto, CA.

Ferroelectric films with extended dielectric inhomogeneity, like a "passive layer", are always split into domains [1]. Here we address the question of how this state is reached from a monodomain state by nucleation and growth processes. We prove that the polydomain state cannot be achieved by nucleation and growth of individual domains with reversed polarization, which is the essence of the "paradox of the coercive field". We then show that the interaction between nuclei of a new phase has effectively an infinite range: it decays as a small power of the distance between the nuclei. This interaction is found to be essential for the polarization switching, as demonstrated for a periodic ensemble of nuclei where nucleation proceeds *without a barrier* as soon as the nuclei are comparable to or larger than the domain wall thickness.

[1] A.M. Bratkovsky and A.P.Levanyuk, Phys. Rev. Lett. **84**, 3177 (2000).

SESSION CC8/BB6: JOINT SESSION
DOMAINS IN FERROELECTRIC THIN FILMS
Chairs: Wenwu Cao and Ramamoorthy Ramesh
Wednesday Morning, November 29, 2000
Room 312 (Hynes)

8:30 AM *CC8.1/BB6.1

DOMAIN STRUCTURE AND SWITCHING IN FERROELECTRIC FILMS OBSERVED BY AFM. Angus I. Kingon, NCSU, Department of MS&E, NC; B. Rodriguez and R. Nemanich, NCSU, Department of Physics, NC; C.B. Parker, D.J. Kim and J.-P. Maria, NCSU, Department of MS&E, NC.

Ferroelectric nonvolatile memories are currently entering production. Despite the very significant development of the films and devices over the past many years, there remains a great deal which is not known regarding the ferroelectric domain structure, and the role of the ferroelectric domain walls in determining device switching characteristics and device lifetimes. In the first part of the presentation we describe methods used to characterize the spatial variation of properties of the ferroelectric capacitors by characterizing the spatial distribution of the piezoelectric properties (by AFM). We deduce that the scale of the distribution is far smaller than the grain size, for the case of PZT films. We discuss the significance of the results in terms of the statistical methods used, and the role of domain walls, and contrast the results to previously reported results for SBT. We show that the spatial distribution of properties is markedly increased after fatigue. However, the size of the fatigued regions is generally submicron. We discuss the implications for scaling of PZT-based nonvolatile memories to higher densities. Secondly, we describe experiments in which the extent of local switching is characterized as a function of a single voltage pulse, for samples which include the variables: PZT composition, film orientation, film microstructure, domain wall density, electrode type, capacitor dimensions, and prior fatigue cycling. Implications are drawn for high density devices.

9:00 AM *CC8.2/BB6.2

ELECTROMECHANICAL RESPONSE OF UNPOLED FERROELECTRIC STRUCTURES. Alexander Tagantsev, Olivier Steiner, Ceramics Laboratory, EPFL, Swiss Federal Institute of Technology Lausanne, SWITZERLAND.

The piezoelectric coupling, which basically controls the electromechanical response of poled ferroelectric materials, is averaged down to zero in unpoled structures. Under these conditions, the link between the strain and the electric field becomes quadratic and can be described in terms of an effective electrostrictive coupling. This coupling is controlled by various contributions which are related to variation of the domain structure (extrinsic contribution) and to the anharmonicity of the crystalline lattice of the material (intrinsic contribution). The goal of this talk is to discuss these contributions with an accent on the intrinsic one. Here two results, which do not match the routinely accepted general picture of phenomenon, are reported. First, there is no violation of the correspondence between the direct and converse electrostrictive effects when passing from the paraelectric to ferroelectric phase of the material as it has been proposed by Zang et al. [Q.M. Zang, W.Y. Pan, S.J. Jang, and L.E. Cross, Ferroelectrics v. 88, 147 (1988)]. Second, the effective intrinsic longitudinal electrostrictive coefficient of polydomain structure of a perovskite ferroelectric, Q_{33}, can be negative.

9:30 AM CC8.3/BB6.3

DOMAIN SWITCHING KINETICS OF PZT THIN FILMS AT HIGH FREQUENCIES. Takaaki Tsurumi, Song-Min Nam, Young-Bae Kil and Satoshi Wada, Tokyo Inst. Technology, Dept. of Metallurgy & Ceramics Science, Tokyo, JAPAN.

Domain switching behavior of sol-gel derived PZT thin films at high frequencies have been investigated for ferroelectric memory applications. A measuring apparatus of D-E hysteresis curves was developed using a voltage-current converter with virtual ground circuit. The coercive field of the PZT thin films strongly depended on the measuring frequency, nevertheless their remanent polarization was almost independent of it. The coercive field was also dependent on temperature and electrode area. The domain switching kinetics of PZT thin films could be explained using a nucleation-controlled model. A linear relation was obtained between ln ν and $1/Ec^2$, where ν is a frequency and Ec is a coercive field. The intercept at $1/Ec^2=0$ is a limiting frequency of domain switching. The limiting frequency of domain switching (ln ν_0) increased with decreasing electrode area. The slope of the line was determined by a binding energy between domain wall and defects, domain wall energy and the change in the polarization with domain wall motion. From the results obtained in this study, a guideline to develop ferroelectric films was proposed for ferroelectric memories with high speed and low operating voltage.

9:45 AM CC8.4/BB6.4

ABRUPT APPEARANCE OF THE DOMAIN PATTERN AND FATIGUE OF THIN FERROELECTRIC FILMS. A.M. Bratkovsky, A.P. Levanyuk, Hewlett-Packard Laboratories, Palo Alto, CA.

We study the domain structure in ferroelectric thin films with a "passive" layer (material with damaged ferroelectric properties) at the interface between the film and electrodes within a continuous medium approximation. An abrupt transition from a monodomain to a polydomain state has been found with the increase of the "passive" layer thickness d. The domain width changes very quickly at the transition (exponentially with d^{-2}). We have estimated the dielectric response dP/dE (the slope of the hysteresis loop) in the "fatigued" multidomain state and found that it is in agreement with experiment, assuming realistic parameters of the layer. We derive a simple universal relation for the dielectric response, which scales as $1/d$, involving only the properties of the passive layer. This relation qualitatively reproduces the evolution of the hysteresis loop in fatigued samples and it could be tested with controlled experiments. It is expected that the coercive field should increase with decreasing lateral size of the film. We believe that specific properties of the domain structure under bias voltage in ferroelectrics with a passive layer can resolve the long-standing "paradox of the coercive field".

10:30 AM *CC8.5/BB6.5

FERROELECTRIC THIN FILMS: NANOSCALE CHARACTERIZATION BY SCANNING FORCE MICROSCOPY. Alexei Gruverman, Sony Corporation, Yokohama, JAPAN.

In this paper, results of nanoscale characterization of ferroelectric thin films and capacitors by means of scanning force microscopy (SFM) will be presented. Polarization reversal dynamics and degradation effects, such as fatigue and retention loss, were studied in ferroelectric thin films via direct observation of their domain structures using the SFM piezoresponse method. SFM approach allowed direct nanoscale studies of correlation between crystallinity, domain structure and switching behavior of the ferroelectric films. Results of comparative nanoscale studies of SBT films grown by different techniques will be presented. It will be shown that the SFM data are consistent with the macroscopic parameters. SFM can be used for studying nanoscale variations of switching parameters in ferroelectric films and for investigating the scaling effect on switching performance of submicrometer ferroelectric capacitors. It will be demonstrated that for implementation of reliable high-density ferroelectric memories a certain capacitor/grain size ratio should be maintained. Particular attention will be given to the investigation of the mechanism of polarization retention loss in ferroelectric films. The retention behavior of ferroelectric films was studied as a function of switching conditions, electrode material, surrounding domain patterns and sample prehistory. SFM allowed direct mapping of leakage sites and nanoscale investigation of electrical conduction mechanism at these sites. Results of SFM measurements of leakage current characteristics of submicrometer ferroelectric capacitors will be presented.

11:00 AM CC8.6/BB6.6

GROWTH AND CONTROL OF DOMAIN STRUCTURE OF EPITAXIAL $PbZr_{0.2}Ti_{0.8}O_3$ FILMS GROWN ON VICINAL (001) $SrTiO_3$. V. Nagarajan, C.S. Ganpule, S.P. Alpay, A. Roytburd, R. Ramesh, Univ of Maryland, Dept of Materials Engineering, College Park, MD; D.G. Schlom, Pennsylvania State University, Dept of Materials Engineering, University Park, PA.

Highly tetragonal, epitaxial PZT films with a nominal composition of $PbZr_{0.2}Ti_{0.8}O_3$ exhibit a 2-dimensional grid of 90° domains (a-domains, i.e., c-axis in the plane of the film). Our previous studies have revealed that the 90° domains are preferential sites for the nucleation of 180° reverse domains during polarization switching and relaxation. Furthermore, we have observed that this array of 90° domains effectively isolate neighboring c-axis oriented regions. Therefore, we are studying approaches to control the spacing and periodicity of the 90° domains. Such self-assembled arrays of periodic domain structures can form the templates for novel memory arrays. In this paper, we report on the use of vicinally cut [along [100], [010], and [110] directions in the substrate plane] single crystal substrates to control the 90° domain formation. Epitaxial thin films have been deposited by pulsed laser deposition onto the vicinal substrates, with epitaxial conducting oxide bottom electrodes (LSCO and SRO). We have been able to control the nucleation of the 90° twins to occur preferentially at the steps on the substrate. We show that the orientation of these domains can be controlled such that they exhibit only 2 of the 4 possible variants. By using 4-circle x-ray diffraction,

TEM and Electric Force Microscopy (EFM) we have investigated the structural and electrical properties of these artificially engineered structures. The control of such structures as a function of film thickness and substrate miscut orientation will be presented.

11:15 AM CC8.7/BB6.7
DOMAINS IN $SrBi_2Nb_2O_9$ AND $SrBi_2Ta_2O_9$ FERROELECTRIC FILMS. M.A. Zurbuchen, J. Lettieri, Y. Jia, G. Asayama and D.G. Schlom, Penn State Univ, Dept of Materials Science and Engineering, University Park, PA; S.K. Streiffer, Argonne National Laboratory, Materials Science Division, Argonne, IL; M.E. Hawley, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM.

We recently reported $SrBi_2Nb_2O_9$ films with the highest remanent polarization value attained to date in $SrBi_2Nb_2O_9$ or $SrBi_2Ta_2O_9$ films, $P_r = 15.7\ \mu C/cm^2$ [1]. This was achieved by tilting the c-axis of $SrBi_2Nb_2O_9$ by 57° from the substrate surface normal in order to get a significant component of the polar axis, the a-axis, aligned with the direction of the applied electric field in these (103) $SrBi_2Nb_2O_9$ / (111) $SrRuO_3$ / (111) $SrTiO_3$ epitaxial films. In this talk, the microstructural features of these films, revealed by high-resolution and dark-field transmission electron microscopy (TEM), are reported, including domains, domain boundaries, domain populations, and out-of-phase boundaries. Portions of the same films used for electrical characterization were examined by TEM. Films grow in a 3-fold twin structure on the 3fold symmetric (111) $SrTiO_3$ surface. Dark-field TEM imaging over a 12 μm^2 area shows no evidence of second phases (crystalline or amorphous), which is important for high-density FRAM applications.
[1] J. Lettieri, M.A. Zurbuchen, Y. Jia, D.G. Schlom, S.K. Streiffer, and M.E. Hawley, Appl. Phys. Lett. v76, p2937 (2000).

11:30 AM CC8.8/BB6.8
CELLULAR DOMAIN ARCHITECTURE OF STRESS-FREE EPITAXIAL FERROELECTRIC FILMS. S.P. Alpay, A.L. Roytburd, V. Nagarajan, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; L.A. Bendersky, National Institute of Standards and Technology, Materials Science and Engineering Laboratory, Gaithersburg, MD; R. Ramesh, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD.

Epitaxial ferroelectric films undergoing a cubic-tetragonal phase transformation relax internal stresses due to the structural phase transformation and the difference in the thermal expansion coefficients of the film and the substrate by forming polydomain structures. The most commonly observed polydomain structure is the c/a/c/a polytwin which relieves the internal stresses only partially. Relatively thicker films may completely reduce internal stresses if all three variants of the ferroelectric phase are brought together such that the film has the same in-plane size as the substrate. We provide experimental evidence on the formation of the 3-domain structure based on transmission electron microscopy in 450 nm thick (001) PZT (20/80) films on (001) strontium titanate substrate grown by pulsed laser deposition. X-ray diffraction studies show that the film is fully relaxed. Experimental data is analyzed in terms of a domain stability map. It is shown that the observed structure in epitaxial ferroelectric films is due to the interplay between relaxation by misfit dislocations at the deposition temperature and relaxation by polydomain formation below the phase transformation temperature. The effect of the domain structure on the switching characteristics and physical properties is discussed.
This work is supported by NSF under Grant No. DMR-9903279 and by the NSF-MRSEC program under Grant No. DMR-9632521.

11:45 AM CC8.9/BB6.9
NEAR-FIELD OPTICAL SECOND HARMONIC IMAGING OF THE POLYDOMAIN STRUCTURE OF EPITAXIAL $PbZr_xTi_{1-x}O_3$ THIN FILMS. I.I. Smolyaninov, H.Y. Liang, C.H. Lee, C.C. Davis, Univ of Maryland, Electrical and Computer Engineering Dept, College Park, MD; V. Nagarajan, C. Ganpule, R. Ramesh, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; E. Williams, Univ of Maryland, NSF Materials Research and Science Engineering Center, College Park, MD.

Near-field optical second harmonic microscopy [1] has been applied to imaging of the $c/a/c/a$ polydomain structure of epitaxial $PbZr_xTi_{1-x}O_3$ thin films in the $0 \leq x \leq 0.4$ range. Comparison of the near-field optical images and the results of AFM and x-ray diffraction studies show that the optical resolution of the order of 80 nm has been achieved. Symmetry properties of the near-field second harmonic signal allow us to obtain good optical contrast between the local second harmonic generation in c- and a-domains. Experimentally measured near-field second harmonic images have been compared with the results of theoretical calculations. Good agreement between theory and experiment has been demonstrated. Thus, novel optical technique for nanometer scale ferroelectric domain imaging has been developed. Its main advantage with respect to the other scanning probe techniques is the possibility of fast time resolved measurements using optical pump and probe technique.
[1] I.I. Smolyaninov *et al.*, Opt. Lett. **25**, 835 (2000).

SESSION CC9: PROCESSING, PROPERTIES, AND CHARACTERIZATION

Chairs: Dirk J. Wouters and Debra L. Kaiser
Wednesday Afternoon, November 29, 2000
Room 312 (Hynes)

1:30 PM *CC9.1
ORIENTATION SELECTION MECHANISMS IN FERRO-ELECTRIC PZT THIN FILMS. Gerd Norga, Laura Fë, IMEC vzw, Leuven, BELGIUM.

The recent successful application of sol-gel PZT thin films in non-volatile memories (FERAM) has emphasized the need for tailoring sol-gel processes to increase their process compatibility (by lowering crystallization temperature) and to fit device requirements (by reducing film thickness). An important priority in this regard is to maintain control over the (111) orientation, which features superior ferroelectric switching properties. However, the large number of process variables, which is intrinsic to the sol-gel process, combined with variations in the preparation chemistry, has limited the development of a generally accepted model for orientation control. In the first part of the talk, available literature models, which focus mainly on the role of the pyrolyzed film / crystalline perovskite phase transformation in orientation selection, will be reviewed. Next, we will report on the use of in-situ techniques, such as absorption-reflection-FTIR, to study on a real temperature scale, the transformation mechanism of the spun precursor, over amorphous to crystalline PZT. Monitoring hydrolysis and condensation reactions during subsequent thermal steps revealed significant variations in the condensation rate as a function of Zr/Ti stoichiometry, solvent, and sample history. Specifically, our studies demonstrate that control of the condensation rate below a critical value is a necessary condition for obtaining well oriented PZT films. In conclusion, a comprehensive model which includes epitaxy, compositional, and chemical factors in orientation selection will be presented.

