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 32/2 (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 Streciher, Argonne National Laboratory
Paul Muraki, Swiss Federal Institute

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

8:30 AM *CCL.1
AN OVERVIEW OF F-RAM TECHNOLOGY FOR HIGH DENSITY APPLICATIONS
Christine Delah, Thomas Mokolajicz, Nicolae Nagel, Carlos Miguez, Emisum 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/interconnect 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 processing using SrTiO3/ThO2/SBT as ferroelectric layer, Pt as electrode material as well as 3-layer tungsten/aluminium metallisation are given.

9:00 AM CCl.2
INTEGRATED TiO2/Pt/PLZT/InOx FERROELECTRIC CAPACITOR WITH EXCELLENT FATIGUE AND IMPRINT PERFORMANCE FOR FRAM APPLICATIONS
Fan Chu, Glen Fox, Hamron International Corporation, Colorado Springs, CO.
Yoshinari Hori, Tatsuya Yamazaki, Fujitsu Limited, Iwate, JAPAN.

Doped PLZT [Pb, La]/[Zr, Ti]O3 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 facilitates 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 TiO2 stacking layer, Pt bottom electrode, doped (Ch and Sr) PLZT thin film and InOx top electrode. The ferroelectric performance, such as switching (Qc,r and Vac,r) fatigue and aging performance, was collected after the integration of PZT capacitors (after inter-layer contact process). The doped PLZT capacitor stack showed no fatigue at 5V 1013 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 1012 fatigue cycles at 3V (150V/cm). The excellent imprint performance of this integrated PZT capacitor structure will also be presented.

9:15 AM CCl.3
TWO TYPES OF LOCAL DEGRADATION IN FATIGUED PZT CAPACITORS FOR FRAM
Kimishiko Ito, Yuko Mori imizu, Teru Tatsumi, Takashi Ho, Hiroshiro Hia, Naoya Inose, 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 each other both in the dependence of phase images of piezoresponse. 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 bistable strain effect caused by the piezoelastic 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 new boundary regions and then extends to the interior of grains. On the contrary the pinning of domains is clearly observed in solgel-PZT films, and in fact both types of regions are found to coexist in fatigue processes. 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 solgel-PZT films. The apparent loss of ferroelectricity is explained either by the 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 present AFM study of incremental fatigue steps will be also presented which further support our model.

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

Real-time AFM imaging of domains in Lead Zirconate Titinate (PZT) shows that 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 vector, which is the various of grain boundaries 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 hypothesis, we have modeled the surface displacements at grain boundaries for different misorientations and compared these results to the observed displacements. Finite element analysis (FEO) is used to calculate the residual stresses resulting from these misorientations.

9:45 AM CCl.5
SCALING OF PROPERTIES IN FERROELECTRIC THIN FILMS

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Scaling of the ferroelectric and piezoelectric properties in Pb_0.5(Bi_0.35Na_0.65)O_3-0.25PbTiO_3 (PZNT) and PbTiO_3 thin films with thickness for non-polarized region. The piezoelectric and electrical properties were obtained from non-polarized thin film samples (1x1, 0.1-0.25, 0.05-0.09 and 0.02-0.07,μm). Three additional atomic force microscopy (AFM) based techniques were used to characterize these non-polarized devices. Piezoelectric, electrical polarization and capacitance spectroscopy measurements were done on the same set of films and the study of the correlation between the relative properties studied by these methods has been made. It was found that capacitors as small as 0.5×0.5×μm exhibit good piezoelectric/ferroelectric properties and that the sub-micron capacitors show resistance to bipolar fatigue with up to at least 10^8 cycles.

This work is supported by National Science Foundation - Materials Research Science and Engineering Center (NSF- MRSEC).

10:30 AM *CC1.12
ISSUES AND POINTESTIMATION OF HIGH DENSITY FRAM WITH QUARTER MICRON DESIGN RULE. Soon Oh Park, 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 pluggable buried contact (BC), making fine pattern of capacitor and back-end processing without hydrogen plasma damages. To avoid the oxidation of polysilicate, it is required to do 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 pyrolysis formation and to have the best crystallographic orientation. However, this temperature is too high to obtain the stable BC resistance. Therefore, we are developing MOCDVD PZT process of which deposition temperature is about 550°C. Even with this low temperature, the ferroelectric properties are maintained for the device fabrication. The 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 MOCDVD PZT, the film thickness can be reduced down to 180nm. A high etching slope etching process is very effective in obtaining each 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 ion is influenced by the ILD/EML process is a very serious issue because of the large side wall area. Very thin Al2O3 layer grown by atomic layer deposition is an effective hydrogen barrier. Furthermore, the step coverage of the Al2O3 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 COG 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 Soo Yi, II 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/SiO2/Si substrates using different methods. First approach was changing the spin speed 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 the solvent based PZT solution. In addition, to enhance the crystallization, the effect of PPO 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 results. The coercive voltage and leakage current were not so high. We could obtain 70 nm PZT film with excellent hysteresis 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. Kyoung Soek Lee, Yong Kyun Kim, Sungsoo Bae, Pohang Univ of Science and Technology, Dept. of Materials Engineering, Pohang, KOREA; Jong Kim, II Sub Chung, Samsung Advanced Institute of Technology, Microelectronics Lab., Materials Device Sector, Yongin, 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 the ferroelectric P-E hysteresis curve can be estimated. The electric field illuminated region was made confined exactly normal to the film substrate interface by patterning an isolated cap (1×2×1.2 mm²) and etching off the remainder in order to eliminate mechanical constraint from non-etched regions. The polarization under 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 the 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 MOCDVD. Takayuki Watanabe, Tomohiro Sakai and Hiroshi Fukunishi, Department of Innovative and Engineering Materials, Tokyo Institute of Technology, Kajino, JAPAN; Keisuke Saito, Application Laboratory, Analytical Department, Philips Japan, Ltd. Kawasaki, 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 BL SF thin films with different m numbers, i.e., Bi80.5Sb16.5O24.5 (BVO) (m = 1), Bi22Te2O58 (SBT) (m = 2), Bi12TeO22 (BIT) (m = 3), by MOCDVD and compared their ferroelectric properties. BVO, SBT and BIT films prepared on (110)SrRuO3/110SrTiO3 substrates are transparent 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 on (100) SrRuO3/100 SrTiO3 substrates showed (001)-orientation. In the case of SBT film, (001)-oriented did not show ferroelectricity, but (116)-oriented one showed ferroelectricity with spontaneous polarization (Ps) of 11.4 μC/cm². From these results, Ps value along a-axis of SBT can be calculated to be 2μC/cm² and this value almost agreed with the estimated one from SBT powder. On the other hand, in the case of BIT film, both of (001) - and (118)-oriented epitaxial grown films showed ferroelectricity with Ps of 4 and 27 μC/cm² 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 μC/cm² respectively. Those values were almost agreed with the reported values of BIT single crystal by S.E. Cuninns 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 BIT film was found to be almost same as that of powder. This is strongly related to the existence of large number of lattice distortion 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
MOCDVD OF Ir and IrO_2 Thin Films for PZT Capacitors. Manabu Shizuma, Kenzou Kitagawa, Masahiro Fujisawa and Hiroshi Niu, Himeji Institute of Technology, Dept. of Electronics, Himeji, Hyogo, JAPAN.

Highly oriented Ir and IrO_2 thin films were successfully prepared on SiO2/Si at 300-400°C by MOCDVD using a new Ir precursor, Ir(C5H4CH3)1.5(C5H5)2), and O2. This precursor was first used in our experiments. In a liquid at room temperature and a high vapor pressure (85°C/10 Torr) compared with conventional Ir solid precursors. Ir thin films obtained at 300-400°C were highly reflecting, and had a smooth surfaces (rms roughness : 1.434nm) and low resistivities of 23-44μΩcm. Values of rms roughness and resistivity were nearly threetimes those of sputtered Ir films prepared at 300°C MOCDVD-Ir films showed good step coverage of 73-80%, 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 MOCDVD-Ir bottom electrode at 600°C by MOCDVD. PZT capacitors with evaporated Au top electrodes showed good ferroelectric D-E hysteresis loops. Auger analysis for PZT/ Ir/SiO2/Si interface indicated that MOCDVD-Ir bottom electrode was a good diffusion barrier for PZT components (Ir, Zr, Ti). Fabrication of PZT capacitors with both top and bottom Ir-based electrodes using all MOCDVD process will also be reported.

SESSION CC2: INTEGRATION AND ELECTRODES

Chairs: Yoichi Miyawaki and Scott R. Simmerfelt
Monday Afternoon, November 23, 2008
Room 312 (Hynes)
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 high stability of this electrode will be discussed.

2:30 PM CST 2.4
STUDIES OF CONDUCTING DIFFUSION BARRIER THIN FILM GROWTH AND PROPERTIES VIA IN SITU SURFACE SENSITIVE ANALYTICAL TECHNIQUES. A. M. Driener1, D. M. Grimes1, O. Ascierto2, A. R. Kortan3, 4 and R. Ramesh4. Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL. 1 Material and Nuclear Engineering Department, University of Maryland, College Park, MD. 2 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 for integration of ferroelectric capacitors with CMOS devices. The Ti-Al layer can provide the double functionality of diffusion barrier and bottom electrode. The LSCO/Ti-Al layer exhibited a good chemical behavior where the Ti-Al layer had an amorphous microstructure. We are exploring the possibility of implementing Ti-Al and TiN as a conducting diffusion barrier for integration of FERAms with CMOS.

2:00 PM CST 2.2
OXIDATION RESISTANCE OF Ta2S3 DIFFUSION BARRIERS FOR STACKED CAPACITORS. E. Lelievre1, M. C. Hoag1, F. Brack1, J. M. Desvages1, B. Agius1, T. Vickeridge1, D. J. Kim2 and A. I. Kingon. 3Laboratoire Charles Fabry, Groupe Physique des Films M即使是, Université Paris Sud, Orsay, FRANCE. 4GPS, Université Paris 6, Paris, FRANCE. 5Dept of MSE, North Carolina State University, Raleigh, NC.

The integration of high permittivity perovskite oxides such as (Ba,Sr)TiO3 (BST) in advanced memory devices requires high temperature processing on O2 containing atmosphere. To prevent plugging 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. Therefore new materials have to be developed. In this paper we compare new results for the Ta2S3 system with earlier results for the TiN system. We report on the properties and the resistance to oxidation of Ta2S3 thin films deposited by reactive sputtering using a TaS3 target. The sheet resistance and the thickness of the Ta2S3 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 concentration). Films were then processed by rapid thermal annealing (RTA) at 500 °C and 750 °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 TaO were measured after the RTA treatments in order to extract information on the film compositions. The relationship between the depth profiles and the oxidation curves were deduced with the aid of the MEA simulations program. Oxide thicknesses after oxidation were measured by X-ray reflectometry. Significant differences were observed between the Ta2S3 and TiN systems in terms of oxidation rates, crystallinity, N loss during oxidation and conductivity.

2:15 PM CST 2.3
HIGHLY STABLE In2O3 ELECTRODE FOR FERROELECTRIC MATERIAL DEPOSITION. Fangyun Zheng, Zhiqiang Zhang, Sheng Hua, Jia-xu Man, Yishia Ouyang, Hong Ying, Weizhe Zhang, Sharp Laboratories of China, Ltd., Guangdong, China. Ohtsubo, Wendong Zhen, Norio Fujimura, Sharp Corporation, Nara City, Nara, JAPAN.

In2O3 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 In2O3 bottom electrode and annealed at 800 °C for accumulated 50 min. Excellent device performance was obtained. No intermixing and peeling of the bottom electrode were observed. This electrode was also used as electrode for other ferroelectric materials deposition for FERAms and DRAM devices. After depositing PGO on top of In2O3 bottom electrode by O2 plasma immersion, a smooth surface PGO can be obtained with well saturated hysteresis loop. SEM, TEM, XRD, AES, and XPS have been used to characterize the In2O3 bottom film and the interfaces between the ferroelectric material, In2O3 bottom electrode, and Si substrate. The composition and conductivity...
Ferroelectrics used in a memory device such as (Pb, Ln)/ZrTiO3 (PLZT) are vulnerable to reducing atmosphere and low 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 crumpled shape when the baking was carried out on a virgin capacitor. Although remanent polarization diminished in all cases, saturation polarization was not suppressed. The crumpled hysteresis loop can be described as an average of two loops shifted to positive and negative. 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 non-remanent hysteresis. In the secondary processes, oxygen gas is generated both from deposition gas of interlayer dielectric and from reaction between metal and moisture in the dielectric. Improvement of remanent polarization is required for the planarization and multi-layer application for the future devices. Reduction of remanent polarization is related to the impurities of the capacitor and can be improved by controlling the deposition condition of solgel PLZT and annealing IrOx electrode in oxygen.

4:00 PM CC2.7
DEGRADATION OF FERROELECTRIC Pb(Zr,Ti)O3 UNDER REDUCING CONDITIONS. Yuichi Shimakawa and Yoshimichi Kubo, Fundamental Research Laboratories, NEC Corporation, Tsukuba, JAPAN.

Solid-state chemistry analysis of Pb(Zr,Ti)O3 (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 SrBi2Ta2O9 (SBT) due to decomposition, the weight of PZT samples changes little during H2 annealing at typical process temperatures. Although no significant 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 0.02%) even after 45-H2-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 samples strongly suggest that the defects are introduced into PZT during H2-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. PzTiO3 decomposes through oxygen dissociation more easily than PbTiO3. 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 A SHOOTER PROCESSES. Choon Park, O-Song Kwon, Sun-Soo Seol, Jin-Woo Kim, and Hee-Koo Yoon, Hyundai Electronics Industries, Memory R&D Div, Icheon, KOREA.

Damage induced by metal etching and photoresist(PR) strip processes has been investigated for Pt/SrBi2Ta2O9 ferroelectric capacitors. Interconnect metal lines consisting of TiN/Ai/Ti/TiN/Ti layers was patterned by Cr/Au/Au chemistry and PR was stripped by O2/N2 plasma. Each 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 each machine nor each parameter 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 plasmas, helicon source plasma has very high plasma density. In this study, we correlated plasma density and charging of ferroelectric capacitors, and discussed discharge 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/SrBi2Ta2O9/Pt CAPACITORS FOR FERROELECTRIC MEMORY.

Suk-Kyoung Hong, B. Yang, Young Ming Kong, Seok Won Lee, Chang Goo Lee, Chang Won Suh, Nam Soo Kang, and K.H. Yoon, Peram 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/SrBi2Ta2O9/Pt (STO) capacitors was investigated. The electrical performance of the fine-patterned STO capacitors (2x2 100x100 mm²) as measured after Al-based metallization strongly depends on the ILD oxide types. Tetraethylorthosilicate (TEOS)-based undoped (U) or (U) doped (D) oxide films (ITO) 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 mm². While the ILD oxide of STO+TEOS-doped borophosphosilicate glasses (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 25-800°C and Transmission Electron Microscopy analysis indicate that the degradation of the USG-covered Pt/SBT/Pt capacitors was caused by pinhole, small Pt hillocks developed mainly on the bottom Pt electrode during recovery anneal processes performed at 700 or 800°C. 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 mm² 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 SiNx PASSIVATION FILMS FOR PZT FERROELECTRIC CAPACITORS BY CATALYTIC CVD. Toshitaka Masumura1, Yasuto Yonemura2, Yoshihide Fujimoto1, Takashi Nakamura2, Atsushi Matsuoka1, Hideto Masumura1, and Japan Advanced Inst. of Science and Technology, Ishikawa, JAPAN.

2nd Industrial Inst. of Ishikawa, Ishikawa, JAPAN. "Recm Co., Ltd., Kyoto, JAPAN.

