

# SYMPOSIUM U

## Materials Science of Novel Oxide-Based Electronics

April 24 – 27, 2000

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\* Invited paper

## SESSION U1: APPLICATIONS

Chairs: David S. Ginley and Hiroshi Kawazoe  
Monday Morning, April 24, 2000  
Nob Hill A/B (Marriott)

### 8:30 AM \*U1.1

#### BURIED OXIDE CHANNEL FIELD EFFECT TRANSISTOR.

J.A. Misewich and A.G. Schrott, IBM-T.J. Watson Research Center, Yorktown Heights, NY.

An oxide channel field effect transistor was recently demonstrated at IBM [1] which showed switching characteristics similar to conventional silicon FETs. In this paper we introduce a new architecture for the oxide channel transistor where the oxide channel material is buried below the gate oxide layer. This architecture has several significant advantages over the first generation in coupling capacitance, channel mobility, and channel stability. We will discuss the design and fabrication of this second generation oxide FET and we will present results from second generation devices which demonstrate a higher transconductance.

[1] D.M. Newns, J.A. Misewich, C.C. Tsuei, A. Gupta, B.A. Scott, and A. Schrott, Appl. Phys. Lett. 73, 780 (1998).

### 9:00 AM U1.2

SIMULATION OF A SIMPLIFIED DESIGN FOR AN ALL METAL-OXIDE NANOSCALE MOTT TRANSITION FIELD EFFECT TRANSISTOR. Dennis M. Newns, Pratap C. Pattnaik, Wilm M. Donath, IBM-T.J. Watson Research Center, Yorktown Heights, NY.

We describe simulations on a simplified design for an all metal-oxide nanoscale Field Effect Transistor (FET). The device uses a high dielectric constant ferroelectric dielectric as the gate insulator. The channel material is a metal oxide and may be a Mott Insulator. In the present model, the gate and source/drain electrodes are unconventionally placed on opposite sides of the channel. Simulations are quantum mechanical and are based on a simplified transport model. Results show that the device has adequate conductance and that short channel effects are not large, even at 10 nm. channel length. Quasistatic simulation of a ring oscillator yields an estimated device switching time of 300 fs. for a single FET device.

### 9:15 AM U1.3

OPTIMIZING FABRICATION OF BURIED OXIDE CHANNEL FIELD EFFECT TRANSISTORS. A.G. Schrott, J.A. Misewich, M. Copel, D.W. Abraham and D. Neumayer, IBM-Thomas J. Watson Research Center, Yorktown Heights, NY.

The buried oxide channel field effect transistors (BOCFET) recently demonstrated at IBM [1] offer the potential to scale beyond the limits of silicon technology. In these devices the gate oxide/channel interface quality and gate oxide dielectric strength are critical to the device performance. Kawasaki and coworkers [2] have demonstrated that surface termination plays a substantial role in addition to atomic smoothness of the perovskite substrates in obtaining perfect two dimensional epitaxy of the heterostructures used in BOCFET architecture. It is well known that substrates with the highest degree of smoothness are obtained through an etching process which leaves a strontium titanate substrate terminated in titanium. Unfortunately, titanium termination leads to precipitates in the epitaxial growth of cuprates. We have examined methods of producing strontium terminated surfaces for BOCFET fabrication. The influence of substrate treatment and temperature on channel conductivity in BOCFET structures will be presented. In addition methods for optimizing the quality, dielectric constant, and dielectric breakdown potential of gate oxides for BOCFET architecture will be presented. [1] A.G. Schrott, J.A. Misewich, B.A. Scott, A. Gupta, D.M. Newns, and D. Abraham, Proc. Mat. Res. Soc. 574, in press (1999); A.G. Schrott and J.A. Misewich, to be published. [2] T. Ohnishi, K. Takahashi, M. Nakamura, M. Kawasaki, M. Yoshimoto, and H. Koinuma, Appl. Phys. Lett. 74, 2531 (1999); P. Tsuchiya, M. Kawasaki, H. Kubota, J. Nishino, H. Sato, H. Akoh, H. Koinuma, Appl. Phys. Lett. 71, 1570 (1997).

### 9:30 AM U1.4

ELECTRICAL CHARACTERISTICS OF LSMCD-DERIVED  $\text{SrBi}_{2.4}\text{Ta}_2\text{O}_9$  THIN FILMS USING  $\text{TiO}_2$  BUFFER LAYER FOR METAL/FERROELECTRIC/INSULATOR/SEMICONDUCTOR FIELD EFFECT TRANSISTOR DEVICES. Joo-Dong Park, Tae-Sung Oh, Hong Ik Univ, Dept of Metallurgical Engineering and Materials Science, Seoul, KOREA.

Using  $\text{TiO}_2$  buffer layers of 10~200 nm thickness,  $\text{SrBi}_{2.4}\text{Ta}_2\text{O}_9$  (SBT) thin films of 400 nm thickness were prepared on the Si(100) substrates by Liquid Source Misted Chemical Deposition (LSMCD), and their electric characteristics were investigated for nondestructive read out (NDRO) MFIS-FET device application. The 400 nm-thick

SBT film on Pt/Ti/SiO<sub>2</sub>/Si(100) substrates exhibited 2P<sub>r</sub> of 8.9  $\mu\text{C}/\text{cm}^2$  and E<sub>c</sub> of 28 KV/cm at 5 V. C-V characteristics of Pt/SBT/TiO<sub>2</sub>/Si structures exhibited hysteresis loops due to the ferroelectric switching behavior of SBT films, and the maximum capacitance of MFIS structures increased with decreasing the thickness of TiO<sub>2</sub> buffer layers. The memory window of 1.2 V was obtained for SBT films on Si substrates using 50 nm-thick TiO<sub>2</sub> buffer layer.

### 9:45 AM U1.5

STUDY OF  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  (GGG) and  $\text{ZnGa}_2\text{O}_4$  / GaAs INTERFACE FOR MOS DEVICE APPLICATIONS. S. Pal, D.N. Bose, Advanced Technology Centre, Indian Institute of Technology, Kharagpur, INDIA.

One of the key remaining issues in GaAs technology is the lack of insulating layers providing low interface state density for stable MOS device operation. The present approach is to use gallium oxide-containing compounds  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  (GGG) and  $\text{ZnGa}_2\text{O}_4$  as insulating layers on n-GaAs to provide high resistivity gate dielectric with low  $D_{it}$ . For the first type of oxide, both single crystal GGG and sintered polycrystalline material were used. A stoichiometric mixture of  $\text{Ga}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$  was sintered at 1450°C for 12 hrs. to prepare the polycrystalline powder. Stoichiometric  $\text{ZnGa}_2\text{O}_4$  powder was used in the second case. The oxide films were deposited by electron beam evaporation on (100) n-GaAs single crystals of carrier concentration  $4.5 \times 10^{15} \text{cm}^{-3}$ . The GGG film thickness was varied from 500 Å to 5000 Å. Pretreatment of the GaAs substrates involved removal of native oxide in 50% HCl followed by immediate deposition of oxide films. Au-Ge metallization was used for ohmic back contacts. MIS structures were fabricated by depositing gold dots on the oxide films. Post-deposition annealing of GGG films at 370°C was found essential to obtain modulation of C-V. The dielectric constants of the GGG and  $\text{ZnGa}_2\text{O}_4$  films were found to be 13.2 and 12.4 respectively while the resistivities were found to be  $10^{11}$  ohm-cm and  $10^9$  ohm-cm. The C-V curves for GGG/ GaAs showed high positive threshold voltages which decreased with increase in oxide thickness with no appreciable change in  $D_{it}$ . From the high frequency (1MHz) C-V measurements interface state densities  $D_{it}$  were estimated using Terman's method.  $D_{it} = 1.68 \times 10^{11} \text{eV}^{-1} \text{cm}^{-2}$  was observed on the GGG (from single crystal) / GaAs interface compared with  $3.89 \times 10^{11} \text{eV}^{-1} \text{cm}^{-2}$  for GGG (from poly) / GaAs and  $6.9 \times 10^{11} \text{eV}^{-1} \text{cm}^{-2}$  for  $\text{ZnGa}_2\text{O}_4$  / GaAs interface. The hysteresis in C-V for GGG / GaAs was found to be very small while it was larger for  $\text{ZnGa}_2\text{O}_4$  / GaAs. PL carried out using an Argon ion laser (488 nm) on bare and passivated GaAs surfaces showed increase in intensity after oxide deposition showing the efficacy of oxide passivation.

### 10:30 AM \*U1.6

ELECTRONIC PHASE SEPARATION AND ITS IMPLICATION FOR OXIDE ELECTRONIC DEVICES. T. Venkatesan, University of Maryland, College Park, MD.

In the last decade some of the most exciting materials systems to have been studied are the doped antiferromagnets. The high temperature superconducting cuprates and the colossal magnetoresistive manganites are two excellent examples of widely studied systems with a fascinating array of properties and interactions. From the fundamental point of view the idea that these systems even in the presence of a stoichiometric, single material phase can exhibit an inhomogeneity with respect to charge distribution, also referred to as an electronic phase separation, has become quite popular. In this talk I will discuss some of the effects of this electronic phase separation on the response of the materials to external perturbations and also discuss implications for potential devices.

### 11:00 AM \*U1.7

ALUMINUM OXIDE FILMS FOR GATE INSULATOR APPLICATIONS GROWN BY PULSED LASER DEPOSITION. Sherwood D. Silliman, Hans M. Christen, K.S. Harshavardhan Neocera, Inc., Beltsville, MD; Roland Chin, Zhiyong Ma, Intel Corporation, Technology & Manufacturing Group, Hillsboro, OR.

Thin insulating films of aluminum oxide were grown on hydrogen-terminated p-type silicon substrates by Pulsed Laser Deposition (PLD). Stoichiometric  $\text{Al}_2\text{O}_3$  targets and an Ar background gas were used in an off-axis growth geometry with no direct line-of-sight between the laser spot and the substrate surface. Capacitance values as high as  $1.5 \text{mF}/\text{cm}^2$  were measured on films with thicknesses below 40 Å, corresponding to a dielectric constant of 6.5. Forward leakage current densities of  $-0.5 \text{A}/\text{cm}^2$  at  $-1\text{V}$  are observed on 25 Å thick films at room temperature. Cross-sectional TEM shows good coverage uniformity but indicates the existence of an interfacial layer. The potential of these films for gate insulator applications and ways to further improve the film quality are discussed.

**11:30 AM U1.8**

WORK FUNCTION STUDY FOR THE SEARCH OF EFFICIENT TARGET MATERIALS FOR USE IN HYPER-THERMAL SURFACE IONISATION USING A SCANNING KELVIN PROBE. Uwe Petermann, Iain D. Baikie, Bert Lägler, Konrad M. Dirscherl, Robert Gordon Univ, Dept of Applied Physics, Aberdeen, UNITED KINGDOM.

In order to search for efficient target materials for use in Hyper-thermal Surface Ionisation (HSI), a new mass spectroscopy ionisation technique, we have performed a study of high and low work function (wf) surfaces as part of an ongoing project. HSI relies on high and low wf surfaces for the production of positive (pHSI) and negative (nHSI) ions, respectively. Using a novel UHV Scanning Kelvin Probe we have followed the oxidation kinetics of polycrystalline Re at different temperatures and examined the effects of oxidation, flash annealing and sputter-anneal cleaning cycles via high resolution wf topographies. Our results indicate that oxidised Re is the best candidate for pHSI in terms of ionisation efficiency and wf change. The peak wf change of 2.05 eV occurred at 950K. For the nHSI materials Calcium exhibited the best performance with respect to the ionisation efficiency indicating a wf of 2.8 eV. We will present data in terms of ionisation efficiency using an HSI-TOF system and time stability of the wf.

**11:45 AM U1.9**

SURFACE INVESTIGATIONS ON SINGLE CRYSTAL ANATASE TiO<sub>2</sub>. R. Hengerer, L. Kavan, B. Bolliger, M. Erbudak and M. Graetzel, EPFL, Lausanne, SWITZERLAND.

In charge separation/injection devices based on nanocrystalline TiO<sub>2</sub> films like dye-sensitized solar cells or 'rocking chair' lithium batteries, anatase TiO<sub>2</sub> shows superior performance in comparison to the more stable and common polymorph of TiO<sub>2</sub>, rutile. In contrast to rutile, however, surface investigations that help to elucidate the charge transfer processes are missing for anatase due to the lack of large and clean crystals. We succeeded in growing suitable anatase single crystals by a chemical transport reaction. The surfaces of these crystals could be characterized by standard physical and electro-chemical techniques. The examination of the structure of the clean (101) and (001) faces by low energy electron diffraction (LEED) and secondary electron imaging (SEI) showed that these surfaces are bulk terminated and thermodynamically stable. The discussion of molecular adsorption on anatase surfaces can now be based on reliable structural data. Impedance spectroscopy in aqueous solution revealed a slight difference in the flatband potential between the (101) and the (001) faces. This shift is also manifested in a different photocurrent onset potential and can be rationalized by a different water adsorption on the two surface structures. Voltammetry in aprotic solutions showed a different lithium insertion behavior for the two surfaces. This is explained by a different structural transparency of the anatase lattice in the two directions. Both findings favor the (001) over the (101) surface. This orientational dependence could have some important technological relevance for the mesoscopic TiO<sub>2</sub> films used in solar cells and lithium batteries.

SESSION U2: NEW IDEAS AND MAGNETISM  
Chairs: Dennis M. Newns and T. Venky Venkatesan  
Monday Afternoon, April 24, 2000  
Nob Hill A/B (Marriott)

**1:30 PM \*U2.1**

TRANSPARENT OXIDE NANOPARTICLES FOR ADVANCED ORGANIC/INORGANIC COMPOSITE THIN FILM SENSORS AND EMITTERS. Sue A. Carter, Alison Breeze, University of California, Santa Cruz, CA; Alexi C. Arango, E-Ink Corp., Cambridge, MA; H.H. Horhold, Fredrich Schiller University, GERMANY; P.J. Brock, IBM Almaden Research Center, San Jose, CA; David S. Ginley, NREL, Golden, CO.

I will discuss how transparent semiconducting oxide nanoparticles can be used to dramatically improve the optical and electrical properties of solution-processed thin film organic/inorganic composite optoelectronic devices. By controlling the organic-oxide interface and the composite morphology, I will show that efficient photovoltaic and light emitting diode operation can be achieved in the same material system. Finally, I will address the implication of these results for the use of semiconducting oxides in other novel organic-oxide based devices, including biosensors, transistors and optical switch.

**2:00 PM \*U2.2**

EPITAXIAL PIEZOELECTRIC HETEROSTRUCTURES FOR HIGH FREQUENCY MEDICAL ULTRASOUND TRANSDUCER APPLICATIONS. C.B. Eom, Duke University, Department of Mechanical Engineering and Materials Science, Durham, NC.

The recent developments of relaxor ferroelectrics such as Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)-PbTiO<sub>3</sub> (PMN-PT) PMN-PT and Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)-PbTiO<sub>3</sub> PZN-PT, yielding significantly higher electromechanical coupling coefficient than conventional polycrystalline ferroelectrics, have propelled single crystal materials to the forefront of research and development of piezoelectric devices. A major challenge is to prepare these materials in single crystal epitaxial thin films between metal electrodes, and integrate them so that these properties can be utilized in piezoelectric devices with all the advantages of microelectronic technology. We have fabricated PMN-PT/SrRuO<sub>3</sub> single crystal epitaxial heterostructures on miscut (001) SrTiO<sub>3</sub> substrates employing conductive oxide SrRuO<sub>3</sub> bottom electrode. The SrRuO<sub>3</sub> conductive oxide is a pseudo-cubic perovskite, which could be an ideal electrode for piezoelectric devices. Scanning tunneling microscopy and x-ray diffraction revealed that the SrRuO<sub>3</sub> films on miscut (001) SrTiO<sub>3</sub> substrates grow by step flow mechanism in one direction, which leads to single crystal film. Transmission electron microscopy images of a cross-sectional PMN-PT/SrRuO<sub>3</sub> heterostructure show that the PMN-PT layer is single domain and grows epitaxially on the single crystal SrRuO<sub>3</sub> thin film bottom electrode. These epitaxial heterostructures look promising for the fabrication of integrated single crystal piezoelectric devices for electromechanical systems. We will discuss the materials science issues in fabricating high frequency medical ultrasound transducers.

**2:30 PM \*U2.3**

MATERIALS DESIGN FOR THE LOW-RESISTIVITY p-TYPE ZnO AND TRANSPARENT FERROMAGNET WITH TRANSITION METAL ATOM DOPED ZnO: PREDICTION vs. EXPERIMENT. H. Katayama-Yoshida, K. Sato, Department of Condensed Matter Physics, The Institute of Scientific and Industrial Research, Osaka Univ., Osaka, JAPAN; T. Yamamoto, Department of Electronic and Photonic System Engineering, Kochi University of Technology, Kochi, JAPAN.

Based upon ab initio electronic structure calculation using supercell-ASW method, we report that co-doping using reactive codopants of donors, such as Al, Ga or In, enhances the incorporation of N acceptors in p-type codoped ZnO. We find the delocalized states of N in p-type ZnO in which N acceptors are codoped with Ga, In and Al donors [1]. We propose a new valence control method for the fabrication of a low-resistivity p-type ZnO upon codoping, based upon the calculation [1]. We compare our materials design to fabricate a low resistivity p-type ZnO [1, 2] with the recent successful codoping experiments using Ga and N codoping in ZnO [3]. Based upon ab initio electronic structure calculation using supercell-KKR method, we propose a materials design to fabricate the ferromagnetic Mn-doped p-type ZnO. It is shown that the anti-ferromagnetic states is more stable than the ferromagnetic ones due to the anti-ferromagnetic super-exchange interaction, if we have no mobile holes. However, upon codoping with the mobile holes, it is shown that the ferromagnetic states becomes more stable than the anti-ferromagnetic ones due to the ferromagnetic double-exchange interaction. We obtain a large exchange splitting and small crystal field splitting with highly localized and satulated magnetic moment, which indicates a strong ionicity with a high-spin ground states [4]. We discuss the roles of the codoping, hole and electron concentration dependences, and chemical trend (3d transition metal) of the ferromagnetic states. Based upon the calculations for V-, Cr-, Fe-, Co- and Ni-doped ZnO, we also propose the materials design for the fabrication of the transparent ferromagnets with almost saturated magnetic moment [5]. We compare our prediction with an available experiment.

- [1] T. Yamamoto and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 38 (1999) pp. L166-L169.
- [2] H. Katayama-Yoshida and T. Yamamoto, Japanese Patent (Fabrication method of a low-resistivity p-type ZnO using codoping: JP H10-287966), and submitted to USP and ECP.
- [3] M. Joseph, H. Tabata, T. Kawai, to be published in JJAP, 38 (1999) No. 11A.
- [4] K. Sato and H. Katayama-Yoshida, unpublished results.
- [5] H. Katayama-Yoshida and K. Sato, Applied Japanese Patent (Fabrication method and new materials of ferromagnetic p-type ZnO: JP H11-247959).

**3:00 PM U2.4**

FABRICATION AND PROPERTIES OF 1-3 PZT/POLYMER COMPOSITES FOR TRANSDUCER APPLICATIONS VIA RAPID PROTOTYPE METHOD. Xiaodong Yin, Li Lu and J.Y.H. Fuh, National University of Singapore, Dept. of Mechanical and Production Engineering, Singapore, SINGAPORE.

Piezoelectric ceramic/polymer composites with 1-3 connectivity for transducer applications were fabricated by rapid prototype techniques. PZT ceramic preforms containing uniform rods aligned in a precise array were produced. The PZT preforms contain 500 rods which are 200 μm diameter and 2-5 mm long. The PZT structures were sintered, poled, encapsulated into a polymer matrix. Composites

have been produced with both flexible and rigid polymers. Several transducers with the same composition but different thickness and PZT volumes have been fabricated and evaluated. Measurement of the 1-3 PZT composites revealed good performance both as projectors and hydrophones. Ultrafine scaled 1-3 PZT composites with uniform arrays of 80 nm diameter, 5000 nm long PZT fibers in an epoxy matrix have also been produced. The properties of both PZT composites were investigated.

### 3:30 PM U2.5

**THERMAL STABILITY AND SEMICONDUCTING PROPERTIES OF EPITAXIAL  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  FILMS.** K.S. So, K.H. Wong, W.B. Wu, The Hong Kong Polytechnic Univ, Dept of Applied Physics, Hung Hum, Kowloon, Hong Kong, PR CHINA.

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) perovskite oxide films have been grown on (001)  $\text{LaAlO}_3$  (LAO) by pulsed laser deposition. The films were deposited in an ambient oxygen pressure of 0.1 mTorr to 200 mTorr and under different substrate temperatures. Their structural properties were examined by X-ray diffractometry. Heteroepitaxial growth was confirmed for films deposited at 650°C or above. Electrical measurements suggest that the charge carrier concentration of the films varies with their oxygen content and shows high stability against further thermal treatment. Semiconducting LSMO films at room temperature were obtained for deposition at oxygen pressure  $\leq$  60 mTorr. The epitaxial LSMO films have been used as the semi-conducting channel of a ferroelectric field effect transistor. Hetero-epitaxial  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ /LSMO/LAO structures have been fabricated and characterized.

### 3:45 PM U2.6

**THE ENHANCEMENT OF ELECTRICAL CONDUCTIVITY AND LOW-FIELD MAGNETORESISTANCE BY POINT DEFECTS IN  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  FILMS.** Hsiung Chou, M.N. Ou, National Sun Yat-Sen University, Department of Physics, Kaohsiung, TAIWAN; M.T. Hong, National Sun Yat-Sen University, Department of Electrical Engineering, Kaohsiung, TAIWAN; Y.C. Yu, Academia Sinica, Institute of Physics, Taipei, TAIWAN.