2:00 PM CC9.2
INFLUENCE OF Zr-ALKOXIDE MODIFICATION ON THE PROPERTIES OF PZT THIN FILMS. Barbara Malic, Marija Kosec, Zoran Samardzija Jozef Stefan Institute, Ljubljana, SLOVENIA.

The crystallization, microstructure and functional response of ferroelectric thin films are influenced by the solution chemistry. Clustering of zirconium species in PZT based sols, prepared by a reaction between lead acetate and transition metal alkoxides in 2-methoxyethanol, has been observed by EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy. In order to obtain a more homogeneous distribution of constituent metal atoms in the solution, zirconium alkoxide was prior synthesis modified by acetic acid or acetylacetone. Both compounds are commonly used as reagents for the chemical modification of simple alkoxides, forming less reactive alkoxoacylates. 2-methoxyethanol based PZT sols were prepared from lead acetate, titanium n-propoxide and zirconium n-propoxide. The latter was either used as-received or mixed with acetic acid or acetylacetone prior synthesis. The sols were spin-coated on platinized silicon substrates, pyrolyzed at 350°C and annealed at 500 - 650°C for 15 minutes. EXAFS results show a decrease of Zr-O-Zr links in the acetic acid modified PZT sol implying a more homogeneous constituent metal distribution. No such decrease in comparison to unmodified sol is found in acetylacetone modified PZT. However the two modified PZT samples differ in thermal decomposition pathways, stemming from the variations in sol composition. Higher level of homogeneity achieved in modified PZT sols evokes the perovskite crystallization in thin films and decreases the crystallization temperature on (0001) sapphire. On platinized silicone substrate that promotes heterogeneous nucleation, all PZT films crystallize in the perovskite phase after annealing at 500°C. The modifiers nevertheless affect the relative orientation of the perovskite phase. The paper reports the structural, microstructural and ferroelectric features of the three groups of films in the view of differences induced by the solution chemistry.

2:15 PM CC9.3
SURFACE REACTION MECHANISMS IN CHEMICAL VAPOR DEPOSITION OF $(Ba,Sr)TiO_3$ FILMS. Mikio Yamamuka, Masayoshi Tarutani, Takaaki Kawahara, Tsuyoshi Horikawa, Tatsuo Oomori, and Teruo Shibano, Mitsubishi Electric Corp., Advanced Technology R&D Center, Amagasaki, JAPAN.

3D stacked cells with high-dielectric-constant (Ba,Sr)TiO_3 [BST] films have been proposed for Gbit-scale memories and beyond. Such stacked cell structures require conformal coverage in the BST films prepared by a CVD method. In order to improve the conformality of the films, it is important to understand the chemistry of precursors in gas phase and on deposition surface. In our previous paper, we have investigated the surface reactions in the CVD of BST films at the substrate temperature (T_s) of 480°C. We have found that Ti precursors adsorbed on the film surface inhibited the following adsorption of Ba and Sr precursors. In this paper, we described the dependence of atomic incorporation rates (I_r) on the precursor fluxes incident onto the film surface (Γ) at different T_s of $420 - 520$°C. We showed the effects of the oxygen gas concentration on the surface reactions. In the dependence of I_r on Γ, each value of I_r for Ba, Sr, and Ti monotonously increased with the increasing Γ of corresponding precursors, and then gradually saturated at high Γ. The gradients of I_r to Γ in the unsaturated region and the saturated values of I_r increased with increasing T_s. The sticking coefficient of Ba and Sr precursors (β_{Ba}, β_{Sr}) greatly depended on Γ of Ti precursors. In the results of extrapolations, both β_{Ba} and β_{Sr} for $T_s = 520$°C were estimated to be about 1×10^{-3} without Ti precursors, and about 1×10^{-4} with excess Ti precursors. The values of β for Ba, Sr, and Ti increased with an increasing oxygen gas concentration, respectively. It was certainly concluded that the decomposition of precursors on the surface is enhanced by oxygen. Finally, the surface reaction model was constructed based on a Langmuir isotherm adsorbing mechanism, and it was found to be effectively interpret of the above results.

2:30 PM CC9.4
GROWTH OF (Ba,Sr)TiO_3 THIN FILMS IN A MULTIWAFER MOCVD REACTOR. P. Ehrhart[1] , F. Fitsilis[1], S. Regnery[1,2], R. Waser[1], F. Schienle[2], M. Schumacher[2], M. Dauelsberg[2], P. Strzyzewski[2], H. Juergensen[2]. [1]IFF, Forschungszentrum Julich GmbH, Julich, GERMANY. [2]AIXTRON AG, Aachen, GERMANY.

We report on the performance of a planetary multi-wafer MOCVD reactor which handles 5 six inch wafers simultaneously. The reactor is combined with a liquid delivery system which mixes the liquid precursors from three different sources: 0.35 molar solutions of $Ba(thd)_2$ and $Sr(thd)_2$ and a 0.4 molar solution of Ti(O-i-Pr)$_2$(thd)$_2$. The thickness of the BST film was varied between 10 and 100 nm. The microstructure and the film stress were investigated by X-ray diffraction. The composition of the films was routinely determined by X-ray fluorescence analysis, using different calibration standards prepared by chemical solution deposition. As a direct consequence of the reactor design we obtain a high uniformity of the films over 6 inch wafers, i.e.: a few percent deviation in thickness and off-stoichiometry, as well as high efficiencies for the precursor incorporation in the order of 40%, which promise a big advantage in the cost of ownership. Details of the microstructure were investigated by scanning electron microscopy, and by transmission electron microscopy. The surface topology was investigated by scanning force microscopy and the chemistry of the interface by secondary ion mass spectrometry. Film growth on different substrates is discussed within a wide parameter field. The finally achieved electrical properties, e.g., permittivity, loss tangent, leakage current, are discussed in relation to the microstructural properties.

2:45 PM CC9.5
PROCESS OPTIMIZATION FOR THE METAL-ORGANIC CHEMICAL VAPOR DEPOSITION OF SBT THIN FILMS. D. Burgess, R. Barz, F. Schienle, M. Schumacher, J. Lindner, and H. Juergensen AIXTRON AG, Aachen, GERMANY; S. Narayan, L. McMillan and C. Paz de Araujo Symetrix Corp., Colorado Springs, CO; K. Uchiyama and T. Otsuki Panasonic Technologies Inc., Colorado Springs, CO.

The metal-organic chemical vapor deposition (MOCVD) of ferroelectric thin films is being widely investigated for the manufacture of devices requiring both volatile and non-volatile memory. The deposition of multi-component thin films with uniform characteristics requires superior hardware engineering to control a large number of variables. In this regard, AIXTRON has combined the TriJet liquid delivery system and a dual-chamber showerhead design with its established knowledge of temperature and pressure control for the deposition of strontium bismuth tantalate (SBT). For example, the MOCVD of SBT has yielded films having 2Pr = 13μC/cm^2 at 5V with leakage current density Jl = 1E-8 A/cm^2 at < 5V were obtained. In addition, films with excellent thickness uniformity with 3s = 2.25% at 180 nm have been deposited on 6-Pt/TiO$_x$/Si wafers. Currently various Bi and ST precursors and precursor solvents are being investigated to further optimize film qualities and the deposition process. Data demonstrating the effects of major reactor components and process parameters on the magnitude and uniformity of film characteristics will be reported.

3:30 PM *CC9.6
IN-SITU STUDIES OF METAL-ORGANIC CHEMICAL VAPOR DEPOSITION OF $PbTiO_3$ THIN FILMS. S.K. Streiffer, G.B. Stephenson, J.A. Eastman, M.V. Ramana Murty, O. Auciello and G.-R. Bai, Materials Science Division, Argonne National Laboratory, Argonne, IL; Carol Thompson, Dept. of Physics, Northern Illinois University, Dekalb, IL and Materials Science Division, Argonne National Laboratory, Argonne, IL; A. Munkholm, Chemistry Division, Argonne National Laboratory, Argonne, IL.

We have constructed an MOCVD system on BESSRC-CAT beamline 12-ID-D of the Advanced Photon Source, for studies of oxide thin film growth behavior. Single crystal $PbTiO_3$ films are being deposited using tetraethyl lead, titanium isopropoxide, and O_2 as precursors. Grazing incidence, real time x-ray scattering and fluorescence techniques are used to characterize growth modes and resulting film structures in the high-pressure, high-temperature MOCVD environment. An overview will be presented of our results on the initial deposition of $PbTiO_3$ on $SrTiO_3$ (heteroepitaxy) followed by continued deposition of $PbTiO_3$ on $PbTiO_3$ (homoepitaxy), and of the effect of process parameters on the microstructure of the growing film. A brief summary will be given of other types of *in-situ* experiments that we are performing in this system, including diffuse scattering to measure the island size during layer-by-layer growth. The potential for optimization of growth processes with correlated improvements in ferroelectric properties will be discussed.
This work is supported by the U.S. Department of Energy, Office of Science, under Contract W-31-109-Eng-38, and by the State of Illinois, under HECA.

4:00 PM CC9.7
DEPOSITION OF STOICHIOMETRIC $LiTaO_3$ AND $LiNbO_3$ THIN FILMS BY CONTROLLING THE VAPORIZATION PROCESS IN MOCVD. Ruichao Zhang, Rensselaer Polytechnic Institute, Dept of Electrical, Computer and Systems Engineering, Troy, NY; Ren Xu, IBM Almaden Research Center, San Jose, CA.

$LiTaO_3$ and $LiNbO_3$ are important ferroelectric materials used in integrated optics. $LiTaO_3$ phase and $LiNbO_3$ phase are both known to exist over a relatively wide composition range, primarily on the lithium-poor side of stoichiometry. The compositional defects caused by Li_2O deficiency from stoichiometry can affect the physical properties, especially the optical properties of $LiTaO_3$ and $LiNbO_3$ films. Stoichiometric $LiTaO_3$ and $LiNbO_3$ films were successfully deposited in this study using autostoichiometric MOCVD. In this process, depositions were carried out autostoichiometricly using double alkoxide precursors, and the stoichiometry of the films deposited could be controlled precisely on the molecular level because it was independent on the precursor flow rates. It was found that the composition of the vapor phase as the result of vaporization of double alkoxide was determined by the stability of the double alkoxide as well as the relative volatility between single and double alkoxides. The stoichiometry of the deposition could be achieved by controlling the vaporization process of the double alkoxide precursors. An analysis method, including vapor pressure measurement on double and single alkoxides and sublimate composition analysis, was provided to study the stoichiometry of double alkoxide vaporization processes. The results were used to choose suitable double alkoxide precursor and to determine favorable deposition conditions. The vaporization processes of Li-Ta and Li-Nb double alkoxides with different carbon chains were studied systematically using this precursor analysis method. Stoichiometric $LiTaO_3$ and $LiNbO_3$ crystalline films were obtained on both silicon and sapphire substrates using LiTa(n-OC$_4$H$_9$)$_6$ or LiTa(i-OC$_4$H$_9$)$_6$ as precursor for the deposition of $LiTaO_3$ films and LiNb(n-OC$_4$H$_9$)$_6$ as precursor for the deposition of $LiNbO_3$ films. The vapor species in the vapor phase were analyzed by Mass Spectrometry, and the films were characterized by X-ray diffraction (XRD), SEM, AFM and other analytical methods.

4:15 PM CC9.8
EFFECT OF GROWTH TEMPERATURE ON THE DIELECTRIC PROPERTIES OF Pb(ScTa)$_{1-x}$Ti$_x$O$_3$ (PSTT) THIN FILMS GROWN ON LaNiO3 BUFFERED Si USING MOCVD. C.H. Lin, P.A. Friddle, C.H. Ma and Haydn Chen, Department of MS&E, University of Illinois at Urbana-Champaign, Urbana, IL; T.B. Wu, Department of MS&E, National Tsing Hua University, Hsinchu, TAIWAN ROC.

Highly (002) textured Pb(ScTa)$_{1-x}$Ti$_x$O$_3$ (PSTT) (x=0-0.3) thin films were deposited using metal-organic chemical vapor deposition (MOCVD) technique at temperature ranging from 600°C to 685°C. Dielectric properties of these PSTT thin films showed strong dependency on the growth temperature. For PSTT thin films with composition near its morphotropic boundary (x=0.3), the room temperature dielectric constants increased from 980 to around 1600 as the growth temperature increased from 650 to 685°C. In addition, the dielectric dispersion behaviors of films grown at different

temperatures were compared. Detailed chemical analytical results showed that growth temperature greatly affected the chemical state of Pb ions in these PSTT films. The variation in the ionic state of Pb could result in the misplacement of Pb ions in the lattice. Thus, the space charge induced by the misplaced Pb ions degraded the dielectric properties of those PSTT thin films grown at lower temperature. Work was supported by the U.S. Department of Energy through the Frederick Seitz Materials Research Laboratory at University of Illinois.

4:30 PM CC9.9
ELECTRICAL PROPERTIES OF PLZT THIN FILM SPUTTERED ON Pt/IrO_x BOTTOM ELECTRODE FOR FERROELECTRIC MEMORY APPLICATION. Yusuke Miyaguchi, Koukou Suu, ULVAC Japan, Ltd., Chiba, 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 auti-oxidation barrier is needed in between ferroelectric capacitor and plug. In this study, we chose IrOx as oxygen barrier to form PLZT/Pt/IrOx/plug structure. PLZT thin films were deposited on Pt/IrOx 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.

4:45 PM CC9.10
SPECTROSCOPIC ELLIPSOMETRY STUDY OF THE STRUCTURE AND OPTICAL CONSTANTS OF $Pb(Zr,Ti)O_3$ THIN FILMS DEPOSITED BY SOL-GEL SPIN COATING. Soumana Hamma, Jobin Yvon/Horiba, Thin Film Group, Edison, NJ; Ronald G. Polcawich, Army Research Laboratory, AMSRL-SE-RL, Adelphi, MD.

Ferro electric thin films are increasingly investigated for a wide range of applications ranging from electronic and opto-electronic to micro-machine systems. For many applications the film thickness and its dielectric function as well as the interface integrity are key issues in film performance characteristic. In addition, optical applications required uniform and smooth surface. Lead zirconium titanate $Pb(Zr,Ti)O_3$(PZT) is one of the most studied perovskite-type ferroelectric materials. In this study, we use spectroscopic ellipsometry as a non-destructive tool to determine the thickness; the dielectric function and interface properties of $PbZr_{0.52}Ti_{0.48}O_3$ films deposited by sol-gel spin coating on Pt-coated silicon substrate. The dielectric functions were determined in the visible and UV spectral range (below and above the absorption edge of PZT). The dependence of the dielectric function on the thickness was investigated over the thickness range of 0.2 - 2 μm. Below the band gap, the dielectric function can be described by classical oscillator dispersion but above the gap a direct inversion of the ellipsometric data is required. The interface between the PZT and the Pt substrate can be modeled as a mixture of the two materials and extend over few nanometers. The uniformity of the films was investigated by X-Y scan measurements and was found to be excellent (less than 0.5% deviation in the thickness).

SESSION CC10: POSTER SESSION FUNDAMENTALS OF FERROELECTRIC THIN FILMS

Chair: Ajit Krishnan
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

CC10.1
STRUCTURAL DISTORTION AND FERROELECTRIC PROPERTIES OF $SrBi_2(Ta_{1-x}Nb_x)_2O_9$. Yuichi Shimakawa and Yoshimi Kubo, Fundamental Research Labs, NEC Corp, Tsukuba, JAPAN; Yuuki Tauchi, Takashi Kamiyama, and Hajime Asano, Inst for Matls Scie, Univ of Tsukuba, Tsukuba, JAPAN.