Feasibility of SiNx 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 films are prepared by Cat-CVD. However, deposition on the substrate surface due to active hydrogen in Cat-CVD processes may occur, since SiH4 and NH3 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[Zr0.52Ti0.48]O3 (PZT) capacitors occurs by exposure to active ammonia cracking on catalyzer, when the sample temperature is lowered below 200°C by controlling the heat flow from the catalyzer. Therefore, SiNx films were prepared at low substrate temperatures of 175°C and 200°C using Cat-CVD. A ratio of the on-state current to the off-state current of SiNx/NH3, the refractive index of SiNx 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 2.13, deposited at 170°C was oxidized during air exposure for 10 days. After the deposition, 2) After 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 SiNx film, which is resistive for oxidation in air exposure, is prepared at 200°C. It is concluded that the SiNx films prepared at 200°C by Cat-CVD instead of degragation for ferroelectricity, are expected in 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 Rambani and John David Banack

Monday Evening, November 27, 2000

8:00 PM
Exhibition Hall D (Hynes)

CC3.1
INDUCTIVE-COUPLED RF MAGNETRON PLASMA PHYSICAL VAPOR DEPOSITION OF [Sr,Sr0.7T0.3] TiO3 (BST) FILMS TO CONTROL CRYSTALLITY AND MICROSTRUCTURE

An inductive-coupled plasma (ICP) in conjunction with a radio frequency (RF) magnetron plasma was applied to physical vapor deposition (PVD) of Barium Strontium Titanate Oxide (Bax Sr1-x) TiO3 (BST) films to control crystallinity and microstructure. 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-02 mixture gas (Ar-02 = 1) ambient at 20 Pa at 80°C indicated (200), (100), and (110) peaks. It is found that the ratio of (110) to (200) was not changed by the pressure but the ratio of (200) to (100) 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 work functions at BST/SiO2 and BST/Si interfaces were determined to be 3.55 eV and 1.96 eV, respectively. The work function of Ru was obtained to be 4.99 eV by photocell yield spectroscopy. An energy band diagram of Ru/BST/SiO2/Si illustrates system is determined.

**CC3.2**

**THICKNESS DEPENDENCE OF THE DIELECTRIC CONSTANT IN Sr0.5Ba0.5TiO3 (SBT) AND THE EFFECT OF TOP ELECTRODE MATERIAL.** Lesley G. Riemann, Robert Bowman, Marty Greg, Queen's University of Belfast, Department of Pure and Applied Physics, Belfast, Northern Ireland, UNITED KINGDOM.

Thin film capacitor structures of MgO/SrRuO3/SiO2/SrTiO3/Au prepared by Pulsed Laser Deposition. XRD showed perovskite SrRuO3 (SRO) and SrTiO3 (STO) layers with good crystallinity and respective orientations of (100)/(001) and (110). A nano-crystalline BST structure was observed from bright field TEM images. The capacitance exhibited low frequency dispersion and loss tangents: typically C(1kHz)/C(10kHz) is 0.05 and tan δ < 0.05. The dielectric constant was measured for BST thicknesses from 15 to 60nm and found to be consistent with the series capacitor model. Parameters from the model yielded information on the quality of the film capacitor structure. The effect of electrode properties of different top electrode materials deposited on the BST film was studied in an attempt to understand the role of the interfaces in the thickness dependence of the dielectric constant.

**CC3.3**

**ULTRA-TILN BST FILMS DEPOSITED BY METAL-ORGANIC DEPOSITION.** D.L. Kaiser, J.J. Ritter, J. Levin, P.K. Schenck, J.E. Blendell, J. Parke, J. Pask, Oxford University, NIST, Gaithersburg MD, H. Berstein, Raytheon Systems, TX.

Ba0.9Sr0.1TiO3 (BST) films with thicknesses down to 2 mm have been deposited on 5 cm diameter silicon wafers by spin coating. The coating solution was composed of a barium strontium titanium oxynitride acetate solution [([BaSe] / Ti = 1.00 / 0.01), glyceric acid acetate, isopropyl alcohol, and ethyl ether glycolic 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 was determined by electron microprobe analysis with dispersive spectrometry was 0.20 + 0.01 and (BaSe / Ti = 1.00 ± 0.05. The films were continuous, with RMS surface roughness of less than 1 nm as measured by atomic force microscopy. Film thicknesses were measured by light diffraction electron microscopy (HREM), reflectance mode spectrophotometry, and X-ray reflectivity. HREM examination also revealed a 2 mm to 7 mm thick amorphous interlayer between the BST film and the substrate. Films that were less than 5 mm thick were amorphous, even after annealing at 700°C.

**CC3.4**


Currently there is a considerable interest in the use of semiconducting oxides as candidate materials for next-generation MOSSFETS, in conjunction with high-k dielectrics such as SrTiO3 and ferroelectrics such as PZT. We have examined the interface electrical properties of epitaxially grown SrTiO3 (STO) / La0.6Sr0.4CuO (LSCO) and La0.6Sr0.4MgO (LSMO) (MOS) heterostructures on Nb-SrTiO3 (Nb-STO) substrates using C-V and I-V techniques. C-V studies indicate that the Nb-STO interface shows features corresponding to that of a oxide-semiconductor. No noticeable injection effects were observed indicating a “good” interface between STO and the semiconducting oxides. Major 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 ~2 ×1019/cm3 and is seen to increase with increasing temperature. LV studies show that the leakage current levels of these structures are as low as ~10−5 A/cm2 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 results of our structural, microscopic 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-9635251.

**CC3.5**

**PREPARATION AND CHARACTERIZATION OF MF AND MFS STRUCTURES USING SrTiO3, Nb2O5, AND THIN FILMS BY PULSED LASER DEPOSITION.** M. Ohkawa, T. Nakano, T. Yano, M. Nakano, and Minoru Noda, Graduate School of Engineering, Osaka Univ., Osaka, JAPAN.

SrTiO3 (STO)-La2O3 (STO) ferroelectric thin films have been prepared on Pt/SiOx/Si and SiO2/Si substrates by pulsed laser deposition (PLD) method. (111) oriented STO thin films were deposited at a low temperature of 60°C in N2 ambient gas of 0.001 Torr with composition ratio of x = 0.3. A x = 0.3 STO LSJ heterostructure of the STO 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/cm2, which is enough from theoretical analysis to control Si surface potential. A dielectric constant at room temperature is as low as 5. The remanent polarization of post-annealed films was not changed after 105 oscillations of polarization reversal. A counter electrode C-V hysteresis was observed in Metal-Ferroelectric-Insulator-Semiconductor (MFIS) structure using SrTiO3 (STO)-La2O3 (STO) on SiO2/Si at deposition temperature of 600°C, where a memory window of 1.5 V was obtained with measuring frequency, sweep voltage rate and width were 1 MHz, 0.25 V/sec and 0.1 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 V/sec. This result indicates that the hysteresis is originated from the ferroelectric property in the STO film. The gate retention time was about 20 sec when the voltage and time of pulse write were 0.2 V and 1 sec, respectively, and hold bias was -10 V. The time is in the same order as that in SrTiO3 (STO) previously we reported, although leakage in the STN is about by one 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/Be/La2O3/TiO2/Si, Si3N4/Si MFIS STRUCTURE FOR FET-TYPE FERROELECTRIC CORE MEMORIES BY THE SOL-GEL METHOD.** Takeshi Kijima, Yoshishina Fujisaki, Research and Development Association for Future Electron Devices, Tokyo Institute of Technology, Frontier Collaborative Res. Center, Yokohama, JAPAN; Takeki Ito, Eiunke Tokumatsu, Tokyo Institute of Technology, Precision & Intelligence Lab., Yokohama, JAPAN; Hiroshi Ishiiwa, Frontier Collaborative Res. Center, Tokyo Institute of Technology, Yokohama, JAPAN.

For FET-type ferroelectric memories, c-axis oriented (Be/La2O3/TiO2/Si) BLT films with small remanent polarization Pr of 4μC/cm2 have been investigated. BLT films were fabricated by the sol-gel method on a Si3N4 amorphous film formed by atomic nitrogen radicals. Using stereometric solgel solution, BLT crystallization could 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 thin film substrate of Si3N4/Si (Metal/ferroelectric/insulator/semiconductor) structure showed a C-V hysteresis property with a memory window of about 1V, which corresponded to the coercive voltage of 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 BiTTe2O6 THIN FILMS DEPOSITED DIRECTLY ON Si BY PULSE INJECTION MOCVD.** Jian Hyeong Kim, Jin Yang Kim, and Hyeong Joong Kim, School of Materials Science and Engineering, Seoul National University, KOREA.

Bi2Te3O6 (BTO) is a promising gate dielectric material for a ferroelectric field effect memory because it can offer considerable value of remanent polarization and low coercive force with good fatigue.
endurance. However, BIT thin films deposited on Si have been reported to have quite low polarization value for this application as well as a high fatigue endurance. Recently, In-doped BIT (BLT) thin film in MnF multi-layered structure was reported to have larger value of P, 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 8° Si MOSFET devices, which is advantageous to process integration. In this study, In-doped bismuth titanate (BLT), LiTaO\textsubscript{3}, LiNbO\textsubscript{3}, and TiO\textsubscript{2} films were very difficult to control the film composition as well as to obtain a good interface between the film and substrate. Hence, the pulse injection method was used to deposit the films, 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 physical and electrical properties of BLT thin films. In addition, we investigated the In doping effect on the ferroelectric properties in comparison with a Bi\textsubscript{2}Ti\textsubscript{4}O\textsubscript{9} thin film. The BLT thin films obtained by pulse injection showed a good interface and stoichiometric composition. The MFS capacitors exhibited a good ferroelectric phase transition, 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 writing pulses varied from 3 to 9 V. The properties of (Bi\textsubscript{2}La\textsubscript{0.8}Ti\textsubscript{0.2})O\textsubscript{3} thin films were strongly dependent on pulse injection conditions.

**C3.9**

**LOW TEMPERATURE PROCESSING OF LEAD BASED FERROELECTRIC CAPACITORS INTEGRATED ON Si USING DIFFUSION BARRIERS**

B.T. Liu, S. Agarwal, A.P. Monga, Y. Wang, R. Ramesh, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD.

Pb(Zr,Ti)O\textsubscript{3} based ferroelectric random access memories (FeRAMs) have received great attention because of its low operating voltage, low remanent polarization and fast switching speed. However, the integration into the high-density CMOS architecture, is restricted by high processing temperatures (typically 650°C) and the identification of electrically conducting diffusion barriers between the polycrystalline Si substrate 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 PtZrO\textsubscript{2} 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 DMR9639521 and Bellcore.

**C3.10**

**THE PROPERTIES OF MnF MOS CAPACITORS WITH HIGH k DIELECTRICS FOR ONE TRANSISTOR MEMORY APPLICATION**

K. Ono, T. Fujihara, Marubun, Tochigi, Japan.

MnF (Metal/Ferroelectric/Metal/Oxide/Silicon) capacitors with high k dielectrics have been proposed as one transistor memory applications. P type Si wafers were used as the substrates of MnF MOS capacitors. In the first, 3.5-15 nm thermal Si\textsubscript{2}, Zr\textsubscript{2}, Hf\textsubscript{2}, Y\textsubscript{2}, La\textsubscript{2}O\textsubscript{3}, and etc. thin films were formed on the Si substrates. Then, the upper layer Ti (20 nm thick) was deposited on the oxide layer by sputtering. After that, bottom electrodes (150 nm thick Ir) were deposited by electrochemical beam evaporation techniques. An oxide MOCDR window was further used for the growth of 260-300 nm thick c-axis oriented PbGe\textsubscript{0.9}Si\textsubscript{0.1} thin films on the Ir electrodes. Finally, the top electrodes (100 nm thick Pt) were deposited by electrochemical beam evaporation techniques to form the MnF MOS capacitors. The MFM capacitors with c-oriented PbGe\textsubscript{0.9}Si\textsubscript{0.1} thin films showed a good ferroelectric and electrical properties. Pt and TiC values were measured from 2 to 3.8 μC/cm\textsuperscript{2}, and from 30 to 35 kV/cm at an applied voltage 5V respectively. The leakage current of 3.6 × 10\textsuperscript{-7} A/cm\textsuperscript{2} at 100kV/cm and dielectric constants of 45 – 55 were obtained. The operation voltages of MnF MOS 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 MnF MOS capacitors. It was found that the memory windows increased with increasing Pr values of MnF capacitors, which was consistent with the calculation formula of the memory windows of MnF MOS capacitors. The basic mechanism were also investigated and discussed.

**C3.11**

**IMPROVEMENT OF RETENTION PROPERTY OF YMnO\textsubscript{3}/Y\textsubscript{2}O\textsubscript{3}/Si MnF CAPACITOR**

Norifumi Fujihara, Daiwa Inc., Kusako Kato, and Tatsuo Ito.

We have been proposing YMnO\textsubscript{3} with low remanent polarization and permittivity as a transistor type FeRAM, and reported that c-oriented YMnO\textsubscript{3} films are obtained on [111] Si with Y\textsubscript{2}O\textsubscript{3} buffer layer. Ferroelectric nature was confirmed by phase transition measurement.[1] However, the memory retention properties was not satisfied because of the poor crystallinity. We attempted to fabricate epitaxial YMnO\textsubscript{3} films on epitaxial Y\textsubscript{2}O\textsubscript{3}/Si structure in order to obtain highly oriented YMnO\textsubscript{3}/Y\textsubscript{2}O\textsubscript{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.[2]


**SESSION C04: POSTER SESSION**

**INTEGRATION AND ELECTRODES**

Chair: Katherine L. Swanger and Sunjung Aggarwal

Monday Evening, November 27, 2000

**C04.1**

**OXIDATION AND CONTACT RESISTANCE OF [Ti,Al]N AND TaSiN BARRIERS.** Francisco Aygunwes, Sungjin Kim and Angus I. Kingon, NC State, Dept of MSE, Raleigh, NC.

The preparation of ferroelectrics and high-permittivity perovskite materials, which are 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 also be correlated with O\textsubscript{18} depth profiling measurements undertaken at the University of Paris Sud. Determination of diffusion coefficients and activation energy, as well as electrical properties measurements reveal that the oxide for such a barrier is a compromise between electrical and oxidation resistance which depends 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 on the formation of a thin oxide component at the surface of the film.

**CC4.2**

**SUPPRESSION OF OXIDATION OF AN EPITAXIAL [100] ZnFILM ON Si DURING THE DEPOSITION OF THE IR FILM**

Sadashio Horii* and Susumu Horii, 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. To form bottom electrode, we have proposed the double layer structure of Ir on barrier metal Zn for PZT. However, the Zn film was oxidized by residual oxygen during the Ir film deposition. So, in this study, we tried to suppress the oxidation of Zn film during the Ir film deposition. The Zn film was deposited on Si (100) substrate with the temperature of 1100°C by RF sputtering with Ar and N₂ gas containing 4% H₂ at 850°C. At N₂/ArN₂ gas flow rate ratio of 5:50, we obtained an epitaxial [100]-oriented Zn film on Si with a cube-on-cube relationship and at 20%, the Zn film had the lowest resistivity of 1.41 μΩcm. The Ir film was deposited by RF sputtering with N₂ gas containing 4% H₂ instead of Ar at 600°C on the epitaxial [100] Zn/[100] Si structure. Although the sputtered Ir film was removed by a base pressure of less than 7x10⁻⁶ Pa, the Zn film was fully oxidized at the deposition rate of 0.5 mm/min. Then, by increasing the deposition rate to 25 nm/min, about 25% of entire Zn film was oxidized. In order to suppress the oxidation further, we placed 10 pieces of 10x10 mm² Zr metal plates on the non-erosion area of the Ir target with a thickness of 0.1 mm, because it is known that Zr particles can be expected to have high selectivity to granular roughness of the Zn film. In this condition, no oxidation of the Zn film was observed during the 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**

Hong-Kuk Yuh, Euijoon Yoon, School of MKE, Seoul National University, Seoul, KOREA; Sang Il 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 (IILD) deposition, passivation layer (Si₃N₄ 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 ferroelectric material. Also, it is well-known that 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 Pt bottom electrodes were prepared and exposed to hydrogen for 24 hours in a hydrogen atmosphere at 400°C. PZT films with Pt top and bottom electrodes (Pt/PZT/Pt), PZT film with a Pt bottom electrode (PZT/Pt), and PZT film with Pt and a metal electrode (Pt/Pt/MCVD) were used for the hydrogen annealing. After the hydrogen annealing, the Pt layer of the Pt/PZT/Pt capacitor dropped to almost zero. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed. The Pt/PZT/Pt capacitor was removed.