The effects of uniform point defects produced by irradiation with 1.7, 3 and 6 MeV protons on electrical conductivity and the magnetoresistance (MR) in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (001) films have been investigated. The doses were varied from  $1 \times 10^{11}$  to  $2 \times 10^{15}$  protons/cm<sup>2</sup>. The point defects by local structures and spin disorder generated dramatically enhancement on MR from -0.1% to -6% at a field lower than 2000 Oe at 77K. The MR decreased with increasing of temperature. At room temperature, low-field MR remained to -0.8% where the original sample exhibited an intrinsic MR of -0.1%. The dependence of MR to temperature suggested a spin-flip tunneling mechanism through a s-d impurities interaction. The point defects were found to give rise a new conduction channel for carrier that outweighed the electron-lattice scattering which was usually attributed to an excess resistivity as in irradiation experiments. As a result of that, they lowered the overall resistivity over 4 orders of magnitude.

### 4:00 PM U2.7

**TRANSPORT ANISOTROPY IN EPITAXIAL PLD-MADE  $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$  FILMS.** S.I. Khartsev, P. Johansson, A.M. Grishin, Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN.

Sequence of epitaxial  $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$  (LSMO) films, ranged from 240 to 5 nm, have been prepared by pulsed laser deposition onto (110)  $\text{SrTiO}_3$  (STO) substrates. Compared with our previous results on LSMO/ $\text{SrTiO}_3$ (100) films (MRS Spring 99' Proceedings), films on STO(110) substrates exhibit strong anisotropy of electrical resistivity R. R measured in [1-10] direction is comparable with the resistivity of LSMO/STO(100) film, while R in [100] direction 25 times larger than in STO(100) case. The maximum value of  $R[100]/R[1-10] = 25$  anisotropy reaches at low temperature of 90 K. Distinct crossover from 3D to 2D case has been observed. For thick films anisotropy monotonously decreases with the temperature increase. Films thinner than 200 angstrom exhibit peak of anisotropy at temperature, which shifts to lower temperatures with the thickness decrease. Maximum temperature coefficient of resistivity (TCR) was found to be around 2%, if measured along [100] direction, and about 3 times higher in [1-10] in-plane direction. We explain the observed effects in terms of the crystalline properties of fabricated films.

### 4:15 PM U2.8

**MAGNETORESISTANCE AT GRAIN BOUNDARIES IN La-Ca-Mn-O CMR FILMS.** D.J. Miller, Y.K. Lin, V. Vlasko-Vlasov, U. Welp, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Structural defects play a large role influence on the properties of the CMR manganites. In this work, we have studied the effect of grain

boundaries on magnetoresistance in La-Ca-Mn-O thin films. Thin film bicrystals were prepared by pulsed laser deposition onto bicrystal substrates. In contrast with the highly meandering boundaries typically observed in bicrystals of high temperature superconductors, the boundaries in these films are relatively straight and well defined. However, the magnetic character of such boundaries varies from that of the grains on either side, with the local magnetization oriented out of the plane at the boundary while it is oriented within the plane in the grains on either side. This change in local magnetization leads to enhanced magnetoresistance across the boundary in low fields, and a model describing this behavior will be discussed.

This work was partially supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under contract W-31-109-ENG-38 and by the National Science Foundation through the Science and Technology Center for Superconductivity under contract DMR 91-20000.

### 4:30 PM U2.9

**GRAIN BOUNDARY MODIFICATIONS IN POLYCRYSTALLINE  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  DUE TO ADDITIVES.** V. Ravindranath, K.S.P. Phani Kumar, P.V. Suresh, Sriram Thirumalai and M.S. Ramachandra Rao, Materials Science Research Centre and Department of Physics, Indian Institute of Technology, Madras, Chennai, INDIA.

Hole doped manganese perovskites such as  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  (M= Ca and Sr) have attracted considerable attention in recent years because of the colossal magnetoresistance (CMR) they exhibit close to the ferromagnetic transition temperature. Although, a number of structural and magnetotransport studies have been carried out on bulk polycrystalline samples, single crystals and thin films of these materials, the physics of the grain boundaries in these materials is not well understood. The role of grain boundaries in the magnetotransport properties of these compounds is being increasingly realized<sup>1,2</sup>. With better understanding it may be possible to exploit the grain boundary properties for device applications. In the present study, polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (LCMO) was prepared by the solid state reaction method. High quality LCMO powder was thoroughly mixed with 5wt% and 10wt% silver oxide (AgO). The mixture was pressed in to pellets and sintered at 1300°C for 24 h. Essentially, metallic silver addition is affected in this process as AgO dissociates in to Ag and oxygen at very low temperatures. Resistivity of the silver-added compounds showed nearly an order decrease compared to the pure compound (LCMO), the peak resistivity temperature being same in both the cases. Scanning electron micrographs of the compounds show an increase in the average grain size for the silver added compounds. Preliminary analysis of the data show that addition of silver oxide makes the material more crystalline and hence decreases the average area of the grain boundaries. Though a decrease in resistivity is not suitable from the point of view of device applications, these studies show the role of additives in modifying the grain boundaries on the magnetotransport properties of these materials. Further work is in progress to increase the resistivity of these compounds by using insulating additives such as  $\text{PbO}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{CrO}_2$ ,  $\text{YbFeO}_3$  etc.

<sup>1</sup>A. Gupta et al., Phys. Rev. B. 54 (1996) R15629.

<sup>2</sup>R. Gross et al. (to appear in JMMM 1999).

### 4:45 PM U2.10

**MAGNETIC AND MAGNETO-OPTIC PROPERTIES OF PULSED LASER DEPOSITED  $\text{Ce}_x\text{Y}_{3-x}\text{Fe}_5\text{O}_{12}$  FILMS.** Hyonju Kim, Alex Grishin, K.V. Rao, Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN.

We report magnetic, crystalline, and magneto-optic (MO) properties of Ce-substituted yttrium iron garnet (Ce:YIG) thin films epitaxially grown onto single crystal  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (111) substrates using Nd:YAG pulsed laser deposition technique. Oxygen ambient pressure is found to be the critical parameter to grow Ce:YIG films with good crystalline and magnetic properties as well as large MO effect. The film fabricated at 50 mTorr oxygen pressure exhibits the maximum Faraday rotation  $\text{FR} = 0.7$  and  $1.6$  deg/um @ 633 nm and 429 nm respectively, the minimum in-plane coercivity  $H_c = 35$  Oe, and the narrowest full width at half maximum  $\text{FWHM} = 0.06$  deg of (444) rocking curve. Analog of the Verdet constant  $V = \text{FR}/4\pi\text{mT}$  is also found to be dependent on the ambient pressure and reaches the value as high as  $1.41 \times 10^{-3}$  deg/um\*G @ 633 nm, indicating this material is promising for MO applications. Energy dispersion FR spectra, measured in visible region 400 to 840 nm, clearly demonstrate Ce substitution prominently enhances Faraday effect at 690 nm and at the 429 nm blue-wavelength region. Three times lower value of FR, compared with the films fabricated by sputtering technique, correlates with anomalous low saturated magnetization  $4\pi\text{mT}$ s, lower by the same factor. To clarify the role of strain, induced by film/substrate lattice mismatch, and the change of  $\text{Fe}^{3+}$  and  $\text{Ce}^{3+}$  valence states, deposition onto the  $\text{Gd}_3(\text{Ga},\text{Sc})_5\text{O}_{12}$  single crystal as well as post-deposition heat treatment have been performed in various ambient gases.

SESSION U3: FERROELECTRICS I  
Chairs: David S. Ginley and Alexander Grishin  
Tuesday Morning, April 25, 2000  
Nob Hill A/B (Marriott)

**8:15 AM \*U3.1**

**FERROELECTRIC THIN FILM BASED TUNABLE MICROWAVE COMPONENTS FOR SATELLITE COMMUNICATIONS: A PROGRESS REVIEW.** Felix A. Miranda, Robert R. Romanofsky, Fred W. Van Keuls, Carl H. Mueller and Joseph D. Warner, NASA-Glenn Research Center, Cleveland, OH; Guru Subramanyam, University of Dayton, Dayton, OH.

The quality of thin ferroelectric films for satellite communications at microwave frequencies has improved considerably in recent years. This has prompted demonstrations of tunable microwave components such as filters, resonators, oscillators, and phase shifters with applicability at frequencies ranging from L-band to Ka-band. Thus, the use of ferroelectric technology is evolving from a single, "stand-alone" component, to more ambitious hybrid communication subsystems such as filter-LNAs and resonators-FETs based tunable oscillators, and self-integrated, multi-element systems such as, for example, electronically steerable reflectarray antennas. In this work we will discuss the current trends of ferroelectric thin film based tunable subsystems for communication applications in terms of the following aspects: most promising materials for implementation of these subsystems at room and cryogenic temperatures, advantageous geometry for circuit design, ferroelectric film thickness, doped films, post annealing treatments, crystalline quality, less expensive substrates (e.g. sapphire and silicon), among others. Practical examples of how these factors were taken into account to perform effective demonstrations of this technology will be discussed, and the current state of development of some multi-element subsystems such as linear phased array for ranging and collision avoidance applications will be presented.

**8:45 AM \*U3.2**

**FUNDAMENTAL UNDERSTANDING OF MATERIALS ISSUES IN FERROELECTRIC THIN FILMS.** X.X. Xi, Department of Physics, The Pennsylvania State University, University Park, PA.

The properties of ferroelectrics in the thin film form are often different from those of their bulk counterparts. In pulsed-laser-deposited SrTiO<sub>3</sub> thin films, we have found that under strain, the thin films are in a tetragonal structure at room temperature. The cubic-to-tetragonal structural phase transition, which occurs in single crystals at about 105 K, is shifted to above 800 K. In films with little strain, the transition occurs at 125 K. In both cases, Raman scattering shows the symmetry-forbidden optical phonons, indicating the reduction of symmetry, caused most likely by local defects such as oxygen vacancies. The line shape of the polar phonon shows a Fano asymmetry, indicating the interaction with a polar continuum of excitation, which we suggest to be due to the micro polar regions around the oxygen vacancies. The temperature dependence of the low-frequency complex dielectric constant shows markedly distinct behaviors from those of the single crystals, which is consistent with the 2D Ising model in transverse field if one assumes a stronger ferroelectric coupling with respect to the quantum fluctuations in the thin films. The dielectric constant decreases as the film thickness decreases. We have measured the soft mode in the thin films using far infrared ellipsometry, and the result shows that the soft mode is considerably hardened in the thin films compared to the single crystals. After the correction for the dead layers effect, the lower dielectric constant in thin films is completely explained by the soft-mode hardening, in agreement with the LST relation. The phonon frequencies are also measured under the electric-field bias using Raman scattering, and a non-vanishing field-induced soft-mode hardening is observed up to room temperature. These lattice dynamics results are important for the understanding of the dielectric and ferroelectric properties in the thin films.

**9:15 AM U3.3**

**PYROELECTRIC COEFFICIENT OPTIMIZATION THROUGH GRAIN SIZE CONTROL IN (Ba,Sr)TiO<sub>3</sub> THIN FILMS.** Lawrence F. Schloss and Eugene E. Haller, Materials Science Division, Lawrence Berkeley National Laboratory and Department of Materials Science and Mineral Engineering, University of California at Berkeley, Berkeley, CA.

The effects of columnar grain size on the dielectric properties of (Ba,Sr)TiO<sub>3</sub> (BST) thin films being developed for utilization as the active layer in pyroelectric detector arrays have been explored. Thin, epitaxial bilayers of Ba<sub>0.2</sub>Sr<sub>0.8</sub>TiO<sub>3</sub> and SrRuO<sub>3</sub> were grown by pulsed laser deposition on SrTiO<sub>3</sub> substrates at pulsed laser repetition rates varying from 1 to 20 Hz during BST growth. Room temperature

dielectric constants were found to increase with increasing laser pulse rate. Temperature dependent capacitance studies revealed a Curie temperature decrease of more than 60 K with increasing laser pulse rate. However, the rate of dielectric constant change with temperature did not show a monotonic dependence on the laser pulse rate. For films with SrRuO<sub>3</sub> deposited at 5 Hz, the pyroelectric coefficient was largest for BST films also grown at 5 Hz. While the pyroelectric coefficient was almost identical at low and high repetition rates, the pyroelectric coefficient at this intermediate laser pulse rate was approximately three times larger. High resolution x-ray diffractometry, in conjunction with cross-sectional scanning electron microscopy and Rutherford backscattering spectroscopy, were employed in order to explain the relation between the electrical properties and the microstructure of these films.

**9:30 AM U3.4**

**THE EFFECTS OF Mg DOPING ON THE MATERIALS AND DIELECTRIC PROPERTIES OF Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> THIN FILMS.** M.W. Cole, P.C. Joshi, R.L. Pfeffer, C.W. Hubbard, M. Wood, M. Ervin, U.S. Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD.

We have investigated the materials and dielectric properties of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> thin films with 0 to 20 mol% Mg. Films were fabricated via metalorganic decomposition technique using barium acetate, strontium acetate, titanium isopropoxide as precursors to form BST. Acetic acid and 2-methoxyethanol were used as solvents and magnesium methoxide was employed as the dopant. The precursor films were spin coated onto Pt-coated silicon substrates. Subsequent to coating, the films were pyrolyzed at 350°C in order to evaporate solvents and organic addenda and form an inorganic film. The spin coat-pyrolyzation process was repeated until a film thickness of 500 nm was achieved. Post-deposition annealing was performed in an oxygen ambient at 750°C. The doped and undoped films were characterized for structural, compositional, dielectric and insulating properties. Specifically, x-ray diffraction was used to assess film crystallinity, phase formation and film orientation. Atomic force microscopy and field emission scanning electron microscopy and were employed to access surface morphology and plan view grain formation. Cross-sectional transmission electron microscopy, combined with energy dispersive spectroscopy analysis, was used to detail the film microstructure, film-substrate interfacial properties, and elemental diffusion. Rutherford backscattering spectrometry was employed to access film thickness and composition. The electrical measurements were conducted in the metal-insulator-metal capacitor configuration. Dissipation factor, and dielectric permittivity were measured with an HP 4192A impedance analyzer. The films insulating properties, leakage current, were evaluated via I-V measurements. Our results demonstrate that the dielectric and insulating properties of BST thin films are strongly dependent on processing temperature, film composition, microstructure, crystal structure and the quality of the electrode-film interface. The details of the materials, dielectric and electrical properties will be examined, correlated and discussed.

**10:00 AM \*U3.5**

**A MICROSCOPIC MODEL OF FERROELECTRICITY IN PbTiO<sub>3</sub> THIN FILMS.** Karin M. Rabe, Dept of Applied Physics, Yale University, New Haven, CT; Philippe Ghosez, Institut de Physique, Universite de Liege, Liege, BELGIUM.

Ultrathin ferroelectric films have recently attracted interest as components in novel field-effect devices. Sample geometry, surface properties and electrical and mechanical boundary conditions are all expected significantly to affect the ferroelectric instability and spontaneous polarization in these films, complicating the interpretation of experimental observations. We have studied ferroelectricity in ultrathin PbTiO<sub>3</sub> films through the construction of an microscopic effective Hamiltonian with parameters determined from first-principles calculations. Under short-circuit electrical and stress-free mechanical boundary conditions, (001) films with thickness as low as three unit cells are found to have a perpendicularly polarized ferroelectric ground state with significant enhancement of the polarization at the surface. This theoretical framework also permits the investigation of structural phase transitions, as well as the calculation of the dielectric and piezoelectric response of the films under applied electric fields and stresses both in the ground state and at nonzero temperature. Selected results will be presented.

**10:30 AM \*U3.6**

**ELECTROSTATIC MODULATION OF SUPERCONDUCTIVITY USING A FERROELECTRIC FIELD EFFECT.** C.H. Ahn, S. Gariglio, P. Paruch, T. Tybell, L. Antognazza, J.-M. Triscone DPMC, University of Geneva, Geneva, SWITZERLAND.

We have investigated the modulation of superconductivity using a ferroelectric field effect in epitaxial Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub>/GdBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub> heterostructures. Using the polarization field of the ferroelectric oxide

Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub>, we have shifted the doping level of the high temperature superconductor GdBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub> without introducing chemical or structural disorder. For slightly underdoped samples, a reversible change of the superconducting transition of 7 K was observed, whereas for more underdoped samples, an insulating state was induced. This approach demonstrates the route to a nonvolatile superconducting switch, a device that is dissipationless in one of its states.

C.H. Ahn, S. Gariglio, P. Paruch, T. Tybell, L. Antognazza, J.-M. Triscone, Science 284, 1152 (1999).

#### 11:00 AM U3.7

DEPENDENCE OF DIELECTRIC PROPERTIES ON THICKNESS (25 NM-200 NM) FOR METAL-ORGANIC CHEMICAL VAPOR DEPOSITED PZT THIN FILMS. C.H. Lin, P.A. Friddle, A. Daga, D.A. Payne, Haydn Chen, Department of Materials Science and Engineering, Frederick Sietz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL; T.B. Wu, Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, TAIWAN ROC.

Textured, (001)-oriented Pb(Zr,Ti)O<sub>3</sub> (PZT) thin film capacitor were prepared using metal-organic chemical vapor deposition (MO-CVD) on LaNiO<sub>3</sub> (LNO) buffered platinized Si. With thickness varying from 25 nm- 200 nm, the dependence of electrical properties on the film thickness was studied using several techniques, including temperature variable current-voltage (I-V), capacitance-voltage (C-V) and polarization-electrical field (P-E) measurements. The effects of the interfacial layer on the dielectric properties of the PZT thin films are described. Such interfacial layer was characterized to be possibly due to Pb-deficient layer at the interface between PZT and LNO. The dielectric constant of the interfacial layer is analyzed to be around 150 with the thickness being about 5 nm, while the true dielectric constant of the PZT layer is 667. It was also found that the dielectric behavior of the PZT thin film capacitors became interfacial layer dominant as the thickness of PZT layer gets below 50 nm. Moreover, the potential barrier for the charge injection from LaNiO<sub>3</sub> conductive layer to PZT is characterized to be about 0.2 eV.

\*Work was supported by the U.S. Department of Energy through the Frederick Sietz Materials Research Laboratory, University of Illinois at Urbana-Champaign.

#### 11:15 AM U3.8

INFLUENCE OF LaNiO<sub>3</sub> AS AN ELECTRODE ON THE PROPERTIES OF FERROELECTRIC OXIDES. M. Vedawyas, R. Katare, Md. Yaesin A. Kumar, University of South Alabama, Dept. of Electrical & Computer Engineering, Mobile, AL.

An electrode plays an important role in realising a ferroelectric thin film as a potential memory device. We have investigated LaNiO<sub>3</sub> (LNO) as a potential electrode material and evaluated the ferroelectric properties of oxide materials like Barium Strontium Titanate (BST) and Lead Zirconium Titanate (PZT). We have successfully deposited epitaxial films of LNO on Pt coated Si(100) and LaAlO<sub>3</sub> (LAO) substrates using the pulsed excimer laser deposition technique. We are able to grow high quality BST and PZT films on top of this LNO layer. The transmission electron microscopy studies revealed the smooth interface between the substrate and the LNO layer as well as between LNO and the ferroelectric film. The X-ray diffraction revealed the epitaxy of the LNO films. The ferroelectric properties of BST and PZT were investigated using the HP9412A impedance analyzer, Keithley 617 electrometer and RT66A.

#### 11:30 AM \*U3.9

NOVEL PROPERTIES IN MAGNETIC AND MAGNETO-RESISTIVE OXIDE ARTIFICIAL LATTICES, Tomoji Kawai, Osaka University, Mihogaoka, Ibaraki, JAPAN.

This talk includes following topics:

- 1) Basic principle of the magnetic oxide artificial lattices.
- 2) Fabrication of the oxide artificial lattices by laser MBE.
- 3) Spin control by crystal orientation in (Fe,Cr) oxides and (Mn,Fe) oxides.
- 4) Enhanced magnetoresistance in spin frustrated Mn oxide lattices.
- 5) Photo-induced magnetization of spinel oxides.

#### SESSION U4: FERROELECTRICS II

Chairs: Felix A. Miranda and J.-M. Triscone

Tuesday Afternoon, April 25, 2000

Nob Hill A/B (Marriott)

#### 1:30 PM \*U4.1

JUNCTION PROPERTIES OF METAL/SrTiO<sub>3</sub> SYSTEMS. Takashi Shimizu and Hideyo Okushi, Electrotechnical Laboratory, Tsukuba, Ibaraki, JAPAN.

Electrical properties of Nb-doped SrTiO<sub>3</sub> Schottky junctions have been investigated in detail for a comprehensive understanding of metal/oxide interfaces. In the first topic, we present importance of surface treatment for oxides to improve controllability and reproducibility of the electrical properties of the oxide interfaces. With a high-purity ozone surface treatment, rectification ratio over 9th order of magnitudes has been successfully obtained, while without the surface treatment, anomalous large reverse bias leak currents were observed in the current-voltage characteristics. This suggests the effectiveness of the surface treatment for oxides after performing lithography or etching process in device application of perovskite oxides. In the next topic, we show the chemical trend of the Schottky barrier height and temperature dependence of the electrical properties of the junctions. We present existence of intrinsic low permittivity layer at the metal/SrTiO<sub>3</sub> junction and suggest structural modulation of SrTiO<sub>3</sub> at the interface. This structural model for the intrinsic low permittivity layer is consistent with the effectiveness of the epitaxial growth of oxide-electrodes in order to suppress the reduction of the permittivity of the dielectric oxide films. In the final topic, photo-capacitance spectroscopy of electronic states in the metal/ SrTiO<sub>3</sub> systems will be described. It is found the photocapacitance spectroscopy is one of the most effective tools for the deep level characterization of the oxides compared with the conventional transient capacitance methods, such as deep level transient spectroscopy (DLTS), which shows anomalous transient behavior originated from characteristic dielectric properties of SrTiO<sub>3</sub>. Deep levels in Au/SrTiO<sub>3</sub> Schottky junctions of the order of 10<sup>13</sup> - 10<sup>15</sup> cm<sup>-3</sup> are characterized and band diagram of the junction will be discussed.