Ferroelectric materials of the $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ solid-solution system were synthesized, and their structural and ferroelectric properties were investigated. Structure refinement using high-resolution neutron diffraction data can reveal the detailed crystal structures of these displacive ferroelectric oxides. Atomic displacements of the ions in the $(Ta,Nb)O_6$ octahedron significantly increase as x increases, which leads to more structural distortion of the perovskite-type unit. The Bi_2O_2 layer, in contrast, is less distorted in $SrBi_2Nb_2O_9$ than in $SrBi_2Ta_2O_9$. The contribution of the perovskite-type unit to total ferroelectric polarization is greater in the $SrBi_2Nb_2O_9$ sample, while that of the Bi_2O_2 layer is less; consequently, the total calculated polarization slightly increases. This change in polarization is similar to a recent observation in $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ thin film capacitors where both remanent polarization and the coercive field slightly increase with increasing x. The ferroelectric Curie temperature also increases from 300 ($SrBi_2Ta_2O_9$) to 440°C ($SrBi_2Nb_2O_9$). Three short (Ta,Nb)-O bonds in the $(Ta,Nb)O_6$ octahedron, whose lengths are less than 2 Å, have a covalent character, and the substitution of Nb for Ta makes the bonds more covalent. The strong covalent interaction of the (Ta,Nb)-O bonds increases the structural distortion resulting in the higher ferroelectric Curie temperature and the larger contribution of the perovskite-type unit to the total spontaneous ferroelectric polarization.

CC10.2
EFFECT OF CATION ORDERING ON DIELECTRIC PROPERTIES OF SC SUBSTITUTED $Pb(Mg_{1/3}Nb_{2/3})O_3$ RELAXOR FERROELECTRICS. L. Farber[1], M.A. Akbas[2], and P.K. Davies[1]. [1]Dept. of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA. [2]Vishay Inc, Bridgeport, CT.

The chemistry and stability of the B-site cation ordering and its relevance to the relaxor ferroelectric behavior of the $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) family of perovskites has been the subject of considerable debate. Latest results on PMN-type relaxors implied that the chemical randomness (and associated random fields) on the B' cation sub-lattice, and not the actual ordered domain size, is critical in mediating the ferroelectric coupling. However, experiments aimed toward enhancing the degree of ordering and growing ordered domains in pure PMN by annealing met with no success. Recently, we demonstrated that the cation order was responsive to thermal treatment for Sc substituted PMN. In this presentation we report the effect of cation ordering on dielectric properties of solid solutions in the (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$ - (x)$Pb(Sc_{1/2}Nb_{1/2})O_3$ (PMN-PSN) system. We demonstrate that the size of chemically ordered domains does not affect the relaxor behavior of PMN-rich compositions. At higher levels of substitution the dielectric response is dependent upon the degree of order: disordered samples are relaxors and ordered samples exhibit normal ferroelectric behavior. The crossover from relaxor to normal ferroelectric behavior occurs between x = 0.5 - 0.6. Additionally, spontaneous relaxor-to-normal FE phase transformation is observed in disordered forms of samples with higher than ~50 mole % PSN. The structural changes and the associated modifications in the dielectric properties will be discussed in relation to the "random site" model for the chemical ordering in PMN.

CC10.3
ORDERING IN $(La,Sr)(Al,Ta)O_3$ SUBSTRATES AND ITS INFLUENCE ON THE STRUCTURE OF FERROELECRIC THIN FILMS. Hao Li, T. Tran, C.L. Canedy, L. Salamanca-Riba and R. Ramesh, Materials Research Science and Engineering Center (MRSEC), Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD. J.H. Scott, National Institute of Standards and Technology, Gaithersburg, MD.

Recently, a new substrate $(La,Sr)(Al,Ta)O_3$ (LSAT), formulated as $0.29(LaAlO_3){:}0.35(Sr_2AlTaO_6)$ is becoming widely used for the deposition of ferroelectric thin films. Unlike $LaAlO_3$ (LAO), which has a cubic to rhombohedral transition at 800K, LSAT does not have any phase transformation within the temperature range of interest (from 1200K to 150K) and it is less expensive than $SrTiO_3$ substrates. In addition, LSAT is cubic and well lattice matched with many of the ferroelectric materials, such as $Pb(Zr,Ti)O_3$ and $(Ba,Sr)TiO_3$. However, there has been a relative dearth of detailed materials characterization of this new substrate. We used bright/dark field TEM, HREM and computer image simulation as well as EDS and four circle X-ray diffraction to characterize this substrate. We found that LSAT contains partially ordered regions of 5 -50 nm in size at room temperature. The disordered regions have a perovskite structure with a=0.3868 nm and the ordered regions have an f.c.c. structure with double the lattice parameter. Using EDS analysis, we determined that the chemical composition of these two regions is identical. X-ray analysis of the FWHM of the 111 peaks confirmed the size of the ordered regions. We will also present detailed atomic arrangement obtained using through focus HREM and computer image simulation. The influence of this ordered structure on the crystallinity of the ferroelectric thin films will be discussed.
This work was funded by NSF-MRSEC.

CC10.4
PIEZORESPONSE MEASUREMENT FOR $Pb(Zr,Ti)O_3$ ISLAND STRUCTURE USING SCANNING PROBE MICROSCOPY. H. Fujisawa, K. Morimoto, M. Shimizu and H. Niu, Himeji Institute of Technology, Department of Electronics, Himeji, JAPAN; T. Kimura, K. Honda and S. Ohtani, Fujitsu Laboratory Ltd, Atsugi, JAPAN.

Piezoresponse measurement using scanning probe microscopy(SPM) was performed for island structure at initial growth stage of $Pb(Zr,Ti)O_3$(PZT) thin films. PZT island structure was prepared on (111)$Pt/SiO_2/Si$ substrate by metalorganic chemical vapor deposition(MOCVD). Deposition times were changed from 1 to 7min. When deposition times were 1 and 3min, (111)-oriented triangular-shaped PZT islands before becoming a continuous film were observed by atomic force microscopy(AFM). The width of PZT islands were increased from 50 to 100nm as the deposition time increased from 1 to 3min. The height was almost constant at 20-30nm. In piezoresponse measurement, the phase difference between a tip vibration signal and displacement of PZT island surface changed from 0 to 180° drawing a hysteresis loop when dc bias voltage was changed from 0, 10, -10 to 0V. This result proves that PZT islands with width of 100nm and height of 30nm had a spontaneous polarization which can be switched by external voltage, that is, ferroelectricity. Observations using raman microscopy will also be reported.

CC10.5
FEM ANALYSIS OF DOMAIN EVOLUTION IN EPITAXIAL PZT THIN FILMS. Kilho Lee, Kyeong Seok Lee, and Sunggi Baik, Pohang University of Science and Technology, Dept of Materials Science and Engineering, Pohang, KOREA.

Equilibrium domain structures commonly observed in epitaxial Pb-based ferroelectric thin films are analyzed by finite element method (FEM) using a commercial package, ABAQUS. Evolution of periodic 90°-domain structures in epitaxial $PbTiO_3$ thin films on cubic single crystalline substrates is analyzed as a function of decreasing temperature in order to simulate cooling process after the film deposition at elevated temperature (T_G). The degree of c-axis orientation (α) is determined as a function of temperature below the Curie temperature and compared to the experimental results. It is then possible to calculate the magnitude of misfit strain during film growth and its relaxation due to dislocation generation. The dependence of domain structures on the selection of cubic substrate and the chemical composition in epitaxial PZT thin films is also analyzed with the assumption that the major driving force for domain structures is thermo-elastic strains arising from the film-substrate interaction and the cubic-tetragonal phase transformation. The FEM analysis also suggests that initial misfit stress at TG is not fully relaxed and inversely proportional to c-domain abundance.

CC10.6
THE FERROELECTRIC PROPERTIES OF $Pb(Zr_{0.3}Ti_{0.7})O_3$ THIN FILMS. Feng Yan, Peng Bao,Yening Wang, National Laboratory of Solid State Microstructures, Department of Physics, Nanjing University, Nanjing, PR CHINA; Helen L.W. Chan, Chung-Loong Choy, Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, PR CHINA.

The grain size strongly influences the fatigue properties of PZT thin films with Pt electrodes. A film with smaller grain size has better fatigue properties. We assume the fatigue is mainly due to the pinning of domain walls in the PZT grains by space charge or charged point defects near Pt electrodes. The point defects always accumulate near the PZT/Pt interface for the internal electric field is very strong near the interface. Therefore the film with lower fraction of the grains touched Pt electrodes has better fatigue properties. The permittivity of the thin film decreases with the decrease of grain size. It may be due to that the mobility of domain walls decreases with grain size. The coercive fields of the PZT thin films with Pt electrodes are higher than that with oxide electrodes. During the deposition process of Pt electrodes, the films may be damaged and the hysterisis loops become unsymmetrical.

CC10.7
FERROELECTRIC PHASE TRANSITIONS IN FILMS WITH DEPLETION CHARGE. A.P. Levanyuk, A.M. Bratkovsky, Hewlett-Packard Laboratories, Palo Alto, CA.

We consider ferroelectric phase transitions in both short-circuited and biased ferroelectric-semiconductor films with a space (depletion) charge which leads to some unusual behavior. It is shown that in the presence of the charge the polarization separates into 'switchable' and 'non-switchable' parts. The electric field, appearing due to the space charge, does not wash out the phase transition, which remains second order but takes place at a reduced temperature. At the same time, it leads to a suppression of the ferroelectricity in a near-electrode layer. This conclusion is valid for materials with both second and first order phase transitions in pure bulk samples. Influence of the depletion charge on thermodynamic coercive field reduces mainly to the lowering of the phase transition temperature, and its effect is negligible. The electric field estimated in the literature and supposed to favor the switching actually corresponds to the nonswitchable part of the polarization and is obviously irrelevant to the problem. The depletion charge can, however, facilitate an appearance of the domain structure which would be detrimental for device performance (fatigue). We discuss some issues of conceptual character, which are generally known but were overlooked in previous works. The present results have general implications for small systems with depletion charge.

CC10.8
FATIGUE IN PZT THIN FILMS. Vladimir Ya. Shur, Ekaterina V. Nikolaeva, Eugene I. Shishkin, Ivan S. Baturin, Ural State Univ., Inst. of Phys.& Appl. Math., Ekaterinburg, RUSSIA; Dierk Bolten, Rainer Waser, Inst. fuer Werkstoffe der Electrotechnik, RWTH Aachen, Aachen, GERMANY.

We have used the new approach to fatigue phenomenon for analysis of the evolution of the current pulses during cyclic switching measured in PZT thin films. It is proposed that the evolution of nonuniform spatial distribution of bias field during periodical switching is responsible for fatigue phenomenon. We have shown that fatigue behavior corresponds to the spreading of the bias field distribution function during ac switching which has been extracted by mathematical treatment of the switching current data. The investigated $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films (120-140-nm-thick) have been deposited by sol-gel method on $Si/SiO_2/Ti/Pt$ substrate. Fatigue-induced evolution of the shape of current pulses measured during ac switching under the action of triangular pulses in frequency range 10 - 100 Hz (amplitude of applied voltage ranged from 5 to 7 V) has been analyzed. We suppose that the current pulse shape for switching at low frequency (in slow increasing field) is determined by spatial distribution of bias field. We have fitted the switching current data proposing the normal distribution of bias fields. The observed fatigue induced increasing of switching time and changing of the switching current shape have been related to growth of the bias field dispersion. Therefore proposed fatigue mechanism is related to spatially inhomogeneous imprint effect.
The research was made possible in part by Program "Basic Research in Russian Universities" (Grant No.5563) and by Grant No.97-0-7.1-236 of the Ministry of Education of the Russian Federation.

CC10.9
NEW MODEL OF FATIGUE AND REJUVENATION PHENOMENA IN FERROELECTRICS. 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.

We have proposed a new approach to the explanation of the fatigue kinetics based on self-organized evolution of the spatially nonuniform bias field. In order to explain the fatigue kinetics we consider the model based on the fact that during any switching cycle the ratio of stay in the states with opposite polarization direction ranges over the sample volume/area. The local value of this ratio defines the change of the bias field at the given point by the end of considered switching cycle. Thus the bias field spatial distribution turns out to depend on the whole domain evolution prehistory. Application of proposed approach to explanation of the rejuvenation effect is presented also. Computer simulation of this model demonstrates that both fatigue and rejuvenation effects are caused by self-consistent change of bias field distribution function with ac switching. The observed fatigue induced increasing of switching time is related to increasing of the dispersion of bias field distribution function, which leads to freezing of the sample regions with maximum of bias field. The strong dependence of endurance on the screening time constant, ratio of switching cycle period to switching time and initial domain structure is revealed. The simulated domain evolution at different fatigue stages shows the irreversible change of the geometry of switching area. Moreover computer simulation allows to investigate the change of switching current during fatigue. These results allow to choose the appropriate formulas for fitting the current data thus describing the fatigue kinetics quantitatively. The comparison with experimental data for PZT thin films and PZN-PT crystals confirms the validity of our model.
The research was made possible in part by Program "Basic Research in Russian Universities" (Grant No.5563) and by Grant No.97-0-7.1-236 of the Ministry of Education of the Russian Federation.

CC10.10
THERMODYNAMICS OF CONSTRAINED FERROELECTRIC FILMS. A.L. Roytburd, C.S. Ganpule, S.P. Alpay, V. Nagarajan, Dept. of Materials and Nuclear Engineering, University of Maryland, MD; E.D. Williams, A. Stanishevsky, J. Melngailis, Materials Research Science and Engineering Center, University of Maryland, MD; R. Ramesh, Dept. of Materials and Nuclear Engineering, University of Maryland, MD.

The relations between electrical and mechanical properties of constrained ferroelectric films are analyzed. It is shown that the

internal stresses and the elastic constants can be determined through the measurement of the electrical response. The change in the polarization is proportional to internal stresses due to film-substrate misfit whereas the linear electrical and electromechanical responses to external field do not depend on the misfit and are determined by the film constraint. Significant recovery in the piezoelectric constant and susceptibility is theoretically predicted and experimentally verified for specific film configurations which reduce the degree of constraint. The displacement of the surface of a film clamped on the substrate under electrical field can be not less and even larger than surface displacement of a free-standing film. The theoretical results are successfully applied to (001) PZT (20/80) films on (001) LAO substrate and polycrystalline PNZT films on Si substrate.
The support by the NSF under Grant No. DMR-9903279 and by the NSF-MRSEC program under Grant No. DMR-9632521 is gratefully acknowledged.

CC10.11
RESPONSE OF THE ELECTRIC FIELD GRADIENT IN ION IMPLANTED $BaTiO_3$ TO AN EXTERNAL ELECTRIC FIELD.
M. Dietrich, M. Deicher, Universität Konstanz, Fachbereich Physik, Konstanz, GERMANY; S. Unterricker, TU Bergakademie Freiberg, Institut für Angewandte Physik, Freiberg, GERMANY; J. Bartels, K. Freitag, Universität Bonn, Institut für Strahlen- und Kernphysik, Bonn, GERMANY.