**CC4.4**

**MICROSTRUCTURES OF SrRuO₃ THIN FILMS EPITAXIALLY GROWN BY PULSED LASER DEPOSITION**

Sang Suk Kim, Byung II Kim, Sunchon National University, Depart. of Materials Science & Metallurgical Engineering, Sunchon, KOREA; The Soong King, Jung Ho Je, Pohang Science & Technology, Dept. of Materials Science Engineering, Pohang, KOREA; The Yeon Sung, Kwangju Institute of Science & Technology, Dept. of Materials Science, Kwangju, KOREA.

As one of the conducting oxides, SrRuO₃ has been receiving great attention due to its various useful properties. Along with its metallic conductivity, good compatibility 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 SrRuO₃ thin films have been successfully grown on different single crystal substrates by various deposition methods. However, understanding of mechanical behaviors and microstructures seem to be lacking. In this work, we prepared a series of ultrathin epitaxial SrRuO₃ thin films on SrTiO₃(001) using pulsed laser deposition. We then analyzed their microstructural properties mainly focusing on surface characterization and transmission electron microscopy. We discuss the early stage growth behavior and domain evolution of SrRuO₃ thin films.

**CC4.5**

**PROPERTIES OF REACTIVELY SPUTTERED HUIDUM OXIDE THIN FILMS**


The preparation of ferroelectric and high dielectric perovskite materials, which is required for memories, has been reported to be carried out by rapid thermal annealing (RTA) at temperatures ranging from 550°C to 750°C in nitrogen or oxygen environments. The presence of stress and the correct alignment of the electric field with respect to the domain walls is of importance. In order to overcome the problem of stress, we have developed a new technique using fluoride corrosion. We used a mixture of 10% KOH and 90% water as the etchant and we have observed anisotropic etching of the perovskite material. The result was that the etching rate of SrRuO₃ was higher than that of SrRuO₂. Therefore, we used SrRuO₃ as the etchant and we were able to obtain a good alignment of the domains. Finally, the material was deposited by reactive sputtering in oxygen plasma. The deposited and annealed samples were characterized using Rutherford backscattering spectroscopy (RBS) for Ti content and nuclear reaction analysis (NRA) for Ti content and nuclear reaction analysis (NRA) for Ti content. The relationship between the depth profiles and the measured excitation curves was deduced with the aid of the SPACES simulation program.
Technique, using RuCl₃ and H₂O 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 resistivity of 29 × 10⁻⁵ cm-ohm when annealed at 700°C. The presence of P₂, A₁g, and B₂g modes is consistent with the Raman spectrum of rutile. These modes as well as an additional unknown band at about 477 cm⁻¹ were investigated by temperature-dependent Raman studies. Based on the results, the band at 477 cm⁻¹ that disappears above 300 K is attributed to the hydrated RuO₂ present in the films. A detailed XPS analysis shows that the stoichiometry of RuO₂ in the films is close to the value of 1:2. The X-ray absorption measurements of RuCl₃, RuO₂, and hydrated RuO₂ were also detected. The presence of hydrated RuO₂ in the films by XPS analysis corroborates the Raman results. RuO₂ as a bottom electrode was found to enhance the ferroelectric properties of La modified lead titanate (PLT) films.

Temperature-dependent ferroelectric characterization of these films will be presented in detail.

This work is supported in part by DAAG55-98-1-0012 and DE-FG02-ER75764 grants.

CC4.8

REACTIVE ION ETCHING OF SOL-GEL DEPOSITED LEAD ZIRCONATE TITANATE THIN FILMS ON SF₆ PLASMAS


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. The reaction of PbO, ZrO₂, and TiO₂ with water, structure, dry etch processes are required to provide materials of etching patterned PZT. Reactive ion etching (RIE) has shown promise for dry etching of these films. This paper presents results obtained on RIE of PZT sol-gel films in a Plasma-Therm 720 RIE system with SF₆ etch gas, and compares them with results obtained in the past using H₂O/CF₄ (Fremont 124) etch gas. Pb/(Zrₐ,Tiₜ)O₂ sol-gel deposited onto SOI/Si substrates, patterned with a photoresist layer, and then etched in a photoresist etch mask. Previously, RIE of PZT in Fremont 124 plasma has resulted in relatively low etch rates (≥20 nm/min), and in the photoresist being scored with a carbon-type layer that made its subsequent removal difficult. Significant increases in etch rates with SF₆ plasma, etch rate increases up to 60 nm/min, and etch rates with applied power up to 75 nm/min at 300 W. Etch rates decreased with pressure increase due to distributed photodecomposition of ions and electron bombardment energy, suggesting an etch process that is dependent on ion-induced mechanisms. In addition, photoresist masks could be removed subsequent to etching, demonstrating that solvent RIE with SF₆ plasma is compatible with the common manufacturing technology of the silicon substrate. Scanning electron microscopy (SEM) revealed that smooth etched surfaces with anisotropic profiles were achieved.

SESSION C55 POSTER SESSION

FERROELECTRIC NON-VOLATILE MEMORIES - FUNDAMENTALS AND TECHNOLOGY

Chun-Chieh F. E. Demh and Shigenari Omori

Monday Evening, November 27, 2000

8:00 PM

Exhibition Hall D (Hynes)

C5.5.1 Properties of Au/Pt/Bi/Ti/Pt-Si FERROELECTRIC MEMORY DIODES. Jun Yu, Hua Wang, Xiaoming Dong, Wenli Zhou, Yunbo Wang, Lili Zhu, Hunzhang University of Science & Technology, Department of Electronic Science & Technology, Wuhan, CHINA.

A ferroelectric memory diode that consists of Au/Pt/Bi/Ti/Pt-Si multi-layer configuration was fabricated by pulsed laser deposition (PLD) techniques and were investigated. The P-E curve of the Pt/Bi/Ti/Pt-Si film system had a symmetric hysteresis loop with Pe=290 μC/cm² and Ec=84kV/cm, and the decay in remnant polarization was only 10% after 10⁶ switching cycles. The C-V curve and VPEI pulses were obtained from the ferroelectric polarization of Pt/Bi/Ti/Pt film. The current density was 6.7×10⁻³ A/cm² at a voltage of 4V, and the conductivity behavior is discussed. The results suggest that the growth of the Bi ferroelectric layer is helpful to increase the memory window and to reduce the current density by improving the serious interduction.

C5.5.2 PREPARATION AND CHARACTERIZATION OF SrBi₂Ta₂O₈ THIN FILMS ON [100]-ORIENTED LaNiO₃ ELECTRODES. J. H. Xu, G. D. Hu, H. H. Wilson, C. P. Li, and S. P. Wong, Department of Electronic Engineering, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, CHINA.

We have prepared SrBi₂Ta₂O₈ (SBT) thin films on [100]-oriented LaNiO₃ (LNO) electrodes at annealing temperatures of 600°C and 650°C on Pt/Ti/SiO₂/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 fabricated a (200)-oriented SBT thin film on LaNiO₃/Pt/Ti/SiO₂/Si substrate at 600°C. We have studied the effects of the LNO oxide electrode on the structure, surface morphology, dielectric, and ferroelectric properties of SBT thin films annealed at 600°C and 650°C. Although the remnant polarization of the (200)-oriented SBT thin film is not as large as expected, the film can be uniformly poled and imaged using an atomic force microscope in the piezoelectric mode.

C5.5.3 DIRECT COMPARISON OF STRUCTURAL AND ELECTRICAL PROPERTIES OF EPITAXIAL (001), (110), AND (103) ORIENTED SrBi₂Ta₂O₈ THIN FILMS. Ho Nyung Lee, Alina Vinicu, Stephan Seng, Nikola D. Zakharenko, Alina Pignolet and Dietrich Hesse, Max-Planck-Institut für Mikrostrukturphysik, Halle/Saale, GERMANY.

Epitaxial SrBi₂Ta₂O₈ (SBT) thin films with well-defined (001), (110), and (103) orientations have been grown by pulsed laser deposition (PLD). Relatively high remnant polarization (110) is valid for all cases of SBT films on STO substrates irrespective of their orientations. The measured remnant polarization and coercive field of (110)-oriented SBT films were 4.8 μC/cm² and 84 kV/cm, respectively, at a maximum applied electric field of 320 kV/cm. A higher remnant polarization (5.2 μC/cm²) and lower coercive field (52 kV/cm) than those of SBT (110) 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), (110), 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.

C5.5.4 FATIGUE-FREE La-SUBSTITUTED BISMUTH TITANATE THIN FILMS GROWN USING CHEMICAL SOLUTION DEPOSITION. Young Chon, Sun Hwan Lee, Gyu Chul Yi, and Hyun Myung Kang, 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 lanthanum strontium bismuth titanate (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 reliability 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, acetoacetic-based precursors were employed. The films were crystalized 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 remnant polarization and a coercive field of the BLT films annealed at 650°C are 6.9×10⁻⁴ μC/cm² and from 5 to 10 of μm, respectively. Furthermore, the films did not show any fatigue behavior after 10⁸ 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.

C5.5.5 MOVING KINETICS OF PRECURSORS FOR FERROELECTRIC SBF FILMS A. Berri, G. G. Condorelli, I. Fragnoli, Dipartimento di Scienze Chimiche, Università di Catania, Catania, ITALY.
MOCVD fabrication of SBT ferroelectric films is of great interest for Pb-Ra-M application. It is well suited for highly conformal layers when deposited by non-volatile memory technology and Laser ablation deposition. In this context kinetics and deposition mechanism poses a critical role as far as industrial scaling is concerned.

This paper reports on SBT deposition process adopting Sr(hfa)2(�), Bi(C6H4O2)3 and Ta(C5H5NO)3 precursors. Experiments were performed in a reduced pressure, horizontal cold wall reactor for single and multi component depositions. Surface morphologies were analyzed 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 technique (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 pressures and pulse parameters. Depending upon the experimental conditions, deposition processes occur either in the reaction rate limited regime or in the mass transport regime. Kinetics controlled by reaction rates (T=300°C to 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 SrBi2Ta2O9 THIN FILMS AND POYDYERS.**
R.R. Dua, P.S. Dhakal, A. Dixit, W. Perge, R.S. Kheriy, Department of Physics, University of Puerto Rico, San Juan, PR; R.E. Meghjani and M.S. Tamin, 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 SrBi2Ta2O9 powders with Ba (A site) and Nb (B site) substitutions using a novel solution based route. These powders were then pressed and sintered at 1050°C to obtain high quality targets. Thin films were prepared from these ceramic targets on Si(100) and Pt/TiO2/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) were 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 DAA15-94-1-0012, DAAD19-94-1-0062, and NSF DMR 9801759 grants.

**CC5.7**

**ROLE OF THE ELECTRODE MORPHOLOGY AND DOMAIN ORIENTATION ON THE DIELECTRIC PERFORMANCE OF BaTiO3, PbTiO3, AND Pb(Zr0.35Ti0.65)O3 THIN FILMS.**
José Guerrero, Florencio Sanchez, Jose Roldan, Marla V. Garcia-Cuecen, Cesca Ferrarin, Manuel Vecrila, Universitat de Barcelona, Departament de Fisica Aplicada i Optica, Barcelona, SPAIN.

Epitaxial ferroelectric Pb(Zr,Ti)O3 (PZT) thin films have been fabricated by pulsed laser ablation of a ceramictarget with the composition of the tetragonal to rhombohedral morphotropic phase boundary (MPB). Lattice matched La0.8Sr0.2TiO3 and SrTiO3, as well as [100] Silicon substrates have been used for the preparation of epitaxial Sr0.8La0.2TiO3 and La0.8Sr0.2TiO3 bottom electrodes with room-temperature electrical conductivities in the range of 150 Ohm-cm for both materials. Square hysteresis loops with remanence exceeding 40 μC/cm² are obtained for the PZT films on La0.8Sr0.2TiO3, which form in the tetragonal phase at lower temperatures, whereas for the rhombohedral phase above 75°C. The long-range stress is lost when PZT is grown on SrTiO3 due to orthorhombic domain pattern formation in the electrodedipole, along with its slightly rougher surface morphology. As a result, the rhombohedral phase typically has amplitudes of hysteresis loops lower than the tetragonal phase, as shown by P-V curves. We show that the phase formation can be tuned by modifying the deposition parameters, e.g. tetragonal PZT can be obtained on SrTiO3 when deposited at higher substrate temperature (75°C) than on La0.8Sr0.2TiO3. On the contrary, the influence of the electrode on the Zr/Ti ratio of 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 applications, especially for Solgate and Capacitance vs. Voltage measurements are also included. The role of the top electrode (Al, Au, SrRuO3, LaNiO3) is also studied: intrinsic and induced imprint is observed when symmetric electrode configurations are used.

**SESSION CC6: BST FOR DRA AND GATE ELECTRICS**
Chairs: Orlando Aubiello and Rainer Waer
Tuesday Morning, November 28, 2000
Room 312 (Hynes)

8:30 AM **CC6.1**

**THE EFFECT OF FORMING GAS ANNEALING ON METAL/ (Ba,Sr)TiO3/METAL THIN FILM CAPACITORS FOR FUTURE DRAM APPLICATIONS: ELECTRICAL PROPERTIES AND DEGRADATION MECHANISMS.**

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, which is commonly used to control SiO2/Si interface states, on the electrical properties of Pt/BSTO/Pt thin film capacitors. In the talk we will present the results of studies we have made on the electrical properties of passivated Pt/BSTO/Pt thin film capacitors that have been annealed in forming gas (5% Ar 5% H2 or D2) at temperatures between 280°C and 350°C. The BSTO film thickness is 150-100 nm thick) were prepared by metalorganic 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 to 1.05. Deuterium SIMS depth profiles for metal/BSTO/metal capacitor structures with thick, 50-nm, electrode metals (catalytic Pt vs non-catalytic Au) will also be presented. 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-Nordheim) formulation. We show that the data can be understood in terms of thermally 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 DOING AND REMOVAL FROM PEROVSKITE DIELECTRIC THIN FILMS.**
Rory V C. Wang, Wee-Lung Altm, Robert J. Becker and Paul C. Mhinterer, Department of Materials Science and Engineering, Stanford University, Stanford, CA; Steven R. Gilbert, Agilent Laboratories, Palo Alto, CA; Michelle Schulberg, Novellis Systems, San Jose, CA.