#### 2:00 PM U4.2

HETEROEPITAXIAL BARIUM HEXAFERRITE FILMS ON (111) MAGNESIUM OXIDE SUBSTRATES. Steven A. Oliver, Center for Electromagnetic Research, Northeastern University, Boston, MA; Izabella Kozulin, Ming Ling Chen, Soack Dae Yoon, Xu Zuo and Carmine Vittoria, Dept. of Electrical and Computer Engineering, Northeastern University, Boston, MA.

The development of methods for growing highly oriented barium hexaferrite films is of great importance for planar nonreciprocal devices operating at millimeter wavelengths. To date, sapphire has been the substrate of choice for growing barium hexaferrite films. However, the barium hexaferrite/sapphire combination has significant mismatches in both lattice constants and thermal expansion coefficients, such that thicker films incur large tensional stresses and thus crack and delaminate from the sapphire substrate. One candidate substrate material for improved barium hexaferrite film growth is (111) MgO, which provides an interfacial surface of close-packed oxygen planes that have a structure similar to the basal plane of (000n) barium hexaferrite. Here, the lattice mismatch is -0.01, while the thermal expansion coefficient of MgO is greater than that of barium hexaferrite, such that the deposited film will be under compression. To study this system, heteroepitaxial films of barium hexaferrite and scandium-substituted barium hexaferrite having thicknesses of 0.5 - 2 micrometers were deposited onto (111) MgO substrates by pulsed laser deposition at temperatures of 900C. X-ray diffraction measurements showed that these films were phase-pure and had only (000n) diffraction peaks. Magnetometry results on pure barium hexaferrite films showed magnetization values near 4.0 kG, lower than those measured in bulk materials. Torque magnetometry measurements showed the films to have excellent c-axis orientation out of the film plane, with no indication for an in-plane c-axis crystallographic orientation. Ferromagnetic resonance linewidth values of 0.70 kOe were obtained for as-produced films at 54 GHz. Substrate curvature measurements showed the MgO substrates to be under tensile stress. One potential difficulty for this method may be the low tensile strength of the MgO substrates, as the deposition of thicker (> 30 micrometer) non-oriented barium hexaferrite films on (111) MgO has caused the substrates to shatter upon cooling.

#### 2:15 PM U4.3

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

There has been a lot of activity on preparation of PZT films since they have potential to be used for NVRAMs. Integration of these films with silicon for industrial applications have also been an issue that is being extensively investigated in the recent days. We have been successful in the fabrication of (100) oriented epitaxial PZT films on SrRuO<sub>3</sub>/SrTiO<sub>3</sub>/MgO/TiN/Si heterostructures by pulsed laser

deposition; SrRuO<sub>3</sub> being used as the bottom electrode. The films were observed to be single phase by X-ray diffraction. The thickness of the film was around 400 nm. Temperature of the substrate and the oxygen pressure was varied to get the best film. Transmission electron microscopy was done to study the microstructure and composition of the films. Dielectric measurements were performed on the films at room temperature and at a frequency of 100 kHz. P-E hysteresis loop measurements were carried out with evaporated Ag electrodes. The value of saturation polarization P<sub>s</sub> was between 20-25 mC/cm<sup>2</sup> and the coercive field E<sub>c</sub> varied from 35-45 kV/cm. Growth of films for better values of P<sub>s</sub> and E<sub>c</sub> is in progress. The variation of the properties of the films with thickness will also be studied in detail.

#### 2:30 PM U4.4

UV RADIATION EFFECTS IN SOL-GEL PROCESSING OF FERROELECTRIC PZT THIN FILMS. Kyle S. Brinkman and Robert W. Schwartz, Department of Ceramic and Materials Engineering, Clemson University, Clemson, SC.

Sol-gel processing of ferroelectric thin films, such as lead zirconate titanate (PZT), is being investigated for a range of applications including thin film capacitors, non-volatile memory devices, electrooptic switches, and infrared detectors. Recent cost and environmental concerns have led to the development of water-based precursor solutions that are stable in ambient conditions, and that demonstrate lower crystallization temperatures. Another key technical challenge for the development of these applications is the patterning of the films for device fabrication. It is known that the structural evolution of these materials (i.e., film processing behavior and microstructural development) may be adjusted through the incorporation of chemical modifying, or "chelating" agents. In this research, hydrogen peroxide has been used to improve the wetting behavior and stability of precursor solutions. Our results indicate that peroxide in conjunction with known  $\beta$ -diketone UV absorbing ligands lead to increased photosensitivity for enhanced device patterning. Texture/orientation development in the films is affected by the addition of peroxide and the exposure to UV radiation. The structural evolution of this system was explored by XRD, TGA/DTA, FTIR, NMR and FESEM.

#### 2:45 PM U4.5

PERFECTLY C-AXIS ORIENTED FERROELECTRIC Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> THIN FILMS ON SiO<sub>2</sub>/Si(001) BY PULSED LASER DEPOSITION. Choong-Rae Cho, Alex Grishin, Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN.

Highly polar axis oriented ferroelectric films on Si substrates with conventional buffer layers are considered to be of great necessity for practical applications, since Si is the essential material in various ferroelectric thin films devices (memories and MEMS) while ferroelectric performance (remnant polarization, coercive field and dielectric permittivity) are strongly controlled by microcrystalline structure. Perfectly c-axis oriented Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> (NKN) thin films have been prepared on thermally grown ultrathin (<20 nm) SiO<sub>2</sub>/Si(001) structures by pulsed laser deposition technique. X-ray diffraction shows multiple-cell structuring of NKN/SiO<sub>2</sub>/Si(001) films along the polar axis. Through the comparison with NKN films grown onto amorphous ceramic glass as well as thicker SiO<sub>2</sub> template layers, we suggest a small amount of distributed SiO<sub>2</sub> crystals, which populates SiO<sub>2</sub>/Si interface, maintains an epitaxial relation with the Si substrate and plays an important role in oriented NKN film growth. Ferroelectric measurements yield induced polarization P = 22  $\mu$ C/cm<sup>2</sup> at 100 kV/cm, remnant polarization Pr = 12  $\mu$ C/cm<sup>2</sup>, and film resistivity of the order of 10<sup>10</sup> Ohm\*cm @ 5 kV/cm. The dielectric permittivity and dissipation factor have been found to vary from 114.0 to 107.2 and from 0.016 to 0.009 respectively in the frequency range 1 kHz to 1 MHz.

#### 3:30 PM \*U4.6

THIN Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> FILMS FOR VARACTOR APPLICATIONS. Choong-Rae Cho, Jung-Hyuk Koh, Alex Grishin, Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN; S. Abadei, P. Petrov, S. Gevorgian, Department of Microelectronics, Chalmers University of Technology, Göteborg, SWEDEN.

There has been considerable recent interest in developing microwave devices using ferroelectric thin films. At present most of thin film devices proposed for microwave applications are based on SrTiO<sub>3</sub> (STO), BaTiO<sub>3</sub> (BTO) or solid solutions of these materials: BaSrTiO<sub>3</sub> (BSTO). Very little is known about other ferroelectrics suitable for microwave applications. Recently, several considerably interesting characteristics of Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> (NKN) thin films for microwave device applications have been reported: strong electric field dependence of dielectric permittivity at room temperature and high piezoelectric coefficient with self-assembling textures on polycrystalline

substrates (Appl. Phys. Lett., 73, 927, (1998), Appl. Phys. Lett., 75, 268 (1999)). We report on perfectly c-axis oriented NKN thin films prepared on thermally grown ultrathin SiO<sub>2</sub>/Si(100) by pulsed laser deposition. Based on this structure, interdigital gold upper electrodes have been fabricated to make small size high Q-factor varactors. Optimum design of interdigital capacitor, the performance of device at GHz range frequency, temperature stability and fatigue against tuning electric field will be discussed.

#### 4:00 PM U4.7

RETENTION PROPERTIES OF FERROELECTRIC Pb(Zr,Ti)O<sub>3</sub> THIN FILMS FOR NANOSTORAGE MEDIA APPLICATIONS. William Jo, Stanford University, Edward L. Ginzton Lab, Stanford, CA; J.W. Hong, PSIA, Seoul, KOREA; M. Kim, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN; D.C. Kim, LG Corporate Institute of Technology, Devices and Materials Lab. Seoul, KOREA.

We report charge retention in preferentially c-axis oriented ferroelectric Pb(Zr,Ti)O<sub>3</sub> (PZT) thin films on LaNiO<sub>3</sub> by electrostatic force microscopy. Surface charge density of the PZT films was observed as a function of time in a selected area where a region is single-poled and another region is reverse-poled. Retention behaviors of the regions are very different: the single-poled region shows a declined response and the reverse-poled region reveals a retained characteristic. Decay and retention mechanisms of the regions are explained by space charge redistribution and trapping of defects in the films. Furthermore, an electrical characterization of polarization-voltage loop shows that charge retention is correlated to imprinted nature of the PZT films.

#### 4:15 PM U4.8

BARIUM STRONTIUM TITANATE THIN FILMS FOR BROAD-BAND SATELLITE COMMUNICATION APPLICATIONS. C.H. Mueller, S.A. Alterovitz, F.W. Van Keuls, J.D. Warner, R.R. Romanofsky and F.A. Miranda, NASA-Glenn Research Center, Cleveland, OH; C.M. Carlson, T.V. Rivkin, P.A. Parilla, J.D. Perkins and D.S. Ginley, National Renewable Energy Laboratory, Golden, CO.

Next-generation low-earth orbiting (LEO) satellite communication systems will require communication channels with much higher data rates than current systems, as well as satellite tracking capabilities. Paraelectric Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> (BST) thin films are being developed for applications that require frequency and/or phase tuning at K-band (18 - 26 GHz) and higher frequencies. One of the most pressing needs for broadband satellite communications systems is a low-cost, beam-steerable antenna at the user terminal. The objective of this work is to develop BST films that are tailored towards the development of beam-steerable reflectarray antennas. BST films were deposited on single-crystal MgO substrates using in-situ pulsed laser deposition. The film compositions had Ba/Sr compositions of 40/60 or 60/40, and were either 300 nm or 1200 nm thick. The film microstructures were characterized using high resolution x-ray diffraction (HRXRD), ellipsometry, and ultraviolet transmission spectroscopy. HRXRD indicates the film crystalline quality is slightly higher in the 60/40 than the 40/60 films, and for films with the same composition, is similar for the 300 and 1200 nm films. Asymmetric omega scans show that film strain is completely relieved via dislocations at the film/substrate interface. Ellipsometry measurements show that the film thickness had a much larger impact on extinction coefficient than did film composition; for both compositions, the extinction coefficients of the 300 nm are virtually identical. However, the extinction coefficients of the 1200 nm films have additional absorption peaks near the bandgap energy. Correlations between microstructural data and microwave performance of the phase shifters will be presented.

#### 4:30 PM U4.9

(Ba,Sr)TiO<sub>3</sub> AND (Ba,Sr)TiO<sub>3</sub>-MgO COMPOSITE THIN FILMS FOR TUNABLE DEVICES. C.M. Carlson<sup>1</sup>, T.V. Rivkin<sup>1</sup>, P.A. Parilla<sup>1</sup>, J.D. Perkins<sup>1</sup>, D.S. Ginley<sup>1</sup>, L.C. Sengupta<sup>2</sup>, L. Chiu<sup>2</sup>, X. Zhang<sup>2</sup>, Y. Zhu<sup>2</sup>, S. Sengupta<sup>2</sup>, A. Kozyrev<sup>3</sup>, V. Osadchy<sup>3</sup>, A. Pavlov<sup>3</sup>, A. Golovkov<sup>3</sup>, M. Sugak<sup>3</sup>, D. Kalinikos<sup>3</sup>. <sup>1</sup>National Renewable Energy Laboratory, Golden, CO, <sup>2</sup>Paratek Microwave, Inc., Columbia, MD, <sup>3</sup>Electrotechnical University of St. Petersburg, St. Petersburg, RUSSIA.

The optimization of ferroelectric materials for microwave communications applications requires a balance of the tuning and loss properties for a particular application. To do this in a meaningful way requires an understanding of the relationships between the structural and dielectric properties. In this paper we will discuss both our elucidation of the film strain during pulsed laser deposition and post-anneal for very high quality epitaxial films and a novel approach employing (Ba,Sr)TiO<sub>3</sub>(BST)-MgO composite thin films. We will also report on the performance of tunable microwave devices made from these films. We deposited thin films of pure BST and BST-MgO

composite films using laser ablation on single crystal substrates. Pure epitaxial BST films exhibit peak dielectric constants  $\epsilon/\epsilon_0 > 6000$  with a change in dielectric constant of  $> 65\%$  with an applied dc field of  $\sim 7 \text{ V}/\mu\text{m}$ , but had a loss tangent  $> 0.06$  at only 2 GHz. Both the BST and MgO materials in BST-MgO composite films were also epitaxial on single crystal substrates. After post-annealing, these composite films had 19% tuning of the dielectric constant with a loss tangent of only 0.03 at 10 GHz.

#### 4:45 PM U4.10

**BARIUM STRONTIUM TITANATE (BST) THIN FILMS FOR HIGH FREQUENCY TUNABLE DEVICES.** P.K. Baumann, S.K. Streiffer, O. Auciello, Argonne National Laboratory, Materials Science Division, Argonne, IL; D. Kauffman, R.A. Erck and J. Giunarra, Argonne National Laboratory, Energy Technologies Division, Argonne, IL.

Barium strontium titanate (BST) thin films have been studied for applications such as capacitors for resonant circuits and high-frequency tunable phase-shifters. We have deposited BST thin films at 650°C to 750°C on platinized silicon with good thickness and composition uniformity using a large area vertical metal organic chemical vapor deposition (MOCVD) system. A computer-controlled liquid delivery system was used to inject precursors into the deposition chamber to control the films composition and ensure good reproducibility. The Ti content of the BST films was varied from 50-55%, and the Ba/Sr ratio was 70/30. The pressure in the deposition chamber was varied from 1.5 - 2.5 Torr. The composition of the BST films has been analyzed using x-ray fluorescence (XRF) and Rutherford backscattering spectrometry (RBS). Patterned Pt top electrodes were deposited onto the BST films at 350°C through a shadow mask using electron beam evaporation. A dielectric constant of approximately 900 and a dielectric loss of as low as 0.02% was measured at room temperature, zero field and 1 kHz for 120nm thick films. Dielectric tunability as high as 3.5:1 and was measured for an electric field of 400 kV/cm. We will report on a systematic study of the electrical properties as a function of BST growth conditions and annealing conditions of the entire capacitor structure.

\*Work supported by the U.S. Department of Energy, BES-Material Sciences, under Contract W-31-109-ENG-38, and by DARPA, contract 978040.

#### SESSION U5: POSTER SESSION: MATERIALS SCIENCE OF NOVEL OXIDE-BASED ELECTRONICS

Chairs: John D. Perkins and Dennis M. Newns  
Tuesday Evening, April 25, 2000  
8:00 PM  
Salon 1-7 (Marriott)

#### U5.1

**TWO STEP PROCESS FOR THE GROWTH OF A THIN LAYER OF SILICON DIOXIDE FOR APPLICATION IN SIS SOLAR CELLS.** Jorge Pedro, Hugo Aguas, Elvira Fortunato, Isabel Ferreira, Rodrigo Martins, New Univ. of Lisbon, Fac. of Science and Technology, Materials Science Dep., CENIMAT and CEMOP/UNINOVA, Monte da Caparica, PORTUGAL.

In the SIS (Semiconductor-Insulator-Semiconductor) solar cells the insulator plays the main role in the device performances. It should be very thinner (below 4 nm thickness) and also compact, to form the desired tunnelling effect between the two semiconductor layers, the silicon and the semiconductor oxide. The silicon oxidation method proposed consists in a two step process. First the silicon wafer is oxidised in a furnace at a temperature of 560°C, using a mixture of oxygen and nitrogen gases. This permits a very slow oxidation that can be easily controlled by the time of oxidation. In spite of this, ellipsometric measurements of this oxide revealed a poor compact oxide. To improve the compactness of the oxide, we use a second step process that consists in oxygen plasma treatment of the oxide, which under appropriate conditions can lead to the improvement of the compactness of the silicon dioxide film, as revealed by ellipsometric studies. These results, together with SIMS and RBS data, were correlated with the data obtained from the C-V measurements performed aiming to establish the best oxide properties and thickness that lead to the production of cheap and efficient solar cells.

#### U5.2

**EPITAXIAL GROWTH MODES, GROWTH-INDUCED LINEAR DEFECTS ARRAYS AND VORTEX PINNING ANISOTROPY IN  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  FILMS.** V.L. Svetchnikov, V.A. Komashko, V.S. Flis, and V.M. Pan, Institute for Metal Physics, Kiev, UKRAINE; C.L. Snead and M. Suenaga, Brookhaven National Laboratory, Upton, NY; H.W. Zandbergen, National Centre for HREM, TU Delft, Delft, THE NETHERLANDS.

HREM study are performed for YBCO films epitaxially-grown on different substrates and buffer layers by sputtering or PLD. Linear defect (dislocations) arrays are identified in films, depending on growth modes: 1) Edge dislocation arrays: a) misfit dislocations; b) dislocation loops associated with stacking faults, their lines are parallel to  $ab$ -plane; c) dislocations in low-angle domain boundaries (up to  $10^{11}$  lines/cm<sup>2</sup>), forming (i) at 2D epitaxial growth mode via rotational relaxation of mismatch; (ii) due to specific growth mode due to rotational incompatibility; (iii) at coalescence of misoriented growing islands. 2) Screw dislocation arrays: a) dislocations on interface low angle twist boundaries; b) dislocations at spiral-mediated growth mode with cores parallel to  $C$ -axis. Note, screw dislocations are unlikely to contribute to net pinning force, having core diameter by order of magnitude larger than in edge dislocations and density by two-three orders of magnitude lower. Critical current density,  $J_c$ , is studied in range of applied field, temperature, angle between field vector and  $C$ -axis of YBCO films. Two-peaked angular  $J_c(H)$  dependencies are detected while field vector rotates, preserving constant Lorenz force configuration. Two  $J_c(H)$ -maxima correspond to  $H \parallel C$  and  $H \parallel ab$ , relative height changing with temperature, applied field,  $E_c$ -criterion and growth conditions. Analysis of  $J_c(H, T, \theta)$ -data allows to suggest  $J_c(H \parallel \cdot)$ -peak is due to pinning on  $a[100]$  edge dislocation lines as well as due to edge dislocations, lying in  $ab$ -plane. In the latter case vortices intersect  $ab$ -plane dislocations, interacting like with point-like defects.  $J_c(H \parallel ab)$ -peak is due to the  $ab$ -plane dislocations pinning as well as Hirr-anisotropy.  $J_c(H)$ -dependencies at  $H \parallel$ -axis are shown to consist of three parts. Low field part is weakly field dependent. There is single-vortex pinning regime. The intermediate field part of  $J_c(H \parallel C)$  is linear in double-log scale:  $J_c \propto H^{-q}$ , where  $q$  is close to 0.5. At higher fields  $J_c(H)$  starts to fall down faster.

#### U5.3

**STOICHIOMETRY EFFECTS OF ON THE ELECTROCHEMICAL PROPERTIES OF  $\text{Li}_x\text{Mn}_2\text{O}_4$  FILMS GROWN BY LASER ABLATION.** D. Singh, R. Houriet, R. Giovanini, R. Vacassy and H. Hofmann, Dept. of Materials Science, Swiss Federal Institute of Technology, Lausanne, SWITZERLAND; V. Craciun and R.K. Singh, Dept of Materials Science and Engineering, University of Florida, Gainesville, FL; J. Perriere, Groupe des Physique des Solides, Universites Paris VII et VI, Paris, FRANCE.

Li stoichiometry and Mn oxidation state play a key role on the electrochemical properties of  $\text{Li}_x\text{Mn}_2\text{O}_4$  films. The ultraviolet-assisted pulsed laser deposition (UVPLD) technique was used to deposit  $\text{Li}_x\text{Mn}_2\text{O}_4$  films on Si and stainless steel grids. By changing the deposition temperature and oxygen pressure, films having different crystalline structure and stoichiometry were produced. The crystallinity was assessed by x-ray diffraction and transmission electron microscopy, while stoichiometry was investigated by Rutherford backscattering spectrometry, nuclear reaction analysis and x-ray photoelectron spectroscopy. The effect of the Li content and Mn oxidation state on the electrochemical properties of the grown films has been investigated. Electrochemical measurements were carried out in a glove box using cyclic voltammetry, electrochemical cycling and AC impedance spectroscopy in a half-cell configuration with lithium metal as anode and reference electrode and the grown  $\text{Li}_x\text{Mn}_2\text{O}_4$  films as cathode. The results obtained indicate that differences in film stoichiometry have a significant impact upon electrochemical kinetics of Li intercalation and de-intercalation. The films grown under optimized conditions exhibited good electrochemical characteristics such as high rate capability, very slow capacity fading even at high discharge rates (100-500 microA), good coulombic efficiency and rechargeability up to 400 cycles. Based on these results, a correlation between stoichiometry and kinetics of Li intercalation and deintercalation was established.

#### U5.4

**SEEDING EFFECT IN LANTHANUM NICKEL OXIDE CERAMIC/CERAMIC NANOCOMPOSITE FILMS.** Yu Zhang, QiFa Zhou, Helen Lai-Wa Chan, Chung-loong Choy, The Hong Kong Polytechnic University, Dept. of Applied Physics and Material Research Centre, Hong Kong, CHINA.