In solids, the electric field gradient (EFG) at a certain lattice site is determined mainly by the atoms in its nearest neighborhood, i.e. their electronic properties and the distances to each other. Therefore, variations of lattice constants lead to changes in EFG. The influence of sample temperature on EFG has been studied in detail with perturbed γ-γ-angular correlation spectroscopy (PAC) for many cases. PAC spectroscopy observes the hyperfine interaction of radioactive probe nuclei with the EFG at their position. We report on experiments in which we applied uniaxial stress with help of the inverse piezoelectric effect in order to influence the EFG. Single crystalline, ferroelectric $BaTiO_3$ as material with the highest piezoelectric constants among the perovskites with ordered sublattices suits best for this investigation. We have implanted $^{111}In(^{111}Cd)$ (160 keV, 2.2×10^{13} cm^{-2}) with a mean depth of 45 nm. The probe atoms $^{111}In(^{111}Cd)$ substitute Ti and are exposed to an axially symmetric EFG with a strength of $V_{zz} = 173(1)\times10^{18}$ V/m^2. PAC measurements reveal a quadratic dependence of the EFG on the external electric field strength E (-3 ... 4 kV/mm, parallel to polar c-axis): $V_{zz}(E) = (173(1)$ 8.0(2) E/kV/mm 4.0(1) $E^2/kV^2/mm^2)\times10^{18}$ V/m^2. Point charge model calculations which take into account the changes of the lattice parameters according to the inverse piezoelectric effect reproduce the linear change of V_{zz}, but not the quadratic term. The polarizability of the host ions of $BaTiO_3$ is known to result in a quadratic shift of electron density with respect to an electric field strength carried by photons. When a static electric field is applied externally, the polarization occurs in a similar way. The resulting quadratic shift of the electron density is reflected in the strength of the EFG.
This work has been supported by the BMBF (03-DE5KO1-6, 03-DE5KO2-9).

CC10.12
CALCULATION OF FERROELECTRIC PHASE TRANSITIONS RESPONSE IN KDP, TGS and $NaNO_2$ NANOPARTICLES AND THIN FILMS.
Juan D. Romero and Luis F. Fonseca, Dept. of Physics, University of Puerto Rico, San Juan, PR.

Order-disorder ferroelectrics can be described theoretically by the Transversal Ising Model (TIM) Hamiltonian, which includes the four-pseudospin interaction terms. By using Monte Carlo simulations method, we report our calculations of the averaged electrical polarizations at different temperatures for typical order-disorder ferroelectrics such as KDP, TGS and $NaNO_2$. With this method we studied the phase transition behavior of nanoparticles and thin films and its dependence on the size of the particles, surface interactions and thickness of the films. To accomplish our objective with each material mentioned above, we first selected the appropriate microscopic parameters of our Hamiltonian that simulate the bulk behavior and compared those values with the reported coefficients derived from the Landau phenomenological theory. Then, we proceeded to study the ferrolectric phase transition of the nanoparticles and films as a function of their size and thickness. We found that our simulations fitted very well the bulk experimental behavior, though the microscopic parameters obtained for our Hamiltonian are slightly different of those deduced by the phenomenological theory of Landau. We could also describe the size dependence of the critical temperature and of the characteristics of the transition. We report the shifting of the critical temperature of such materials as a function of the characteristic size of each system. Finally, we were able to explain a variety of experimental contradictory results about the behavior of the critical temperature of the nanostructured materials as the competition between size effects and surface interactions in the system.

CC10.13
DISTINCTION METHOD BETWEEN FERROELECTRIC $SrBi_2Ta_2O_9$ PHASE AND PARAELECTRIC FLUORITE AND PYROCHLORE IMPURITY PHASES.
Keisuke Saito, Isao Yamaji, Takao Akai, Philips Japan Ltd., Analytical Division, Kanagawa, JAPAN; Peter Munk, Philips Analytical B.V., NETHERLANDS; Masatoshi Mitsuya, Norimasa Nukaga, Hiroshi Funakubo, Tokyo Institute of Technology, Interdisciplinary Graduated School of Science and Engineering, Department of Innovative and Engineered Materials, Kanagawa, JAPAN.

It is well known that fluorite type and pyrochlore type of impurity phases in Sr-Bi-Ta-O system often coexist with ferroelectric bismuth layer structured $SrBi_2Ta_2O_9$ phase. Fluorite phase is expected to grow under low temperature deposition and bismuth excess film composition, while pyrochlore phase is expected to grow under bismuth deficient film composition. In conventional XRD characterization, it is almost impossible to distinguish between $SrBi_2Ta_2O_9$ phase and impurity phases because fluorite phase has almost the same lattice parameters as one perovskite unit cell of $SrBi_2Ta_2O_9$ and pyrochlore has almost twice as large lattice parameters as that. In the present study, we employed X-ray diffraction reciprocal space mapping technique to distinguish them and these phases were successfully distinguished from each other in very precisely and quantitatively. For example, in the case of $SrBi_2Ta_2O_9$ thin film prepared on conventional $Pt/Ti/SiO_2/Si$ substrate by MOCVD, it is widely reported that the $SrBi_2Ta_2O_9$ has strong its (115) preferred orientation owing to the strongest intensity of its diffraction in conventional θ-2θ scan. However, strong 103 orientation, not 115 orientation, was ascertained by the novel characterization method. Moreover, it was also ascertained that the film included approximately 3 percent of pyrochlore phase. Consequently, from the novel characterization method, it was concluded that the $SrBi_2Ta_2O_9$ thin films prepared by MOCVD on conventional Pt/Ti/SiO2/Si substrate has strong 103 orientation and the films included fairly small amount of pyrochlore phase. Moreover, the strong diffraction believed as $SrBi_2Ta_2O_9$ (115) diffraction was not the one but the pyrochlore (222) diffraction. From this result, it was well demonstrated that the X-ray diffraction reciprocal space mapping technique is effective method to distinguish crystallographic phases when more than two phases show their diffraction at very close angle in conventional θ-2θ scan. Furthermore, it is ascertained that correct quantitative distinction between ferroelectric $SrBi_2Ta_2O_9$ phase and impurity phases, especially fluorite phase, by this method is essential to lowering the growth temperature.

CC10.14
USE OF AN EXTERNAL ELECTRIC FIELD TO CONVERT THE PARAELECTRIC PHASE TO THE FERROELECTRIC PHASE IN ULTRA-THIN COPOLYMER FILMS OF P(VDF-TrFE).
Matt Poulsen, S. Adenwalla and Stephen Ducharme, Department of Physics and Astronomy, Center for Materials Research and Analysis University of Nebraska-Lincoln, Lincoln, NE; V.M. Fridkin, S.P. Palto, N.N. Petukhova and S.G. Yudin Institute of Crystallography, The Russian Academy of Science, Moscow, RUSSIA.

X-ray diffraction was used to probe the structural changes associated with the conversion of the paraelectric phase to the ferroelectric phase that results from the application of a large external electric field. The samples under study are ultra-thin (150 to 250 Å) Langmuir-Blodgett copolymer films of vinylidene fluoride (70%) with trifluoroethylene (30%) deposited on aluminum-coated silicon. θ-2θ X-ray diffraction was used to measure the change in inter-layer spacing perpendicular to the film surface. Upon heating at zero external electric field, the crystalline films undergo a structural phase transition, at $100^\circ \pm 5^\circ$C, from the all-trans ferroelectric phase to the trans-gauche paraelectric phase [1,2]. Above the phase transition temperature, the non-polar paraelectric phase can be converted back to the polar ferroelectric phase, in a smooth continuous process, using a large external electric field ($\approx$1 GV/m). For example, at 100°C the ferroelectric phase first appears above 0.2 GV/m and increases steadily in proportion while the paraelectric phase decreases until complete conversion to the ferroelectric phase is achieved at approximately 0.6 GV/m. This technique allows us to construct the ferroelectric-paraelectric phase coexistence region in the E-T plane, from the zero field transition temperature to the critical point.
[1] Stephen Ducharme, A.V. Bune, L.M. Blinov, V.M. Fridkin, S.P. Palto, A.V. Sorokin and S.G. Yudin, Phys. Rev. B 57, 25 (1998).
[2] Jaewu Choi, C.N. Borca, P.A. Dowben, A.V. Bune, Matt Poulsen, S. Pebley, S. Adenwalla, and Stephen Ducharme, Phys. Rev B 61, 5760 (2000).

SESSION CC11: POSTER SESSION
PIEZOELECTRIC, PYROELECTRIC, AND
OPTICAL MATERIALS AND DEVICES
Chairs: Mareike Klee and Michael Sayer
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

CC11.1
EFFECTS OF FERROELASTIC BUFFER LAYERS ON THE PROPERTIES OF $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ AND $Pb(Zr,Ti)O_3$ THIN FILMS ON Pt COATED SILICON WAFERS. Eunki Hong, Takeshi Yoshimura, Susan Trolier-McKinstry, The Pennsylvania State University, Department of Materials Science and Engineering, Materials Research Laboratory, University Park, PA.

Ferroelectric materials such as PZT and PMN-PT have been investigated for high performance piezoelectrics. However, many relaxor materials don't exhibit good thermal stability at high temperatures due to their low Curie temperatures. For this reason, PYbN-PT which has high Curie point (360°C) at the morphotropic phase boundary should be expected to improve the high temperatue stability of piezoelectric properties. In this work, we deposited both PZT and PYbN-PT thin films on $Pt/Ti/SiO_2/Si$ substrates by using either pulsed laser deposition or sol-gel technique. Either a $SrRuO_3$ single layer or $SrRuO_3/YNbO_4$ double layer was used as buffer layer between the substrate and the ferroelectric film. $YNbO_4$ is a ferroelastic materials, and may potentially act to reduce the local or global residual stress between the ferroelectric film and the substrate. Compared to the bare Pt-coated Si-substrate, the buffer layers effectively suppressed pyrochlore phase formation in PYbN-PT thin films. PYbN-PT thin films deposited with $SrRuO_3$ buffer layers exhibited (110) and (111) orientation. PYbN-PT thin films deposited on $SrRuO_3/YNbO_4$ show strong (110) orientation. The resulting PYbN-PT films exhibit well-developed hysteresis loops with remnant polarizations (P_r) as high as 14-20 $\mu C/cm^2$. The effect of the ferroelastic buffer layer on the dielectric and piezoelectric properties of the films will be reported.

CC11.2
ROLE OF SUBSTRATE ON THE DIELECTRIC AND PIEZO-ELECTRIC BEHAVIOR OF EPITAXIAL LEAD MAGNESIUM NIOBATE-LEAD TITANATE RELAXOR THIN FILMS.
V. Nagarajan, Pamir Alpay, Chandan Ganpule, Brindha Nagaraj, Sanjeev Aggarwal, Alexander Roytburd, Ellen Williams and R. Ramesh, Univ of Maryland, Dept of Materials Engg, College Park, MD.

The effect of various substrates on the electrical and electromechanical properties of epitaxial $0.9[Pb(Mg_{1/3}Nb_{2/3})O_3]$-$0.1[PbTiO_3]$ (0.9PMN-0.1PT) thin films is investigated. (001) 0.9PMN-0.1PT films are grown on (001) $LaAlO_3$ (LAO), $(La,Sr)(Al,Ta)O_3$ (LSAT), $SrTiO_3$ (STO), and MgO substrates with 40 nm thick top and bottom $La_{0.5}Sr_{0.5}CoO_3$ electrodes by pulsed laser deposition. X-ray diffraction results indicate that the films on LAO, LSAT, and STO are stressed biaxially in compression in the film-substrate interface whereas the films on MgO are stressed in tension. We observe a systematic decrease in the phase transition temperature (temperature at which a maximum in dielectric response occurs), from around 150°C to around 60°C as the relaxor thickness is increased from 100 nm to 400 nm for the films grown on LAO. It is accompanied by an increase in the relative dielectric constant (ϵ_r), measured at room temperature and 10kHz, from 300 to 3000 respectively. Correspondingly the piezoelectric responses, measured using a scanned probe microscope, shows a strong dependence on the film thickness. For 100 nm thick PMN-PT films grown on various substrates a decrease in the temperature of dielectric maximum (T_m) together with an increase in the dielectric constant and the longitudinal piezomodulus is observed with decreasing in-plane epitaxial stresses for LAO, LSAT, and STO substrates. The film on MgO substrates has the highest dielectric constant and piezomodulus with Tm below room temperature. The variation in Tm may be attributed to the shift in the transformation temperature from the paraelectric state to the relaxor state due to internal stresses in the film-substrate interface. Electrical and electromechanical properties should depend strongly on internal stresses in the vicinity of the phase transformation, which is reflected in our experimental observations.

CC11.3
FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF EPITAXIAL $Pb[Yb_{1/2}Nb_{1/2}]O_3$-$PbTiO_3$ FILMS. Takeshi Yoshimura and Susan Trolier-McKinstry The Pennsylvania State University, Materials Research Laboratory, University Park, PA.

Epitaxial relaxor ferroelectric films have attracted much attention for micro-electromechanical systems (MEMS), because relaxor based ferroelectric single crystals exhibit ultralarge piezoelectric responses. In this study, we investigated ferroelectric and piezoelectric properties of epitaxial (1-x)$Pb[Yb_12Nb_12]O_3$-x$PbTiO_3$ (PYbN-PT) films. Since PYbN-PT has the highest Curie point (∼360°C) near the morphotropic phase boundary (x ∼ 0.5) of the known relaxor ferroelectric-$PbTiO_3$ solid solutions, MEMS devices with temperature stable can be expected. (100)$LaAlO_3$ single crystals were used as substrates. $SrRuO_3$ bottom electrodes and PYbN-PT films were deposited by pulsed laser deposition. (001)PYbN-PT (50/50) films were obtained at the deposition temperature of 650°C. Typical full width at half maxima of the rocking curve for PYbN-PT 002 are 0.6°. The dielectric constant and dielectric loss at room temperature and 10 kHz are ∼1000 and 0.05, respectively. Ferroelectricity with the remanent polarization of 30 $\mu C/cm^2$ was also obtained. For such samples, the product of d_31•Young's modules is 4 C/m^2.

CC11.4
PMN-Pt THIN FILMS DEPOSITED ON (100)-ORIENTED $LaNiO_3$ BOTTOM ELECTRODES. Zhenshan Zhang and Susan Trolier-McKinstry, Materials Research Laboratory, Pennsylvania State University, University Park, PA.

$(100)_{pc}$-oriented thin films of $LaNiO_3$ (LNO) were deposited by DC magnetron sputtering onto Si substrates (pc = pseudo cubic indices). A lattice parameter a_{pc} of 3.845 Å and thermal expansion coefficient of 16.3 × 10^{-6}/°C were measured for LNO thin films using high temperature X-ray diffraction. (001)-oriented thin films of $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ (PMN-PT) were fabricated by a sol-gel method on $(001)_{pc}$-textured LNO metallic oxide electrodes. The analysis of the rocking curve revealed the full width half maximum (FWHM) of 200 reflection of PMN-PT films is 5.6°. The dielectric constant of PMN-PT films decreased with increasing electric field and had a 32% change at a field of 50 kV/cm. A d_{31} of -76 pC/N (assuming a Young's modulus of 45 GPa) and aging rate of 6.8% were measured on 1.1 μm thick PMN-PT films. The films exhibited a leakage current density of less than 10^{-6} A/cm^2 when an electric field of 100 kV/cm was applied.

CC11.5
CRYSTALLINE AND ELECTRICAL PROPERTIES OF FERRO-ELECTRIC SILVER NiOBaTe-TANTALATE THIN FILMS.
Jung-Hyuk Koh, S.I. Khartsev, Alex Grishin, Dept of Condensed Matter Physics, Royal Institute of Technology, SWEDEN; Vladimir Petrovsky, Dept of Ceramic Engineering, Univ of Missouri-Rolla, Rolla, MO.

We report on new ferroelectric $Ag(Ta,Nb)O_3$ (ATN) films grown by pulsed laser deposition technique onto polycrystalline Pt and $(La,Sr)CoO_3/LaAlO_3$ single crystal substrates. ATN films on Pt have been found to be (001) preferentially oriented, while the epitaxial quality of $ATN/LSCO/LaAlO_3$ heterostructures has been ascertained. The sequence of the coupled structural-ferroelectric phase transitions in the temperature range 77 to 420 K has been compared in films and bulk ceramics and high temperature stability of dielectric constant and loss tangent delta in ATN films was observed in extended temperature range. Weak frequency dispersion of the dielectric performance, low loss tan delta (100 kHz) ∼ 0.008, ferroelectric state at low temperature with the remnant polarization around 0.4 $microC/cm^2$ and electrical tunability as high as 32% @77 K promise new ATN films for various applications. Results on dielectric spectroscopy performed both for vertical and interdigital capacitive cells will be presented.
This work was supported by the Swedish Agency NUTEK.