Exposure to hydrogen-containing environments may cause severe leakage current degradation and/or polarization degradation in high-k perovskite thin films. Charged hydrogen defects act as delocalized dopants and, in the case of leakage current degradation, their concentration to the space-charge layer within the dielectric film, 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 deuterium forming gas anneals. Distribution of deuterium in the films was probed by SIMS sputter-depth-profiling analysis. Post-doping gas recovery times in both inert and oxygen-containing ambient used 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 IMPPLICATIONS FOR DEVICE RELIABILITY IN LS-MOCVD (Ba,Sr)TiO3 THIN FILMS.**
C.B. Park, S-J Kim, and A.T. Kingon, North Carolina State University, Raleigh, NC.
(Bal7, 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 shift, AC shift, soft breakdown, and high temperature AC failure. Previous investigations of failure have focused on high temperature AC degradation, however, this failure under low temperature and AC stress appears to be a more closely approximates the real operating conditions of a BST capacitor. To understand the relationship between AC stress, and the resulting degradation of failure under low temperature DC and AC conditions has been performed under varying fields and frequencies. These measurements were also performed to determine the failure mechanisms of BST and thereby determine if this additional stress produces additional failure modes or accelerated rates. This work has combined 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 above yields 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 high density memories. While systematic structure-property studies and some reliability data have been reported for BST thin films grown by MOVCD 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 our investigation of the compositional, microstructural, and electrical properties of BST thin films deposited by low-temperature R.F. 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)TiO3 ON Ru. Minoroshi Tawatari, Takahiko Sato, Mikio Yamamoto, Takashi Kishinami, Tatsuo Horikiri, Takashi Takehashi, Yoshikazu Yonezawa, Takeshi Kuriyama, Tengo Shibano, Mitsubishi Electric Corp., Advanced Technology R&D Center, Hyogo, JAPAN.

Metal-insulator-metal [MIM] (Ba,Sr)TiO3 [BST] capacitor has attracted much interest for applications in future high density memories. Ru is promising as a top electrode material because of its feasibility in micro-machining 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 BST on Ru, including the plasma-annihilation by Ru annealing, the optimization of CVD process, and the control of Mo source flow-rate, which enables thin BST films of high-permittivity with a good leakage property. BST films were deposited by the flash 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 adjusting 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-cracks or micro-hilllocks in these films, which were confirmed to be caused by Ru oxidation. Therefore, an annealing process of the Ru electrode was added for its plasma-annihilation, 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<sub>eq</sub> ~ 0.45 nm and leakage current < 2 x 10<sup>-7</sup> A/cm<sup>2</sup>. 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 Bong, 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 >4 Gb DRAM applications. It is well known that etching BST/PT electrodes 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 redeposit on the etched Pt profile as well as on the side surfaces of the etch chambers, 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/PT capacitors, as well as how to overcome the problem of etching BST/PT with the etch by-products, thus controlling CD and improving productivity. The feasibility of etching <0.13 µm Pt electrodes in a Metal Etch DMS Century platform will be shown, as well as the good process repeatability and low particle counts. The results will be presented to demonstrate the manufacturability of etching Pt electrodes, BST defect prevention after etching and 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 / SrTiO3 / Pt CAPACITORS. Mitsuki Izuka, Tomomori Aoyama, Masahiro Kyotoku and Kazuhiko Fukuji, 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 easily oxidizable. Taking into account post-thermal stress 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 deposited highly c-axis oriented Ru films by CVD and applied them to the bottom electrode of Ru / SrTiO3 / Pt capacitors. Ru films were deposited using Ar-carried Ru-ethyl cyanoacetate (Ru[(CH<sub>3</sub>)<sub>2</sub>CN]<sub>2</sub>)[6] and Ru in a halogenated hexane-type nematic. By lowering the deposition temperature to 300°C, good step coverage (>95%, <0.13 µm hole, aspect ratio=5:4) were achieved. For 300°C deposition, lower partial pressure of O<sub>2</sub> tends to cause smoother surface morphology and lower resistivity (30 µΩcm). In order to obtain highly (092) orientation observed by XRD, in addition, the ratio between the partial pressure of Ru[(CH<sub>3</sub>)<sub>2</sub>CN]<sub>2</sub>] and O<sub>2</sub> was found to be important. If the partial pressure of Ru[(CH<sub>3</sub>)<sub>2</sub>CN]<sub>2</sub>] is close to that of O<sub>2</sub>, Ru[(CH<sub>3</sub>)<sub>2</sub>CN]<sub>2</sub>] probably dissolves to Ru and 2[(CH<sub>3</sub>)<sub>2</sub>CN] and so the Ru film grows on c-axis orientation. In the case of excess O<sub>2</sub> circumstance, by-products of Et-CN possibly impede the growth of c-axis oriented Ru films. Furthermore, we fabricated Ru / SrTiO3 / Pt capacitors using the highly c-axis oriented CVD-Ru films as a bottom electrode. Even after post-annealing at 650°C, the SiO<sub>2</sub> equivalent thickness was low (t<sub>eq</sub>=0.38 nm) and the degradation of leakage current was small (J<sub>leak</sub> ~ 1E-7 A/cm<sup>2</sup> at ±0.7V). As result, highly c-axis oriented Ru films by CVD were suggested to be excellent electrodes for threedimensional capacitors in next-generation DRAMS.

11:15 AM *CC6.8
PROPERTIES OF Ba,Sr,<sub>1−x</sub>TiO<sub>3</sub> THIN FILMS ON SILICON (100) SUBSTRATES GROWN BY MOLECULAR BEAM EPITAXY. J. Ramdehi, LL. Hie, Z. Yu J.A. Barlow, C.D. Overgaard, J. Finder, K. Eisenbeiser, R. Droopad, W.J. Ooms, Physical Sciences Research Laboratories, Motorola Labs, Phoenix, AZ. Digital DNA 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, SrOyTiO3-x (STO) and Ba,Sr,<sub>1−x</sub>TiO<sub>3</sub> (BOTO) are excellent candidates for CMOS gate dielectric and ferroelectric materials. In the present work, we will report on the growth and characterization of STO, Ba,Sr,<sub>1−x</sub>TiO<sub>3</sub> (BOTO) on Si, Ge, and Si<sub>1−x</sub>Gex, and MBE on Si by using a 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, HREM were used to characterize the films. As grown, STO/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 5±5 nm. The optimization of growth sequence has led to an amorphous layer as thin as 7±4 nm. The C-O character lines show an excellent oxide formation, as thin as 9±9 nm for a 50±5 thick STO and a leakage current as low as 0.2 mA/cm<sup>2</sup> at -1 Volt. We will discuss the origin of this amorphous layer its stability and impact on the material and electrical properties. BTO will be characterized using the same 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 (\(120 \mu \text{m}\)) 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 \(\text{SrTiO}_3/\text{Si}
\)
HETEROSTRUCTURES BY HRTEM. G.Y. Yang, R. Ramaswamy,
University of Maryland, Materials Research Science and Engineering
Center, College Park, MD. J. Finder, E. Wang, J. Yu, J. Ramdani, R.
Droegemeier, K. Eisenbeiser, Motorola Inc., Physical Science Research
Laboratory, 3001 ZJ, W. Germany, School of Materials Science and Engineering, Atlanta, GA.

Deposition of \(\text{SrTiO}_3\) (STO) dielectric films on silicon substrates is of much interest since \(\text{SrTiO}_3\) 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 electrical characteristics 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 \(\langle 001 \rangle_{\text{STO}}/\langle 001 \rangle_{\text{Si}}, \langle 100 \rangle_{\text{STO}}/\langle 110 \rangle_{\text{Si}}\). It was established that, under appropriate processing conditions, the \(\text{SrTiO}_3/\text{Si}
\)
interface was abrupt to within one atomic plane and the interface most likely consists of Si bonded with O in \(\text{SrTiO}_3\), forming 2x1 and 1x1 domains. Latent rotation of \(\text{SrTiO}_3\) on \(\langle 001 \rangle_{\text{Si}}\) surface of Si substrate by 45°

Under these conditions, the minimum difference in crystallographic parameters and crystal chemistry between \(\text{SrTiO}_3\) 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. Misorientation directly correlated with the Si substrate surface roughness. Stacking faults confined within the STO might be revealed from layer by layer deposition. In this paper, we present results of our HRTEM imaging and corresponding image simulation studies to carefully examine the structure and chemistry of the interface.

This work is partly supported by a NSF-MRSEC under grant No. DMR-9623521.

SESSION CC7 FUNDAMENTAL PROPERTIES OF FERROELECTRIC THIN FILMS
Chair: 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. Ramaswamy,
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 extensive studies in the composition of the 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 (cations and vacancy defects, and alkali or alkaline earth 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 \(\text{Si-H}\) ) and cationic defects (specifically local ionic 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 MICROSCOPES OF FERROELECTRIC SURFACES.

In the last few years a wide spectrum of non-contact, intermittent contact and contact scanning probe microscopies have been applied to investigate ferroelectric surfaces. The imaging mechanism of 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 electro-mechanical coupling and surface charge via capacitive interactions. Quantification of surface properties from SPM data represents a largely unresolved problem. In this paper we analyze the contact formation mechanism in PFM using an analytical approach for the piezoelectric phase 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 electrostrictive 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. Various temperature PRI imaging was performed and the temperature dependence of the piezoresponse compared with the Ginzbarg - Devonskaya theory. To simultaneously study surface potential and polarization distribution a novel dual scan-line modification of PRI was implemented. Relevant theory, existing differences and experimental results are discussed.


2:15 PM CC7.3

Two scanning probe microscopy modes have been used for the characterization and manipulation of ferro-electric (FE) films. TUNNELLing-AM (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 sample. The current flow through the probe is measured using a linear low current amplifier, which has a range of 80 nA 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 observed in the Barium Titanate sample. A second technique, SCM has been used to investigate microhysteresis and image the domain polarization in different FE films, including PZT and SiBT 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 comparable 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 MEASUREMENTS IN FERROELECTRIC THIN FILMS USING SCANNING NONLINEAR DIELECTRIC MICROSCOPY. Hirotsugu Odaigawa, 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 crystalline anisotropy of dielectric materials, and termed “scanning nonlinear dielectric microscopy” (SNDM). Using this system we observed a ferroelectric polarization distribution in various ferroelectric materials with nanometer resolution, and reported the results in this paper. Using this new technique, we observe new types of scanning nonlinear dielectric microscopy (SNDM), with additional function of simultaneous observation of surface morphology, is developed. This technique uses a novel technique of scanning nonlinear dielectric microscopy, with nanometer spatial resolution, and reported the results. In this paper, this new technique of scanning nonlinear dielectric microscopy (SNDM), with an additional function of simultaneous observation of surface morphology, is developed. It 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 domain patterns 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 results show that nanosized 180° c-o ferroelectric domain with the width of 1.5 nm for PZT film having a good correlation with a topography image are observed. The result also shows that the resolution of the microscope is less than 0.3 nm for PZT thin film. Thus the SNM system with the function of simultaneous observation of surface morphology is very useful for understanding domain structures and domain dynamics of ferroelectric thin film.


2:45 PM C7.5

LATITUDE VIBRATIONAL PROPERTIES OF SrB$_2$Ti$_3$O$_9$, Ran Liu, Motozora, Materials and Structures Labs, Meizan, AZ; Peir Chen, Motozora, Materials and Structures Labs, Aizu, TX; Xinling Lu, Pengda Huang, University of Illinois at Urbana-Champaign, Department of Materials Science, Urbana, IL.

SrB$_2$Ti$_3$O$_9$ is one of the layered perovskite ferroelectrics with excellent fatigue resistance and thus has gained great interest in 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 behavior. In this work, we carried out Raman spectroscopy study of thin film, powder and single crystal SrB$_2$Ti$_3$O$_9$. At temperature above the Curie temperature, all 12 Raman modes expected from the tetragonal (I4/mmm) structure have been observed. These Raman modes were assigned to combinations of A$_1$, E$_g$, and T$_{2g}$ modes based on 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$_2$ modes were observed when the films were detected by laser. The Raman mode with electric field was found to be of A$_1$ symmetry and appearing only when light polarization lay in the a-b plane.

3:30 PM C7.6

TRANSIENT BEHAVIOR OF THE POLARIZATION IN FERROELECTRIC THIN FILM CAPACITORS. Rainer Winter, IFF, Research Center Juelich, GERMANY; Oliver Jäger, Michael Grassmann, METRIT GmbH, Ulrich Bätzner, Uh-Werke. Osterr. STEU. 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 rectangular pulse measurements. Decreasing the voltage level of the excitation pulses decreases 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 PbZT thin films on the switching properties are investigated. The films are produced by means of ion beam sputtering. A set of samples with different temperatures was prepared for the investigation. As a result 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 a phenomenological approach, which takes into account the Curie-van Schrödinger behavior, which can be observed in non-polar high-K materials as well as in ferroelectric thin films.

4:00 PM C7.7

SELF-POLARIZATION OF TEXTURED PZT THIN FILMS FORCED BY ELECTRODE-PZT INTERACTION. G. Schneeb Tillman, G. Gehrke, Dresden University of Technology, Institute for Solid State Electronics, GERMANY; P. Powolka, 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 fabricated uniformly. For this reason high and high elementary electric fields must be presented to model maring of the ferroelectric domain area and high resolution by pyroelectric spectroscopy of thermal wave distribution [inner intensity modulation method - 1LMM]. The reducing interaction of the metal electrodes with PZT during film deposition and cooling down leads to the formation of the electrically deficient a-axis phase. An asymmetric $\pi$-junction forms with a space charge distribution consisting of the positive space charge of the a-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$^3+$ 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 polaron condensation while electron hopping between Ti$^3+$ and Ti$^4+$ ions. By this way, a stable interface is formed above the Curie temperature Ti$^3$-Ti$^4$ dipole complexes are formed which nucleate domain formation and determine domain orientation during cooling down below the Curie temperature.

4:15 PM C7.8

STRESS-INDUCED ELEVATION OF THE SPONTANEOUS POLARIZATION IN Bi$_4$Ti$_3$O$_{12}$ (BTO) FILMS. W. D. M. Y. Y. Fang, X. Q. Pan, Dept. of Materials Science and Engineering, The Univ. of Michigan, Ann Arbor, MI; J. H. Hsu 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 Bi$_4$Ti$_3$O$_{12}$. 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 Bi$_4$Ti$_3$O$_{12}$/SrTiO$_3$ superlattice with a bilayer period of 10 nm was synthesized by reactive molecular beam epitaxy (MBE) on (100) SrTiO$_3$ substrate. Atomically abrupt interfaces between two constituents were achieved. Despite the large lattice mismatch between Bi$_4$Ti$_3$O$_{12}$ and SrTiO$_3$ (~3.0%), the high-resolution transmission electron microscope (HREM) 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 Bi$_4$Ti$_3$O$_{12}$ 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 ~50 GPa. Quantitative HREM studies revealed an enhanced displacement of Ti cations with respect to oxygen octahedra in the Bi$_4$Ti$_3$O$_{12}$ layers. Based on these results, the spontaneous polarization of the strained Bi$_4$Ti$_3$O$_{12}$ is determined to be about three times that of the bulk Bi$_4$Ti$_3$O$_{12}$, which agrees well with the prediction using the modified Landau-Ginsburg-Devonshire theory.

4:30 PM C7.9

FATIGUE DEGRADATION MODEL BASED ON FOWLER-NORDHEIM ELECTRON INJECTION. S. Sugama, N. Shinto, Toshikin 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 a 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 electrode to the ferroelectric film by Fowler-Nordheim tunneling, and are trapped at domain boundaries (and/or transition region-ferroelectric film interfaces). These electrons cause a fatigue polarization by inducing thermoelastic stress. 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/D dependence of fatigue characteristics on external stress voltage.

4:45 PM C7.10

EASY COLLECTIVE POLARIZATION SWITCHING IN FERROELECTRICS. A.M. Baskov, A.P. Levanyuk, Hewlett-Packard Laboratories, Palo Alto, CA.