Lanthanum nickel oxide (LNO) is a conducting ceramic which has potential to be used as interleaving electrodes in multilayer ceramic actuators. Thicker LNO films have been formed by incorporating nanosized LNO powder (annealed at 700°C, with diameter around 100nm) into a LNO matrix prepared by a metal-organic deposition (MOD) method. Three different weight percents, 2%, 4%, and 10% of LNO powder have been added. The structure variation of the ceramic/ceramic composite film with annealing temperature was studied by differential thermal analysis, thermogravimetry and X-ray diffraction. The crystallization temperature of LNO composite film is found to be lowered from 580°C to 510°C, and according to this, the annealing temperature of this film can also be decreased from 700°C to 630°C, due to a seeding effect introduced by the nanopowder.



#### U5.5

PREPARATION AND CHARACTERIZATION OF  $\text{LiCoO}_2$  THIN FILMS ON POROUS Ni/NiO CATHODES FOR MCFC BY COMPLEX SOL-GEL PROCESS (CSGP). W. Lada, A. Deptula, B. Sartowska, T. Olczak, A.G. Chmielewski, Institute of Nuclear Chemistry and Technology, Warsaw, POLAND; M. Carewska, S. Scaccia, E. Simonetti, L. Giorgi, A. Moreno, ENEA-CRE-Casaccia, ITALY.

NiO cathodes are most frequently used in Molten Carbonate Fuel Cells (MCFC). The major disadvantage of its application is dissolution of NiO in K/Li electrolyte that significantly decreases cell life. The goal of the presented work is preparation of  $\text{LiCoO}_2$  thin film on Ni/NiO in order to protect the cathode body against dissolution. Sol-gel dipping technique was selected. For preparation of starting sols Complex Sol-Gel Process (CSGP) has been applied. These starting sols have been prepared by adding of LiOH to aq. acetates solution of  $\text{Co}^{2+}$  with ascorbic acid and then alkalinizing with aqueous ammonia to pH=8. Cathode plates of various dimensions (several to several hundreds  $\text{cm}^2$ ) have been dipped in these sols and withdrawn at various rates (2-34 mm/sec). Sometimes commercial sintered Ni plates were initially oxidized by heating in various temperatures. Changing of the microstructure and mechanical properties were observed. The best non folded plates were obtained at 600°C for 1h. Thermal treatment procedure for covered plates has been elaborated on the basis of thermal analysis of gel powders prepared by evaporation of respective parent sols. The covered substrates were soaked at 160°C for 48h, then at 200 for 72h, and calcined (using low heating rate 1°C/min) at 650°C for 1h. Heat treatment should be carried out under pressure of inert ceramic plates in order to avoid of waving. The presence of  $\text{LiCoO}_2$  in deposited coating has been proved by EDS patterns. Resultant film thickness were measured by Scanning Electron Microscopy (SEM) of polished cross sections. It ranged from 1 to several  $\mu\text{m}$  and depended strongly on concentration, viscosity, and coating withdrawal rate. It has been found, in a 300 hours test in molten carbonate, that covering of Ni/NiO cathode bodies completely prevent dissolution of Ni in molten K/Li electrolyte. Also dissolution of  $\text{LiCoO}_2$  coating was not observed. In contrast separate prepared  $\text{LiCoO}_2$  powders exhibit small solubility (several ppm of Co). After several hundreds hours treatment in molten electrolyte SEM observations do not show any changes in microstructures and morphology of covered cathodes. Characterization of covered cathodes in MCFC working conditions are currently studied.

#### U5.6

EFFECTS OF THE FINAL HEAT-TREATMENT CONDITIONS ON MICROSTRUCTURES OF  $\text{YbBa}_2\text{Cu}_3\text{O}_{7-\delta}$  SUPERCONDUCTING FILMS FORMED ON  $\text{LaAlO}_3(001)$  SUBSTRATES BY THE DIPPING-PYROLYSIS PROCESS. Junko Shibata, Tsukasa Hirayama, Japan Fine Ceramics Center, Nagoya, JAPAN; Katsuya Yamagiwa, Izumi Hirabayashi, Superconductivity Reserch Laboratory, ISTE, Nagoya, JAPAN; Yuichi Ikuhara, Dept of Materials Science, The University of Tokyo, Tokyo, JAPAN.

The dipping-pyrolysis process is a promising method for producing high-temperature superconducting films inexpensively. It was also reported that  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  films with critical current densities excess  $10^5 \text{ A/cm}^2$  were successfully prepared by using this method. In this method, it is important to control the nucleation and growth of the crystals during initial heat-treatment and final heat-treatment for obtaining good superconducting properties. We investigated effects of the final heat-treatment conditions on microstructures of  $\text{YbBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\text{Yb123}$ ) films formed on  $\text{LaAlO}_3(\text{LAO})$  substrates. First, we prepared precursor films by spin-coating the LAO substrates with a solution dissolving metal naphthenates of Yb, Ba, and Cu in toluene, and then by heat-treating the substrates at 425°C in air. Subsequently, these precursor films were heated under various conditions of heating rate and holding time at 750°C in an Ar gas flow. Microstructures of the final films were characterized by X-ray diffraction method and by transmission electron microscopy(TEM). We used in this work transmission electron microscope, JEM-2010, working at 200kV. Studies by TEM revealed that the film prepared by heating the precursor films at 20°C/min to 750°C was a c-axis oriented Yb123 film. However, the films formed by heating the precursor films at 0.5°C/min found to be polycrystalline. Furthermore, the film produced by heating the precursor film at 3°C/min and by holding for 2hours was also polycrystalline, in contrast, the film formed by heating at the same rate and by holding for 10hours changed to the c-axis oriented Yb123 film. In conclusion, rapid heating rate at the final heat-treatment is necessary for the epitaxial growth of the films, and long holding time is effective for the grain growth of the crystals.

#### U5.7

STRUCTURE AND PROPERTIES OF OXIDE FILMS ON ZINC SELENIDE SINGLE CRYSTALS. Yu. A. Zagoruiko, N.O. Kovalenko,

T.S. Teplytska, O.A. Fedorenko, P.V. Mateychenko, Institute for Single Crystals, National Academy of Sciences of Ukraine, Kharkov, UKRAINE.

Oxide films are obtained on different crystallographic surfaces of ZnSe single crystals by the methods of thermal and photothermal oxidation. Determined are the rates of oxidation processes depending on the technological conditions of oxidation (temperature, intensity and spectral composition of optical irradiation). The methods of X-ray structure analysis and electron-probe microanalysis are used to investigate the phase composition and structure of oxide coatings obtained under different conditions of oxidation of ZnSe crystallographic surfaces. Studied is the influence of surface treatment quality on the structure perfection of the formed oxide films. Within a wide temperature range, investigated are optical and electrical characteristics of oxide coatings obtained on different surfaces of the semiconductor samples. Examined are the mechanical strength and laser damage threshold (wavelength = 10.6 micrometers) of ZnO coatings. The results of mechanical testing performed on the samples with oxide films point to a high adhesion of the films to the crystal surface. On the closely packed (111) face revealed is the formation of "islets" of oxide films characterized by higher values of hardness and crack resistance in comparison with uncoated zinc selenide single crystals. It is found that more perfect structure of the oxide films is obtained at photostimulated oxidation of the crystal surface. Such films are characterized by lower values of optical absorption (wavelength=10.6 micrometers), higher transmission within 2.5 - 12.0 micrometers spectral range and higher adhesion. The method of photostimulation allows to make strong, homogeneous thermostable high-textured ZnO coatings. The obtained heterostructures of ZnO-ZnSe type possess high thermal stability of mechanical and optical (in the IR region) properties. Presented are the results of practical use of such heterostructures as photoconverters, varistors, antireflecting IR optical elements.

#### U5.8

Abstract Withdrawn.

#### U5.9

INFLUENCE OF LOW TEMPERATURE-GROWN GaAs ON LATERAL THERMAL OXIDATION OF  $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$ . J.C. Ferrer and Z. Liliental-Weber, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley CA; H. Reese and E. Hu, Department of Electrical and Computer Engineering, University of California, Santa Barbara, CA.

The incorporation of an excess of As in GaAs by low temperature growth (LT GaAs) has been shown to provide some interesting physical properties for device applications due to the formation of Ga vacancies. We report on a transmission electron microscopy study of the lateral oxidation of  $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$  layers grown by molecular beam epitaxy. Samples with LT GaAs layers placed below the oxidized  $\text{Al}_{0.98}\text{Ga}_{0.02}\text{As}$  and reference samples without LT GaAs and are compared. The effect of addition of a SiN cap is also discussed. Results show that reference samples, with and without a cap layer, tend to accumulate As in the oxide interface with the surrounding layers. Numerous small voids are found at the oxide/GaAs interface that may cause layer delamination. For samples exposed to a similar oxidation process, with a LT GaAs layer grown below the oxide, occasionally some As precipitates were found. These interfaces were abrupt and did not show void formation. This different behavior can be explained by the high Ga vacancy concentration present in the LT GaAs and by their diffusion toward the layer, providing a mechanism for enhanced As migration.

#### U5.10

FABRICATION OF  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  SUPERCONDUCTOR THICK FILMS ON Cu SUBSTRATES. Sang-Chul Han, Tae-Hyun Sung, Young-Hee Han, Jun-Seong Lee, Sang-Joon Kim, Korea Electric Power Research Inst, Power System Lab, Taejon, KOREA.

Well oriented  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8(\text{Bi}2212)$  superconductor thick films were formed successfully on Cu tapes by liquid reaction between Cu-free precursors and Cu tapes. Cu-free Bi-Sr-Ca-O powder mixtures were screen-printed on Cu tapes and heat-treated at 850-870°C for several minutes in air. Cu-free precursors were composed of  $\text{Bi}_x\text{SrCaO}_y$  ( $x=1.2-2$ ). In order to obtain the optimum heat-treatment condition, we studied on an effect of the precursor composition on the superconducting properties of Bi2212 films and the reaction mechanism of their rapid formation. Microstructures and phases of films were analyzed by XRD and optical microscope. The electric properties of superconducting films were examined by the four probe method. At heat-treatment temperature, the specimens were in a partially molten state by liquid reaction between CuO in the oxidized copper tape and the precursors which were printed on Cu tapes. The non-superconducting phases in the molten state are mixtures of Bi-free phases and Cu-free phases. During the heat-treatment

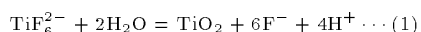
procedure, Bi2212 superconducting particles nucleate at interfaces between Bi-free phase and liquid and grow in preferred orientations. It was confirmed that the phase colony from the phase diagram of  $\text{Bi}_2\text{O}_3\text{-(SrO+CaO)/2-CuO}$  system correspond to the observed result.

**U5.11**  
GROWTH MORPHOLOGY AND ELECTRONIC STRUCTURE OF ULTRA-THIN  $\text{TaO}_x$  FILMS ON  $\text{Ag}(100)$ . Carl A. Ventrice, Jr., Marc M. Howard, Sten N. Thornburg, Christina K. Davis, Univ. of New Orleans, Dept. of Physics, New Orleans, LA; Heike Geisler, Xavier Univ., Dept. of Chemistry, New Orleans, LA; Dustin A. Hite, Phillip T. Sprunger, Louisiana State Univ., CAMD/Dept. of Physics, Baton Rouge, LA.

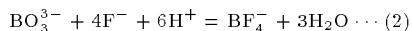
As device sizes in integrated circuits continue to shrink, high dielectric constant metal-oxides such as  $\text{TaO}_x$  are beginning to replace  $\text{SiO}_2$  for use in storage capacitors and as gate dielectrics. Despite the widespread use of  $\text{TaO}_x$  films, there have been relatively few studies of their crystal structure and electronic properties. We present a study of the growth morphology and electronic properties of  $\text{TaO}_x$  films on the  $\text{Ag}(100)$  substrate using LEED and synchrotron-based, angle-resolved, photoelectron spectroscopy. The  $\text{Ag}(100)$  substrate was chosen to prevent the formation of a mixed interfacial oxide (e.g., a  $\text{TaO}_x/\text{SiO}_2$  interface for growth on Si). In addition, the  $\text{Ag}(100)$  substrate has a relatively close lattice match with  $\text{TaO}$ , and the metallic Ag substrate allows characterization of the insulating  $\text{TaO}_x$  films without sample charging. The  $\text{TaO}_x$  films were grown by thermal evaporation of Ta in an oxygen atmosphere of  $10^{-6}$  Torr. Growth on a  $\text{Ag}(100)$  surface held at room temperature results in an amorphous  $\text{TaO}_x$  overlayer. Subsequent annealing of these films to  $600^\circ\text{C}$  for 10 min. results in a LEED pattern that has tentatively been assigned to a 2-domain epitaxial  $\text{Ta}_2\text{O}_5$  overlayer structure. Photoemission measurements of these films show the onset of Ta-5d emission at 4 eV below the Fermi level. No indication of either Ta or  $\text{TaO}_x$  was observed with photoemission or LEED for deposition onto a  $\text{Ag}(100)$  substrate held at temperatures above  $200^\circ\text{C}$ . This indicates that the Ta is either forming large islands or going sub-surface at these elevated temperatures.

**U5.12**  
MICRO PATTERN OF  $\text{TiO}_2$  THIN FILM FORMATION BY DIRECT SYNTHESIS FROM AQUEOUS SOLUTION AND TRANSCRIPTION OF RESIST PATTERN. Takeshi Yao, Yoshiharu Uchimoto, Hiroki Yab, Graduate School of Energy Science, Kyoto University, Kyoto, JAPAN.

Direct synthesis from aqueous solution (DSAS) is the method for synthesizing ceramic oxides in crystalline state directly from aqueous solution at ordinary temperature and ordinary pressure. DSAS is advantageous because of the applicability to making films with wide areas and/or complicated shapes with no requirement of vacuum or high temperature, and because of lower cost. Micro patterning of materials having high dielectric constant is important for manufacturing electronic devices such as DRAM, FeRAM and so on. We prepared a glass plate printed micro pattern on the surface by commercial organic photo-resist material. The glass plate was soaked as the substrate in ammonium hexafluorotitanate solution, in which the chemical equilibrium holds as in reaction(1),



We added boric acid to the solution. The fluoride ion is consumed by reaction (2),



then the chemical equilibrium in reaction (1) is shifted from left to right in order to increase the amount of fluoride ion, resulting in the formation of titanium oxide. After the soaking, the substrate was washed with distilled water and dried at room temperature. No heat treatment was conducted. The substrate was coated with dense, hard and homogeneous thin film. Characteristic XRD peaks for anatase  $\text{TiO}_2$  were observed. Then the substrate was soaked in acetone with ultra sonic vibration. The resist material was dissolved off with  $\text{TiO}_2$  film on. Micro pattern of  $\text{TiO}_2$  thin film transcribing the resist pattern with line width of  $1 \mu\text{m}$  was obtained.

**U5.13**  
MOCVD LEAD MAGNESIUM NIOBATE EPITAXIAL THIN FILMS FOR FERROELECTRIC AND PIEZOELECTRIC APPLICATIONS. P.K. Baumann, S.K. Streiffer, G.R. Bai, O. Auciello, Materials Science Division, Argonne National Laboratory, Argonne, IL; S. Stemmer, Department of Physics, University of Illinois at Chicago, Chicago, IL; K. Ghosh, C. Thompson, Dept. of Physics, Northern Illinois University, DeKalb, IL and Materials Science Division, Argonne National Laboratory, Argonne, IL.

Relaxor-based ferroelectrics such as lead magnesium niobate (PMN) and lead magnesium niobate titanate (PMN-PT) have excellent properties that could make them suitable candidates for dielectric and piezoelectric applications. We have grown epitaxial PMN and PMN-PT thin films by metalorganic chemical vapor deposition at  $700^\circ\text{C}$  on  $\text{SrRuO}_3/\text{SrTiO}_3$  substrates. The zero-bias dielectric constant and loss measured at room temperature and 1 kHz for 350 nm thick pure PMN films were 1300 and 1.1%, respectively. For PMN-PT films the small-signal permittivity ranged from 900 to 1800 depending on deposition conditions and Ti content; correspondingly low values for the dielectric loss between 1 and 3% were determined for all specimens. We will report on a systematic study of the dielectric and ferroelectric properties as a function of temperature and Ti content, and on initial piezoelectric measurements of these films.

**U5.14**  
HYDROTHERMAL PREPARATION OF  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  THIN FILMS FROM Ti-Zr METALLIC ALLOYS ON SILICON SUBSTRATES. Chang-Tai Xia, V.M. Fuenzalida and R.A. Zarate Universidad de Chile, Facultad de Ciencias Físicas y Matemáticas, Departamento de Física, Santiago, CHILE.

Hydrothermal preparation of  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  thin films from sputtered Ti-Zr metallic alloys was achieved on silicon substrates. A Ti-Zr 66:34 a/o alloy target was used as the sputtering source. X-ray diffraction indicated that a 4 hour hydrothermal treatment in 0.5 M  $\text{Ba}(\text{OH})_2$  aqueous solution was enough to fully react a  $\sim 55$  nm Ti-Zr alloy thin film on silicon substrate. A 2 hour treatment in 1 M solution resulted in a similar degree of crystallinity in the thin films. However, the morphology, roughness, and cracks in the formed  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  films were different for the different preparation conditions. XPS analysis showed that the Ti/Zr ratio in the prepared  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  films were different from that in the sputtered Ti-Zr alloy films. Preliminary capacitance measurement revealed that a dielectric constant  $\sim 200$  for the hydrothermal 300 nm  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  films. This relatively low dielectric constant value could be due to the poor density of the hydrothermal films. The formation mechanism will be discussed.

**U5.15**  
PREPARATION OF THICK PZT FILMS BY TAPE CASTING TECHNIQUES. Ralph Nonninger, Norbert Bendzko, Helmut Schmidt, INM Institut für Neue Materialien, Department of Chemistry and Technology of Non-Metallic Inorganic Materials, Saarbrücken, GERMANY.

For the production of thick PZT films / nanocrystalline PZT powders an aqueous precursor system based on a mixture of Pb-, Zr- and Ti-hydroxid was synthesized and precipitated by using an organic base. The resulting mixture was treated in an autoclave system at  $250^\circ\text{C}$  to crystallize the PZT powder in a pure perovskite phase. The PZT powder based on this process has a density of  $7,8 \text{ g/cm}^3$  (97% of th.), a primary particle size of 20 nm, which are aggregated to an average particle size of 100 nm and a specific surface area of  $8 \text{ m}^2/\text{g}$ . Green PZT-films in the range of 5 to  $20 \mu\text{m}$  have been prepared by slip casting. This films are blankable and cutable and can be transferred to the surface of Si and Pt wafers. After sintering by  $600^\circ\text{C}$  the PZT films are dense, crack-free and pure perovskite phase.

**U5.16**  
PHASE TRANSFORMATIONS IN SOL-GEL PZT THIN FILMS. D.P. Eakin, M.G. Norton and D.F. Bahr, Mechanical and Materials Engineering, Washington State University, Pullman, WA.

Piezoelectric thin films, particularly those based on the perovskite crystal structure, are becoming more common in MEMS for both sensing and actuating components. A common way of depositing these films is using solution deposition routes, wherein solutions or sol-gel components containing the proper chemistry are deposited upon platinized substrates via spin coating. The amorphous gel thus produced is then heat treated to form the desired crystal structure. However, there is still debate over the mechanism by which the proper crystal structure forms. Lead - zirconate - titanate (PZT) can form both cubic and tetragonal crystal structures, and only the tetragonal is desired for MEMS applications. To study the transformations which occur between the initial amorphous (or nanocrystalline) structure to the final desired structure, an in situ study of the phase transformations has been undertaken using transmission electron microscopy (TEM). A PZT solution (52/48) was spun onto single crystal sodium chloride, and then heated to 100 and 350 degrees Celsius to pyrolyze the solution. The substrate was then dissolved and the films were collected onto grids for TEM analysis. The crystal structure and grain morphology of the films was recorded as a function of heat treatment time and temperature. The films begin in a very diffuse nanocrystalline state, and at temperatures of approximately  $700^\circ\text{C}$  the films transform with time to the cubic and then the perovskite crystal structure. Additionally, these films have been compare to samples formed outside of the TEM to ensure the

effects of vacuum annealing are minimal. Finally, a similar study using films with 20 nm of platinum deposited on the initial nanocrystalline film has been undertaken to determine if the underlying platinum is responsible for the phase transformations observed through x-ray diffraction of films on platinized substrates.

#### **U5.17**

**X-RAY DIFFRACTION OF EPITAXIAL PEROVSKITE PZT FILMS GROWN UNDER MILD HYDROTHERMAL CONDITIONS.**  
K. Mikulka-Bolen, Rutgers Univ, Dept of Ceramic and Materials Engineering, Piscataway, NJ; T.W. Ryan, Philips Analytical, Natick, MA; V.A. Kogan, Philips Analytical, Almelo, NETHERLANDS; L.E. McCandlish, Ceramare Inc, Highland Park, NJ; W.E. Mayo, R.E. Riman, Rutgers Univ, Dept of Ceramic and Materials Engineering, Piscataway, NJ.

Reciprocal space mapping, texture measurements and conventional powder diffraction have been used to determine the crystal quality and orientation of epitaxial perovskite films. XRD was used as a characterization tool to distinguish between good and poor quality films, in order to delineate the hydrothermal reaction conditions and substrate characteristics that produce epitaxial, textured polycrystalline or discontinuous growth. Measurements were conducted using a Philips Analytical X'pert Materials Research Diffractometer System (Philips MRD) equipped with parabolic mirror optics collimating the incident and diffracted beams. XRD was used to characterize perovskite  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (PZT) films of various compositions ( $x > 0.5$ ), grown hydrothermally on (100) oriented  $\text{SrTiO}_3$  substrates. Films synthesized under mild hydrothermal conditions formed either continuous epitaxial or continuous textured polycrystalline layers, or discontinuous pseudocubic crystal "islands". Conventional  $\theta$ - $2\theta$  scans were conducted to determine the exact position of the (200) film peak. Vegard's Law was applied to calculate the expected peak location as a function of the compositional value of  $x$  in PZT. For film compositions with  $x > 0.5$ , a series of overlapping tetragonal and rhombohedral film peaks was observed, indicating that film composition (Zr:Ti ratio) and lattice parameter may vary normal to the substrate interface to reduce lattice mismatch between the substrate and film. Rocking curve scans gave FWHM values as low as  $0.25^\circ$  for smooth epitaxial layers. Pole figure texture measurements of the {301} film planes showed four-fold symmetry in the smooth epitaxial films. Textured polycrystalline films were observed to have multiple broad peaks with four-fold symmetry, indicating some degree of misorientation. Reciprocal space mapping was used to determine the quality of epitaxy by measuring the broadening of intense symmetric and asymmetric reflections in reciprocal space. The support of ONR, DARPA and the ONR AASERT Program is gratefully acknowledged.