CC11.6
MODELING OF BENDING-TYPE MICROACTUATORS USING PZT THIN FILMS. Baomin Xu, Jindong Zhang and L. Eric Cross, Materials Research Laboratory, Pennsylvania State University, University Park, PA.

Bending structure, in which a thin layer of PZT film is supported by a thin silicon structural membrane, is the most popular design for micromachined piezoelectric sensors and actuators. In this work, the actuation behavior of the bending-type microactuators using both the novel, in-plane poled PZT films and the conventional, through-thickness poled PZT films has been studied by using FEA (Finite Element Analysis) method. The in-plane polarization can be realized by depositing PZT films on silicon substrates buffered by an insulating oxide layer such as ZrO_2 and using top surface interdigitated electrode systems for the cantilever structure or annular electrode systems for the diaphragm structure. The FEA modeling demonstrates that, with the same input electric energy, the displacement of the microactuators using the in-plane poled PZT films can be more than 1.5 times of the displacement of the microactuators using the through-thickness poled PZT films. This is because the in-plane polarization enables d_{33} mode to be used for the microactuators and d_{33} is about two times of d_{31} for PZT films, which overcomes the deficiency that in-plane polarization may cause

some incomplete strain development due to the non-uniformity of electric field.

CC11.7
DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF PZT 52/48 THICK FILMS WITH (100) AND RANDOM CRYSTALLOGRAPHIC ORIENTATION. Q. Zhou, E. Hong, R. Wolf, S. Trolier-McKinstry, Materials Research Laboratory, The Pennsylvania State University, University Park, PA.

Ferroelectric $Pb(Zr_{1-x}Ti_x)O3$ (PZT) films have been extensively studied for active components in micro-electromechanical systems. The properties of PZT films depend on many parameters, including composition, orientation, film thickness and microstructure. In this study the effects of crystallographic orientation on the dielectric and transverse piezoelectric properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT 52/48) films will be reported. Crack free random and highly (100) oriented PZT(52/48) films up to $\sim$ 7 μm thick were deposited using a sol-gel process on $Pt(111)/Ti/SiO_2/Si$ and $Pt(100)/SiO_2/Si$ substrates, respectively. The dielectric permittivity (at 1 kHz) for the (100) oriented films is 980-1000, and for the random films $\sim$ 930-950. In both cases, tand is less than 0.03. The remanent polarization ($\sim$ 25 $\mu C/cm^2$) of random PZT films is larger than that of (100) oriented PZT films (20 $\mu C/cm^2$). The transverse piezoelectric coefficient (d_{31}) of PZT films was measured by wafer flexure method. The d_{31} coefficient of random PZT thick films (-80 pC/N) is larger than that of (100) oriented films (-60 pC/N) when poled at 80 kV/cm for 15 min. Aging rates for the dielectric permittivity and piezoelectric coefficients of PZT films with different orientation will also be presented.

CC11.8
IMAGING & MAPPING OF THE DIELECTRIC PROPERTIES AND PIEZORESPONSE IN MICROMACHINED PZT THIN FILMS. Carles Morros, Robert Bowman, Marty Gregg, Department of Pure and Applied Physics, Queen's University of Belfast, Belfast, UNITED KINGDOM.

Lead zirconate titanate (PZT) thin films have been made by pulsed laser deposition using a target of bulk PZT-5H. The films are fully characterised and their piezoelectric coefficient d_33 is compared to that in commercial PZT-5H. A modified scanning probe microscope is used for the piezoresponse scanning. PZT thin films are then fashioned into device structures by laser micro-machining. The laser machining results in damaged areas along the cut edges. Mapping of the piezoresponse and topograhy on these devices is presented and the implications for transducer fabrication discussed.

CC11.9
A DIELECTRIC BOLOMETER BEHAVIOR OF BST THIN FILM PREPARED BY METAL-ORGANIC-DECOMPOSITION WITH EXCELLENT REPRODUCIBILITY IN THERMAL CYCLING TEST. Minoru Noda, Hong Zhu, Huaping Xu, Tomonori Mukaigawa, Kazuhiko Hashimoto and Masanori Okuyama, Osaka Prefecture Super-Eye-Image-Sensor (SEIS) Project, Osaka, JAPAN.

We have proposed a new type of simple detector pixel circuit and device structure for application of dielectric bolometer mode (DB) of infrared (IR) image sensor. The DB mode IR detector merits in uncooled room temperature operation, chopperless, low power dissipation, and high-sensitivity like a pyroelectric operation. In this work, we have successfully developed a stable $Ba_{1-x}Sr_xTiO_3$ (BST) thin film as an IR detecting material by Metal-Organic-Decomposition (MOD) method. The film was prepared on both $Pt/Ti/SiO_2/Si$-bulk and $Pt/Ti/NSG/Si_3N_4/SiO_2$ membrane structures, where an IR light is detected at the membrane as a change in dielectric constant ε. So, the important issue for realizing a reliable IR sensor with high-sensitivity is to have a good thermal stability in ε against change in the detector temperature. XRD patterns and D-E hysteresis curves were measured and revealed that the BST film has a good perovskite structure and shows an adequate ferroelectric loops even on the micromachined structure, especially for final annealing temperature higher than 700 degree Celsius. Temperature Coefficient of Dielectric constant (TCD), which decides the IR sensitivity, of the MOD made BST film on the micromachined structure is about 1%/K. The reproducibility in ε, namely IR detector capacitance, was found to be very good in temperature ranging from about 10 to 80°Celsius within a relative change of 2%. Finally, the stabilities in both the temperature dependence of ε and the output level have become significantly improved and enabled us to obtain 1-D(1x16) and 2-D(16x16) images with a fairly large IR detectivity, where R_v and D^* were about 1 kV/W and 1e8 $cmHz^{1/2}/W$, respectively.

CC11.10
SOL-GEL DERIVED PYROELECTRIC BARIUM STRONTIUM TITANATE THIN FILMS FOR INFRARED DETECTOR APPLICATIONS. Jian-Gong Cheng, Jun Tang, Shao-Ling Guo, Jun-Hao Chu, National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, CHINA.

$Ba_xSr_{1-x}TiO_3$ (BST) is currently one of the most interesting ferroelectric materials due to its high dielectric constant and composition dependent Curie temperature from 30 to 400 K. However, the sol-gel derived BST films always fail to display pronounced ferroelectricity, which make it unsuitable for uncooled infrared detector applications. In this work, we developed a novel sol-gel technique to prepare $Ba_{0.8}Sr_{0.2}TiO_3$ thin films using a highly diluted precursor solution. A columnar structure with grain size close to 200 nm was obtained with layer-by-layer homoepitaxy due to a very small thickness of individual layer. The prepared $Ba_{0.8}Sr_{0.2}TiO_3$ thin films have been studied for possible infrared detector applications. The measured pyroelecrtic coefficient is larger than 3.1×10^{-4} C/m^2K at the temperatures ranging from 10 to 26°C and reaches the maximum value of 4.1×10^{-4} C/m^2K at 16°C. The infrared detectivity of 4.6×10^7 $cmHz^{1/2}W^{-1}$ has been obtained at 19°C and 10 Hz in the $Ba_{0.8}Sr_{0.2}TiO_3$ films deposited on thick (500 mm) platinum coated silicon substrates. The better infrared response can be expected by the improvement in the thermal isolation of pyroelectric element and the electrode materials.

CC11.11
A MODIFIED SBN SYSTEM FOR PYROELECTRIC SENSORS. Harvey Amorín, Jorge Portelles, Michel Venet, Abel Fundora, Facultad de Física-Instituto de Materiales y Reactivos Universidad de la Habana, Vedado, La Habana, CUBA; Fidel Guerrero, Facultad de Ciencias Naturales, Universidad de Oriente, Santiago de Cuba, CUBA; Jesús M. Siqueiros, Centro de Ciencias de la Materia Condensada, UNAM, Ensenada, MEXICO.

The Thermally Stimulated Depolarization Current (TSDC) and pyroelectric properties of the modified SBN ferroelectric ceramic system are studied for different lanthanum and titanium doping concentrations in thin film and in the bulk. The TSDC measurements for the titanium modified SBN system show the pyroelectric peak for all compositions while a second smaller peak at higher temperature, possibly associated to induced vacancy-impurity dipoles, is also observed in all cases. The second peak contribution was experimentally and mathematically eliminated to determine the remanent polarization and pyroelectric coefficient, both associated only to permanent ferroelectric dipoles. The activation energies and the relaxation times of both processes are determined. The figures of merit for sensor devices are determined for all compositions and compared with those of other pyroelectric systems. The $La_{0.03}Sr_{0.255}Ba_{0.7}Nb_{1.95}Ti_{0.05}O_{5.975}$ sample, in particular, has excellent pyroelectric response, making this material very suitable for pyroelectricity-derived applications.

CC11.12
SENSING PROPERTIES OF $Ba_{1-x}La_xNb_yTi_{1-y}O_3$ (x=0.25, y=0.25) THIN-FILM ON SiO_2/Si SUBSTRATE. Bin Li, P.T. Lai, Department of Electrical and Electronic Engineering, University of Hong Kong, HONG KONG; G.Q. Li, S.H. Zeng, M.Q. Huang, Department of Applied Physics, South China University of Technology, Guangzhou, CHINA.

With the progress of automatic control applications, the need for miniaturized, intelligent and programmable sensors has become an important issue. To achieve these goals, exploiting thin-film sensors on silicon substrates is always the target of investigations. Therefore, desirable sensing thin-film materials have been actively sought. Perovskite-type oxides (ABO_3) attract much attention in recent years because these oxide not only can be used as high-permittivity dielectric in non-volatile memory, but also can be used as sensing materials. Moreover, sensing properties of these oxides may be modified by appropriate combination of cationic constituents. Our previous works [1,2] have found that even though both $Ba_{1-x}La_xTiO_3$ and $SrNb_xTi_{1-x}O_3$ thin film have photo-, thermal and humidity sensitivity characteristics, but photo sensing characteristics is better in La-doped film and thermal sensing characteristics is better in Nb-doped film. Therefore, in this work, $Ba_{1-x}La_xNb_yTi_{1-y}O_3$ (x=0.25, y=0.25) thin-film is proposed with a view to achieving better photo, thermal and humidity sensing properties. Based on three terminals device structure – thin-film resistor and metal-insulator-semiconducting (MIS) capacitor on SiO_2/Si, the sensing performances are investigated. Results reveal that the thin-film resistor has good sensitivity for visible light and good thermal sensitivity within the temperature range of 28$\sim$400 °C. The MIS capacitor is sensitive to change of relative humidity (RH), with a 200% change of current for a humidity change from 12% to 92% RH at a test frequency of 500 Hz, and with short response times of 5 s and 3.5 s for adsorption and desorption of water vapor respectively. Effects of test frequency on photo, thermal and humidity sensitivity performances are also investigated. In conclusion, compared with $Ba_{1-x}La_xTiO_3$ and $SrNb_xTi_{1-x}O_3$ thin film, photo-, thermal and humidity sensing

properties of $Ba_{1-x}La_xNb_yTi_{1-y}O_3$ (x=0.25, y=0.25) thin-film are reasonably improved. So, sputtered $Ba_{1-x}La_xNb_y\ Ti_{1-y}O_3$ (x=0.25, y=0.25) thin-film is a promising material for multi-sensing devices.
Reference:

[1] G.Q. Li, P.T. Lai, S.H. Zeng, M.Q. Huang and B. Li, "A new thin-film humidity and thermal micro-sensor with $Al/SrNb_xTi_{1-x}O_3/SiO_2/Si$ structure", *Sensors and Actuators A*, Vol. 75, pp. 70-74, 1999.
[2] B. Li, P.T. Lai, G.Q. Li, S.H. Zeng and M.Q. Huang, "A new multi-function thin-film microsensor based on $Ba_{1-x}La_xTiO_3$", *Smart Materials and Structure* (in press).

CC11.13
ELECTRIC FIELD EFFECT THERMOELECTRICS. Vladimir Sandomirsky, Bar-Ilan Univ, Dept of Physics, Ramat-Gan, ISRAEL.

It is proposed to use the ferroelectric electric field effect (FEFE)to increase the figure of merit (FM)of the thermoelectric semiconductor (TS). The capacitive structure is considered "Gate-Polarized ferroelectric film (PFF)-TS film".FEFE allows to surpress in the intrinsic TS film one (any) kind of the carriers and to increase simultaneously till an optimal value the quantity of other carriers. The theory of the structure has been developed. The influence of different parameters on the value of FM is analyzed. It is shown that a crucial significance has the value of the static dielectric constant of TS. FM is the more the dielectric constant is more. The results of numerical calculations for the TS PbTe are presented. Its dielectric constant at 300K equals 512. For PFF with the electric displacement 10^8V/cm FM>1 at the enrichment of PbTe-film (500AA) with holes. The perspective themoelectric also is the semimetal Bi with dielectric constant ~150.

SESSION CC12: POSTER SESSION
THIN FILM PROCESSING
Chairs: Gerd J. Norga and Mikio Yamamuka
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hynes)

CC12.1
QUANTITATIVE ANALYSIS OF THE GRAIN BOUNDARY EFFECTS ON THE HYDROGEN-INDUCED DEGRADATION IN LEAD ZIRCONATE TITANATE THIN FILMS. Jang-Sik Lee and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

It is well known that exposing lead zirconate titanate (PZT) thin films to hydrogen severely degrades the electrical properties. This phenomenon has been the subject of intensive study, however there is no electrical evidence relating the hydrogen-induced degradation with the grain boundary in the films. In this work, using the large-grained PZT thin films of about 40 μm in grain size, we could measure the effects of the grain boundary on the hydrogen-induced degradation in PZT thin films by locating the upper Pt electrode (8 μm × 8 μm square) sequentially from the middle of the grain to the grain boundary in a controlled manner. Hydrogen annealing was carried out in a conventional quartz furnace with pure H_2 gas at 400 °C for 30 minutes. We measured the electrical properties before and after the hydrogen annealing in order to determine the extent of the degradation. It was found that the grain boundary was mainly responsible for the electrical degradation caused by the exposure to the hydrogen. However, little degradation with hydrogen exposure was observed when the Pt top electrode was located in the center of grain. This is the first quantitative analysis of the grain boundary effects on the hydrogen-induced degradation in PZT thin films. The experimental evidence will be presented in detail and a new model, i.e. the sequential degradation from the grain boundary to the center of grain will be suggested.

CC12.2
ANALYSIS OF THE GRAIN SIZE SATURATION IN LEAD ZIRCONATE TITANATE THIN FILMS BY THE CONTROL OF INTERFACE ENERGY. Jang-Sik Lee and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

We previously reported that the laterally grown length of lead zirconate titanate (PZT) thin films by SNLC (Selectively Nucleated Lateral Crystallization) was saturated at certain temperature. It was interesting to notice that there existed the maximum lateral growth length and the length did not increase with increasing heat treatment time. In our previous work, only the phenomenological assumption was presented without providing a clear reason. In this study, we will present the analysis of the saturation of grain size in PZT thin films through the control of the interface energy. The saturation of grain size was analyzed by the interface energy during the crystallization process of PZT thin films. The factors affecting the saturation of grain size were found to be the interface energy between perovskite and pyrochlore phase and the one between PZT thin film and the bottom Pt electrode. When the ion damage was introduced to the grain-size saturated PZT thin films to control the interface energy between perovskite and pyrochlore phase, further lateral growth occurred. Pt bottom electrode thickness was changed in order to alter the interface energy between the PZT thin film and the Pt bottom electrode. The increase of the bottom Pt electrode thickness resulted in the enlargement of the PZT grain size, because the lattice parameter of Pt films approached that of the PZT thin films. The phenomena and reasons of the grain size saturation at certain temperature will be discussed in detail.