Ferroelectric films with extended dielectric inhomogeneity, so called 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 is observed as soon as the nuclei are comparable to or larger than the domain wall thickness.
SESSION C8/B6.1 JOINT SESSION
DOMAINS IN FERROELECTRIC THIN FILMS
Chairs: Wen Wu, Tsao and Ramamurthi Ramas
Wednesday Morning, November 29, 2000
Room 313 (Hynes)

8:30 A.M. **C8.1/B6.1**
DOMAIN STRUCTURE AND SWITCHING IN FERROELECTRIC FILMS OBSERVED BY AFM. Angos L. Kinnun, NCSU, Department of Physics, NC; B. Rodriguez and D. Nemanich, NCSU, Department of Physics, NC; C.B. Parker, D.J. Kim and J-P. Marin, NCSU, Department of Microsystems, 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 wall in determining device switching characteristics and device lifetimes. In the first part of the presentation, we describe methods used to characterize the spatial variations of properties of the ferroelectric capacitors by characterizing the spatial distribution of the piezoelectric domains (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 wall in determining 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 fatigue regions is generally submicron. We discuss 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 simple which include the variables: PZT composition, field orientation, film microstructure, domain wall density, electrode type, capacitor dimensions, and prior fatigue cycling. Implications are drawn for high-density devices.

9:00 A.M. **C8.2/B6.2**
ELECTROMECHANICAL RESPONSE OF UNPOLED FERROELECTRIC STRUCTURES. Alexander Tagantsev, Olivier Steinic, Ceramics Laboratory, EPEL, 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 strains 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 crystal structure (spontaneous polarization) 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 ones. Here two results, which do not match the recent compiled general phenomenological predictions, are reported. First, there is no violation of the correspondence between the direct and converse electrostrictive effects when passing from the paraelectric ferroelectric phase of the material as it has been proposed by Zhang et al. [Q.M. Zhang, W.Y. Pan, S.J. Zhang, and L.E. Cross, Ferroelectrics v. 88, 147 (1988)]. Second, the effective intrinsic longitudinal electrostrictive coefficient of the polymer of structure of a perovskite ferroelectric, Z33, can be negative.

9:30 A.M. **C8.3/B6.3**
DOMAIN SWITCHING KINETICS OF PZT THIN FILMS AT HIGH FREQUENCIES. Takashi Tsuim, Song-Min Nam, Young-Hse 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 devices. A measurement apparatus of DME having a variable voltage circuit was developed using a voltage-source-current converter with virtual ground. The coercive field of the PZT thin films strongly depended on the measurement frequency. Nevertheless, their permanent polarization remained 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 fast polarization was obtained between In u and 1/En2 where u is a frequency and E is a coercive field. The intercept line (1/En2) is a limiting frequency of domain switching. The limiting frequency of domain switching (ln u) 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 design ferroelectric films was proposed for ferroelectric memories with high speed and low operating voltage.

9:45 A.M. **C8.4/B6.4**

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 polidomain 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-3). We have estimated the dielectric response d3/dE (the slope of the hysteresis loop) in the "passive" 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 "passive" layer 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".

10:00 A.M. **C8.5/B6.5**
FERROELECTRIC THIN FILMS: NANOSCALE CHARACTERIZATION BY SCANNING FORCE MICROSCOPY. Alexei Grunze, 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. Direct observation of their domain structure by the SFM piezoelectric technique was performed. 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 submicron ferroelectric capacitors will be presented.

11:00 A.M. **C8.6/B6.6**
GROWTH AND CONTROL OF DOMAIN STRUCTURE OF EPITAXIAL PbZr0.52Ti0.48O3 FILMS GROWN ON VITCIAL [001]. SeTo, V. Naganuraj, C.S. Gangule, S.P. Alpy, A. Roybnd, R. Ramesh, Univ. of Maryland, Dept of Materials Engineering, College Park, MD; D. G. Schom, Pennsylvania State University, Dept. of Materials Engineering, University Park, PA.

Highly tetragonal, epitaxial PZT films with a nominal composition of PbZr0.52Ti0.48O3 exhibit a 2-dimensional grid of 90° domains ( blocking 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 reversal and relaxation. Furthermore, we have observed that this arrays 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 vicinal cut [hkl] [001], [110], and [111] directions in the substrate plane) single crystal substrates to control the 90° domain formation. Epitaxial thin films of PbZr0.52Ti0.48O3 are 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 90° blocking domains 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 interactions of such structures with film thickness and substrate miscut orientation will be presented.

11:15 AM CCR.7/BB6.7
DOMAINS IN SrBi2Nb2O9 AND SrBi2Ta2O9 FERROELECTRIC FILMS. M.A. Zurbechun, J. Lettieri, Y. Jin, G. Asnaya and D.G. Schoum, Penn State Univ, Dept of Materials Science and Engineering, University Park, PA; SK. Streifer, Argonne National Laboratory, Materials Science and Engineering, Argonne, IL; M.E. Hawley, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM.

We recently reported SrBi2Nb2O9 films with the highest remanent polarization value attained to date in SrBi2Nb2O9 or SrBi2Ta2O9 films, P = 1.57 μC/cm² [1]. This was achieved by tilting the α-axis of SrBi2Nb2O9 by 9° from the substrate surface normal in order to get a significant component of the polar axis, the α-axis, aligned with the direction of the applied electric field in these [103] SrBi2Nb2O9 / [111] SrBi2Ta2O9 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-plane boundaries. Portions of the same films used for electrical field measurements were examined by TEM. Films grown in a 3-fold twin structure on the SrBi2Nb2O9 surface. Dark-field TEM imaging over a 12 μm² area shows evidence of second phases (crystalline or amorphous), which is important for high-density FRAM applications.

11:30 AM CCR.8/BB6.8
CELLULAR DOMAIN ARCHITECTURE OF STRESS-FREE EPITAXIAL FERROELECTRIC FILMS. S.P. Alpay, A.L. Boydurd, V. Nagarajan, U. of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; L.A. Benderly, 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-to-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 polidomain structures. The most commonly observed polidomain structure is the c/a/c/a polycrystalline, which relaxes the internal stresses only partially. Relatively thicker films may completely relax 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. 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 interface and relaxation by polidomain formation below the phase transformation temperature. The effect of the domain structure on the switching characteristics and physical properties is discussed.

This work was supported by NSF under Grant No. DMR-9983279 and by the NSF-MUSEC program under Grant No. DMR-9432921.

11:45 AM CCR.9/BB6.9
NEAR-FIELD OPTICAL SECOND HARMONIC IMAGING OF THE POLYDOMAIN STRUCTURE OF EPITAXIAL PbZr0.85Ti0.15 O3 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. Gargule, 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 has been applied to imaging of the c/a/c/a polycrystalline structure of epitaxial PbZr0.85Ti0.15 O3 thin films in the 0 ≤ x ≤ 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 nearer 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.

SESSION C9: PROCESSING, PROPERTIES, AND CHARACTERIZATION

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

1:30 PM C9C.1
ORIENTATION SELECTION MECHANISMS IN FERROELECTRIC PZT THIN FILMS. Gerd Norga, LauraFlex, Inc, 250 West Ave, Louvain, 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 spin 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 C9C.2
INFLUENCE OF Zr-ALKOXIDE MODIFICATION ON THE PROPERTIES OF PZT THIN FILMS. Barbara Malic, Marija Kasec, Zoran Stamenzija 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 crystalline and amorphous phases, 2-methoxyethanol based PZT sols were prepared from lead acetate, titanium n-propoxide and zirconium n-propoxide. The latter was used as received or mixed with acetic acid or acetonitrile prior synthesis. The sols were spin-coated on platinum 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 acetonitrile 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 eases the perovskite crystallization in thin films and decreases the crystallization temperature on (001) substrate. On platinum silicon 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 C9C.3
SURFACE REACTION MECHANISMS IN CHEMICAL VAPOR DEPOSITION OF Ba0.5Sr0.5TiO3 FILMS. M. Imai, M. Yamada, M. Kajii, T. Hara, Osaka University, M. Maeyama, T. Tanaka, Kawasaki, T. Honda, Waseda University, S. Tani, Tokyo University, T. Nishioka, T. Shibano, Mitsubishi Electric Corp., Advanced Technology R&D Center, Amagasaki, JAPAN.
3:30 PM C09.4
GROWTH OF BaSrTiO3 THIN FILMS IN A MULTIAVAPOR MOCVD REACTOR. P. Ehrhart1, F. Fisula2, S. Regens1, R. Waser1, F. Schielen3, M. Schulzeiner4, M. Drueck2, P. Strzyz2, H. Juergens5, JFF, Forschungszentrum Julich GmbH, Julich, GERMANY. 1AXTRON 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: 0.5 mol solutions of Ba(thd)2 and Sr(thd)2 and a 0.4 mol solution of Ti(O-tPr)2(thd)2. The thickness of the BST film was varied between 1.0 and 100 nm. The microstructure and the film stress were examined 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 promises 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 with regard to the different physical properties, especially the optical properties of LiTaO3 and LiNbO3 films. Stoichiometric LiTaO3 and LiNbO3 films were successfully deposited in this study using autoclave MOCVD. In this process, deposits are grown at atmospheric pressure 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 substrate composition analysis, was provided to study the stoichiometry of double alkoxide vaporization processes. The results used to choose suitable double alkoxide precursors to determine favorable deposition conditions. The vaporization processes of LiTa and LiNb double alkoxides with different carbon chains were studied systematically using this precursor analysis method. Stoichiometric LiTaO3, LiNbO3 and LiTaO3:LiNbO3 films were successfully grown on LiTaO3 and LiNbO3 substrates using both silicon and sapphire substrates using LiTa(x)OC4H9-x+LiNb(x)OC4H9-x as precursor for the deposition of LiTaO3 films and LiNb0(x)OC4H9-x as precursor for the deposition of LiNbO3 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 C09.8
EFFECT OF GROWTH TEMPERATURE ON THE DIELECTRIC PROPERTIES OF Pb(Sr1-x-Ba0 5)TiO3 THIN FILMS GROWN ON LA2O3 BUFFERED SIO2 USING MOCVD. C.H. Lin, P.A. Friddle, CH. Ma and Huygh Chen, Department of Materials Engineering, University of Illinois at Urbana-Champaign, Urbana, IL. T.B. Wu, Department of Materials Engineering, National Tsing-Hua University, Hsinchu, TAIWAN ROC.

Highly (002) textured Pb(Sr1-x-Ba0.5)TiO3 thin films were deposited using metal-organic chemical vapor deposition (MOCVD) technique at temperature ranging from 600°C to 650°C. Dielectric property of MOCVD thin film showed a large dependence on the growth temperature. For PST thin films with composition near its morphotropic boundary (x=0.3), the room temperature dielectric constant increased from 650 to around 1600 as the growth temperature increased from 600°C to 650°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 Pr ions in these PSTT films. The variations in the ionic state of Pr ions could result in the misalignment of Pb ions in the lattice. Thus, the space charge induced by the misplaced Pb ions degraded the dielectric properties of these 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 C9.9

ELECTRICAL PROPERTIES OF PLZT THIN FILMS SPUTTERED ON Pt/ArO⁻ BOTTOM ELECTRODE FOR FERROELECTRIC MEMORY APPLICATION. Yasuak Miyasugi, Koukos Sou, ULVAC Japan, Ltd., Chiba, Japan.

To realize high-density ferroelectric memory over 1Gb, ITIC cell architecture with ferroelectric capacitor stacked on plug structure (Studied Type: Capacitor, STC) is considered to be necessary to be introduced. The ferroelectric capacitor structures with Pt/ArO⁻ or Pt/ArO⁻/Ti bottom electrodes (BEs) which is being used in current planar 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 oxidation barrier is needed in between ferroelectric capacitor and plug. In this study, we chose ArO⁻ as oxygen barrier to form PLZT/Pt/ArO⁻/plug structure. PLZT thin films were deposited on Pt/ArO⁻ BEs using RF sputtering technique. The PLZT capacitors were evaluated in terms of orientation, PLZT film composition and characteristics performance. Good ferroelectric properties were obtained by optimizing sputtering conditions and PLZT film composition.

4:45 PM C9.10

SPECTROSCOPIC ELLIPSOMETRY STUDY OF THE STRUCTURE AND OPTICAL CONSTANTS OF Pb(Zr,Ti)O₃ THIN FILMS DEPOSITED BY SOL-GEL SPIN COATING. Masanari Hamana, John Yuen/Horton, Thin Film Group, Edison, NJ./Ronald G. Polkewich, Army Research Laboratory, AJSRL-SE-RL, Adelphi, MD.

Ferroelectric thin films are increasingly investigated for a wide range of applications ranging from electronic and electro-optic to micro-machining 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)O₃ (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 Pb(Zr₀.₅₂Ti₀.₄₈)O₃ 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 thickness was investigated over the wavelength 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 Pt 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: Aji Krishan Wednesday Evening, November 29, 2000

8:00 PM

Exhibition Hall D (Hyatt)

CC10.1

STRUCTURAL DISTORTION AND FERROELECTRIC PROPERTIES OF Sr₂Ba₂Ti₂O₇ and Cu₃Sr₂Ti₂O₇. Yoshie Shinkami and Yoshimi Kubo, Fundamental Ferroelectric Lab., NEC Corp., Tsukuba, JAPAN; Yuuki Tsuji, Takashi Kamiyama, and Hajime Asano, Inst for Mobi Sci, Univ of Tsukuba, Tsukuba, JAPAN.

Ferroelectric materials of the Sr₂Ba₂Ti₂O₇ and Cu₃Sr₂Ti₂O₇ 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 compounds having the same general framework. The distortive displacements of the ions in the [(Ba₂₋ₓSrₓ)O₂₋ₓ] layers significantly increase as x increases, which leads to more structural distortion of the perovskite-type unit. The Bi₂O₃ layer, in contrast, is less distorted in Sr₂Bi₄Nb₂O₁₁ than in Sr₂Bi₂Ta₂O₇. The contribution of the perovskite-type unit to total ferroelectric polarization is greater in the Sr₂Bi₄Nb₂O₁₁ sample, while that of the Bi₂O₃ layer is consequently, the total calculated polarization slightly increases. This change in polarization is similar to a recent observation in the Sr₂Bi₂Ta₂O₇ sample. Three short (Ta₂O₇)₇B₆O₁₄ octahedron, whose lengths less than 2 Å, have a common octahedron, and the substitution of Nb for Ta makes the bonds more covalent. The strong covalent interaction of the (Ta₂O₇)₇B₆O₁₄ octahedron increases the structural distortion resulting in the higher ferroelectric Curie temperature and the larger enhancement of the perovskite-type unit to the total spontaneous ferroelectric polarization.

CC10.2

EFFECT OF CATION ORDERING ON DIELECTRIC PROPERTIES OF SC SUBSTITUTED Pb(Mg₁/₃Nb₂/₃)O₃ RELAXOR FERROELECTRICS. L. Farber, M.A. Akbar, and P.K. Davies. 3rd Dept. of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA. Vishay Inc, Bridgeport, CT.

The chemistry and stability of the Bi-site cation ordering and its relevance to the relaxor ferroelectric behavior of the Pb(Mg₁/₃Nb₂/₃)O₃ (PMN) family of perovskites has been the subject of considerable debate. Latest results on PMN-type relaxors imply that the chemical randomness and associated random fields on the Bi 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 meet with no success. Recently, we demonstrated that the cation ordering was responsive to thermal treatment for Sc substituted PMN. In this presentation we report the effect of cation ordering on dielectric properties of Sc substituted Pb(Mgₓ/₃Nb₂/₃−ₓ)O₃ (S-PMN) evaluated in the x ≤ 0.5 x ≤ 0.5 domain.

CC10.3

ORDERING IN [La₆Sr₅][Al₆Ta₈]O[sub 34] SUBSTRATES AND ITS INFLUENCE ON THE STRUCTURE OF FERROELECTRIC THIN FILMS. Hae-L. Trun, T. Trun, C.L. Comley, L. Salmun-See-Riba and R. Ramesh, Materials Research Science and Engineering Center (MUSEC), Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD 20742 National Institute of Standards and Technology, Gaithersburg, MD.