#### **U5.18**

**ACHIEVING ROOM TEMPERATURE MAGNETORESISTANCE IN  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  BY GRAIN BOUNDARY MODIFICATION.** V. Ravindranath, Mary Sheela Bobby and M.S. Ramachandra Rao, Materials Science Research Centre and Department of Physics, Indian Institute of Technology, Madras, Chennai, INDIA.

Doping studies in colossal magnetoresistance (CMR) manganese perovskites such as  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  where  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$  etc. throw light on the understanding of the underlying physical mechanisms that would pave way to envisage device applications. Giant magnetoresistive (GMR) magnetic multilayers (Fe-Cr, Co-Cr) yield changes in magnetoresistance (MR) of the order of 20 - 45% at room temperature (RT) and find applications in magnetic recording heads and sensors<sup>1</sup>. On the other hand, very large MR ratios could be realised in CMR manganites only at low temperatures. Device applications require large changes in resistivity at temperatures close to RT and over a broad temperature range. It has been shown that grain boundaries play an important role in determining the MR in these materials<sup>2</sup>. Presence of grain boundaries in polycrystalline bulk CMR compounds result in higher MR ratios over a large temperature range<sup>3</sup> around the Curie temperature ( $T_C$ ). In the present study, grain boundary modifications of  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  and Y-doped  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  have been attempted.  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  ( $x = 0.175, 0.2$ ) and  $\text{La}_{0.7-x}\text{Y}_x\text{Sr}_{0.3}\text{MnO}_3$  ( $x = 0.05, 0.075, 0.175, 0.3, 0.4 \& 0.5$ ) compounds were prepared by the solid state reaction method. The interest was to improve the MR by modifying the grain boundaries in compounds having the peak resistivity temperature close to RT using insulating additives like  $\text{PbO}, \text{Sb}_2\text{O}_3, \text{CrO}_2$  etc. Preliminary studies showed a 25% MR in pure  $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$  at RT. Further work is underway to increase the resistivity of this compound using the above mentioned additives. Thin films of these compounds would be grown using the PLD technique. CMR manganites with considerable changes in MR at RT are the potential candidates for device applications like magnetic proximity switches and sensors.

#### References:

- <sup>1</sup>J. Doughton et al. IEEE Transactions on Magnetics, 30 (1994) 4608.
- <sup>2</sup>A. Gupta et al. Phys. Rev. B. 54 (1996) R15629.
- <sup>3</sup>H.Y. Hwang et al. Phys. Rev. Lett. 75 (1995) 914.

#### **U5.19**

**ELECTRIC AND MAGNETIC PROPERTIES OF NON-STOICHIOMETRIC  $\text{Fe}_{2-x}\text{Ti}_x\text{O}_{3+\delta}$  FILMS.** Tatsuo Fujii, Takuya Yano, Makoto Sadai, Makoto, Nakanishi, Jun Takada, Okayama Univ, Dept of Applied Chemistry, Okayama, JAPAN; Mitsugu Sohma, Kenji Kawaguchi, Natl Inst Materials Chemical Res, Tsukuba, JAPAN.

$\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$ , a solid solution between  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{FeTiO}_3$ , is a half-metallic ferrimagnet with Curie temperature of 250-600 K. Electric and magnetic properties of  $\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$  is very sensitive to the cation arrangement in the octahedral interstices of a hcp oxygen lattice. The ferrimagnetism appears only when the octahedral cation sites are ordered into two nonequivalent layers along the c-axis; one is a  $\text{Ti}^{4+}$ -rich layer and another is a  $\text{Fe}^{2+}$ -rich layer. Moreover the formation of mixed valence states between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the  $\text{Fe}^{2+}$ -rich layer gives an anisotropic electrical conductivity along the c plane. We have already succeeded to prepare well-crystallized epitaxial  $\text{Fe}_{2-x}\text{Ti}_x\text{O}_{3+\delta}$  films by activated reactive evaporation method. However the observed spontaneous magnetization of the films was less than a half of the ideal value expected from fully ordered layers. And the electric conductivity of the films was still large in comparison with that of  $\text{Fe}_3\text{O}_4$  films. We will report here the effects of nonstoichiometry on electric and magnetic properties of the  $\text{Fe}_{2-x}\text{Ti}_x\text{O}_{3+\delta}$  films. Sample films were prepared on  $\alpha\text{-Al}_2\text{O}_3(0001)$  single crystalline substrates by two ways. One is an  $\text{O}_2$ -reactive MBE system with an analysis chamber of in situ x-ray photoelectron spectroscopy (XPS), and another is an  $\text{O}_2$ -reactive magnetron sputtering system with high temperature oven. High purity Fe and Ti metals were evaporated or sputtered individually to control the Fe/Ti deposition ratio. Total evaporation rate and thickness were about 0.1nm/s and 200 nm for both films, respectively. The substrate temperature of MBE films was fixed to 773 K, while that of sputtered films was heated up to 1273 K. The deposited films were examined by energy dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD), magnetization (VSM), conversion electron Mössbauer spectroscopy (CEMS) and dc Hall measurements.

#### **U5.20**

**THE GROWTH OF La-(Sr-Ca)-Mn-O FILMS BY RF SPUTTERING.** Hsiung Chou, C.C. Hsu, M.N. Ou, National Sun Yat-Sen University, Department of Physics, Kaohsiung, TAIWAN; M.T. Hong, National Sun Yat-Sen University, Department of Electrical Engineering, Kaohsiung, TAIWAN; C.L. Huang, H.L. Kao, Chung Yuan Christian University, Department of Electronic Engineering; Y.C. Yu, Academia Sinica, Institute of Physics, Taipei, TAIWAN.

La-(Sr-Ca)-Mn-O (001) films on  $\text{SrTiO}_3$  (001) have been grown by the on and off-axis RF sputtering. It was found that the film properties were very sensitive to the growth conditions. In the on-axis geometric growth, the strong back sputtering effect of negative oxygen ions changed the composition of the films and so did the metal-insulation transition temperature ( $T_p$ ) and the magnetoresistance (MR). The total pressure and the substrate to target distance were important in suppressing the back sputtering. The growth temperature was found to have more sensitive effect on the film than those of pulse laser ablation. In this report the detail of the growth conditions to the surface morphology, the composition, the conductivity and the magnetoresistance of films will be presented.

#### **U5.21**

**NEW STRUCTURE MODEL FOR LITHIUM NICKEL BATTERIES.** María Angeles Monge, Enrique Gutiérrez-Puebla, Isidoro Rasines, Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco, Madrid, SPAIN; Juan Campa, Facultad de Ciencias Geológicas, U.C.M., Madrid, SPAIN.

Single crystals of  $\text{Li}_{0.27}\text{Ni}_{0.73}\text{O}$  have been grown for the first time. They have led to establish a novel structure type which is a superstructure of known rhombohedral  $\text{LiNiO}_2$ . Unit-cell dimensions, atomic positions, temperature factors, interatomic distances and angles will be given. The new structure consists in a close packing of oxide anions in which the cations occupy half of the octahedral holes, giving rise along the c direction to the alternation of mixed layers containing Li and Ni in various proportions that will also be given. Since the magnetic behavior of polycrystalline  $\text{LiNiO}_2$  has been interpreted in all the ways imaginable, magnetization measurements performed on mentioned crystals have allowed to determine their intrinsic magnetic properties, which will be reported.

## U5.22

**RADICAL CHANGE IN THE APPROACH TO ELECTRONIC PROPERTIES OF OXIDES.** Valery P. Kisel, Inst. of Solid State Physics, Chernogolovka, RUSSIA.

Charged ion conductivity, electroplastic and electrical breakdown effects evidenced for the crucial role of deformation mechanisms in the electric properties of crystalline (CS) [1] and organic (OS) [2] solids. This approach allows one to describe the insulator-metal-superconductor transition (IMST) through the increase of crystal work-hardening (WH) which decreases the plastic-deformation losses for nucleation and motion of charges thus lowering the electrical resistivity of CS, OS [1]. The works [2-5] directly evidenced for the strict correlation between the mechanical (WH, structural instabilities) and electrical properties of solids. The same features of the motion of deformation units in CS [6] and OS [7] confirm the universality of WH-mechanisms in CS and OS. The change of resistance in strained (due to hydrostatic pressures, inhomogeneous phases, compacted powder, etc.) samples closely varies with the hardening of soft crystals and the softening of hardened samples [2-8]. The sharp increase of WH at low temperatures means the sudden decrease in electrical resistivity (the IMST), the higher WH of crystal prompts the higher transition temperatures of low-temperature WH abrupt rise and of the insulator- superconductor transition and vice versa. The remarkable finding of this work is the scaling of mechanical [9-10] and electrical parameters of super- conductors in different scales of observation, which confirms the new approach to IMST.

References:

- [1] V.P. Kisel, The 2nd Int. Conf. on Cryocrystals and Quantum Crystals, Polanica-Zdroj, 7-12.9.1997, Poland, Abstracts No P1-13, P2-24.
- [2] P. Murray, G.M. Spinks, G.G. Wallace et al, Synth. Metals, 1998, v. 97, p 117-122.
- [3] C.C. Chang, J.B. McKinnon, C. Rose-Innes, Phys. Stat. Sol., 1969, v. 36, p 205-9.
- [4] K. Bechgaard et al, Mol. Cryst. Liq. Cryst., 1982, v. 79, No 1-4, pp 271-275.
- [5] J.P. Pouget, R. Moret, R. Comes, K. Bechgaard et al, Ibid. 1982, v. 79, pp 129-143.
- [6] V.P. Kisel Mater. Sci. Forum, 1993, v. 119-121, pp 233-238.
- [7] M. Mukoujima, K. Kawabata et al, Solid State Comm, 1996, v. 98, No 4, pp 283-6.
- [8] R. Konig, A. Schindler et al, Phys. Rev. Lett. 1999, v. 82, No 22, pp 4528-4531.
- [9] V.P. Kisel, Mater. Sci. Engr. A, 1993, v. 163, No 2, pp 356-359.
- [10] V.P. Kisel, Phys. Stat. Sol., 1995, v. 149A, No 1, pp 61-68.

## U5.23

**PROPERTIES OF A NOVEL AMORPHOUS TRANSPARENT CONDUCTIVE OXIDE, InGaO<sub>3</sub>(ZnO)<sub>m</sub>.** Masahiro Orita, Hiromichi Ohta, Masahiro Hirano, Hideo Hosono, Hosono TEAM Project, ERATO, JST, Kawasaki, JAPAN; Hiroaki Tanji, Hiroshi Kawazoe, R&D Center, HOYA, Tokyo, JAPAN.

Amorphous thin films of InGaO<sub>3</sub>(ZnO)<sub>m</sub> were prepared by a pulsed laser deposition method in which a quartz substrate was used at room temperature. It was found that this compositional system is a novel 4s type amorphous transparent conductive oxide (TCO), where extended 4s orbital plays dominant roles. It is well accepted that extended 5s orbital of metal ions are attributed to the conductivity of amorphous TCOs (5s-type) such as In<sub>2</sub>O<sub>3</sub>, AgSbO<sub>3</sub> and 2CdO GeO<sub>2</sub>, while any amorphous TCO of extended 4s states (4s-type) has not been reported so far. By utilizing 4s orbital in place of 5s one, one would expect TCO with wider energy band gaps or transparent in shorter wavelength. We have already reported that polycrystalline thin films of the system prepared by a sputtering method realized good electric conductivity and high optical transparency simultaneously. In this work, a pulsed laser deposition method was employed with a hope to obtain amorphous state because of the slow deposition rate inherent to the technique. The crystallographic structure of the films was confirmed as an amorphous in terms of XRD and TEM measurements. Compositional ratio of ZnO to GaO<sub>3/2</sub> in the films analyzed by means of XRF was sensitive both to KrF laser power and to oxygen pressure, that is, the ratio enlarged with an increase in laser power or in oxygen pressure. For laser power of 80 mJ and oxygen pressure of 0.8 Pa, the electrical resistivity varied from  $1 \times 10^{-2}$  ohm-cm to  $4 \times 10^{-3}$  ohm-cm by increasing the m values from 1 to 4. Optical band gaps (E<sub>g</sub>) obtained from optical absorption spectra were in the range from 3.8 eV to 3.6 eV, which should be compared to that of ITO (3.2 eV).

## U5.24

**METAL-DISPERSED SnO<sub>2</sub> THIN FILMS BY SOL-GEL METHOD FOR CO-SENSING.** Carmen Canevali, Norberto Chiodini, Franca Morazzoni, Roberto Scotti, Univ. Milano-Bicocca, Dept. Scienza dei Materiali, Milano, ITALY.

SnO<sub>2</sub> is a semiconductor metal oxide sensitive to the gas composition

of the surrounding atmosphere and used for gas sensor devices based on resistance variations. The addition of small amount of an appropriate noble metal, which has to be chosen depending the kind of gas to be detected, improves the sensing properties. This promoting effect of the metal arises by the activation of the gas molecules or by the electronic sensitization resulting from an electron transfer from the oxide to the metal. This implies that the amount and the homogeneous distribution of the metal affect the electric response amplitude and reproducibility. Previous works<sup>1</sup> suggested that also the intimacy of the metal-semiconductor contact plays an important role to improve the electronic exchange between the gases and the metal/oxide system. Aim of this work was to obtain films of Pt- and Ru-dispersed SnO<sub>2</sub> by a sol-gel method which allows the simultaneous gelation of tin (tin tetraterbutoxide) and metal (Pt or Ru acetylacetonate) precursors and a more intimate metal-semiconductor contact. Films of 100-150 nm of thickness were produced by spin-coating technique on silica or silicon substrates and were morphologically characterized by Scanning Electronic Microscopy and Atomic Force Microscopy. The sensing properties of the metal-dispersed SnO<sub>2</sub> films were tested by measuring the variations of resistance and selectivity in revealing CO. X-ray Photoelectron Spectroscopy and Electron Paramagnetic Resonance were used to recognize surface centers and defects responsible for the material functionality and the change in the oxidation state of the loaded metal. Correlations between the film electric properties and the species involved in the reaction between CO and the oxide were discussed to understand the role of the metal in the surface reaction mechanism and the influence of metal dispersion into the oxide in order to improve the sensitivity of the material.

1. N. Chiodini, C. Canevali, F. Morazzoni, R. Scotti, Mat. Res. Soc. Symp. Proc., 547, 209, (1999).

## U5.25

**THE PREPARATION AND PROPERTIES OF CADMIUM OXIDE FILMS PRODUCED BY METALORGANICS CHEMICAL VAPOR DEPOSITION.** Xiaonan Li, David Young, Timothy Coutts, National Renewable Energy Laboratory, Golden, CO.

Among the various TCOs materials including the oxides of Sn, In, Zn, Cd and their alloys, least work has been done on the cadmium oxide (CdO) thin films. Several groups have reported the properties of CdO thin films made by reactively sputtering, spray pyrolysis, and activated reactive evaporation. However no production has been done by metalorganics chemical vapor deposition (MOCVD). The purpose of this paper is to provide the initial information on the processing parameters of MOCVD; and the quality of MOCVD formed CdO films.

CdO is an n-type semiconductor with band gap of 2.4 eV. The highest mobility ever achieved was 100 cm<sup>2</sup>/V-s by K. Gurumurugan and others with dc reactive magnetron sputtering.

In this study, we found the properties of CdO films are very sensitive to CVD parameters. A deposition rate from 10 to 90 nm per minute for CdO film has been achieved at the CVD chamber pressure of 20 to 150 Torr and substrate temperature of 100 to 400 centigrade degrees. The surface roughness and the texture of CdO films changed with deposition temperature. Without any extrinsic doping, the carrier concentration of CVD produced CdO films could reach to low of 10<sup>21</sup>/cm<sup>3</sup>. As carrier concentration decreasing, the Hall mobility increased from less than 10 to 220 cm<sup>2</sup>/V-s, which was about twice height as it ever reached previously. The optical data indicated that the CdO band gap increased to 3.27 eV because of conduction band degeneracy. Four coefficients method measurement conformed that, with the increasing of carrier concentration, the increment of energy band gap was about 1eV.

## U5.26

**COMPLEX METHOD TO PRODUCE NOVEL OXIDE-BASED MATERIALS AT NANO/MOLECULAR SCALE.** Weixing Wang, Kecheng Gong, Polymer Structure & Modification Research Lab, South China University of Technology, Guangzhou, CHINA.

Homogeneous ultrafine mono/multi-element oxide powders are the key to produce high-performance electronic materials. It's well to known that many biominerals such as bone, shells and tooth can be produced at the ambient conditions. Oxide-based materials and biological assembly can be conceptually linked. Here, we describe an aqueous/organic solution complex method in biological view to produce novel oxide-based materials at nano/molecular scale. This biomimetic method can produce homogeneous ultrafine mono/multi-element oxide powders, self-standing inorganic films with special functions from inexpensive and non-toxic or relatively non-toxic reagents. The properties of inorganic oxide film are promising, it's self-standing, can withstand temperature to 1000°.

## U5.27

**FABRICATION OF MgIn<sub>2</sub>O<sub>4</sub> THIN FILMS WITH LOW RESISTIVITY ON MgO(100) SURFACE BY PLD METHOD.**

Ryuichi Noshiro, Kazushige Ueda, Hideo Hosono, Hiroshi Kawazoe<sup>1</sup>, Tokyo Inst. Tech., Materials & Structures Lab., Yokohama, JAPAN. <sup>1</sup> Present address: HOYA Corp., R&D Center.

Magnesium indium spinel oxide (MIO) is one of the recently discovered n-type conducting transparent oxides. Spinel lattice includes linear chains of edge-sharing oxygen octahedra and vacant octahedral and tetrahedral cation sites. We have pointed out that the former structural units can be viewed as a highway of carrier electrons. The latter is to be effective doping sites for accommodating excess atoms. Relatively large spatial separation of the highway from the doping sites may reduce the scattering of the carriers by ionized impurities. In the present study epitaxial thin films of the spinel oxide were fabricated on MgO(100) surface in order to reduce the scattering by grain boundaries and crystal imperfections. This is an essential process to confirm if our proposition actually works or not. MIO thin films were deposited on the MgO substrates by using a ceramic target by PLD under two different conditions in atmosphere: one was fabricated under an oxygen pressure of 0.23 Pa to introduce electron carriers from oxygen vacancies. Another was fabricated by using an oxygen radical source to suppress formation of the oxygen vacancies under high oxygen partial pressure. Proton was implanted to the thin films, which was grounded, to generate electron carriers: the implanted hydrogen atoms are expected to be ionized in the spinel lattice. Optical transmission, electrical transport properties, surface morphology, and interface structures of the thin films were examined. Thin films were found to be epitaxially grown on the substrate by X-ray pole figure measurements, and transmission electron microscopic observations. Structural imperfections are included in the thin films such as dislocations and amorphous regions. These may be the primary scattering centers. The highest conductivity was obtained for the thin films fabricated under the reducing atmosphere;  $4500 \text{ Scm}^{-1}$ . The carrier density, Hall mobility and Burnstein-Moss shift observed for the thin film were, respectively,  $2.1 \times 10^{21} \text{ cm}^{-3}$ ,  $14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $0.6 \text{ eV}$ .

SESSION U6: TRANSPARENT CONDUCTORS I  
Chairs: Sue Anne Carter and Jeremy Levy  
Wednesday Morning, April 26, 2000  
Nob Hill A/B (Marriott)

#### 8:30 AM \*U6.1

FUNDAMENTAL ADVANCES IN TRANSPARENT CONDUCTING OXIDES. Timothy J. Coutts, Xiaonan Li and David L. Young  
National Renewable Energy Laboratory, Golden, CO.

Very large-volume markets for large-area, flat-panel displays and photovoltaic panels are likely to be established in the early years of the next century. Transparent conducting oxides (TCOs) of improved opto-electronic properties will be required to enable these applications to be reduced to practice. Our work is focusing on improving both the fabrication-limited properties of the materials (extrinsic), and materials-limited properties (intrinsic). The achievement of improved electrical and optical properties hinges on realizing a higher electron mobility via intrinsic and/or extrinsic properties. To this end, we have investigated the properties of several TCOs including cadmium oxide, tin oxide, zinc oxide, cadmium stannate and zinc stannate. All of these may be deposited by chemical vapor deposition (CVD) and we have the capability to fabricate compounds and alloys in the cadmium oxide, tin oxide, zinc oxide ternary phase diagram. The properties of the materials have been investigated using a wide variety of techniques including high-resolution electron microscopy, atomic force microscopy and X-ray diffraction, as well as Mössbauer, Raman and UV/visible/NIR spectroscopies. We have measured the transport properties (conductivity, Hall, Seebeck and Nernst coefficients) and have obtained the effective mass, relaxation time, Fermi energy, and scattering parameter. This information has been obtained as a function of deposition and annealing parameters, as well as doping. We have found that the mobilities of free-electrons in the cadmium-bearing compounds are greatly superior to those in the other materials, because they have much longer electron relaxation times. In the case of cadmium oxide, there is also great benefit from a much lower effective mass. We are gaining a clearer understanding of the fundamental microscopic attributes needed for TCOs that will be required in more demanding applications early next century.

#### 9:00 AM \*U6.2

$\text{In}_2\text{O}_3$  BASED MULTICOMPONENT OXIDE TRANSPARENT CONDUCTING FILMS PREPARED BY RF MAGNETRON SPUTTERING. Tadatsugu Minami and Toshihiro Miyata, Kanazawa Institute of Technology, Ishikawa, JAPAN.