CC12.3
MICROSTRUCTURE AND PROPERTIES OF Mn-DOPED PMN-Pt THIN FILMS ON LSCO-BUFFERED Si-WAFER. Y. Wang, K. Mori, V. Nagarajan, M. Wuttig, R. Ramesh, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; K. Chandra, Wilcoxon Research Company, Gaithersburg, MD.

Lead magnesium niobate - lead titanate (PMN-PT) thin films have attracted much attention recently due to their potential applications in micro-electronic-mechanical systems (MEMS). In order to improve the dielectric, ferroelectric and piezoelectric properties of such films, one of the key issues is to get pure perovskite phase of PMN-PT and prevent the formation of pyrochlore phase. In this work, we tried to deposit 70PMN-30PT thin films on ($La_{0.5}$, $Sr_{0.5}$)CoO_3-buffered platimized silicon (LSCO/Pt/Si) wafers by sol-gel and spin-coating techniques. The X-ray diffraction tests revealed that under the same deposition conditions, PMN-PT grown on LSCO/Pt/Si has a higher ratio of perovskite/(perovskite pyrochlore) than the film on Si-wafer without LSCO template, indicating that LSCO assists the formation of perovskite PMN-PT and suppresses the pyrochlore phase. The effect of Mn doping on perovskite phase formation was systematically studied. The electrical property measurements and microstructure observation by means of AFM are also reported.

CC12.4
THICKNESS DEPENDENCE OF MICROSTRUCTURE AND PROPERTIES OF PZT 40/60 THIN FILMS. Y. Wang, K. Mori, B.T. Liu, B. Nagaraj, H. Li, C. Ganpule, R. Ramesh, M. Wuttig, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; K. Chandra, Wilcoxon Research Company, Gaithersburg, MD.

The microstructure as well as dielectric and ferroelectric properties as a function of thickness is investigated on PZT40/60 films deposited by sol-gel and spin-coating techniques. The films prepared on three different substrates were found to show quite different orientation vs thickness relationship. When grown on platimized silicon wafer (Pt/Si), PZT has a polycrystalline structure with a dominant (110) peak in X-ray diffraction. The relative intensity of the major XRD peaks, I_{rltv}= I(001)/[I(110) I(001)], increases with the film thickness. When deposited on ($La_{0.5}$,$Sr_{0.5}$)CoO_3-buffered Pt/Si, PZT exhibits (001) texture and as the film gets thicker, the relative intensity decreases. When deposited on LSCO-buffered $SrTiO_3$ single crystal, PZT films were found to grow epitaxially but random orientation begins to appear when the thickness is above a critical value. The dielectric and ferroelectric properties of the films were also studied.

CC12.5
ROTATING DISK METAL-ORGANIC CHEMICAL VAPOR DEPOSITION AND CHARACTERIZATION OF LEAD ZIRCONIUM TITANATE (PZT) THIN FILMS FOR INTEGRATED CIRCUIT APPLICATIONS. J. McAleese, G.S. Tompa, J. Cuchiaro, L.G. Provost, Structured Materials Industries Inc.; D. Hadnagy, G. Fox, S. Sun, Ramtron International Corporation.

Lead zirconium titanate (PZT) ferroelectric oxide thin films have been successfully integrated into non-volatile memory (NVRAM)products creating increased demand for advanced architectures. Consequently a compatible deposition technology, such as Rotating Disk Reactor Metal-Organic Chemical Vapor Deposition (RDR-MOCVD, is required to successfully meet the integration challenges. Conformal, ferrolectric films need to be deposited over shrinking capacitor area and reduced thickness, a prerequisite being that as aspect ratios increase, compositional uniformity of the multi-element oxides must be maintained. To achieve this, the effect of CVD parameters including substrate temperature, gas flow rates and reactor pressure must be studied in order that successful process can be integrated. A compatible ferroelectric layer deposition must not adversely effect the underlayer circuitry that could lead to the destruction of necessary electrical responses desired for memory and data retention. These performance characteristics become more critical in scaled films and are subject to varied response due to the capacitor substrate. We will evaluate electrical performance of PZT capacitor structures suitable

for implementation in advanced integration schemes on a thermally stable electrode and the corresponding process conditions of the RDR-MOCVD deposited PZT thin films.

CC12.6
Abstract Withdrawn.

CC12.7
EPITAXIAL FERROELECTRIC ($Pb(Zr,Ti)O_3$) THIN FILMS ON $SrRuO_3$ THIN FILM BOTTOM ELECTRODE GROWN BY HYDROTHERMAL PROCESS. D.M. Kim, S.D. Bu, M.K. Lee, C.B. Eom, Department of MS&E, University of Wisconsin-Madison, Madison, WI; S.K. Streiffer, Argonne National Laboratory, Argonne, IL.

We have grown epitaxial ferroelectric $Pb(Zr,Ti)O_3$ thin films on $SrRuO_3$ thin film bottom electrode on (001) SrTiO3 substrate by hydrothermal process. The hydrothermal process allows us to grow oxide films from aqueous solution at low processing temperature. $SrRuO_3$ is a pseudocubic perovskite structure and chemically stable metallic oxide which allow us to grow epitaxial PZT thin films. We have prepared the reaction mixture with titanium dioxide(anatase, TiO_2), zirconium oxychloride ($ZrOCl_2$) and lead nitrate ($PbNO_3$) in an alkaline aqueous solution and fabricated the film under 200°C in a teflon-lined autoclave reactor. Four-circle x-ray diffraction analysis revealed the PZT layer is purely {001} normal to the substrates with cube-on-cube in-plane epitaxial arrangement. They show well saturated hysteresis loops, strongly asymmetric polarization switching and the occurrence of imprint phenomenon. Their dielectric constant and loss tangent are 460 and 0.035 at 10^4 Hz. They also show low leakage current and its value is $2Wtimes$ 10^{-6} A/cm^2 at 100 kV/cm. We will discuss the morphology and microstructure of the heterostructures.

CC12.8
ELECTROPHORETIC DEPOSITION OF $Ba_{1-x}Sr_xTiO_3$°VMgO COMPOSITE THICK FILMS FOR MICROWAVE APPLICATION. E. Ngo, P.C. Joshi, M. Cole, C. Hubbard.

Barium Strontium titanate (BST) composite is being investigated as one of the major dielectric material candidate, suitable for tunable microwave devices, bypass capacitor, IR detector and DRAMs application. BST can be tailored over a broad range to meet the requirements for these various applications. Bulk ceramic of Barium Strontium titanate-composite have been reported to show significantly reduced dielectric constant and dielectric loss compared to pure BST . Excellent dielectric loss and dielectric tunability characteristics have been obtained at X-band and K-band frequencies by optimizing the Ba/Sr ratio and MgO content such that the Curie temperature shifts below the room temperature making the material paraelectric under normal operating conditions. We have investigated the electrophoretic deposition (EPD) method as a low cost and conformal way of depositing thick films of the patented composites of barium strontium titanium oxide. The materials were deposited on platinum substrate in acetone base slurry under bias and at controlled rate. Conformal BST thick films of 10-50 m were obtained, acetone-aerosol OTS surfactant dispersion was used as dispersive medium. Dielectric constant and dielectric loss were 603.3 and .029, 327.0 and .002 for Ba0.60Sr0.40TiO3 and Ba0.60Sr0.40TiO3 V 20wt%, respectively. Electronic properties at low frequency of the electrophoretic films will also compared with those of the bulk ceramics and pulsed laser deposition films. In addition, analyses including surface roughness, SEM, FT-IR and will also be discussed.

CC12.9
SYNTHESIS AND ELECTRICAL PROPERTIES OF SBT HETEROSTRUCTURES ON SILICON BY DOMAIN MATCHING EPITAXY. S. Chattopadhyay, J. Narayan, NSF Center for Advanced Materials and Smart Structure, NC A&T State University, Electrical Engineering Dept., Greensboro, NC & North Carolina State University, Materials Science Dept., Raleigh, NC; V.S. Knight, W. Gilmore, C.B. Lee, NC A&T State University, Electrical Engineering Dept., Greensboro, NC.

Ferroelectric thin films of $SrBi_2Ta_2O_9$ (SBT) have been investigated extensively in the recent years because of their potential application in nonvolatile random access memories and dynamic random access memories. Hence, integration of SBT with silicon is very important for the device application of this compound. We have been successful in growing c-axis oriented thin films of $SrBi_{2.2}Ta_2O_9$ by pulsed laser deposition on silicon (00l) substrates by domain matching epitaxy, using titanium nitride as the buffer layer and platinum as the bottom electrode. The films are phase pure and have been found to possess good grain structure as observed by scanning electron microscopy and atomic force microscopy. Measurement of electrical properties of the films have revealed the dielectric constant for the films to be between 220 and 245 and the loss tangent have been found to vary from 0.01 to 0.02. Hysteresis loop measurements have indicated the spontaneous polarization (Ps) and the remanent polarization (Pr) to be 27 microcoulomb/cm^2 and 11.6 microcoulomb/cm^2, respectively, and the coercive field (Ec) is 54 kV/cm. The properties of these c-axis oriented films have been found to be better than those of SBT polycrystalline films grown on Pt/TiN/MgO(001) heterostructures. Fatigue measurements of these films are being done.

CC12.10
A PLD-BASED CONTINUOUS COMPOSITIONAL-SPREAD TECHNIQUE APPLIED TO EPITAXIAL FILMS AND HETEROSTRUCTURES. Hans M. Christen, Sherwood D. Silliman, and K.S. Harshavardhan, Neocera, Inc., Beltsville, MD.

We present a novel continuous-compositional spread technique based on the non-uniformity of the deposition-rate typically observed in pulsed laser deposition. Using rapid (sub-monolayer) sequential deposition of the phase spreads constituents, a pseudo-binary or pseudo-ternary phase diagram is deposited without the need for masks and without the requirement of a post-anneal. Therefore, combinatorial materials synthesis can be carried out under optimized film growth conditions (for example, complex oxides can be grown at high temperature). Additionally, lifting the need for post-annealing renders this method applicable to heat-sensitive materials and substrates (e.g. films of transparent oxides on polymer substrates). Composition determination across the sample and mapping of physical properties onto the ternary phase diagram is achieved via a simple algorithm using the parameters that describe the deposition-rate profiles. Experimental verification using EDX and RBS measurements demonstrates the excellent agreement between the predicted and the calculated composition values. Results are shown for the high-temperature growth of crystalline perovskites, including (Ba,Sr)TiO3 and the formation of a metastable alloy between SrRuO3 and SrSnO3. Applications of the method to the growth of heterostructures and superlattices are discussed.

CC12.11
GROWTH AND CHARACTERIZATION STUDIES OF $ABi_2Ta_2O_9$ (A = Ba, Sr, and Ca) FERROELECTRIC THIN FILMS. R.R. Das, W. Pérez, R.J. Rodríguez , E. Ching-Prado*, P.S. Dobal and R.S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR. *Faculty of Science and Technology, Technological University of Panamá, Tocumen, PANAMA.

Thin films of ferroelectric $ABi_2Ta_2O_9$ bismuth-layered structure, where A = Ba, Sr, and Ca, were prepared by a Pulsed Laser Deposition technique on Si, $Pt/TiO_2/SiO_2/Si$, and $LaAlO_3$ substrates. The influence of substrate temperature, between 500 to 750°C, and oxygen partial pressure, from 100 to 600 mTorr, on the structural properties of the films were investigated. The films deposited above 600°C substrate temperature shown the complete Aurivillius layered structure. All films were annealed at 750°C for 30 minutes in oxygen atmosphere have shown improved in electrical properties. We discuss the influence of the A-site cation substitution on the structural and ferroelectric properties of the films. Results of Raman spectroscopy, X-ray diffraction, atomic force microscopy, and X-ray photo electron spectroscopy techniques showing the A-site substitution will be presented. This work is supported in parts by DAAG55-98-1-00112, DAAD19-99-1-0362, and NSF DMR 9801759 grants.

CC12.12
FERROELECTRIC AND FATIGUE PROPERTIES OF ALKOXY-DERIVED $CaBi_2Ta_2O_9$ THIN FILMS. Kazumi Kato[1,2], Kazuyuki Suzuki[1], Kaori Nishizawa[1], Takeshi Miki[1]. [1]National Industrial Research Institute of Nagoya, Nagoya, JAPAN. [2]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN.

$CaBi_2Ta_2O_9$ (CBT) is one of layer-structured perovskite compounds and has not been well-known for ferroelectric properties as $SrBi_2Ta_2O_9$ (SBT) which has a similar crystal structure. The CBT thin films were successfully prepared on Pt-passivated quartz glass substrates using a triple-alkoxide solution. The thin film crystallized to a single phase of perovskite at 750°C via a mixture of fluorite and perovskite phases. The 750°C-annealed thin film showed random orientation and consisted of fine grains with a diameter of about 80 nm. Pt top electrodes in a circular shape with 0.5 mm diameter were deposited on the 300 nm-thick CBT film by r.f. sputtering. The dielectric constant and loss factor were 124 and 0.04, respectively, and were constant in the frequency range of 10 kHz to 2 MHz. The thin film exhibited P-E hysteresis loops at relatively high voltages. The remanent polarization and coercive electric filed were 6.9 μC/cm^2 and 170 kV/cm at 13 V, respectively. The fatigue behaviors against various electric pulse sequences were examined. The polarization did not change when the pulse width was short such as 10^{-6}s, however, it increased gradually with number of switching cycles when the pulse

width was relatively long such as 10^{-3}s. The thin film exhibited no change of polarization after 10^{10} cycles of switching with the pulse width of 10^{-6}s. This work was financially supported by the Industrial Science and Technology Frontier Program being promoted by AIST, MITI, Japan.

CC12.13
HYDROTHERMAL PROCESSING OF BARIUM STRONTIUM TITANATE FOR HIGH FREQUENCY APPLICATIONS.
K. Zelonka, L. Zou, M. Sayer, Dept of Physics, Queen's University, Kingston, ON, CANADA; H. Hammad, A.P. Freundorfer, Dept of Electrical Engineering, Queen's University, Kingston, ON, CANADA.

A novel technique for fabrication of high quality barium strontium titanate (BST) ceramic coatings is being explored both experimentally and through detailed thermodynamic analysis. The hydrothermal method allows BST coatings to be fabricated at low temperatures on GaAs high frequency circuits with inexpensive processes and precursors. This technique is potentially useful in the processing of many other ceramics, and is advantageous due to its simplicity and relatively mild conditions. Crystallographic BST films with good low frequency electric characteristics have been achieved below 180° C using the hydrothermal method. Techniques for high frequency (30 - 70 GHz) characterization of these films are being investigated. The coatings are being considered as dielectric layers to optimize on-chip antenna design for GaAs microcircuits.

CC12.14
ELECTRICAL CHARACTERISTICS OF SOL-GEL DERIVED Nd^3 DOPED PZT (53/47) THIN FILMS IN PLANAR ELECTRODE CONFIGURATION. S.B. Majumder, B. Perez, B. Roy, A. Martinez and R.S. Katiyar, Dept of Physics, Univ of Puerto Rico, San Juan, PR.