Recently, a new substrate [La₆Sr₅][Al₆Ta₈]O[sub 34] (LaSATS) was synthesized and it has a cubic to rhombohedral transition at 800K. LaSATS does not have any phase transformation within the temperature range of interest (1200K to 1500K) and it is less expensive than STO substrates. In addition, LAPO and LaSATS is cubic and has lattice matched with many of the ferroelectric materials, such as Pb(Zr,Ti)O₃ and Ba₀.₅Sr₀.₅TiO₃. However, there has been a relative dearth of detailed material characterization of this new substrate. We used bright field TEM, HREM and computer image simulation as well as EDS and four circle X-ray diffraction to characterize this substrate. We found that LaSATS contains partially ordered regions of 5.50 nm in size. The ordered regions have a perovskite structure with an (00l) miller plane and the ordered regions have a [00c] structure with the double 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 are also present in a detailed atomic arrangement obtained using high resolution HREM and computer image simulation. The influence of this ordered structure on the crystallinity of the ferroelectric thin films discussed in this work was funded by NSF-MRSEC.

CC10.4

FREQUENCY MEASUREMENT FOR Pb(Zr,Ti)O₃ ISLAND STRUCTURE USING SCANNING PROBE MICROSCOPY. H. Fujita, K. Morimoto, M. Shimizu and H. Nari, Institute of Technology, Department of Electronics, Himeji, JAPAN; T. Kusama, R. Honda and S. Oiwa, Fujitsu Laboratory Ltd., Atsugi, JAPAN.
Piezoelectric measurement using scanning probe microscopy (SPM) was performed for island structure at initial growth stage of Pb(Zr0.52Ti0.48)O3 (PZT) thin films. PZT island structure was prepared on [111]Pt/SiO2/Si substrate by metalorganic chemical vapor deposition (MOCVD). Deposition times were changed from 1 to 7 min. When deposition times were 1 and 3 min, orientation of PZT island structures before becoming a continuous film were observed by atomic force microscopy (AFM). The width of PZT islands was increased from 50 to 100nm as the deposition time increased from 1 to 7 min. The height was also increased from 20 to 230 nm. In piezoelectric measurement, the phase difference between a tip vibration signal and displacement of PZT island surface changed from 0 to 180° during a hysteresis loop when dc bias voltage was changed from 0 to 10 V. This result proves that PZT islands with width of 100nm and height of 300nm had a spontaneous polarization which can be switched by external voltage, that is, ferroelectricity. Observations using ramen microscopy will also be reported.

CC10.5

FEA ANALYSIS OF DOMAIN EVOLUTION IN EPITAXIAL PZT THIN FILMS. Kilho Lee, Kyung Seok Lee, and Sanggi Baik. Pohang University of Science and Technology, Dept of Materials Science and Engineering, Pohang, KOREA

Equilibrium domain structures commonly observed in epitaxial Pt-based ferroelectric thin films are analyzed by finite element method (FEM) using a commercial package, ABAQUS. Evolution of periodic 90°-domain structures in epitaxial PtZrO thin films on cubic single crystal substrates is analyzed as a function of decreasing temperature in order to simulate deposition process after the film deposition at elevated temperature (Tg). The degree of c-axis orientation (α) is determined as a function of temperature below the Curie temperature of the PZT film in the material. 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(Zr0.52Ti0.48)O3 THIN FILMS. Fung Yen, Peng Yao, Yening Wang, National Laboratory of Solid State Microstructures, Department of Physics, Nanjing University, Nanjing, PR CHINA; Helen L.W. Chan, Chang-Lung 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 larger grains, however, smaller grains size shows 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 Pt/PZT interface for the internal electric field is very strong near the interface. Therefore, the film with lower fraction of the grains towards Pt electrodes has better fatigue properties. The permittivity of the thin film decreases with the decrease of grain size. It may be due to 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 PZT electrodes, the films may be damaged and the hysteresis loops become unsymmetrical.

CC10.7

FERROELECTRIC PHASE TRANSITIONS IN FILMS WITH DEPLETION CHARGE. A.L. Smidtov, 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 transition. The influence of the depletion charge on thermodynamic coercive fields 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 non-switchable 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


We have used the new approach to fatigue phenomenon for analysis of the evolution of the current pulses during cyclic switching in PZT thin films. It is proposed that the evolution of non-uniform 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(Zr0.52Ti0.48)O3 thin films (120-140-nm-thick) have been deposited by sol-gel method on Si/SiO2/Pt/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 using the normal distribution of bias field. We have shown that 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 spatial inhomogeneous imprint effect. The research was made possible in part by Program "Basic Research in Russian Universities" (Grant No. 55/6) and by Grant No. 97-5-7-1386 of the Ministry of Education of the Russian Federation.

CC10.9


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 switching field and the relaxation field is always the same in the states with opposite polarization directions 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 tends out to depend on the whole domain evolution history. Applying the developed 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.55/6) and by Grant No. 97-5-7-1-386 of the Ministry of Education of the Russian Federation.

CC10.10

THERMODYNAMICS OF CONSTRAINED FERROELECTRIC FILMS. A.L. Boyardov, C.S. Gangule, S.P. Alpy, V. Nagarajan, Dept. of Materials and Nuclear Engineering, University of Maryland, MD, J.D. Williams, A. Smidtov, J. Mehrgull, 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
crystalline net in the external stresses due to interatomic misfit
wherein the linear electrical and electromechanical responses
to external field do not depend on the misfit and are determined by
the film constraints. 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 change of the surface of a film clamped on the substrate under
external field can be not less and even larger than surface
displacement. The influence of radiating film on the electrical and
mechanical results are successfully applied to (001) PZT (20/80) films on (001) LAO
substrate and polycrystalline PNZT films on Si substrate.
The support was from NSF under Grant No. DMR-9632357 and by
the NSF-MRS program under Grant No. DMR-9833252 is gratefully

CC10.11
RESPONSE OF THE ELECTRIC FIELD GRADIENT IN ION
PLAINTED BiTiO₃ TO AN EXTERNAL ELECTRIC FIELD.
M. Dietrich, M. Descher, Universität Konstanz, Fachbereich Physik,
Konstanz, GERMANY, S. Untertrifaller, 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 in the lattice constants lead to changes in the influence
of simple temperature on EFG has been studied in detail with
perovskite materials. PAC spectroscopy observes the hyperfine interaction of
radiative probe nuclei with the EFG at their Larmor frequencies.
This was performed in experiments in which we applied uniaxial stress with the help of the
inverse piezoelectric effect in order to influence the EFG. Single
-crystalline, ferroelectric BiTiO₃ as material with the highest
piezoelectric constants among the perovskites with ordered sublattices
suited best for this investigation. We have implanted 111 In [111]Cd (160
keV, 2.2×10¹⁰ cm⁻²) with a mean depth of 45 nm. The probe atoms
[111] In [111]Cd substrate Ti and are exposed to an axially symmetric
EFG with a strength of Vₐₙ = 1.37(1)×10¹⁰ V/cm². PAC
measurements revealed a quadratic dependence of the EFG on the
external electric field strength [3.4 ... 4 kV/mm, parallel to polar
c-axis]: Vₐₙ(E) = (1.75 ± 0.02)E/keV/mm 4.0±1)
E²/V²/cm²)×10¹⁰ V/m². 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
Vₐₙ, but not the quadratic term. The polarizability of the host ions of BiTiO₃
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 BMFB
(03-DEKO-1-6)
(ß-DEKO2-9).

CC10.12
CALCULATION OF FERROELECTRIC PHASE TRANSITIONS
RESPONSE IN KDP, TGS AND NaNbO₃ 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 [TlM] Hamiltonian, which includes the
four-spin interaction terms. By using Monte Carlo simulation
methods, we report our calculations of the averaged electrical
polarizations at different temperatures for typical order-disorder
ferroelectrics such as KDP, TGS and NaNbO₃. With this method we
studied the phase transitions 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 such
complex systems we find it helpful to use 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 ferroelectric phase transition of the
nanoparticles thin 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 were consistent with the results given 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 material as a function of the size of each system. Finally, we were able to explain a variety of experimental
counterintuitive results about the behavior of the critical temperature of
the nanomaterials as the competition between size effects and
surface interactions in the system.

CC10.13
DISTINCTION METHOD BETWEEN FERROELECTRIC
SrBi₂Ta₂O₇ and PARAELECTRIC FLUORITE AND
PEROVSKITE IMPURITY PHASES: Koosuke Sato, Ikuo Yamanishi,
Tokyo Aksi, Philips Japan Ltd., Analytical Division, Konagawa,
JAPAN; Peter Munk, Philips Analytical B.V., NETHERLANDS;
Masahiro Minaya, Norimann Nakagai, Hiroshi Funakubo, Tokyo
Institute of Technology, Department of Mechanical Engineering,
Graduate School of Science and Engineering, Department of
Innovative and Engineered Materials, Konagawa, JAPAN.

It is well known that ferroelectric type and paraelectric type of impurity
phases in SrBi₂Ta₂O₇ system often exist with ferroelectric bismuth
layer structured SrBi₂Ta₂O₇ phase. Ferroelectric phase is expected to
exist under low temperature deposition and bismuth excess film
composition, while paraelectric phase is expected to grow under
bismuth deficient film composition. In conventional XRD
characterization, it is almost impossible to distinguish between
SrBi₂Ta₂O₇ phase and impurity phases because ferroelectric phase
has almost the same lattice parameters as one perovskite unit cell of
SrBi₂Ta₂O₇ and paraelectric phase 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
SrBi₂Ta₂O₇ thin film prepared on conventional Pt/Ti/SiO₂/Si substrate
by MOCD, it was reported that the film has strongly [115] preferred orientation owing to the strongest intensity of its
diffraction in conventional 8° 2θ scan. However, strong 110
orientation, not 115 orientation, was ascertained by the novel
determination method and it was also ascertained that the film included approximately 3 percent of paraelectric phase.
Consequently, from the novel characterization method, it was
concluded that the SrBi₂Ta₂O₇ thin films prepared by MOCD on
conventional Pt/Ti/SiO₂/Si substrate has strong 110 orientation and
the films included fairly small amount of paraelectric phase. Moreover,
the strong diffraction behavior as SrBi₂Ta₂O₇ [115] diffraction was
not the one but the paraelectric [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 8° 2θ scan. Furthermore, it was ascertained that correct quantitative distinction between ferroelectric SrBi₂Ta₂O₇
phase and impurity phases, especially ferroelectric 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-TIN COPOYLMER FILMS OF P(VDF-TrFE). Maik
Paulsen, S. Adewunmi and N. Perkovich, Physics and Astronomy,
Center for Materials Research and Analysis
University of Nebraska-Lincoln, Lincoln, NE, V. M. Fridkin, S.P.
Pulko, N.N. Perkovich and S.G. Vasin
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 A) Langmuir-Blodgett
copolymer films of vinylidene fluoride (70%) with trifluoroethylene
(30%) deposited on aluminum-coated silicon. 4.2K X-ray diffraction
was used to measure the change in interlayer spacing perpendicular
to the film surface. Upon heating at zero external electric field, the
crystalline films undergo a structural phase transition at 100 ± 5°C,
from the all-trans ferroelectric 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 (3000 to 1500 V/m). For example, at 100°C the ferroelectric phase film appears above 0.2 Gm/m and increases steadily in proportion while
the paraelectric phase decreases until complete conversion to the
ferroelectric phase is achieved at approximately 0.6 Gm/m. This technique
allows us to construct phase diagrams for the ferroelectric phase
existence region in the E·T plane, from the zero field transition
temperature to the critical point.

[1] Stephen, Ducharme, A. V., Bune, L. M., Blenc, V. M., Fridkin, S. P.,
SESSION CC11 POSTER SESSION PIEZOELECTRIC, PYROELECTRIC, AND OPTOELECTRONIC MATERIALS AND DEVICES

Chairs: Seungik Lee and Michael Sayer
Wednesday Evening, November 29, 2000
8:00 PM
Exhibition Hall D (Hyatt)

CC11.1 EFFECTS OF FERROELECTIC BUFFER LAYERS ON THE PROPERTIES OF Pb(Zr1/2Nb1/2)O3–Pt–TiO2 and Pb(2/3Ta1/3)O3–Pt–TiO2 THIN FILMS ON Pt-FOATED SILICON WAFERS. Runki Hsing, Tsukoshi Yoshimura, Susan Troullin-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 piezoelectric devices. However, many relaxor materials don’t exhibit good thermal stability at high temperatures due to their low Curie temperatures. For this purpose, Pt–Y2N–Pb thin films which have high Curie point >360°C at the morphotropic phase boundary should be improved to improve the high temperature stability of piezoelectric properties. In this work, we deposited both PZT and PMN–Pb thin films on Pt/Te/SrO/Si substrates by using either pulsed laser deposition or solgel technique. Either a SrRuO3 single layer or SrRuO3/NbO4 double layer was used as buffer layer between the substrate and the ferroelectric film. NbO4 is a ferroelectric material meant 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 pyroelectric phase formation in Pt–Y2N–Pb thin films. Pt–Y2N–Pb thin films deposited on SrRuO3 buffer layers exhibited (110) and (111) orientation. Pt–Y2N–Pb thin films deposited on SrRuO3/NbO4 show strong [110] orientation. The resulting Pt–Y2N–Pb films exhibit well-developed hysteresis loops with remnant polarization (P_r) as high as 14–20 μC/cm². The effect of the ferroelectric buffer layer on the dielectric and piezoelectric properties of the film will be reported.


The effect of various substrates on the electrical and electromechanical properties of epitaxial Pb(Mg1/3Nb2/3)O3–PbTiO3 [PMN–PT] thin films is investigated. 0.01 0.9PMN–0.1PT thin films were grown on (001) SrTiO3 (STO), (001) La0.5Sr0.5TiO3 (LST), SrTiO3 (STO), and MgO substrates with 40 nm thick top and bottom La2O3/SrRuO3 electrodes by pulsed laser deposition. X-ray diffraction results indicate that the films on LST, STO, and MgO are single crystalline in composition in the filmsubstrate 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 65°C to 0°C with increasing temperature range. The relaxation time is increased from 0.1 nsec to 400 nsec for the films grown on LST. This is accompanied by an increase in the dielectric constant at 1 MHz, measured at room temperature and 10 kHz, from 300 to 1000, respectively. Correspondingly, the piezoelectric response, measured using a scanning probe microscope, shows a strong dependence on the film thickness. 100 nm thick PMN–PT films grown on various substrates a decrease in the temperature of dielectric maximum T_m together with a decrease in the dielectric constant in the longitudinal piezomodulus is observed with decreasing in-plane epitaxial stresses for LST, STO, and MgO substrates. The film on MgO substrates has the highest dielectric constant and piezomodulus with T_m below room temperature. The variation in T_m may be attributed to the shift in the transformation temperature from the pseudocubic to the relaxor state due to internal stresses in the filmsubstrate interface. Electrical and electromechanical properties should depend strongly on internal stresses in the phase transformation, which is reflected in our experimental observations.

CC11.3 FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF EPITAXIAL Pb(Zr1/2Nb1/2)O3–Pt–TiO2 thin films. Takashi Yoshimura and Susan Troullin-McKinstry. The Pennsylvania State University, Materials Research Laboratory, University Park, PA.

Ferroelectric relaxor ferroelectric systems have attracted much attention for microelectromechanical systems (MEMS), because relaxor based ferroelectric single crystals exhibit ultrahigh piezoelectric response.