In this paper, we describe the preparation of transparent conducting thin films using multicomponent oxides consisting of a combination of different  $\text{In}_2\text{O}_3$  based ternary compounds. Multicomponent oxide thin

films were prepared on glass substrates by rf magnetron sputtering using targets composed of  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  and  $\text{SnO}_2$ . The sputter deposition was carried out at pressures of 0.2 to 1.2 Pa in pure Ar gas or a mixture of Ar and  $\text{O}_2$  gases. The resulting electrical, optical and chemical properties of  $\text{GaInO}_3\text{-Zn}_2\text{In}_2\text{O}_5$  films prepared on room temperature (RT) substrates changed monotonically as the  $\text{Zn}_2\text{In}_2\text{O}_5$  content in the target was varied. In addition,  $\text{GaInO}_3\text{-MgIn}_2\text{O}_4$  films prepared at RT exhibited a significant distribution of resistivity on the substrate which depended on the  $\text{MgIn}_2\text{O}_4$  content in the target. The resistivity distribution was mainly related to that of carrier concentration. This result suggests that the resistivity distribution is attributable to distributions of oxygen concentration as well as activity on the substrate surface rather than the bombardment effect of high energy particles.

#### 9:30 AM U6.3

A VERY LOW ELECTRICAL RESISTIVE TRANSPARENT INDIUM-TiN-OXIDE EPITAXIAL FILM ON (100) SURFACE OF YSZ BY PULSED LASER DEPOSITION. Hiromichi Ohta, Masahiro Orita, Masahiro Hirano, Hideo Hosono, Hosono project of Transparent ElectroActive Materials, Exploratory Research for Advanced Technology, Japan Science and Technology Corporation, Kawasaki, JAPAN; Hiroshi Kawazoe, Hiroaki Tanji, R&D center, Hoya Corporation, Tokyo, JAPAN.

Tin doped indium oxide (ITO) thin films were grown heteroepitaxially on (100) surface of YSZ by a pulsed laser deposition (PLD) method. The film showed very low electrical resistivity as small as  $7.7 \times 10^{-5} \Omega \text{ cm}$  and simultaneously high optical transparency of 85% in the visible light range. ITO thin films with resistivity lower than  $1 \times 10^{-4} \Omega \text{ cm}$  are strongly required for liquid crystal displays of a larger size composed of very precise pixels. Enhancement in carrier mobility is important for transparent electrode applications since the transparency in the visible light becomes decreased drastically due to plasma absorption and reflection when the carrier density exceeds more than  $2 \times 10^{21} \text{ cm}^{-3}$ . A PLD method using single crystal substrates was employed in this study with a motivation to obtain well-crystallized ITO thin films, which would make the electron mobility very large. YSZ (100) single crystal substrates were annealed at  $1350^\circ \text{C}$  for one hour in an air atmosphere to obtain atomically flat terrace and step structures. ITO films were deposited on the substrate, which was rotating and heating at  $600^\circ \text{C}$ , under an oxygen pressure of  $1.2 \times 10^{-3} \text{ Pa}$  by focusing a KrF ( $\lambda=248 \text{ nm}$ ) excimer laser onto a rotating ITO target. An in-plane rocking curve showed four diffraction peaks every  $90^\circ$  in a  $2\theta$  curve indicating that ITO was grown heteroepitaxially on the YSZ (100) surface. A cross sectional TEM image implied that the ITO film was grown cube-on-cube with edge and misfit dislocations. Randomly shaped grains with a size of 100-200nm were observed in AFM images. With an increase in  $\text{SnO}_2$  concentration in the target, the carrier density was increased, but saturated around  $1.9 \times 10^{21} \text{ cm}^{-3}$ . On the other hand, the mobility decreased monotonously for all concentration range. The lowest resistivity of  $7.7 \times 10^{-5} \Omega \text{ cm}$  was obtained when the carrier density and Hall mobility were  $1.9 \times 10^{21} \text{ cm}^{-3}$  and  $42 \text{ cm}^2/\text{Vs}$ , respectively.

#### 9:45 AM U6.4

DENSITY-OF-STATES EFFECTIVE MASS AND SCATTERING PARAMETER MEASUREMENTS ON TRANSPARENT CONDUCTING OXIDES USING SECOND-ORDER TRANSPORT PHENOMENA. David L. Young, Timothy J. Coutts, Xiaonan Li, National Renewable Energy Laboratory, Golden, CO.

TCOs have relatively low mobilities, which limit their performance optically and electrically, and which limit the techniques that may be used to explore their band structure via the effective mass. We have used transport theory to directly measure the density-of-states effective mass and other fundamental properties of TCO films. The Boltzmann transport equation can be solved to give analytical solutions to the resistivity, Hall, Seebeck, and Nernst coefficients. In turn, these may be solved simultaneously to give the density-of-states effective mass, the Fermi energy relative to either the conduction or valence band, and a scattering parameter,  $s$ , which is related to the relaxation time and the Fermi energy. The little-known Nernst effect is essential for determining the scattering parameter and, thereby, the effective scattering mechanism(s). We constructed equipment to measure these four transport coefficients on the same sample over a temperature range of 30 - 350 K for thin films deposited on electrically insulating substrates. We measured the resistivity, Hall, Seebeck, and Nernst coefficients for rf magnetron-sputtered zinc stannate and aluminum doped zinc oxide. We found that the effective mass for zinc oxide increases as the carrier density increases indicating a nonparabolic conduction energy band. In addition, our measured density-of-states effective mass matches previously reported values of the conductivity effective mass estimated from the plasma frequency, denoting a single energy minimum with a nearly spherical, constant-energy surface. The measured scattering parameter, along with Seebeck coefficient values, characterize ionized impurity

scattering in the ZnO:Al and neutral impurity scattering in the undoped material. Preliminary data shows zinc stannate, with a carrier concentration of  $8 \times 10^{18} \text{ cm}^{-3}$ , to have an effective mass of 0.19 m.

#### 10:30 AM \*U6.5

**CONTROL OF VALENCE STATES IN ZnO BY CODOPING METHOD.** Tetsuya Yamamoto, Kochi Univ, Dept of Electronic and Photonic Engineering Systems, Kochi, JAPAN; Hiroshi Katayama-Yoshida, Osaka Univ, Dept of Condensed Matter Physics, Osaka, JAPAN.

We have investigated the electronic structures of p- or n-type doped ZnO based on ab initio electronic band structure calculations in order to control valence states in ZnO for the fabrication of good p-type ZnO. We find unipolarity in ZnO; p-type doping using Li or N increases the Madelung energy while n-type doping using Al, Ga, In or F species decreases the Madelung energy. We proposed that codoping using N acceptors and reactive codopants, Al and Ga, enhances electric properties in p-type codoped ZnO. It has been already verified by experiments. We find a very weak repulsive interaction between Li acceptors and the delocalization of the Li-impurity states for Li-doped ZnO, in contrast with the case of N-doped ZnO. In addition, we find the compensation mechanism by the formation of O vacancies in the vicinity of the Li-acceptor sites. We will propose a promising candidate for the reactive codopant for ZnO:Li based on the above findings.

References:

- 1) T. Yamamoto and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 38 (1999) L166-L169.
- 2) M. Joseph, H. Tabata, T. Kawai, to be published in Jpn. J. Appl. Phys. Pt2 Express Letter, Vol. 38 (1999) No. 11A.

#### 11:00 AM \*U6.6

**TRANSPARENT P- AND N-TYPE CONDUCTIVE OXIDES WITH DELAFOSSITE STRUCTURE.** Hiroshi Yanagi, Kazushige Ueda, Shuntaro Ibuki, Tomomi Hase, Hideo Hosono, Tokyo Institute of Technology, Materials and Structures Laboratory, Yokohama, JAPAN; Hiroshi Kawazoe, Hoya Corporation, R&D Center, Tokyo, JAPAN.

Double oxides with delafossite structure are candidate materials for preparing transparent p- and n-type conductive oxides and fabricating a transparent p-n junction in the same crystal structure.  $\text{CuAlO}_2$ ,  $\text{CuGaO}_2$  and  $\text{AgInO}_2$  with delafossite structure were recently found to show both optical transparency and electrical conductivity on the bases of our working hypotheses.  $\text{CuAlO}_2$  and  $\text{CuGaO}_2$  show p-type electrical conductivity and  $\text{AgInO}_2$  shows n-type. Thin films of these materials were first prepared respectively by pulsed laser deposition (PLD) method on single crystal substrates. It is advantageous for the fabrication of transparent homo-structural p-n junction that the materials were deposited by the same method. The electrical conductivity of  $\text{CuAlO}_2$  thin films was  $0.3 \text{ S cm}^{-1}$  at room temperature. An optical energy band gap was roughly evaluated at the absorption edge in the ultraviolet region and the value was approximately 3.5 eV.  $\text{CuGaO}_2$  thin films deposited by PLD were highly oriented to c-axis. Their conductivity was  $4 \times 10^{-3} \text{ S cm}^{-1}$ . Optical band gap of  $\text{CuGaO}_2$  thin films was  $\sim 3.4 \text{ eV}$ . No intentional doping was carried out on  $\text{CuAlO}_2$  and  $\text{CuGaO}_2$ . Though  $\text{CuAlO}_2$  and  $\text{CuGaO}_2$  were prepared by ordinary solid state reaction, direct preparation of  $\text{AgInO}_2$  by same method was unsuccessful.  $\text{AgInO}_2$  were prepared by cation exchange reaction using  $\text{NaInO}_2$  and  $\text{AgNO}_3$ . In addition, because non-doped  $\text{AgInO}_2$  sintered disks were almost insulating, we carried out intentional doping by using Sn doped  $\text{NaInO}_2$  for cation exchange reaction. Increase of electrical conductivity of sintered disks was successful by doping.  $\text{AgInO}_2$  thin films fabricated by PLD using these as target. Optical band gap was  $\sim 4.4 \text{ eV}$ . The electrical conductivity of Sn 5% doped  $\text{AgInO}_2$  thin films at 300 K was  $7 \times 10^1 \text{ S cm}^{-1}$  and no remarkable temperature dependence was observed. The carrier concentration and the Hall mobility were  $3.3 \times 10^{20} \text{ cm}^{-3}$  and  $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively.

#### 11:30 AM U6.7

**CHEMICAL SUBSTITUTION OF P-TYPE TRANSPARENT  $\text{CuAlO}_2$ .** Renaud Stauber, University of Colorado, Boulder, CO; John Perkins, Phil Parilla, David Ginley, National Renewable Energy Lab, Golden, CO.

Recent results have shown that  $\text{CuAlO}_2$  is a p-type transparent conductor. This could have considerable consequences in a wide range of devices from photovoltaics to flat-panel displays. However, thin film synthesis is difficult because of the complex Cu:Al:O phase diagram. We report a robust method of making c-axis oriented  $\text{CuAlO}_2$  thin films. Thin film precursors of  $\text{CuAlO}_2$  were deposited on sapphire (001) substrates by radio frequency sputtering and by pulsed-laser deposition (PLD). Subsequent annealing in air at  $1050^\circ\text{C}$  in a closed crucible containing  $\text{Al}_2\text{O}_3$  and  $\text{CuO}$  powders yielded nearly phase-pure, biaxially textured  $\text{CuAlO}_2$ . The films were p-type and

transparent with a gap of 3.5eV, but typical carrier concentrations were low, on the order of  $10^{15} \text{ cm}^{-3}$  to  $10^{16} \text{ cm}^{-3}$ . Oxygen anneals at  $700^\circ\text{C}$  in 1 atm of  $\text{O}_2$  raised the carrier concentration to  $10^{18} \text{ cm}^{-3}$  in some samples. In order to increase the carrier concentration further, we are testing chemical substitution on the metal sublattice. Initial experiments were done with Mg, either by direct solid-state synthesis for bulk materials or by layered deposition of MgO during the PLD growth of thin films. At Mg molar concentrations of 2% or less, the bulk material was phase-pure  $\text{CuAlO}_2$  by x-ray diffraction, but was mixed-phase  $\text{CuO}$ ,  $\text{CuAl}_2\text{O}_4$  and  $\text{CuO}$  when the Mg concentration was increased to 5%. The interspersed  $\text{MgO/CuAlO}_2$  thin films crystallized to  $\text{CuAl}_2\text{O}_4$  after the  $1050^\circ\text{C}$  anneal, in contrast to non Mg-containing films which form the  $\text{CuAlO}_2$  phase at this temperature.

#### 11:45 AM U6.8

**INFRARED-TRANSPARENT ELECTRICALLY-CONDUCTIVE  $\text{CuAl}_x\text{O}_y$  DEPOSITED BY REACTIVE MAGNETRON SPUTTERING.** Linda F. Johnson, Mark B. Moran, Randall R. Kolega and Daniel C. Harris, Naval Air Warfare Center, Weapons Division, Naval Aviation Science and Technology Office, China Lake, CA; Ender Savrun, Sienna Technologies, Inc., Woodinville, WA; Mehmet Sarikaya, University of Washington, Dept of Materials Science and Engineering, Seattle, WA.

Thin films of  $\text{CuAl}_x\text{O}_y$  were deposited by reactive magnetron co-sputtering from the high-purity-metal targets. Fourier transform infrared (FTIR) and electron spectroscopy for chemical analysis (ESCA) were used to understand the relationship between the electro-optical properties and the molecular structure of these  $\text{CuAl}_x\text{O}_y$  films. FTIR absorption bands at 1470 and  $1395 \text{ cm}^{-1}$  are present only in films that exhibit enhanced electrical conductivity. When these bands are absent, the  $\text{CuAl}_x\text{O}_y$  films have high values of resistivity. It is possible that the enhanced conductivity of sputter-deposited  $\text{CuAl}_x\text{O}_y$  films could be a result of the overlapping d-orbitals on neighboring  $\text{Cu}^{1+}$  atoms in the plane perpendicular to the c-axis of the delafossite unit cell. Overlapping d-orbitals also would explain why the sputter-deposited  $\text{CuAl}_x\text{O}_y$  films absorb strongly in the visible. Another possibility is that the 1470 and  $1395 \text{ cm}^{-1}$  bands involve complicated vibrational modes of the entire Cu-O-Al-O-Cu sequence along the c-axis of the delafossite unit cell. The fact that the frequencies of these bands are about twice those of the major phonon frequencies in  $\text{Cu}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  is significant and indicates that these modes have some double-bond character. Double bonds tend to enhance electron mobility. Understanding the origin of the bands at 1470 and  $1395 \text{ cm}^{-1}$  could accelerate the development of  $\text{CuAl}_x\text{O}_y$  as a wide bandgap conductive oxide since the bands are clearly associated with enhanced electrical conductivity and carrier mobility. High-resolution ESCA spectra suggest that several of the most conductive  $\text{CuAl}_x\text{O}_y$  films are Al rich with Al:Cu ratios of more than 2:1. Inductively coupled plasma (ICP) emission spectroscopy also shows that the Al:Cu ratio is about 1.95:1 for one of the most electrically conductive and IR transparent films. High resolution electron microscopy (HREM) and electron energy loss spectroscopy (EELS) indicate that the  $\text{CuAl}_x\text{O}_y$  films consists of islands of cubic-copper crystallites in a Cu-Al-O matrix.

#### SESSION U7: TRANSPARENT CONDUCTORS II AND NOVEL CHARACTERIZATION

Chairs: Robert W. Schwartz and Dave H.A. Blank  
Wednesday Afternoon, April 26, 2000  
Nob Hill A/B (Marriott)

#### 1:30 PM \*U7.1

**A STUDY OF THE AMORPHOUS-TO-CRYSTALLINE PHASE TRANSFORMATION AND POTENTIAL TECHNOLOGICAL OPPORTUNITIES IN INDIUM OXIDE: A C-TYPE RARE EARTH DEFECT STRUCTURE.** David C. Paine, Daniel Sparacin, Eric Chason, Brown University, Division of Engineering, Providence, RI.

The indium oxide crystal structure (bixbyite) is based on the arrangement of two types of non-equivalent  $\text{InO}_6$  structural units to form a 80 atom unit cell. In the crystalline form, slightly sub-stoichiometric indium oxide, with or without tin as a substitutional dopant, is a degenerate semiconductor widely used for transparent electrode applications. PVD deposition onto cool (room T) substrates required for deposition onto heat sensitive polymer substrates can result in an amorphous structure that crystallizes at remarkably low temperatures ( $<150^\circ\text{C}$ ) relative to the indium oxide melting point ( $1910^\circ\text{C}$ ) in a process that is not yet well understood. The transformation from amorphous to crystalline states is characterized by a fundamental electronic change from a wide band gap semiconductor in the amorphous state to a metal-like degenerate state in the crystalline form. The attendant change in carrier density and mobility determine the conductivity and the plasma absorption edge of indium oxide.

These critical properties provide an ideal tool for studying the a/c-transformation that we have used to show that the a/c-transformation occurs in two stages starting with amorphous structural relaxation followed by crystallization. We have studied the a/c-transformation in electron-beam deposited indium oxide using isothermal annealing (110 to 250°C) combined with *in situ* resistivity, *in situ* reflectivity, TEM, glancing incidence angle x-ray diffraction and *in situ* wafer curvature measurements. From these measurements we have determined that the structural relaxation of the amorphous structure occurs via a process that is thermally activated ( $E_a=1.3$  eV) and has a kinetic dimensionality (Avrami parameter) near unity. The amorphous relaxation results in a uniform decrease in the molar volume of the amorphous structure which leads to a measured tensile stress increase in the film of approximately 20MPa. Subsequent crystallization occurs with a surprising increase in molar volume and a kinetic dimensionality of approximately 3 which is consistent with 2-d nucleation and growth. A model that fully describes the kinetics of transformation has been developed and will be presented along with several potential applications of the a/c-transformation in indium oxide.

#### 2:00 PM U7.2

##### ROOM TEMPERATURE GROWTH OF INDIUM TIN OXIDE FILMS BY ULTRAVIOLET-ASSISTED PULSED LASER

DEPOSITION. V. Craciun, R.K. Singh, University of Florida, Materials Science and Engineering, Gainesville, FL; D. Craciun, Laser Dept, National Institute for Laser, Plasma and Radiation Physics, Bucharest, ROMANIA.

The properties of indium tin oxide thin layers grown at room temperature on (100) Si and corning glass substrates using an in-situ ultraviolet (UV)-assisted pulsed laser deposition (UVPLD) technique have been studied. A vacuum compatible low pressure Hg lamp emitting 184 nm photons (6% of the output), which dissociate molecular oxygen and form ozone and atomic oxygen, was fitted into the PLD system. It allows for in-situ UV irradiation during the laser ablation-growth process, exposing each deposited layer to the action of more reactive gaseous species formed by UV photodissociation. The crystalline structure of the grown layers was investigated by x-ray diffraction (XRD) and transmission electron microscopy (TEM), while the chemical composition and bonding were investigated by x-ray photoelectron spectroscopy (XPS). The optical properties of films grown on Si substrates were investigated by spectroscopic ellipsometry and those of films grown on corning glass by spectrophotometry. The electrical conductivity was measured by the four point method. These investigations showed that, with respect to conventional PLD grown films under similar conditions but without UV illumination, UVPLD grown films exhibited improved electrical and optical properties. Layers exhibiting average optical transmission higher than 90% in the visible and near infrared range and resistivities below 0.5 mohm.cm were routinely grown by the UVPLD technique.

#### 2:15 PM U7.3

ELECTRICAL AND OPTICAL PROPERTIES OF Ta-DOPED SnO<sub>2</sub> THIN FILMS PREPARED BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION ON GLASS SUBSTRATE. Sang Woo Lee, Haydn Chen, University of Illinois at Urbana-Champaign, Dept of Materials Science and Engineering, Materials Research Laboratory, Urbana-Champaign, IL.

Undoped and Ta-doped SnO<sub>2</sub> thin films have been deposited on glass substrates using metal organic chemical vapor deposition method at 600°C. The deposited film thickness was about 0.2 μm. The deposited films were characterized by XRD, SEM, XPS, and SIMS. Based on XRD results with structure factor calculation, Ta dopants seemed to be incorporated substitutionally for Sn sites rather than interstitially. The SEM showed the gradual change of the surface morphology of the thin films. The electrical resistivity varies from  $1 \times 10^{-2}$  to  $2 \times 10^{-4}$  Ω·cm depending upon the Ta contents and the minimum resistivity was observed when relative Ta concentration was 3.6%. The average optical transmittance in the visible spectrum was about 89%. The role of Ta incorporation to the evolution of the microstructure will be explained. The change in the resistivity will be also explained in terms of the chemical effects induced from Ta doping in the thin films.

#### 2:30 PM U7.4

MAJOR VARIABLES AFFECTING THE CONDUCTIVITY IN A FIXED-FRAME METAL OXIDE. Flavio M. Vichi, M. Isabel Tejedor-Tejedor and Marc A. Anderson, Water Chemistry Program, University of Wisconsin - Madison, WI.