Electrical characteristics of ferroelectric thin films in planar electrode configuration are important to characterize these materials for their applications in tunable microwave and micro-electro mechanical devices. In the present work we have prepared polycrystalline $Pb_{1-x}Nd_x(Zr_{0.53}Ti_{0.47})_{1-x/4}O_3$ (x = 0.0 to 4 at%) thin films on platinized silicon substrate by sol-gel technique and characterize them in terms of their dielectric and ferroelectric properties by depositing planar interdigital finger electrodes on the surface of the films by electron beam lithography. It was found that the capacitance decreases with Nd addition indicating the dielectric property deteriorates with doping. However the dielectric loss decreases with Nd doping. The capacitance and loss tangent of undoped and 4 at% Nd doped PZT films measured at 100 kHz were found to be 138 pF, 0.033 and 95 pF, 0.019 respectively. The tunabilty, calculated from the measured capacitance vs voltage plot was found to be independent of Nd doping ($\sim$ 0.33). Saturated hysteresis loops were obtained in undoped PZT film by applying 100V across 5 μm electrode separation. Nd doped PZT films, on the other hand, electrically shorted at much lower applied voltage ($\sim$ 50V). AFM micrograph indicates undoped PZT films have smooth surface with uniform grain size distribution, whereas Nd doped PZT films has relatively rougher surface with exaggerated grain growth. The observed electrical characteristics are correlated with the observed surface morphology of these films. This work is supported by DAAG19-19-1-0362 and NSF-DMR-9801759 grants

SESSION CC13: PIEZOELECTRIC MATERIALS, CAPACITORS, AND NOVEL DEVICES

Chairs: Susan Trolier-McKinstry and Paul Muralt
Thursday Morning, November 30, 2000
Room 312 (Hynes)

8:30 AM *CC13.1
SINGLE AND COMPLEX OXIDE FILMS FOR INTEGRATED MODULES. Mareike Klee, Rainer Kiewitt, Wolfgang Brand, Philips GmbH Forschungslaboratorien, Aachen P. Lok, Philips Discrete Semiconductors.

Single oxide as well as complex oxide layers such as Ta2O5 as well as Ba1-xSrxTiO3 or PbZrxTi1-xO3 are intensively studied since more than 10 years as dielectric thin films for high density dynamic random access memories as well as ferroelectric non-volatile memories. These dielectric thin films have, however, not only relevance for active devices. In the last few years, dielectric films with a thickness of 0.1-1 m and relative permittivities of 40-2000 are especially studied for high performance miniaturised circuits. Integrated capacitors, resistors and inductors offer miniaturised circuits with high performance, which gain especially relevance for the mobile communication, wireless data transfer and electronic data processing market. The processing and performance of undoped as well as doped single oxide as well as complex films will be discussed with respect to their performance and application in integrated modules.

9:00 AM CC13.2
THIN FILM SUPERLATTICES OF LEAD BASED RELAXORS.
Michael Corbett, Marty Gregg, Robert Bowman, Queens University Belfast, Department of Pure and Applied Physics, Belfast, Northern Ireland, UNITED KINGDOM.

Previous work has shown exciting potential in superlattice ferroelectric studies replicating many features normally associated with relaxor electroceramics. To date no investigation involving superlattice studies has been performed. We report studies of single layer thin films of the lead based relaxors $PbMg_0.33Nb_0.67O_3$ and $0.2PbZn_0.33Nb_0.67O_3$-$0.8BaTiO_3$ fabricated on MgO(100) substrates using Pulsed Laser Deposition. The effect of pyrochlore on the dielectric constant and curve shape of $PbMg_0.33Nb_0.67O_3$ capacitors is investigated and shown to be less detrimental than reported in bulk. $0.2PbZn_0.33Nb_0.67O_3$-$0.8BaTiO_3$ capacitors are 100% perovskite in content and exhibit relaxor behaviour. Superlattices of the two materials were fabricated with different stacking periodicities starting from a simple bi-layer to 150 layers. Satellite peaks in x-ray diffraction traces of the 30 layer and 60 layer structures were used to estimate layer and film thicknesses. Dielectric results do not show a dramatic increase in dielectric constant as has been previously reported for ferroelectric materials and overall, contrary to ferroelectric superlattice structures, the quality of the capacitors inproved for increasing layer density.

9:15 AM CC13.3
RAMAN MICROPROBE STUDY OF CRYSTALLINE BULK AND THIN-FILM RELAXOR FERROELECTRIC PZN-PT.
Jonathan E. Spanier[a], M. Levy[b], Irving P. Herman[a], Richard M. Osgood, Jr.[a], and A.M. Bhalla[c]. [a]Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY. [b]Department of Physics, Michigan Technological University, Houghton, MI. [c]Materials Research Laboratory, Penn State University, College Park, PA.

We report on the use of polarized micro-Raman scattering as a highly effective and nondestructive probe of the structural and ferroelectric properties of crystalline bulk and thin-film relaxor ferroelectric $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$ - $0.045PbTiO_3$ (PZN-PT). Thin single-crystal PZN-PT films were prepared by ion implantation and slicing [1]. Raman studies conducted in the temperature range of 20°C to 600°C demonstrate that the structural quality of these films is comparable to that of the bulk, opening possibilities for new piezoelectric devices based on this material. The rhombohedral-to-tetragonal (R-T) and tetragonal-to-cubic (T-C) phase transitions are observed by distinctive changes in the Raman scattering polarization selectivity not previously reported. Raman scattering is seen to be a probe of the presence and absence of long-range ferroelectric ordering and nanodomains. The origins of the Raman peaks and their polarization selectivity are discussed. M.L. and R.M.O. gratefully acknowledge support by NSF under Grant No. ECS-9980828. I.P.H. and J.E.S. gratefully acknowledge support by the Joint Services Electronics Program (JSEP) under Contract No. DAA-G05S-97-0166.
M. Levy, R. M. Osgood, Jr., R. Liu, L. E. Cross, G. S. Cargill III, A. Kumar, and H. Bakhru, "Fabrication of Single-Crystal Lithium Niobate Films by Crystal Ion Slicing," Appl. Phys. Lett. **73**, 2293 (1998).

9:30 AM CC13.4
EFFECTIVE BEHAVOIR OF POLYCRYSTALLINE FERRO-ELECTRIC THIN FILMS. Kaushik Bhattacharya and JiangYu Li, California Institute of Technology, Pasadena, CA.

Ferroelectric films are increasingly being used as microactuators in MEMS devices. This talk presents a theoretical study of domain patterns as well as the effective piezo-electric and electro-strictive response of single and polycrystalline ferroelectric films. The results are used to study the comparative advantages of single versus polycrystalline films, and predict the optimal textures in polycrystalline films. A ferroelectric thin film has three relevant length-scales – the domains (or walls), the grain size and the film thickness. These length-scales can have a variety of mutual ratios, but each is much smaller than the lateral extent of the film. Starting with a Landau-Devonshire formulation at the smallest scale, the effective behavior of the film is calculated as the three length-scales become small compared to the lateral extent of the film. Relaxation and homogenization techniques are used to implicitly account for the domain and the grains. The result is an understanding of the effective (piezo-electric and electro-strictive) response of the film as a function of the texture, the grain size, the grain morphology, the film thickness and the crystallography.

9:45 AM CC13.5
EPITAXIAL $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ RELAXOR FERRO-ELECTRIC FILMS GROWN BY A 90° OFF-AXIS SPUTTERING TECHNIQUE. S.D. Bu, M.K. Lee and C.B. Eom, Department of MS&E, University of Wisconsin, Madison, WI.

90° off-axis magnetron sputtering has been attractive and widely used for large area deposition of high quality complex oxide thin films because of its simplicity and reproducibility. It has already been demonstrated that this process can grow various perovskite oxide epitaxial heterostructures with the smooth surfaces required for multilayered device applications. We have grown epitaxial $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (67/33) (PMN-PT) films with various orientations by 90° off-axis magnetron sputtering. The epitaxial $SrRuO_3$ and $BaRuO_3$ sputtered on $SrTiO_3$ substrates were used as electrodes. We found that the geometry of the target to the substrate is an important factor in the growth of epitaxial PMN-PT films. The effect of target composition, in particular Mg, was studied by XRD on the growth of PMN-PT films, its relation with the second phase will be discussed. The (001), (110), and (111)-oriented epitaxial PMN-PT films has been obtained with pure perovskite phase, their full width at half maximum, respectively, were 0.41°, 0.34°, and 0.67°. The correlation with film orientation and electrical properties such as piezoelectric coefficient and remnant polarization will be discussed.

10:30 AM *CC13.6
MACROSCOPIC ACTUATORS USING THICK PIEZOELECTRIC COATINGS. Michael Sayer, Geoffrey Lockwood, Timothy Olding, and Guofeng Pang, Queen's University, Dept of Physics, Kingston, ON, CANADA.

Devices ranging from self-contained biomedical imaging transducers, to piezoelectric transformers to actuated large area surfaces require actuating piezoelectric structures in the thickness range of 10-50/mum. Potential fabrication technologies include the lapping of bulk ceramic, tape casting, screen printing of glass frit based inks and sol gel composite processing. The relative piezoelectric performance and fabrication characteristics of each technology will be reviewed with particular emphasis on their compatibility with silicon based semiconductor process methods. Patterning methods for active device structures using laser machining, ceramic micromolding and screen printing will be discussed. Particularly in the case of laser machined and micromolded sol gel composites and laser machined bulk ceramic, the fabrication of annular and linear ultrasonic biomedical imaging arrays operating in the frequency region of 50 MHz will be described and their performance will be compared. Design issues for larger area piezoelectrically actuated surfaces such as mirrors will be considered.

11:00 AM CC13.7
HIGH FREQUENCY THIN FILM FERROELECTRIC ACOUSTIC RESONATORS. Paul Kirby[a], Qing-Xin Su[a], Eiju Komuro[b], Masaaki Imura[b] and Roger Whatmore[a]. [a]Nanotechnology Group, School of Industrial and Manufacturing Sciences, Cranfield University, Cranfield, Bedford, UNITED KINGDOM. [b]Telecom Technology Development Centre, TDK Corporation, Higashi-Ohwada, Ichikawa-shi, Chiba, JAPAN.

A Thin Film Bulk Acoustic wave resonator (FBAR) is a resonant piezoelectric device, similar to the more familiar bulk acoustic resonators, which typically use thin quartz plates but scaled down in thickness so as to operate at higher frequency. Usually a membrane of thin film piezoelectric material is supported on a silicon structure that is created by silicon micromachining techniques. Combining piezoelectric thin films with micromechanical silicon structures offers a means of producing resonant structures whose impedance varies rapidly in the 1-3GHz frequency range. The devices can be directly integrated with silicon or GaAs high frequency circuits. Multiple FBARs can then be arranged to form compact, low insertion loss filters that could be suitable for applications in mobile communications. To date AlN and ZnO thin films have been used successfully as the piezoelectric layer in the FBAR structure and a range of filter configurations have been investigated. The low electromechanical coupling observed in these materials leads to low-bandwidth filters. Here we have used materials with large electromechanical coefficients. In this talk we will discuss the fabrication processes for combining ferroelectric materials, particularly $Pb(Zr_xTi_{1-x})O_3$, with silicon micromechanical devices. The importance of optimising the growth of PZT on Pt electrode structures will be emphasised. The high frequency performance of ZnO and ferroelectric PZT FBAR structures will be compared. A description will be given of the equivalent circuits that can accurately model the impedance data. Values for the derived electromechanical coefficients, acoustic velocity and loss mechanisms will be discussed. The performance of ZnO and PZT FBAR filters will be compared.

11:15 AM CC13.8
PIEZOELECTRIC STRAIN OF THIN EPITAXIAL FILMS MEASURED WITH TIME-RESOLVED X-RAY DIFFRACTION. Carol Thompson, Northern Illinois University, Dept. of Physics, DeKalb, IL, and Argonne National Laboratory, Materials Science Div., Argonne, IL; S.K. Streiffer, G.B. Stephenson, G.-R. Bai, Argonne National Laboratory, Materials Science Div., Argonne, IL; A. McPherson, J. Wang, Argonne National Laboratory, UPD, Argonne, IL; R.A. Rao, C.B. Eom, Duke University, Dept. of Mech. Eng. and Mat. Sci., Durham, NC.

A time-resolved x-ray diffraction method has been developed for evaluating lattice distortions of piezoelectric thin films simultaneously with the application of high-frequency electric fields to the sample. In this stroboscopic technique, a beam chopper with a 2.45μsec opening time is synchronized to probe the time structure of the lattice response during the application of a periodic electric field. By providing insight into the lattice deformations at the microscopic level, this technique complements methods of piezoelectric characterization that measure the macroscopic piezoelectric response. To illuminate the small thin film capacitors, and achieve sufficient strain resolution, we use the high brilliance provided by the Advanced Photon Source. We report results of real-time measurements of the piezoresponse of $Pb(Mg_{1/3}Nb_{1/3})O_3$ - $PbTiO_3$ films. This work is supported by the U. S. Department of Energy, Office of Science, under Contract W-31-109-Eng-38, and by the State of Illinois, under HECA.

11:30 AM CC13.9
ORIENTATION CONTROL OF $(Bi,La)_4Ti_3O_{12}$ FILMS PREPARED BY THE SOL-GEL TECHNIQUE. Eisuke Tokumitsu, Takeaki Isobe, Takeshi Kijima* and Hiroshi Ishiwara*, Precision & Intelligence Lab. *Frontier Collaborative Res Center, Tokyo Institute of Technology, Yokohama, JAPAN.

Required electrical properties of ferroelectric materials for nonvolatile memory applications depend on the types of FeRAMs. For ferroelectric-gate FET applications, it is necessary to reduce a remanent polarization, Pr, while a large Pr is required for capacitor-type FeRAMs. In this work, we demonstrate that crystalline orientations of sol-gel derived ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) films can be controlled by the growth conditions. It is important to control crystalline orientations of the BLT film to obtain desired electrical properties because BLT has large anisotropy. 25-300nm-thick BLT films were fabricated by the sol-gel technique on $Pt/Ti/SiO_2/Si$ substrates. Crystallization temperature was varied from 600 to 800 °C and Bi composition in the precursors was varied from 3.25 to 3.55. It is shown that the excess Bi can promote the crystallization, hence can reduce the crystallization temperature. (001)-oriented BLT films were obtained using a $Bi_{3.45}La_{0.75}Ti_3O_{12}$ solution when the films were annealed at 750 °C. A remanent polarization of 10 uC/cm2 was obtained for (001)-oriented film. On the other hand, (117)-oriented films can be obtained with BiO_x buffer layers and high crystallization temperatures, Correlation between electrical properties and crystalline orientations will be discussed 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).

11:45 AM CC13.10
EFFECT OF LEAKAGE CURRENT THROUGH THE FERRO-ELECTRIC LAYER ON RETENTION CHARACTERISTICS OF MFIS STRUCTURE. Masanori Okuyama, Mitsue Takahashi, Hideki Sugiyama, Kazushi Kodama, Toshiyuki Nakaiso and Minoru Noda, Graduate School of Engineering Science, Osaka Univ., Osaka, JAPAN.

Metal-Ferroelectric-Insulator-Semiconductor (MFIS) FETs are now being paid much attention as nonvolatile memories with nondestructive readout operation which follow good scaling-down rule. We have been analyzing the retention characteristics regarding the effect of charge injection between the ferroelectric and the insulator layers caused by the leakage current. The theoretical results has been obtained by analyzing a model which used the field dependent saturated polarization loop derived by S.L.Miller *et al.* and the current continuity principle and is based on the band-bending approximation at the surface of silicon. A real $Al/SrBi_2Ta_2O_9$(SBT)/Pt capacitor was prepared and studied in order to obtain some experimental parameters describing leakage current density through the ferroelectric layer as a function of time and applied field. The calculated retention curves of MFIS structures have shown good agreements with our experimental data. The numerical results have indicated that a slight increase of Schottky barrier height for the insulator layer ($\Delta\Phi_b$) provides sufficiently long retention time. When $\Delta\Phi_b$=0.08eV is assumed as an independent variable, retention time over 10 years is exhibited theoretically. This calculation suggests that a decrease of the leakage current through the ferroelectric layer can lead to excellent retention characteristics. In order to decrease drastically the leakage current, we newly propose a Metal-

Insulator-Ferroelectric-Insulator-Semiconductor (MIFIS) structure, which is expected more effective than an MFIS structure in terms of improvement of the retention characteristics. Our physical model has been also applied to an MIFIS structure which has an additional SiO_2 layer inserted between the top electrode and the ferroelectric layer of a MFIS where SiO_2 is assumed as the insulator layer. The calculated result has predicted that the insertion of the additional SiO_2 layer 1/10 as thick as the SiO_2 processed on the silicon is very effective to provide satisfactory retention time for the practical use.