In this study, we investigated ferroelectric and piezoelectric properties of epitaxial [100]Pb(Zr1/2Nb1/2)O3–Pt–TiO2 (PZN–PT) films. Single crystalline films can be grown when the Curie point has the highest morphotropic phase boundary (x ~ 0.5) of the known relaxor ferroelectric–Pt–TiO2 solid solutions. MEMS devices with temperature stable can be expected. [001]La2O3 single crystals were used as substrates. SrRuO3 bottom electrode and Pt–Y2N–Pb films were deposited by pulsed laser deposition. [001]Pt–Y2N–Pb (50/50) films were deposited at the temperature deposition of 650°C. Typical full width at half maximum of the rocking curve for Pt–Y2N–Pb 602 are 0.0°. The dielectric constant and dielectric loss at room temperature and 1.0 kHz are ~1000 and 0.05, respectively. Ferroelectricity with the remnant polarization of 30 μC/cm² was also obtained. For such samples, the product of d33*Young's modulus is 4 C/m².

CC11.4 PMN–PT THIN FILMS DEPOSITED ON (100)-ORIENTED LaNiO3 BOTTOM ELECTRODES. Zhihuan Zhang, and Susan Troullin-McKinstry. Materials Research Laboratory, Pennsylvania State University, University Park, PA.

(100)–oriented thin films of LaNiO3 (LNO) were deposited by DC magnetron sputtering onto Si substrates [p–s pseudo cubic indices]. A lattice parameter a_{LNO} of 3.845 ˚A and thermal expansion coefficient of 1.63 X 10^-5/°C were measured for LNO thin films using high temperature X-ray diffraction. (100)–oriented thin films of 0.70(MgZn2/3Nb1/3)O3–0.3PTiO2 (PMN–PT) were fabricated by a solgel method on (001)–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 5.8°. 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 d33 of ~76 pC/N (assuming a Young's modulus of 45 GPa) and aging rate of 6.8% were observed on 1.1 μm thick PMN–PT films. The films exhibited a large current density of less than 10^-5 A/cm² when an electric field of 100 kV/cm was applied.

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

We report on new ferroelectric Ag0.5Ti0.5O3 (ATN) films grown by pulsed laser deposition technique onto polycrystalline Pt and (La,Sr)CoO3/LaNiO3 single crystal substrates. ATN films on Pt have been found to be (001) preferentially oriented, while the epitaxial quality of ATN/LSCO/LaNiO3 heterostructures has been unachieved. 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 and bulk ceramics. As temperature is increased from 65°C to 300°C the relaxation time is increased from 0.1 nsec to 400 nsec for the films grown on LST. We observed a strong dependence on the film thickness. 100 nm thick PMN–PT films grown on various substrates d decrease in the temperature of dielectric maximum (T_m) together with a decrease in the dielectric constant in the longitudinal piezomodulus is observed with decreasing in-plane epitaxial stresses for LST, STO, and MgO substrates. The film on MgO substrates has the highest dielectric constant and piezomodulus with T_m below room temperature. The variation in T_m may be attributed to the shift in the transformation temperature from the pseudocubic to the relaxor state due to internal stresses in the filmsubstrate interface. Electrical and electromechanical properties should depend strongly on internal stresses in the phase transformation, which is reflected in our experimental observations.

CC11.6 MODELING OF BENDING-TYPE MICROACTUATORS USING PZT THIN FILMS. Haomao Xu, Jingdong 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 normal, in-plane poled PZT films and the conventional, through-thickness poled PZT films has been investigated using FEA (Finite Element Analysis) method. The in-plane poling can be realized by depositing PZT films on silicon substrates buffered by an insulating oxide layer such as Al2O3 or TiO2 surfaces. Surface interdigitated electrode systems for the cantilever structure or annular electrode systems for the diaphragm structure. The FEA modeling demonstrated 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 poling enables the second mode to be used for the microactuators and d33 is about twice of d33 for PZT films, which overcomes the efficiency of in-plane poling 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 CRYSTAL-LOGIC ORIENTATION.** Q. Zhao, F. Hong, R. Wolf, S. Troller-McKinstry, Materiales Research Laboratory, The Pennsylvania State University, University Park, PA.

Ferroelectric 

\( \text{Pb}( \text{Zr}_{x} \text{Ti}_{1-x}) \text{O}_3 \) (PZT) films have been extensively studied for active components in microelectronic 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 \( \text{Pb}( \text{Zr}_{x} \text{Ti}_{1-x}) \text{O}_3 \) (PZT 52/48) films will be reported. Crack free random and highly (100) oriented PZT 52/48 films up to ~7 μm thick were deposited using a sol-gel process on Pt/Si and Pt/SiO2 substrates, respectively. The dielectric constant (1 kHz) for the (100) oriented films is 86+6,000, and for the random films is 390±950. In both cases, tan δ is less than 0.05. The remnant polarization is ~25 μC/cm² for random PZT films and ~35 μC/cm² for (100) oriented PZT films. The transverse piezoelectric coefficient (d33) of PZT films was measured by wafer flexure method. The d33 coefficient of random PZT thick films (85 pC/N) is larger than that of (100) oriented films (60 pC/N) when aged at 80 °C for 1.5 minutes. 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 MICROMICROMACHINED PZT THIN FILMS.** Carlos Morera, Robert Bowman, Marty Gregg, Department of Physics and Applied Physics, Queen 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 characterized and their piezoelectric coefficient d33 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 micromachining. The laser micromaching results in damaged areas along the cut edges. Mapping of the piezoresponse and topography on these devices is presented and the implications for transducer fabrication discussed.

**CC11.9**

**A DIELECTRIC POLARIZER BEHAVIOR OF BST THIN FILM PREPARED BY METAL-ORGANOIC-DECOMPOSITION WITH EXCELLENT REPRODUCIBILITY IN THERMAL CYCLING TEST.** Minoru Noda, Hong Zhu, Huiying Xu, Tohonori Maikagawa, Kazuhiko Hashimoto and Masanori Okumura, 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 hologram mode (DB) of infrared (IR) detecting material. The DB mode IR detector made of uncooled room temperature operation, cheapness, low power dissipation, and high sensitivity like a pyroelectric operation. In this work, we have successfully developed a stable \( \text{Ba}_{2-x} \text{Sr}_{x} \text{Ti}_{4} \text{O}_{9} \) (BST) thin film as an IR detecting material by Metal-Organic Decomposition (MOD) method. The film was prepared on both Pt/Ti/SiO2/Si and Pt/Ti/NSG/SiO2/SiO2 membrane structures, where an IR light is detected 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 almost 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 in comparison with 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 degree Celsius within a relative change of 3%. Finally, the stabilities in both the temperature and thermal cycling (10 times) were also measured. The thin-film derived BST film showed significantly improved and enabled us to obtain 1D(1x106) and 2D(1x106) images with a fairly large IR detectivity, where R∞ and D* were about 1 kW/m² and 18 mmHz1/2/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 Chiu, National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, CHINA.

\( \text{Ba}_2 \text{Sr}_{1-x} \text{Ti}_3 \text{O}_{9} \) (BST) is currently one of the most interesting ferroelectric materials due to its high dielectric constant and composition dependent Curie temperature from 30 to 480 K. However, the sol-gel derived BST films 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 \( \text{Ba}_2 \text{Sr}_{1-x} \text{Ti}_3 \text{O}_{9} \) thin films using a highly diluted precursor solution. A columnar structure with grain sizes below 200 nm was obtained with layer-by-layer homogeneity due to a very small thickness of individual layer. The prepared \( \text{Ba}_2 \text{Sr}_{1-x} \text{Ti}_3 \text{O}_{9} \) thin films have been studied for possible uncooled IR detector applications. The measured pyroelectric coefficient is larger than 3.1 x 10⁻⁴ C/m²K at the temperatures ranging from 10 to 26°C and reaches the maximum value of 4.1 x 10⁻⁴ C/m²K at 16°C. The infrared detection of 4.6 x 10⁻⁴ W/m² has been obtained at 19°C and 10 Hz in the \( \text{Ba}_2 \text{Sr}_{1-x} \text{Ti}_3 \text{O}_{9} \) films deposited on 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 Amerini, Jorge Portelles, Michel Venet, Abel Pandora, Faculdad 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; Jesus M. Siguero, Centro de Ciencias de la Materia Condensada, UNAM, MEXICO.

The Thermally Stimulated Depolarization Current (TSDC) and pyroelectric properties of the modified SBN ferroelectric ceramic system was studied for different lanthanum 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 remnant polarization and pyroelectric coefficient, both associated only to permanent ferroelectric dipoles. The polarization 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 \( \text{La}_{2} \text{Sr}_{2} \text{Ba}_{3} \text{Nb}_{2} \text{O}_{10} \) thin films, in particular, has excellent pyroelectric response, making this material very suitable for pyroelectricity-derived applications.

**CC11.12**

**SENSING PROPERTIES OF \( \text{Ba}_{2-x} \text{La}_{x} \text{Nb}_{2} \text{Ti}_{4} \text{O}_{9} \) THIN-FILM ON \( \text{SiO}_{2}/\text{Si} \) SUBSTRATE.** Bing Li, P.T. Lai, Department of Electrical and Electronic Engineering, University of Hong Kong, HONG KONG: Y. Guo, H.P. Keong, 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 ofinvestigations. Therefore, desirable sensing thin-film materials have been actively sought. Perovskite-type oxides (ABO₃) 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 \( \text{Ba}_{2-x} \text{La}_{x} \text{TiO}_3 \) and \( \text{Ba}_{2-x} \text{La}_{x} \text{Nb}_2 \text{Ti}_4 \text{O}_{9} \) thin film photos have thermal 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, \( \text{Ba}_{2-x} \text{La}_{x} \text{Nb}_2 \text{Ti}_4 \text{O}_{9} \) 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-insulancerectifying (MS) capacitor on \( \text{SiO}_{2}/\text{Si} \), the sensing performances are investigated. Results from these experiments show that the thin-film derived BST film has good sensitivity for visible light and good thermal sensitivity within the temperature range of 28±4°C. The MS capacitor is sensitive to change of relative humidity (RH), with a 20%/% 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 s for absorption and desorption of water vapor respectively. Effects of test frequency on photo, thermal and humidity sensing performances are also investigated. In conclusion, compared with \( \text{Ba}_{2-x} \text{La}_{x} \text{Sn}_2 \text{Ti}_4 \text{O}_{9} \) thin film, photos, thermal and humidity sensing
properties of $\text{Ba}_{2+\alpha}\text{La}_{x}\text{Nb}_{y}\text{T}_{1-x-y}\text{O}_{3}$ ($x=0.25, y=0.25$) thin-film are remarkably improved. So, sputtered $\text{Ba}_{2+\alpha}\text{La}_{x}\text{Nb}_{y}\text{T}_{1-x-y}\text{O}_{3}$ ($x=0.25, y=0.25$) thin-film is a promising material for multi-domain sensing.

Reference:

CC11.13
ELECTRIC FIELD EFFECT THERMOELECTRICS. Vladimir Sadowskis
B. Beniun Univ, Dept of Physics, Ramat-Gan, ISRAEL.

It is proposed to use the ferroelectric-electric field effect (FEFE) to increase the figure of merit (FoM) of the thermoelectric conductor (TE). The capacitive structure is considered the Gate-Polarized ferroelectric film (GF-FEFE) allowing surplus in the intrinsically thin film one (any) kind of carriers and to increase simultaneously to 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 FoM is analyzed. It is shown that a crucial significance has the value of the static dielectric constant of TS. PM is the more the dielectric constant is more. The results of numerical calculations for the TS PdTe is presented. Its dielectric constant at 300K equals 51.2. For PdT with the electric displacement 10^6/cm PPM-1 at the enrichment of PdTe film (500 A) with holes. The perspective thermoelectric also is the semiconductive with dielectric constant ~150.

SESSION CC12 POSTER SESSION
THIN FILM PROCESSING
Chair: Gerd J. Noergaard and Mikko Yamanak
Wednesday, 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. Jung-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 evidence until now that 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 x 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 H2 gas at 400 °C for 30 minutes. We measured the resistance 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. Jung-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 Nuclarized Lateral Crystalization) was saturated at a certain temperature. It was interesting to notice that there existed the maximum interlateral growth length and the length did not increase with increasing heat treatment temperature. In our present work, only the phenomena of the grain growth 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 interference 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 phases, further heating and Pt electrode. When the Pt electrode was introduced to the grain-size saturated PZT thin films to control the interface energy between perovskite and pyrochlore phases, further heating and Pt electrode occurred. Pt 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 enhancement of the 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 different temperature will be discussed in detail.

CC12.3
MICROSTRUCTURE AND PROPERTIES OF Mn-DOPED Pb(1-x)Mn(x)Tb0.75Lu0.25O3 THIN FILMS ON LSCO/Si WAFERS. Jiang Lu, Y. Noguchi, V. Nguyen-Huu, M. Wettig, R. Ramesh, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; K. Chandra, Wilcoxen 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 the formation of pyrochlore phase. In this work, we tried to deposit 70PMN30PT thin films on [La0.5, Sr0.5]CoO2-buffered glass and using SnO2 thermal film (500 A) with holes. The X-ray diffractometer tests revealed that under the same deposition conditions, PMN-PT grown on LSCO/Si has a higher ratio of perovskite/(perovskite + pyrochlore) than the film on SnO2/Si without LSCO template, indicating that LSCO assists the formation of pyrochlore PMN-PT and suppresses the pyrochlore phase. The effect of Mn doping on perovskite formation was systematically studied. The electrical property measurements and microstructure observation by means of AFM were also reported.

CC12.4
THICKNESS DEPENDENCE OF MICROSTRUCTURE AND PROPERTIES OF PbTiO3/40/60 THIN FILMS. Y. Wang, K. Nonomura, B.T. Liu, B. Nagraju, H. Li, C. Gaspule, R. Ramesh, M. Wettig, Univ of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; K. Chandra, Wilcoxen Research Company, Gaithersburg, MD.

The microstructure as well as dielectric and ferroelectric properties as a function of thickness is investigated on PbTiO3/40/60 thin 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 platinum wafer (Pt/Si), PbTiO3/40/60 films grown on Pt/Si, PbTiO3/40/60 film has a polycrystalline structure with a dominant (110) peak in X-ray diffraction. The relative intensity of the major XRD peak, $I_{110}/I_{100}$, increases with the film thickness increases. When deposited on [La0.5, Sr0.5]CoO2-buffered Pt/Si, PbTiO3/40/60 film exhibits (101) texture and as the film gets thicker, the relative intensity decreases. When deposited on LSCO-buffered SrTiO3 single crystal, PbTiO3/40/60 film was found to grow epitaxially by liquid phase epitaxy which appears when the thickness is above a critical value. The dielectric and ferroelectric properties of the films were also studied.

CC12.5

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. Conventional ferroelectric films need to be deposited over shrinking capacitor area and reduced thickness, a prerequisite being that its aspect ratio 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 ferroelectic layer deposition must not adversely affect 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 HDB-MOCVD deposited PZT thin films.

CC12.6

Abstract Withdrawn.

CC12.7


We have grown epitaxial ferroelectric Pb(Zr, Ti)O₃ thin films on SrRuO₃ thin film bottom electrode on [100] SrTiO₃ substrate by hydrothermal process using hydrothermal synthesis of the oxide films from aqueous solution at low processing temperature. SrRuO₃ 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, TiO₂), zinc oxide hydroxide (Zn(OH)₂) and lead nitrate (Pb(NO₃)₂) in an aqueous alkaline 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 cubic-on-cubic in-plane epitaxial arrangement. They show well saturated hysteresis loops, strongly asymmetric polarization switching and the occurrence of imprint phenomena. Their dielectric constant and loss tangent are 460 and 0.025 at 10⁶ Hz. They also show low leakage current and its value is 3×10⁻⁶ A/cm² at 100 V/cm. We will discuss the morphology and microstructure of the heterostructures.