In previous studies, we have shown that TiO<sub>2</sub> nanoporous ceramic materials prepared by firing xerogels obtained via a sol-gel route are potential candidates for use as the electrolyte in proton exchange membrane (PEM) fuel-cells, in substitution to more expensive perfluorosulfonic membranes. In the present work we have studied conductivity of a fixed-frame (constant pore structure and surface

area) nanoporous TiO<sub>2</sub> as a function of relative humidity (RH), temperature, surface acidity, number of surface sites and surface doping with phosphate ions. The effect of RH was studied for samples rehydrated by exposure to water vapor or by subjecting to solutions with pH values of 1.5, 2.5 and 4.0. For the vapor-rehydrated samples a drastic increase in conductivity with RH is observed (from  $4.93 \times 10^{-6}$  S/cm at 33% RH to  $1.34 \times 10^{-3}$  S/cm at 81% RH), whereas for the solution-rehydrated samples there is also an increase, but to less extent (from  $6.46 \times 10^{-4}$  S/cm at 33% RH to  $1.45 \times 10^{-2}$  S/cm at 81% RH for rehydration at pH 1.5). Conductivity was also studied as a function of total water content, as obtained from water adsorption isotherms, and it was found that, for a constant water content, higher conductivities were observed in the samples rehydrated at lower pH. As an example, at a water content of 66 molecules/nm<sup>2</sup>, the conductivity at 25°C and 81% RH increases by one order of magnitude from the vapor-rehydrated sample to the sample treated at pH 1.5. Since the pore structure and surface area are the same in both samples, it follows that the proton mobility in the pore water must be higher in the sample treated at pH 1.5, and therefore the water structure (hydrogen bonding and density) are different in both samples. From the pore volume data, we estimate that the density of water in the pores increases by approximately 20% from the vapor-rehydrated sample to the sample treated at pH 1.5.

#### 2:45 PM U7.5

OXYGEN IONS DIFFUSIVITIES IN DOPED TIN DIOXIDE THIN FILMS. Nick Y. Shishkin, Ivan M. Zharsky, Belarus State University of Technology, Minsk, BELARUS.

Ambipolar diffusion of oxygen ions in tin dioxide thin films was investigated. Electrochemical method with blocking oxygen and electron filters was used.  $D^*$ , which is measured in experiments, can be converted into individual diffusivity as  $D^*=nD_0$  ( $n$  - some factor, about several units). The diffusion equation can be solved in the approximation of fast diffusion and dominant electronic conductivity (really, tin dioxide is an electronic semiconductor). The solution looks like:  $I = [2q(N - N_0) D^* / L] \exp(- (D^* t / 4L^2))$ ,  $I$  - current,  $N$  - concentration of electrons after an establishment of equilibrium, and  $N_0$  - before feeding voltage,  $L$  - thickness of the film,  $t$  - time,  $q$  - charge (electron),  $D^*$  - chemical diffusivity. Were investigated thin film of tin dioxide with a content of a palladium (atomic %) 0; 0.5; 0.7; 1; 2 and 3. Films were obtained by magnetron sputtering of the pure tin target (with appropriate palladium content) and subsequent oxidation. Logarithm of the diffusivity dependence vs inverse temperature has a linear character with two different slopes. The point of transition is 700K. The low temperature region corresponds to the diffusivity and the high temperature region includes defects formation process. For the pure tin dioxide energy of activation of the diffusion is 0.3 eV in both regions. The  $D_0$  is 7.6E-8 in low temperature and 2.3E-7 cm<sup>2</sup>/s in high. This is in good agreement with existing data. Maximum value of the diffusivity was found for the film with 0.7-1 % at Pd for the highest defectivity of the material. Activation energy grows with Pd content. Our previous investigations corresponds to the data obtained. Thus, maximum conductivity changes with CO gas influence can be found for the 0.7-1% at Pd films.

#### 3:15 PM \*U7.6

NANOSCALE OPTICAL PROBES OF OPTOELECTRONIC OXIDE MATERIALS. Jeremy Levy, Charles Hubert, Oleg

Tikhomirov, Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA.

Electro-optic probes provide valuable insight into the electro-optic behavior of thin film materials. We have developed a number of local probes for investigating polarization dynamics in ferroelectric thin films such as Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>. They include: quasi-static, dynamic and temperature dependent confocal scanning optical microscopy (CSOM), and apertureless near-field scanning optical microscopy (ANSOM). For ferroelectric thin films, the electro-optic coefficient is proportional to the ferroelectric polarization, and may be used to image the ferroelectric contribution to dielectric loss. Microwave frequency measurements show a remarkable dependence of the local dielectric loss on electric field bias. This phenomena is believed to be due to the uneven growth of in-plane ferroelectric nanodomains whose dielectric relaxation frequency depends strongly on size. Temperature dependent measurements and high resolution optical measurements also provide strong insight into the optical and electronic properties of these materials.

This work is supported by ONR N00173-98-1-G011, NSF DMR-9701725, and NSF IMR-9802784.

#### 3:45 PM \*U7.7

SPIN-POLARIZED TUNNELING IN OXIDE FERROMAGNETS. Daniel Worledge and T.H. Geballe, Stanford University, Dept of Applied Physics, Stanford, CA.

We have developed the ability to grow reproducible La<sub>0.67</sub>Sr<sub>0.33</sub>

MnO<sub>3</sub>/SrTiO<sub>3</sub>/Al tunnel junctions with high quality gap characteristics for spin-polarization measurements. A YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> counter-electrode was required to prevent current crowding. In order to fit our data, we have numerically solved Maki's equations which include the effects of orbital depairing, the Zeeman splitting of the spin states, and spin-orbit scattering. We consistently measure  $P = +72\%$ , for a variety of deposition conditions.

#### 4:15 PM U7.8

INTERFACE STABILITY IN HYBRID TRANSITION METAL/OXIDE MAGNETIC TRILAYER JUNCTIONS. J.Z. Sun, IBM-T.J. Watson Research Center, NY; K.P. Roche and S.S.P. Parkin, IBM Almaden Research Center, CA.

We show that for hybrid oxide-metal trilayer junctions of Co<sub>0.8</sub>Fe<sub>0.2</sub>-SrTiO<sub>3</sub>-La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> and Fe-SrTiO<sub>3</sub>-La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub>, the sign and field-dependence of junction magnetoresistance are sensitive to the junction interface condition. Both positive and negative magnetoresistance can be obtained in either systems, depending on the state of the junction interface. For high biases above 0.5 V, junction resistance shows time-dependent creep. The magnitude and direction of the creep depend on the magnitude and direction of the applied bias, indicating reversible structural modification of the junction interface. We conclude that junction interface chemistry can often be responsible for the observed sign-change of junction magnetoresistance.

#### 4:30 PM U7.9

HIGH TEMPERATURE BEHAVIOR OF Zr(WO<sub>4</sub>)<sub>2</sub> and Hf(WO<sub>4</sub>)<sub>2</sub>: A RAMAN SCATTERING STUDY. S.K. Deb<sup>1,\*</sup>, S.R. Jacob<sup>2</sup> and P.F. McMillan<sup>1,3</sup>. <sup>1</sup>Center for Solid State Science, <sup>2</sup>Dept of Chemistry & Materials Res Center, <sup>3</sup>Dept of Chemistry & Biochemistry, Arizona State University, Tempe, AZ, \*On leave from Bhabha Atomic Research Center, Bombay, INDIA.

Zr and Hf tungstates (Zr(WO<sub>4</sub>)<sub>2</sub>; Hf(WO<sub>4</sub>)<sub>2</sub>) are unusual materials that show large isotropic negative thermal expansion (NTE) over their entire stability region, and are of interest for their potential for designing ceramic materials and composites with low or zero thermal expansion. The NTE behavior is linked to large amplitude vibrational motions of the oxygen atoms cross-linking the WO<sub>4</sub> and (Zr,Hf)O<sub>6</sub> polyhedra in the structure, causing the centers of the polyhedra to come closer together. In the low temperature structure, each WO<sub>4</sub> group contains one non-bridging oxygen atom directed toward the base of an adjoining WO<sub>4</sub> unit. At 430 K, both materials show a phase transition to a cubic structure. The transition is thought to involve incipient bond formation to form an oxygen bridged W<sub>2</sub>O<sub>7</sub> group in the structure, with O<sup>2-</sup> hopping coupled with inversion of one of the WO<sub>4</sub> units in the transition region. The transition is accompanied by large changes in the dielectric constant at low frequency, and by a large change in the negative thermal expansion coefficient. We used Raman spectroscopy to probe the low frequency librational modes driving the NTE behavior as well as the static and dynamic disorder in O<sup>2-</sup> positions through the transition. With increasing temperature almost all the modes show broadening, but none soften. One mode at 146 cm<sup>-1</sup> due to WO<sub>4</sub> librations shows dramatic changes. The FWHM increases from 30 cm<sup>-1</sup> at 400K to 45 cm<sup>-1</sup> at 430K and its frequency hardens from 146 cm<sup>-1</sup> to 155 cm<sup>-1</sup> at these temperatures. These changes reflect the anharmonicity of the librational modes responsible for the NTE effect. Two W-O stretching modes at 737 cm<sup>-1</sup> and 793 cm<sup>-1</sup> related to the W-O bond along the C<sub>3</sub> axis reveal the effects of the transition, starting at 400K and completing by 430K. The FWHM of both modes sharply increases across the transition while the former hardens by 5 cm<sup>-1</sup> and the later softens by 3 cm<sup>-1</sup>. The changes can be interpreted as dynamic disordering of the O3 atoms across the phase transition.

#### 4:45 PM U7.10

WETTING OF DOMAIN WALLS IN SOME PEROVSKITE ALLOYS. Simon Dorfman, Phys Dept, Technion, Haifa, ISRAEL; Alex Gordon, Dept Math and Phys, Haifa Univ at Oranim, Tivon, ISRAEL; David Fuks, Mat Eng Dept, BGU, Beer Sheva, ISRAEL.

The aim of our study is to consider the effect of the wetting of domain walls in some perovskite alloys. This effect was previously discussed both for liquid-liquid and solid-liquid interfaces near the phase transition temperature and expresses itself in the formation of the third phase, which is formed as a layer at the interface and is thermodynamically unstable in the bulk under the same conditions. The effect of formation of a paraelectric layer of a finite thickness at the interface boundary which separates two ferroelectric domains with antiparallel direction of polarization vectors appears to be sensitive to the concentration of the element alloying the perovskite. We discuss this effect for (Ba,Sr)TiO<sub>3</sub> (BST) and Pb(Zr,Ti)O<sub>3</sub> (PZT) solid solutions.

#### SESSION U8/J6: JOINT SESSION: LASER-BASED DEPOSITION OF OXIDES

Chairs: David P. Norton and John D. Perkins

Thursday Morning, April 27, 2000

Nob Hill (Marriott)

#### 8:30 AM \*U8.1/J6.1

ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION OF THIN FILMS. V. Craciun and R.K. Singh, University of Florida, Department of Materials Science and Engineering, Gainesville, FL.

Pulsed laser deposition (PLD) has emerged as one of the most promising techniques for growing thin films due to several important advantages such as the use of a relatively low substrate temperature. For many applications, a further reduction of the process temperatures is highly desirable to prevent harmful film and/or ambient gas-substrate interaction, unwanted substrate interdiffusion processes, and re-evaporation of volatile components. Unfortunately, most high quality PLD grown materials still require substrate temperatures in excess of 650°C. If one wants to lower the substrate temperature without sacrificing the crystalline quality, stoichiometry, and film properties, then a non-thermal source of energy and a more reactive gaseous atmosphere should be used during growth. Laser-assisted PLD, a process where either a part of the incoming laser pulse used for ablation or a second laser pulse is used to irradiate the growing film showed great promise. However, this technique is rather expensive due to use of a second laser source. The pulsed beam can induce appreciable heating of the outermost surface of the substrate, thereby precluding its application to sensitive substrate materials such as plastics. Moreover, optical interference effects when the growing film is very thin can further complicate this process. A novel version of this technique, where the second laser is replaced by an inexpensive low-pressure Hg lamp is presented here. The short wavelength UV radiation (185 nm) emitted by such lamps can dissociate molecular oxygen and form ozone and atomic oxygen. In addition to the laser-assisted PLD technique, the UV source can be used during the cooling stage as well. We have investigated the microstructure and properties of several oxide and nonoxide thin films grown by UVPLD technique at moderate temperatures and compared them with those obtained from films grown using conventional PLD under similar conditions.

#### 9:00 AM U8.2/J6.2

EPITAXY OF OXIDES ON DISSIMILAR SUBSTRATES USING PULSED-LASER DEPOSITION. David Norton, Chan Park, Yong Lee, John Budai, Stephen Pennycook, Gyula Eres and Matthew Chisholm, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN.

The integration of electronic oxide materials on semiconductor and metal substrates is important in numerous applications. Crystalline oxides on semiconductors may be used in the formation of future generation metal-oxide-semiconductor device structures. Epitaxial oxides on metals are key elements in the development of emerging superconducting wire technologies. In both cases, the formation of epitaxial oxide structures is both enabling and complex. One must consider both the kinetics of film growth on a dissimilar material, as well as the thermodynamic stability of the oxide/non-oxide interface. In this talk, we will discuss the role of plume kinetics and thermodynamics in the formation of epitaxial oxide interfaces on semiconductors and metals using pulsed-laser deposition. The specific cases to be discussed include CeO<sub>2</sub> on (001) Ge and (001) Ni. Reflection high energy electron diffraction is used to characterize the nucleation of ceria on these surfaces. Z-contrast STEM will be used to characterize the epitaxial interface. High resolution four-circle X-ray diffraction will be used to elucidate the epitaxial relationship between the film and crystalline substrate.

This research was sponsored by the U.S. Department of Energy under contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

#### 9:15 AM U8.3/J6.3

MAGNETIC AND MAGNETORESISTANCE PROPERTIES OF PULSED LASER DEPOSITED La<sub>2/3</sub>Ca<sub>1/3</sub>MnO<sub>3</sub> THIN FILMS ON SILICON. D. Kumar<sup>1</sup>, A.K. Sharma<sup>2</sup>, S. Chattopadhyay<sup>2</sup>, J. Narayan<sup>2</sup>, S.V. Pietambaram<sup>1</sup>, Rajiv K. Singh<sup>1</sup>, C.B. Lee<sup>3</sup>, J. Sankar<sup>3</sup>. <sup>1</sup>Department of Materials Science and Engineering, University of Florida, Gainesville, FL, <sup>2</sup>Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, <sup>3</sup>North Carolina A&T State University, Greensboro, NC.

The fabrication of La<sub>2/3</sub>Ca<sub>1/3</sub>MnO<sub>3</sub> (LCMO) thin films on silicon (Si) substrates is very important from the point of view of integrating colossal magnetoresistive films based memory devices with Si for the next generation magnetic random access memory (MRAM) technology. A direct growth of LCMO films on Si, however, is hindered by lattice mismatch and chemical reaction between the film



and the substrate materials. It is in this context that we have tried to grow LCMO film on Si by using a highly conducting barrier layer of TiN, which has emerged as an attractive material because of its low electrical resistivity and its excellent metallurgical stability and reliability when subjected to high temperatures. By suitably changing the growth parameters during pulsed laser deposition, TiN films with resistivity as low as 20-50  $\mu\Omega\text{-cm}$  were obtained. In order to achieve epitaxial growth of LCMO films, MgO and SrTiO<sub>3</sub> films were used as intermediate layers between LCMO and TiN layers. The structural characterizations of single layered and multilayered structures were carried out using x-ray diffraction, transmission electron microscopy, and phi-scan measurements. The magnetic and magnetoresistance properties of LCMO films on Si were examined in the range of 10-300 K using superconducting quantum interference device magnetometer. The results have indicated that the properties of LCMO films on Si substrates, deposited under an optimized condition, are on par with the properties of LCMO films on conventional oxide substrates such as LaAlO<sub>3</sub> and SrTiO<sub>3</sub> in terms of paramagnetic to ferromagnetic transition temperature, insulator to metal transition temperature, and magnetoresistance ratio. The paper will present the details of growth and physical properties of LCMO films in addition to a structural model explaining the epitaxial growth of LCMO films on Si.

#### 9:30 AM U8.4/J6.4

PREPARATION OF PZT-YBCO HETEROSTRUCTURE ON YSZ COATED Si BY KrF LASER ABLATION. Kenji Ebihara, Fumiaki Mitsugi, Tomoaki Ikegami, Kumamoto University, Department of Electrical and Computer Engineering, Kumamoto, JAPAN; Jagdish Narayan, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC.

KrF excimer laser ablation technique is applied to fabricate the ferroelectric Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>)(PZT) capacitor on Si(100) substrate. The YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>(YBCO) bottom electrode was deposited on the Si coated by YSZ buffer layer under the appropriate deposition conditions (laser fluence 2-3 J/cm<sup>2</sup>, O<sub>2</sub> atmosphere pressure 100-200 mTorr, substrate temperature 650-710°C). The plasma plumes during film preparation were studied using ICCD images. The fabricated PZT/YBCO/YSZ/Si capacitor shows the ferroelectric properties of the remanent polarization 25  $\mu\text{C}/\text{cm}^2$  and the coercive force 31 kV/cm which are comparable with the results of the PZT/YBCO/MgO(100) capacitor. The switching fatigue for this sample has been investigated to be 10<sup>9</sup> cycles for the decrease to 10  $\mu\text{C}/\text{cm}^2$  polarization.

#### 9:45 AM U8.5/J6.5

PULSED LASER DEPOSITION OF EPITAXIAL SrVO<sub>3</sub> FILMS ON (100)LaAlO<sub>3</sub> AND (100)Si. P.W. Yip and K.H. Wong, Dept of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, PR CHINA.

Thin films of SrVO<sub>3</sub> have been grown on (100)LaAlO<sub>3</sub> and TiN buffered (100)Si substrates by pulsed laser deposition. The films were deposited in temperature range of 450°C - 750°C and under ambient oxygen pressure between 10<sup>-6</sup> and 10<sup>-2</sup> Torr. Their structural properties were characterized using a four-circle x-ray diffractometer. High quality SrVO<sub>3</sub> films were obtained at growth temperatures above 500°C without post annealing. Heteroepitaxial relationship of <100>SrVO<sub>3</sub>||<100>LaAlO<sub>3</sub> and <100>SrVO<sub>3</sub>||<100>TiN||<100>Si were observed for films deposited at  $\geq 550^\circ\text{C}$ . X-ray photoelectron spectroscopic studies of the films suggest that the vanadium is mainly pentavalent. Charge transport measurements show that the films vary from semiconducting to highly conducting for different growth conditions. Resistivity of a few micro-ohm cm was recorded for some of the epitaxial SrVO<sub>3</sub> films.

#### 10:30 AM \*U8.6/J6.6

IMPOSED LAYER-BY-LAYER GROWTH OF COMPLEX OXIDES WITH PULSED LASER INTERVAL DEPOSITION. Dave H.A. Blank, Guus Rijnders and Horst Rogalla, University of Twente, MESA+ Research Institute, Applied Physics, THE NETHERLANDS.

In oxides electronics the control on an atomic level becomes a central issue. The interface in gate-oxides, electrical, and magnetic junctions has to be controlled with the utmost precision. In order to be able to create a crystal structure by depositing consecutive unit cell layers of different materials, a layer-by-layer growth mode is a prerequisite: nucleation of each next layer may only occur after the previous layer is completed. We introduced a growth method, based on a periodic sequence: very fast deposition of the amount of material needed to complete one monolayer followed by an interval in which no deposition takes place and the film can reorganize. This makes it possible to grow in a layer-by-layer fashion in a growth regime (temperature, pressure) where otherwise island formation would dominate the growth. We present the results obtained for homo- and hetero-epitaxial growth on SrTiO<sub>3</sub> as monitored by high-pressure RHEED.

In addition, Monte Carlo simulations are used to support the applicability of interval deposition. Furthermore, this technique is used to grow superconducting as well as ferromagnetic junctions.

#### 11:00 AM U8.7/J6.7

GROWTH OF ZnO/MgZnO MULTIPLE QUANTUM WELL SUPERLATTICES ON SAPPHIRE BY PULSED LASER DEPOSITION. A.K. Sharma, C. Jin, A. Kvit, J. Narayan, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC; J.F. Muth, C.W. Teng, R.M. Kolbas, North Carolina State University, Department of Electrical and Computer Engineering, Raleigh, NC.

We have recently grown<sup>1</sup> high quality Mg<sub>x</sub>Zn<sub>1-x</sub>O alloy single crystal films on c-plane sapphire by pulsed laser deposition (PLD). The bandgap of these alloys was varied upto 4.27 eV by varying Mg content (x) to 34 at.%. Photoluminescence (PL) spectra from these films obtained at room temperature were very bright characteristic of excitonic nature of emission. This new materials system opens up enormous possibilities for optoelectronic devices such as truly solar blind detectors and uv lasers. In further pursuence of this material system, we have grown ZnO/Mg<sub>0.34</sub>Zn<sub>0.66</sub>O multiple quantum well superlattices on sapphire by PLD. The well thickness was varied from 20-40 Å and the barrier thickness was kept constant in these heterostructures. The characterization of these superlattices was performed by high resolution transmission electron microscopy, transmission measurements and photoluminescence. In optical transmission measurements, the features corresponding to quantum wells were resolved as two excitonic peaks of ZnO blue shifted as the well thickness decreases. The photoluminescence from these wells were extremely bright and blue shifted from the corresponding ZnO band-edge PL value. The results are in agreement with the simple calculations performed assuming a band offset  $\sim 0.5$  eV between ZnO and MgZnO. The PLD has been successfully employed to achieve these ultra thin layers with sharp interfaces.

This work has a potential for fabricating highly efficient optoelectronic devices based on ZnO.

<sup>1</sup>A.K. Sharma, J. Narayan, J.F. Muth, C.W. Teng, C. Jin, A. Kvit, and R.M. Kolbas, and O.W. Holland, Appl. Phys. Lett., 75, 22 Nov. (1999).

#### 11:15 AM U8.8/J6.8

SINGLE QUANTUM WELL STRUCTURE OF MgZnO/ZnO/MgZnO ON C-PLANE SAPPHIRE. Supab Chooapun, Dan Chalk, Wei Yang, R.D. Vispute, S.B. Ogale, R.P. Sharma and T. Venkatesan, CSR, Dept of Physics, Univ of Maryland, College Park, MD.