SESSION CC14/DD6: JOINT SESSION HIGH-FREQUENCY APPLICATIONS OF FERROELECTRICS

Chairs: Quanxi Jia and Jon-Paul Maria
Thursday Afternoon, November 30, 2000
Room 312 (Hynes)

1:30 PM *CC14.1/DD6.1
MICROSTRUCTURE AND CHEMISTRY OF NON-STOICHIOMETRIC (Ba,Sr)TiO_3 THIN FILMS. Igor Levin, NIST, Gaithersburg, MD; Richard Leapman, NIH, Bethesda, MD; Debra Kaiser, NIST, Gaithersburg, MD.

The microstructure and chemistry of (Ba,Sr)TiO_3 thin films deposited on Pt/SiO_2/Si substrates by metalorganic chemical vapor deposition were studied using high-resolution transmission electron microscopy and quantitative spectrum imaging in electron energy loss spectroscopy. The grain boundaries in all films with overall Ti content ranging from 50.7% to 53.4% exhibit a significant increase in Ti/Ba ratio as compared to the grain interiors. The results suggest that the deviations of Ti/(Ba Sr) ratio from the stoichiometric value of unity are accommodated by the creation of Ba/Sr vacancies which segregate to the grain boundary regions. The films with Ti contents equal to or greater than 52% additionally contained an amorphous Ti-rich phase at some grain boundaries and multiple grain junctions; the amount of this phase increases with increasing overall Ti content. The analysis indicates that the amorphous phase can only partially account for the significant drop in dielectric permittivity accompanying increases in the Ti/(Ba Sr) ratio.

2:00 PM CC14.2/DD6.2
MICROSTRUCTURAL AND ELECTRICAL PROPERTIES OF La DOPED $Ba_{1-x}Sr_xTiO_3$ THIN FILMS FOR TUNABLE DEVICE APPLICATIONS. M.W. Cole, P.C. Joshi, E. Ngo, C.W. Hubbard, R.L. Pfeffer, M.H. Ervin, M.C. Wood, U.S. Army Research Laboratory, Weapons and Materials Research Directorate, APG, MD.

$Ba_{1-x}Sr_xTiO_3$ (BST) is a promising ferroelectric material for tunable microwave device applications such as electronically tunable mixers, delay lines, filters and phase shifters. Pure BST in thin film form offers tunabilities upward of 50% at bias voltages of less than 10 V, which is compatible with the voltage requirements of present semiconductor based systems. Unfortunately, the tradeoff to high tunabilities are high loss tangents, that is, $\tan\delta > 0.01$. It is well documented that small concentrations of dopants can dramatically modify the properties of ferroelectric materials such as BST. In this work we investigated the materials and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ solid solution thin films doped with La. The films were fabricated via metalorganic solution decomposition (MOSD) technique. The 0 to 20 mol% La doped films were characterized for materials, dielectric, and insulating properties. Specifically, x-ray diffraction (XRD) was used to assess film crystallinity, phase formation, and film orientation. Atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM) were employed to access surface morphology. Cross-sectional transmission electron microscopy (X-TEM), combined with energy dispersive spectroscopy (EDS) analysis, was used to detail the film microstructure and film-substrate interfacial properties. RBS was employed to access film stoichimetry. The electrical measurements were conducted on films in the MIM capacitor configuration. Our results show that La doping of BST results in a reduction of the film dielectric constant, loss tangent, and leakage current. The dielectric and insulating properties will be discussed and correlated to film microstructure, crystal structure, and the quality of the electrode-film interface in order to determine the trade-offs between material quality and potential device performance.

2:15 PM CC14.3/DD6.3
LINKING THE DIELECTRIC RESPONSE OF CERAMIC AND THIN FILM $Ba_xSr_{1-x}TiO_3$: THE EFFECTS OF STRAIN. Chris M. Carlson, Dept of Physics, Univ of Colorado, Boulder, CO; Philip A. Parilla, Tanya V. Rivkin, John D. Perkins and David S. Ginley, National Renewable Energy Laboratory, Golden, CO.

Ba Sr_{1-} TiO_3 (BST) has long been studied for its potential in a wide array of applications, including tunable microwave and RF devices as well as high-density memories (DRAM). A factor that has limited the performance of devices based on thin film BST and other materials is the differences in dielectric response between bulk ceramic materials and thin films. These differences are typically ascribed, in part, to the presence of residual strain in the film-substrate heterostructures. Here we present the correlation of residual strain, as measured by x-ray diffraction, with dielectric response in epitaxial BST (x=0.4) films grown on MgO substrates by pulsed laser deposition. Using a theory recently developed by Pertsev, et. al., we model the temperature, electric field, and strain dependence of the dielectric constant for a series of BST films with varying biaxial and hydrostatic strain. Both the biaxial and hydrostatic strain components produce linear shifts in the transition temperature and, therefore, the entire temperature dependence. A second effect of the hydrostatic strain is the suppression of the overall dielectric response due to an electric field that is internally generated by growth-induced defects. By means of these effects, the dielectric response of the entire series of BST films can be seen as strain-induced modifications of the bulk response. That is, our modeling shows strain to link the dielectric response of these films with that of the bulk material.

2:30 PM CC14.4/DD6.4
STRESS EFFECTS ON DIELECTRIC PROPERTIES OF EPITAXIAL $Ba_{0.6}Sr_{0.4}TiO_3$ THIN FILMS. B.H. Park, E.J. Peterson, Q.X. Jia, Los Alamos National Laboratory, Superconductivity Technology Center, Los Alamos, NM; J. Lee, Sung Kyun Kwan University, Department of Materials Engineering, Suwon, KOREA; X.X. Xi, The Pennsylvania State University, Department of Physics, University Park, PA.

Dielectric properties of $Ba_{1-x}Sr_xTiO_3$ thin films are strongly dependent on their compositions, microstructures, and stress states. Recently, many researchers have tried to investigate stress effects on the dielectric properties of $Ba_{1-x}Sr_xTiO_3$ thin films. Basic approaches to change the stress include the variation of substrates or variation of deposition conditions, such as oxygen pressure. Here we report our approach to manipulate the stress in the film by inserting a strain layer between the substrate and the main body of the film. In detail, we deposited epitaxial $Ba_{0.6}Sr_{0.4}TiO_3$(BST) thin films on MgO(001) substrates by inserting a very thin $Ba_{1-x}Sr_xTiO_3$ (x = 0.1 - 0.7) interlayer to manipulate the stress of the BST films. Since the only difference of those epitaxial BST films is the lattice constant of the buffer layers, we are very successful in controlling the stress of the BST films. We measured the dielectric properties of those films using coplanar capacitor structures at a 1 MHz frequency. BST films under small tensile stress showed larger dielectric constants and tunability values than those without stress as well as those under compressive stress.

2:45 PM CC14.5/DD6.5
$Ba_{1-x}Sr_xTiO_3$ THIN FILM CAPACITORS WITH COPPER ELECTRODES. Jaemo Im, O. Auciello, Materials Science Division, Argonne National Laboratory, Argonne, IL; A.R. Krauss, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL.

$Ba_{1-x}Sr_xTiO_3$ (BST) films are being intensively investigated for application as capacitor materials for Gbit DRAMs and as high frequency tunable devices. Pt is typically used as an electrode material for BST capacitors, because of its oxygen resistance. In the past few years, Cu has been investigated as an interconnect material for deep sub-micron integrated circuits (IC) due to its low resistivity and high electromigration resistance. Using Cu to replace the conventional Pt as electrodes for BST thin film based capacitors will lead to the low R-C delay for advanced ICs and to reduce conductor losses for high frequency devices. A key issue for the integration of Cu into BST thin film based capacitors is to prevent the oxidation of Cu electrodes at the interface during the BST deposition process. Our approach for this issue is to deposit initial thin BST layer at room temperature with conducting barriers between BST and Cu electrodes. Initial characterization of the Cu/BST/Cu capacitors grown on silicon substrates, using magnetron sputter-deposition, show very low losses ($\tan\delta \sim 0.002$, Q>500) with 25% tunability, measured at room temperature and 1 MHz. The effect of barrier electrode layer thickness and BST deposition temperatures, on the electrical properties of BST thin film capacitors will be discussed.

3:30 PM *CC14.6/DD6.6
MECHANISMS OF LOSS AND TUNABILITY OF FERRO-ELECTRIC THIN FILMS PROBED BY LATTICE DYNAMICAL STUDIES. X.X. Xi, A.A. Sirenko, A.M. Clark, Weidong Si, The Pennsylvania State University, Dept of Physics, University Park, PA.

Lattice dynamics is of central importance for the ferroelectric as well as dielectric properties of ferroelectric materials. For tunable devices using ferroelectric thin films, lattice dynamical studies provide important insights into the mechanisms of dielectric nonlinearity and

losses. Through Raman scattering, with and without bias electric field, and infrared ellipsometry studies in $SrTiO_3$ films grown by pulsed laser deposition, we find that the soft mode in the films is harder than that in bulk crystals. This observation is in agreement with the Lyddane-Sachs-Teller formalism to explain the low dielectric constant in the films. The existence of local polar regions is proposed as a critical factor determining the dielectric properties of ferroelectric thin films such as tunability and loss.

4:00 PM CC14.7/DD6.7

ELECTRIC-FIELD-INDUCED RAMAN SCATTERING OF $SrTiO_3$ AND $Ba_{1-x}Sr_xTiO_3$ THIN FILMS. A.A. Sirenko, I.A. Akimov, A.M. Clark, K. Chen, X.X. Xi, Department of Physics, Pennsylvania State University, University Park, PA.

We have performed Raman scattering experiments on $SrTiO_3$ (STO) and $Ba_{1-x}Sr_xTiO_3$ (BST) thin films grown by pulsed laser deposition. Electric-field-induced Raman scattering was studied using indium-tin oxide(ITO)/STO/$SrRuO_3$ and ITO/BST/$SrRuO_3$ structures in a parallel plate capacitor configuration. Temperature dependence of the phonon frequencies reveals a soft-mode in films higher in frequency than found in bulk crystals. This effect is explained by the existence of local polar regions induced by oxygen vacancies in the thin films. The local polarization due to these defects is the basis for the difference in soft mode frequencies in films and bulk crystals. Electric field measurements demonstrate hardening of the soft mode under applied electric fields, which is consistent with tuning of the static dielectric constant described by the Lyddane-Sachs-Teller (LST) relationship.

4:15 PM CC14.8/DD6.8

PSEUDO-SPIN FLOP TRANSITION IN OXYGEN-DEPRIVED BST THIN FILMS. Charles Hubert, Jeremy Levy, Dept of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA; Chris M. Carlson, Department of Physics, University of Colorado, Boulder, CO; Philip A. Parilla, Tanya V. Rivkin, John D. Perkins, David S. Ginley, National Renewable Energy Laboratory, Golden, CO.

Time-resolved confocal scanning optical microscopy is used to probe the local microwave dynamics of ferroelectric nanoregions in Oxygen-deprived $Ba_{0.4}Sr_{0.6}TiO_3/MgO$ thin films. The films are grown using pulsed laser deposition in an O_2 pressure ranging between 40 mT-250 mT. The biaxial strain is observed through x-ray measurements to cross from in-plane to out-of-plane at a growth O_2 pressure of approximately 85 mT. Both the in-plane and out-of-plane components of the ferroelectric polarization response at microwave frequencies are monitored as a function of a static electric field. Significant dielectric dispersion is observed in the out-of-plane ferroelectric response for the 85 mT sample, indicating the "softness" of this mode. Application of an in-plane field quenches the out-of-plane response. We attribute this behavior to a pseudo-spin flop transition in which the out-of-plane polarization (regarded as a pseudo-spin degree of freedom) reorients due to the externally applied electric field.
This work is supported by DOE contract no. DE-AC36-99G010337 (NREL) and by ONR contract N00173-98-1-G011 (U. Pittsburgh).

4:30 PM CC14.9/DD6.9

EXPERIMENTAL AND THEORETICAL INVESTIGATION INTO THE DIELECTRIC BEHAVIOUR OF FERROELECTRIC THIN FILM SUPERLATTICES. Marty Gregg, Deirdre O'Neill, Gustau Catalan and Robert Bowman, Queens University Belfast, Department of Pure and Applied Physics, Belfast, Northern Ireland, UNITED KINGDOM.

In an attempt to reproduce the physics and dielectric properties of relaxor electroceramics, pulsed laser deposition was used to fabricate thin film capacitor structures in which the dielectric layer is composed of a superlattice of $Ba_{0.8}Sr_{0.2}TiO_3$ and $Ba_{0.2}Sr_{0.8}TiO_3$. The properties of the capacitors were investigated as a function of superlattice periodicity. The dielectric constant was enhanced at stacking periodicities of several unit cells, consistent with relaxors. Enhancement was also associated with relaxation phenomena. However, such properties were found to be associated with relatively high dielectric loss. Analysis of the imaginary permittivity showed that fine scale superlattices conform to Maxwell-Wagner behaviour, indicating that 'relaxor-like' features may well be an artifact of increased carrier mobility. Comparison of data with that already published on superlattices suggests that previous claims of dielectric enhancement in superlattices may also be attributed to Maxwell-Wagner behaviour. In addition, a novel temperature-dependent transport model has been developed, which shows that all dielectric features of superlattice structures observed experimentally to date can be reproduced by Maxwell-Wagner formalism.

4:45 PM CC14.10/DD6.10

EFFECT OF THE LASER ENERGY AND NUMBER OF LASER PULSES ON THE MICROSTRUCTURE, COMPOSITION AND PROPERTIES OF BARIUM STRONTIUM TITANATE THIN FILMS SYNTHESIZED BY PULSED LASER DEPOSITION. C.G. Fountzoulas, J.D. Demaree, Army Research Laboratory, Weapons and Materials Research Directorate, Army Research Laboratory, APG, MD.

Thin films of novel barium strontium titanate (BSTO), deposited by the pulsed laser deposition (PLD) technique exhibit excellent electronic properties including tunable dielectric constants and low electronic loss. The microstructure of the film influences the electronic, and mechanical properties (internal stresses and adhesion), important factors affecting the mechanical integrity and reliability of a device made of these thin films, which in turn influences the performance of the film. The BSTO thin films were synthesized at ambient temperature and 30 mT oxygen partial pressure, with 300, 400 and 500 mJ laser energy at 5, 10 and 20 pulses per second on silicon wafer substrates. All films were subsequently post-annealed at 750°C in an continuous oxygen stream. The thickness of the films increased with increasing laser energy and increasing pulse number. In particular, the thickness of the films synthesized at the same laser energy increased linearly with increasing pulse rate, while the thickness of the films synthesized at the same laser pulse rate increased non-linearly with increasing laser energy. The crystallinity and lattice constant variation of all films were studied with the aid of x-ray diffraction analysis. All post annealed films were crystalline. The microstructure of the films and particulate density were examined with the aid of optical microscopy, scanning electron microscopy (SEM) and FT-Raman spectroscopy. The film stoichiometry, and in particular the oxygen composition prior and after annealing, were studied with the aid of a Rutherford backscattering technique. The nanohardness, modulus of elasticity, cohesion and adhesion and wear properties of the films were studied with the aid of a nanohardness indenter and a ball-on-disk tribometer. The electronic, mechanical, physical properties and an initial microstructural zone model of these films will be discussed as a function of the laser energy and pulse rate. These results will be combined with the results of our previous work on the effect of substrate temperature and oxygen partial pressure on the microstructure and properties of the BSTO films.