CC12.8


Barium Strontium titanate (BST) composite is being investigated as one of the major dielectric material candidates, suitable for tunable microwave device applications. BST capacitors, RF detector and DRA 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 MoO₃ 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 potential composites of barium strontium titanate as BST capacitors were deposited on platinum substrate in acetone base slurry under bias and at controlled rate. Conformal BST thick films of 15-20 microns were obtained, acetone-removal OTS surfactant treatment was used as dispersive medium. Dielectric constant and dielectric loss were 603.3 and 0.29, 327.0 and 0.09 for Ba₀.90Sr₀.10TiO₃ and Ba₀.95Sr₀.05TiO₃ V 200%, respectively. Electronic properties at low frequency of the electrophoretic films will also be discussed. These results of electrical characterizations of 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. Chotopadhyay, J. Narayam, NSF Center for Advanced Materials and Smart Structure, NC A&T State University, Electrical Engineering Department, Greensboro, NC & North Carolina State University, Materials Science Dept., Raleigh, NC. V. S. Knight, W. Gilmore, C.B. Lee, NC & State University, Electrical Engineering Dept., Greensboro, NC.

Ferroelectric thin films of SrBi₂2Ta₂O₉ (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 SrBi₂2Ta₂O₉ by pulsed laser deposition on silicon (Si) 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 these 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 remnant polarization (Pr) to be 27 microcoulombs/cm² and 11.6 microcoulombs/cm² 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/Ti/NiO/MgO (001) heterostructures. Fatigue measurements of these films are being done.

CC12.10

ATTEMPTED CONTINUOUS COMPOSITIONAL-SPEW TECHNIQUE APPLIED TO EPITAXIAL FILMS AND HETEROSTRUCTURES. Han M. Christen, Sherwood D. Silverman, R. S. Harshwardhan, Neocron, Inc., Beltsville, MD.

We present a novel continuous-compositional spread technique based on the nonuniformity of the deposition-rate typically observed in pulsed laser deposition. Using rapid (sub-monochromatic) sequential deposition of the phase assemblage, 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). Characterization determines the ternary phase diagram is achieved via a simple algorithm using the parameters that describe the deposition-rate profiles. Experimental verification using EDX and RHEED measurements demonstrates the agreement between the predicted and the calculated composition values. Results are shown for the high-temperature growth of crystallographic perovskites, including (Ba,Sr)TiO₃ and the formation of a metastable alloy between SrRuO₃ and SrRu3. Applications of the method to the growth of heterostructures and superlattices are discussed.

CC12.11

GROWTH AND CHARACTERIZATION STUDIES OF AlₓBi₂Ta₂O₉ (Al = Ba, Sr, and Ca) FERROELECTRIC THIN FILMS. R.R. Dua, W. Perez, R.J. Rodriguez, E. Ching-Pond9, P.S. Dobal and R.S. Kogley, 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 AlₓBi₂Ta₂O₉ bismuth-layered structure, where x = Ba, Sr, and Ca were prepared by a Pulsed Laser Deposition technique on Sr, Pb/TiO₂/SrO/Si, and LaAlO₃ substrates. The influence of substrate temperature, between 500 to 750°C, and oxygen partial pressure, from 100 to 600 mTorr, on the structural and electrical properties of the films was investigated. The films deposited above 600°C substrates temperature show a 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 relationship of the A-site substitution on the structural and ferroelectric properties of the films. Results of Roman 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 part by DAAH64-96-1-0019, DAAD19-94-1-0002, and NSF DMR 9601755 grants.

CC12.12

FERROELECTRIC AND FATIGUE PROPERTIES OF ALKYOXY- DERIVED CaₓBi₂Ta₂O₉ THIN FILMS. Kazumi Kato, Kazuyuki Suzuki, Kuo Nishimura, Tablei Mi, University of National Research Institute of Nagaoka, Nagaoka, JAPAN. Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN.

CaₓBi₂Ta₂O₉ (CBT) is one of layered-structured perovskite compounds and has not been well-known for ferroelectric properties as SrBi₂2Ta₂O₉ (SBT) which has a similar crystal structure. The CBT thin films were successfully prepared on Pt-coated silicon wafer substrates using a three-alcohol sol-gel process. The thin film crystallized to a single phase of perovskite at 750°C via a mixture of fluoro- 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 capacitance of size 0.05 mm × 0.05 mm 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 remnant polarization and coercive electric field were 6.9 μC/cm² 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 10⁻³ s, however, it increased gradually with number of switching cycles when the pulse
width was relatively long such as 10⁻⁴ m. The thin film exhibited no change of polarization after 10⁴ cycles of switching with the pulse width of 10⁻⁴ s. This work was financially supported by the Industrial Science and Technology Frontier Program being promoted by AIST, JST, Japan.

**CC12.13 HYDROTHERMAL PROCESSING OF BARIUM STRONTIUM TITANATE FOR HIGH FREQUENCY APPLICATIONS**

K. Zehnder, L. Wu, Dept. of Chemistry, Queen’s University, Kingston, ON, CANADA; H. C. Frey, 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 and at much higher 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 interconnect design for GaAs microcircuits.

**CC12.14 ELECTRICAL CHARACTERISTICS OF SOL-GEL DERIVED Nb²⁺ DOPED PZT (3/74) THIN FILMS IN PLANAR ELECTRODE CONFIGURATION**

S. B. Majumder, B. Perez, B. Roy, M. Martinez and R. S. Krishnan, Dept. of Physics, Univ. 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 Pb₁₋ₓ(Nbₓ)₂₋₅(Zr₂Ti₂O₇₋n) films on platinumized 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 Nd doped PZT films measured at 100 kHz were found to be 13.86 pF, 0.033 and 95 pF, 0.019 respectively. The tunability, calculated from the measured capacitance vs voltage plot was found to be independent of Nd doping (~ 0.23). Saturated hysteresis loops were obtained in undoped PZT film by applying 1000 V across 5 µm electrode separation. Nd doped PZT films, on the other hand, electrically shorted at much lower applied voltage (~ 50 V). AFM micrograph indicates undoped PZT films have smooth surface with uniform grain size distribution, whereas Nd doped PZT films have relatively rougher surface with exaggerated grain size. The observed electrical characteristics are correlated with the observed surface morphology of these films. This work is supported by DAAD 1-1131-1032 and NSF-DARPA-08-1759 grants.

**SESSION CC13 PIEZOELECTRIC MATERIALS, CAPACITORS, AND NOVEL DEVICES**

Chair: Susan Trolier-McKinstry and Paul Marshall

Thursday Morning, November 30, 2000
Room 312 (Hytes)


Single oxide as well as complex oxide layers such as Nb₂O₅ as well as Ba₁₋ₓSrₓTiO₃ or Pb₁₋ₓZrₓTi₁₋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 grain devices. In the last few years, dielectric films with a thickness of 0.1-μm and relative permittivities of 40-20000 are especially studied for high performance memory circuits. Integrated capacitors, resistors and inductors offer miniaturized circuits with high performance, which gain especially for the 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.
MEASUREMENT OF TIME-RESOLVED X-RAY DIFFRACTION.
C. Thompson, Northern Illinois University, Dept. of Physics,
DeKalb, IL, and Argonne National Laboratory, Materials Science Div.,
Argonne, IL; S. Streiffer, G-B. Stephenson, G-R. Bui,
Argonne National Laboratory, Materials Science Div., Argonne, IL; A.
McPherson, J. Wang, Argonne National Laboratory, UPD, Argonne, IL.
B. Rice, 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
investigating the lattice dynamics of thin films. The films were measured
by the application of high-frequency electric fields to the sample. In
this technique, a beam chopper with a 24.5 ms opening time is
synchronized to the time structure of the lattice response during the
application of a periodic wave. By

10:30 AM *CC13.6

A new method for studying the mechanical properties of
piezoelectric materials has been developed. The method,

11:00 AM *CC13.7

A thin film piezoelectric wave resonator (FBAR) is a resonant
piezoelectric ceramic device. The resonators, which are

11:45 AM *CC13.10

Metallized Ferroelectric-Insulator-Semiconductor (MIFS) FETs are now
being paid much attention as nonvolatile memories with non-
conductive readout operation which follow good scaling rules.
These have been analyzing the temperature and resistance
characteristics of the effect of charge injection between the ferroelectric and
the insulator layers caused by the leakage current. The theoretical results
have been obtained by analyzing a model which used the following
dependent saturated polarization loop derived by S. Miller et al.
and the current continuity principle is based on the band-bending
approximation at the surface of silicon. A real Ai/SiO2/TiO2
MLT/Pt capacitor was prepared and in order to obtain some
Experimental parameters describing leakage current densities
through the ferroelectric layer as a function of time and applied field.
The simulated retention curves of MIFS structures showed good
agreements with our experimental data. The numerical results have
indicated that a slight increase of Schottky barrier height for the
insulator layer (ΔΦb) provides sufficiently long retention time.
When ΔΦb = 0.6 V is assumed as an independent variable, retention time
over 15 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
dramatically the leakage current, we newly propose a Metal
Insulator-Ferroelectric-Insulator-Semiconductor (MIS) structure, which is expected to be more effective than an MIS structure in terms of insulator barrier characteristics. Our physical model has been also applied to an MIS structure which has an additional SiO₂ layer inserted between the top electrode and the ferroelectric layer of a MIS where SiO₂ is assumed as the insulator layer. The calculated result has predicted that the insertion of the additional SiO₂ layer 1/10 as thick as the SiO₂ processed on the silicon is very effective to provide satisfactory retention time for the practical use.

SESSION CC14/DD6.6 JOINT SESSION HIGH-FREQUENCY APPLICATIONS OF FERROELECTRICS
Chairs: Quanxi Jin and Jon-Paul Marie
Thursday Afternoon, November 30, 2000
Room 312 (Hynes)

1:30 P.M. *CC14.1/DD6.6
MORPHOLOGY AND CHEMISTRY OF NON.
STOICHIOMETRIC (Ba,Sr)TiO₃ THIN FILMS. Igor Levin, NIST, Gaithersburg, MD; Richard Leupin, NIH, Bethesda, MD; Debra Kaiser, NIST, Gaithersburg, MD.

The microstructure and chemistry of (Ba,Sr)TiO₃ thin films deposited on Pt/Al₂O₃/Al substrates by metalorganic chemical vapor deposition were studied in detail by high resolution transmission electron microscopy and quantitative spectrometer in electron energy loss microscopy. The grain boundaries in all films with overall Ti content ranging from 40 to 50 atom% 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 to the stoichiometric value of unity are accounted for by the creation of Ba/Sr vacancies which segregate to the grain boundary regions. The films with Ti contents equal to or greater than 50% 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 increasing in the Ti/(Ba Sr) ratio.

2:00 P.M. CC14.2/DD6.6

Ba₁₋ₓSrₓTiO₃ (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 semiconducting systems. Unfortunately, the tradeoff to high tunabilities is high loss tangents, that is, tan δ > 0.01. It has been documented that small concentrations of dopants can dramatically modify the properties of ferroelectric materials such as BST. In this work we investigated the material and dielectric properties of Ba₁₋ₓSrₓTiO₃ solid solution thin films doped with La. The films were fabricated via metalorganic solution decomposition (MOSD). 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 (FSEM) were employed to assess surface morphology. Cross-sectional transmission electron microscopy (XTEM), 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 stoichiometry. 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 insulator properties of BST 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 P.M. CC14.3/DD6.6
LINKING THE DIELECTRIC RESPONSE OF CERAMIC AND THIN FILM Ba₃₋ₓSrₓTiO₃: THE EFFECTS OF STRAIN. Chris M. Carlson, Dept. of Physics, Univ. of Colorado, Boulder, CO; Philip A. Parilla, Tareq V. Rivkin, John D. Perkins and David S. Ginley, National Renewable Energy Laboratory, Golden, CO.

Ba₃₋ₓSrₓTiO₃ (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 constant characteristics. Our physical model has been applied to an MIS structure which has an additional SiO₂ layer inserted between the top electrode and the ferroelectric layer of a MIS where SiO₂ is assumed as the insulator layer. The calculated result has predicted that the insertion of the additional SiO₂ layer 1/10 as thick as the SiO₂ processed on the silicon is very effective to provide satisfactory retention time for the practical use.

2:30 P.M. CC14.4/DD6.6
STRESS EFFECTS ON DIELECTRIC PROPERTIES OF EPITAXIAL Ba₀八十₉₂TiO₃ THIN FILMS. H.R. Park, E.J. Peterson, Q.X. Jin, Los Alamos National Laborato, 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 Ba₁₋ₓSrₓTiO₃ 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 Ba₁₋ₓSrₓTiO₃ thin films. We developed new approaches to change the stress include the variety of substrates or variation of deposition conditions, such as oxygen pressure. Here we report on 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 Ba₀八十₉₂TiO₃(BST) thin films on MgO(001) substrates by inserting a very thin Ba₁₋ₓSrₓTiO₃ (x = 0.1 - 0.7) interlayer to manipulate the stress of the BST films. Since the only difference of these 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 P.M. CC14.5/DD6.6
Ba₁₋ₓSrₓTiO₃ THIN FILM CAPACITORS WITH COPPER ELECTRODES. Iyong O. Auciello, Materials Science Division, Argonne National Laboratory, Argonne, IL; A.R. Krauss, Materials Science and Chemistry Division, Argonne National Laboratory, Argonne, IL.

Ba₁₋ₓSrₓTiO₃ (BST) films are being investigated for application as capacitor materials for Gbit DRAMS and for high frequency tunable devices. They are typically used as Pt for capacitor 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 IC 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 at the interfaces where 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 δ ~ 0.002, Q = 500) with 25% tunability, measured at room temperature and 1 MHz. The effect of backside electrode layer thickness and BST deposition temperatures, on the electrical properties of BST thin film capacitors will be discussed.

3:30 P.M. *CC14.6/DD6.6
MECHANISMS OF LOSS AND TUNABILITY OF FERROELECTRIC THIN FILMS PROBED BY LATTICE DYNAMICAL STUDIES. X.X. Xi, A.A. Sirenko, A.M. Clark, Weldon 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 dynamic 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 Lydiate-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$_{n-2}$Sr$_n$Ti$_3$O$_{12}$ 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$_{n-2}$Sr$_n$Ti$_3$O$_{12}$ (BST) thin films grown by pulsed laser deposition. Electric-field-induced Raman scattering was studied using indium-tin oxide (ITO)/STO/SrHfO$_3$ and ITO/BST/SrHfO$_3$ 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 soft mode in the 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 Lydiate-Sachs-Teller (LST) relationship.

4:15 PM CC14.8/DD6.8

**PSEUDO-SPIN-FLOP TRANSITION IN OXYGEN-DEPRIVED BST THIN FILMS**

Charles Hiber, Jeremy Levy, Dept of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA; Chris M. Cackowski, Department of Physics, University of Colorado, Boulder, 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$_{n-4}$Sr$_n$Ti$_4$O$_{12}$/MgO thin films. The films are grown using pulsed laser deposition in an $O_2$ pressure ranging between 40 mT-250 mT. The bimodal 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 in 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-AC52-06NA25396 (NREL) and by ONR contract N00173-98-1-0011 (U. Pittsburgh).

4:30 PM CC14.9/DD6.9

**EXPERIMENTAL AND THEORETICAL INVESTIGATION INTO THE DIELECTRIC BEHAVIOUR OF FERROELECTRIC THIN FILM SUPERLATTICES**

Marcy Gregg, Deirdre O'Neill, Gustav Catalis 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$_{n-4}$Sr$_n$Ti$_4$O$_{12}$ and Ba$_{n-2}$Sr$_n$Ti$_3$O$_{12}$. The properties of the capacitors were investigated as a function of superlattice periodicity. The dielectric constant was enhanced at stacking periods 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. Feinstones, 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 dielectric loss. The microstructure of the films 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 influence 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, 15 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 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 particular 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 nanoindenter and a ball-on-disk tribometer. The electronic, mechanical, physical properties and an initial microstructural zone model of these films will be discussed in 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.