The single quantum well structures of MgZnO/ZnO/MgZnO were grown on c-plane sapphire substrate by pulsed laser deposition. Photoluminescence measurement was performed on these samples as a function of the well width. The quantum well width was varied by adjusting the deposition time of ZnO confined layer. Room temperature and 77 K photoluminescence were studied using continuous-wave He-Cd laser (325 nm) and pulsed N-laser (337 nm). From continuous-wave and pulsed photoluminescence spectra, we have observed a blue shift with respect to a thick ZnO reference sample when the well width was decreased. These results were fitting with calculation based on the simple square well model using effective mass of electron (0.24) and hole (0.59). By eliminating the well width parameter, the conduction band quantized-energy as a function of band offset has been obtained. This quantized-energy and the well width as a function of band offset, growth conditions, interface roughness, quantum size effect on MgZnO/ZnO/MgZnO quantum wells will be discussed.

#### 11:30 AM U8.9/J6.9

DEVELOPMENT OF LSCO AND LNO OXIDE ELECTRODES FOR SENSOR PROTECTION DEVICES. Malin Charoenwongsa, Kelly Buddin, Maildil Sebastian and Robert Schwartz, Clemson University, Department of Ceramic and Materials Engineering, Clemson, SC.

Oxide electrodes play a key role in a variety of devices, including protection schemes for sensors that operate in the 3 - 5  $\mu\text{m}$  and 8 - 12  $\mu\text{m}$  ranges. One such protection device currently under development is an electrostatic shutter, which is driven into a closed condition for protection against high energy pulses. For the fabrication of this device, electrodes must be developed that possess a sheet resistance of 300 to 500  $\Omega/\text{sq}$ . and which have a transparency, ideally, of at least 80%. We are evaluating the suitability of (La,Sr)CoO<sub>3</sub> (LSCO) and LaNiO<sub>3</sub> thin films for this application by attempting to achieve the appropriate balance between transparency and conductivity through control of the extent of crystallization, oxygen stoichiometry, composition, and thickness. Films are deposited on both BaF<sub>2</sub> and MgO substrates by sputtering or solution deposition followed by annealing at temperatures as high as 1100°C. Crystallization into the perovskite structure has been studied by x-ray diffraction and optical

properties have been studied by standard FTIR techniques. As expected, both the conductivity and transparency of the films are highly dependent on the heat treatment conditions. For the solution deposited films, heat treatment temperatures in the range of 700 to 800°C are required to fully crystallize the perovskite structure. For films that are approximately 150 nm in thickness, calculations of the extinction coefficient of the LSCO materials indicate that  $\alpha$  may approach  $150,000 \text{ cm}^{-1}$  for films heated at 800°C. Measurements of the resistivity of films fabricated under the same processing conditions indicate that values of  $500 \mu\Omega\text{-cm}$  may be obtained. These results suggest that it should be possible to achieve the required balance of sheet resistance and transparency for the development of the electrostatic shutter. However, target film thickness will be in the range of 15 - 25 nm.

#### 11:45 AM U8.10/J6.10

COMPARISON OF TEXTURED AND EPITAXIAL ZnO FILMS. Y.R. Ryu, Henry W. White, Univ of Missouri, Dept of Physics & Astronomy, Columbia, MO.

Textured and epitaxial ZnO films are grown on GaAs and sapphire by pulsed laser deposition (PLD). They are compared to understand the differences in crystal properties. Crystal qualities for ZnO films are studied by atomic force microscopy (AFM), x-ray diffraction (XRD), and photoluminescence (PL). Optical qualities for textured ZnO films are remarkably excellent, comparable with those for high-quality epitaxial ZnO films grown on sapphire. Textured ZnO films show very strong and narrow bound exciton peaks. These results will be discussed.

#### SESSION U9: ALTERNATIVE DEPOSITION APPROACHES

Chairs: Timothy J. Coutts and Hiroshi Kawazoe  
Thursday Afternoon, April 27, 2000  
Nob Hill (Marriott)

#### 1:30 PM \*U9.1

DEVELOPMENT OF NEW VOLATILE CD PRECURSORS FOR THE GROWTH OF CD-CONTAINING OXIDE THIN FILMS VIA MOCVD. Jason R. Babcock, Anchuan Wang, Nikki L. Edleman, Douglas D. Benson, Andrew W. Metz, Matthew V. Metz, Tobin J. Marks, Materials Research Center, Northwestern University, Evanston, IL.

In an effort to grow cadmium oxide (CdO) and cadmium stannate ( $\text{Cd}_2\text{SnO}_4$ ) via metal-organic chemical vapor deposition (MOCVD), a volatile Cd precursor family was desired.  $\beta$ -ketoiminates of varying substitution were prepared in an attempt to identify structure-property relationships. The nature of the ligand substituents strongly influences the melting point (liquid precursors are desired). Unlike conventional Cd  $\beta$ -diketonates, these complexes are shown to be monomeric by x-ray crystallography. Despite these advantageous characteristics, attempts to grow CdO thin films in a cold-wall MOCVD reactor using two derivatives were not successful. This class of Cd complex appears to decompose with time, a likely cause for the poor performance. Therefore, a new series of more thermally stable Cd complexes was sought. Using the chelating diamine  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA), monomeric  $\beta$ -diketonates were prepared. The molecular structure of  $\text{Cd}(\text{hfa})_2(\text{TMEDA})$  ( $\text{hfa} = 1,1,1,3,3,3$ -hexafluoropentane-2,4-dionate) confirms the monomeric designation above. This series of Cd complexes are appreciably more volatile and sublime more cleanly than the  $\beta$ -ketoiminates first examined, as determined by vacuum thermogravimetric analysis (TGA). The use of the  $\beta$ -diketonate precursors in the preparation of Cd-containing oxide thin films will be presented.

#### 2:00 PM U9.2

LIGHT SCATTERING FROM PULSED LASER DEPOSITED  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  THIN FILMS. R.K. Soni, Anju Dixit, R.S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR; A. Pignolet, K.M. Satyalakshmi, D. Hesse, Max-Planck-Institut für Mikrostrukturphysik, Halle/Saale, GERMANY.

Light scattering investigations are carried out on  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  (BBiT) which is a member of the Bi-layer structure ferroelectric oxide with  $n = 4$ . The BBiT thin films, thickness  $\sim 300$  nm, have been grown on epitaxial conducting  $\text{LaNiO}_3$  electrodes on epitaxial buffer layers on (100) silicon by pulsed laser deposition. Earlier reports<sup>1</sup> on morphology and structure investigations have shown that the films consisted of c-axis oriented as well as mixed (110), (100)- and (001) oriented regions with rectangular and equiaxed crystalline grains. Micro-Raman measurements performed on these regions reveal two sharp low-frequency interlayer modes at  $22 \text{ cm}^{-1}$  and  $48 \text{ cm}^{-1}$  along with broad high-frequency modes corresponding to other lattice vibrations including  $\text{TaO}_6$  octahedra. No temperature dependence of low frequency modes is seen in the c-axis oriented regions while a

weak dependence is observed for the mixed oriented regions. Angular dependence of Raman polarization carried out at room temperature as well as near the phase transition temperature of  $420^\circ\text{C}$  provides a useful information of various phases and the interdependence of Raman activity with morphology and crystallographic orientation in  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  thin films.

#### 2:15 PM U9.3

LATTICE DEFECTS IN EPITAXIAL FERROELECTRIC FILMS OF  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  AND  $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  GROWN BY PULSED LASER DEPOSITION ONTO  $\text{LaNiO}_3$  BOTTOM ELECTRODES. Nikolai D. Zakharov, Claudia Schäfer, Ajit R. James, Alain Pignolet, Stefan Senz and Dietrich Hesse, Max-Planck-Institut für Mikrostrukturphysik Halle, GERMANY.

TEM and HRTEM investigations on the nature and role of lattice defects in ferroelectric thin films of the bismuth-layered perovskites  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ , and  $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  were performed using both plan-view and cross-section samples. The films were grown onto epitaxial  $\text{LaNiO}_3$  (LNO) bottom electrodes in turn grown either on  $\text{CeO}_2/\text{YSZ}$  buffer layers on Si(100), or directly on  $\text{SrTiO}_3(100)$ . Layers and films of the same sample were all grown in one single run by pulsed laser deposition. In the four ferroelectric film materials chosen the layer-perovskite structure systematically varies with the Aurivillius parameter  $n$ , which indicates the number of oxygen octahedra that are stacked along the  $c$ -axis between two consecutive  $\text{Bi}_2\text{O}_2$  layers. Parameter  $n$  ranges from 2 to 5, respectively, in  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ , and  $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ . With respect to the identified lattice defects, the films of these four materials have features in common, but also display characteristic differences. In general the layered perovskite (LP) films consist of regions of  $c$ -orientation, where  $(001)_{LP} \parallel (001)_{LNO}$  and  $[100]_{LP} \parallel [110]_{LNO}$ . Occasionally grains of other orientations are embedded into the  $c$ -oriented regions, all showing definite azimuthal orientations. The  $c$  oriented film regions consist of individual grains of column-like or plate-like shape, respectively, separated by distinct low-angle grain boundaries. Size and shape of the grains differ for the four materials, with  $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  consisting of well-developed, large rectangular plates. Cross section images of the low-angle boundaries at moderate magnifications seem to show that the  $\text{Bi}_2\text{O}_2$  planes bow away from their regular (001) habit at the boundaries. HRTEM images, however, reveal that the bowed structures are formed by a step-like arrangement of many short, distinctly plane sections of  $\text{Bi}_2\text{O}_2$  planes, all of (001) orientation. The nature of these and other observed defects is under investigation.

#### 2:30 PM U9.4

VOLATILE, FLUORINE-FREE PRECURSORS FOR MOCVD OF LANTHANIDE OXIDE THIN FILMS. Nikki L. Edleman, John A. Belot, Anchuan Wang, Jason R. Babcock, Andrew W. Metz, Tobin J. Marks, Northwestern University, Dept of Chemistry and The Materials Research Center, Evanston, IL; Paul R. Markworth, Robert P.H. Chang, Northwestern University, Dept of Materials Science and Engineering and The Materials Research Center, Evanston, IL; Michael P. Chudzik, Carl R. Kannewurf, Northwestern University, Dept of Electrical and Computer Engineering and The Materials Research Center, Evanston, IL.

A proven method of successful oxide film growth is metal-organic chemical vapor deposition, a technique extensively employed in the semiconductor industry. Successful MOCVD hinges upon the availability of suitable metal-organic precursors, which must be volatile and stable to repeated thermal cycling. Furthermore, the ligands must readily combust at the heated substrate to avoid film contamination owing to organic decomposition products. Appropriate complexes are ideally liquid state, inexpensive to synthesize, air and moisture stable, and non-toxic. Previous work in our laboratory has focused on the development of suitable MOCVD precursors for deposition of technologically important materials and optimization of subsequent film growth. A current concentration is on lanthanide oxide-containing materials. Lanthanides are of interest as phosphor dopants, components in magnetic devices, oxide fuel cell constituents, superconductors, and oxide buffer layers in semiconducting and superconducting device multilayers. The classic lanthanide MOCVD precursors, fluorinated or non-fluorinated beta-diketonates, are prone to extensive decomposition and oligomerization or (in the fluorinated cases) are incompatible with certain substrates. Hence, the development of improved lanthanide precursors is currently a great need in the thin film community. In response to this need, our lab has developed a new series of fluorine-free, low-melting, volatile lanthanide complexes. In these complexes, the lanthanide ( $\text{Ln} = \text{Ce}, \text{Nd}, \text{Er}$ ) is completely saturated by three tridentate beta-ketoiminate ligands. The alkyl substituents at the ketone, imino, and ether sites of the ligand are synthetically tailorable for tuning precursor volatility and melting point. Results of a full synthetic study of these complexes will be outlined. The complexes have been fully characterized by NMR, elemental analysis, single-crystal x-ray diffraction, mass spectrometry,

and thermogravimetric analysis. In addition, the successful growth of lanthanide oxide films utilizing these new precursors will be detailed.

#### 2:45 PM U9.5

HYBRID BEAM DEPOSITION (HBD) TECHNIQUE FOR GROWTH OF METAL OXIDE FILMS. Yung R. Ryu, Henry W. White, Univ of Missouri, Dept of Physics & Astronomy, Columbia, MO.

We introduce hybrid beam deposition (HBD) as a novel growth technique. HBD combines pulsed laser deposition (PLD), molecular beam epitaxy (MBE), and chemical vapor deposition (CVD). The flux density of available reactive oxygen for ZnO film growth can be effectively increased by using a (Zn,O)-plasma created by combined laser ablation from a pure ZnO target and radical atomic oxygen from a RF gas cracker. The HBD process is discussed for ZnO film growth, and compared with processes of the other growth techniques such as MBE and CVD.

#### 3:15 PM \*U9.6

GROWTH EVOLUTION, MORPHOLOGY, AND MICRO-STRUCTURE OF EPITAXIAL  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  FILMS. J. Lettieri, M.A. Zurbuchen, Y. Jia, D.G. Schlom, Penn State University, Department of Materials Science and Engineering, University Park, PA; S.K. Streiffer, Argonne National Laboratory, Materials Science Division, Argonne, IL; M.E. Hawley, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM.

There has been considerable interest in the bismuth-based, layered materials of the Aurivillius homologous series, such as  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  ( $n=2$  member), due to their superior fatigue-resistance even after significant ferroelectric cycling. This advantageous property makes  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  films excellent candidates for ferroelectric memories. It has been argued that it is the highly anisotropic crystal structure of this material that makes it superior to other perovskite based ferroelectrics. In this study, we have examined the growth of epitaxial films on (001), (110), and (111)  $\text{SrTiO}_3$  in an effort to understand both the growth phenomena and the technologically advantageous anisotropic properties (polarization and fatigue resistance) found in this ferroelectric. The films grow epitaxially with the c-axis inclined by  $0^\circ$ ,  $45^\circ$ , and  $57^\circ$  from the substrate normal, respectively. Examination of the electrical properties (dielectric loss 2-3% for 5000 Å films) as a function of orientation of these epitaxial thin films is used as a tool to quantify the anisotropy. Growth evolution, defects (out-of-phase boundaries), anisotropic electrical properties, and substrate influences on orientation, microstructure, and morphology are emphasized. Electrical characterization, TEM, AFM, and 4-circle x-ray diffraction will be presented.

#### 3:45 PM \*U9.7

EXPLORATION OF NEW PROPERTIES OF OXIDES BY THE GROWTH CONTROL IN PULSED LASER EPITAXY. Hideomi Koinuma\*, Takao Koida, Daisuke Komiyama, Tokyo Institute of Technology, Ceramic Materials and Structures Laboratory; \*also CREST, Japan Science and Technology Corporation; Mikk Lippmaa, Akira Ohtomo, Masashi Kawasaki, Graduate Course of Interdisciplinary Science and Technology, Yokohama, Japan.

In reflection of compositional and structural multiplicity, metal oxides exhibit a wide variety of properties originating mainly from strong electron correlation. Electronic properties of oxides have been utilized mostly in the form of bulk materials and people frequently observe significant change in such properties when the materials were converted into thin films, say less than  $1 \mu\text{m}$  thick. In today's most advance electronics, trend is thinning, hybridization, and integration of materials in which epitaxial thin film technology is essential. Based on our recent studies with focuses on the following topics, this paper is devoted to stimulate the exploration of oxides as new innovative electronic materials by discussing the control of epitaxial thin film growth. 1, Molecular layer epitaxy for lattice and device engineering; Using the fabrication of high-Tc Josephson tunnel junction as an example, key factors for atomically controlled layer-by-layer growth of oxides under high (MBE) and moderate vacuum conditions are elucidated. 2, Step flow growth of perovskite oxide films with single crystal quality; Our compact laser MBE system using laser heating made it possible to grow a  $\text{SrTiO}_3$  film of its dielectric constant equivalent to single crystal ( $\epsilon > 10,000$  at 4K). 3, Epitaxy on mismatched surfaces; For the fabrication of heterojunction devices and artificially designed lattices, we encounter and have to solve this problem. This task is classified into physical, i.e. lattice mismatch, and chemical, i.e. redox or acid-base, problems and some ideas and results of solving the problems are presented. Sometimes, mismatch can be utilized positively to manifest a new property which is hard to be observed in bulk oxide.

#### 4:15 PM U9.8

THE EFFECT OF MICROSTRUCTURE ON THE IMPEDANCE

AND FREQUENCY RESPONSE OF SOL-GEL-DERIVED NANOPARTICULATE MANGANESE DIOXIDE THIN FILMS. Suh-Cem Pang, Suk-Fun Chin, Marc A. Anderson, Water Chemistry Program, University of Wisconsin, Madison, WI.

Sol-gel-derived nanoparticulate manganese dioxide thin films in unbuffered electrolyte have been studied using electrochemical impedance spectroscopy (EIS) over the frequency range of 10 mHz to 100 kHz. These films showed a distinctive impedance response depending upon the range of frequencies: an almost purely capacitive behavior at low frequencies, a diffusion-controlled behavior at intermediate frequencies, and a purely resistive behavior at high frequencies. These frequency responses were independent of applied dc polarization potentials within the range of 0.0V to +0.9V versus SCE. Capacitance values of these films at various polarization conditions ranged from  $2.6 \text{ mF/cm}^2$  to  $4.5 \text{ mF/cm}^2$ , with contributions from both the double-layer capacitance and pseudocapacitance associated with faradaic processes. While porous electrodes of nanoparticulate materials have resulted in an increase in their utilization, the distributive nature of such electrodes compromises their power delivery at very short times (or high frequencies). The porous matrices of nanoparticulate  $\text{MnO}_2$  system allow only a fraction of the energy stored in such capacitor devices to be drawn at high frequencies. Though porous systems afford high surface areas and enhance the rate of kinetically slow reactions, they possess the inherent drawback of high resistivity associated with the electrolyte and the matrix. However, high capacitance value can possibly be achieved at high frequencies by significantly lowering the electrolyte resistance, and by optimizing the microstructure such as the porosity, pore size and film thickness. The effect of microstructure on the impedance and frequency response of sol-gel-derived nanoparticulate  $\text{MnO}_2$  thin films have been reported, and our research efforts have been directed towards achieving frequency responses of fast charge and discharge required for pulsed power applications.

#### 4:30 PM U9.9

PREPARATION AND CHARACTERIZATION OF EPITAXIAL  $\text{Bi}_2\text{WO}_6$  THIN FILMS PREPARED BY SOL-GEL PROCESS. Chikako Kudo, Keishi Nishio, Tsutomu Nagahama, Yuichi Watanabe and Toshio Tsuchiya, Dep. of Mater. Sci. and Tech., Science University of Tokyo, Chiba, JAPAN.

We have succeeded in the preparation of epitaxial thin films of bismuth tungstate ( $\text{Bi}_2\text{WO}_6$ : BWO), one of the bismuth layer-structure ferroelectrics (BLSF), on  $\text{SrTiO}_3$  (001) single crystal substrates by a spin coating process. BLSF are expected to apply for ferroelectric random access memory (FeRAM). A homogeneous coating solution was prepared with tungsten hexachloride and bismuth 2-ethylhexanoate as raw materials, and 2-(2-methoxyethoxy) ethanol and formamide as solvents. The coating thin films were sintered at temperatures from  $500^\circ\text{C}$  to  $800^\circ\text{C}$  for 1h in air. BWO crystallized at temperature above  $500^\circ\text{C}$ . Any crystal phase was not observed in the thin films except for (001) phases of BWO in the XRD patterns using  $\theta$ - $2\theta$  scan. The grain size increased with increasing heat treatment temperature up to  $600^\circ\text{C}$ . It was confirmed that the thin film was in the epitaxial growth because the diffraction spots were revealed by measurement of XRD pole-figure. The crystallographical relationship of the film and the substrate was  $\text{BWO}(001)//\text{STO}(001)$ ,  $\text{BWO}[110]//\text{STO}[100]$ . This relationship would be also expected from that  $a$  and  $b$  lattice constant of BWO nearly equal to  $2^{1/2}$  times that of STO.

#### 4:45 PM U9.10

PROPERTIES OF AMORPHOUS AND CRYSTALLINE  $\text{Ta}_2\text{O}_5$  THIN FILMS PREPARED BY METALORGANIC SOLUTION DEPOSITION TECHNIQUE FOR INTEGRATED ELECTRONIC DEVICES. P.C. Joshi and M.W. Cole, US Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD.

The development of future generation of DRAMs will require the introduction of new materials with higher dielectric constant than the conventional  $\text{SiO}_2$  or silicon oxide/nitride based systems. Among the dielectric materials under investigation,  $\text{Ta}_2\text{O}_5$  is one of the most promising insulator materials for DRAM cell capacitors. The high dielectric constant and low dielectric loss materials are also attractive for microwave applications.  $\text{Ta}_2\text{O}_5$  thin films have potential for numerous microelectronic applications such as gate dielectric of MIS devices, optical waveguides, electroluminescent display devices, and surface acoustic wave devices. For successful integration into microelectronic devices, extremely reliable  $\text{Ta}_2\text{O}_5$  thin films are desired. The properties of  $\text{Ta}_2\text{O}_5$  thin films have been reported to be strongly dependent on the fabrication method, nature of substrate and electrode material, and post-deposition annealing treatment. An understanding of process-structure-property correlation is important to understand and compare various thin film studies reported in literature and exploit  $\text{Ta}_2\text{O}_5$  thin films for devices. In this paper, we

report on the systematic study of structural, optical, dielectric, and insulating properties of amorphous and crystalline Ta<sub>2</sub>O<sub>5</sub> thin films fabricated by metalorganic solution deposition (MOSD) technique. Ta<sub>2</sub>O<sub>5</sub> thin films were fabricated on Pt-coated Si, n<sup>+</sup>-Si, and poly-Si substrates by spin-coating using room temperature processed precursor solution. The structure and surface morphology of the films were analyzed by x-ray diffraction (XRD) and atomic force microscopy (AFM). The optical properties were measured by variable angle spectroscopic ellipsometry. The film/substrate interfacial characteristics were examined by AES and RBS techniques. The dielectric measurements were conducted on films in MIM and MIS configurations. The insulating properties and dominant conduction mechanism in amorphous and crystalline Ta<sub>2</sub>O<sub>5</sub> thin films were analyzed through the measurements of *I-V* characteristics in MIM capacitors. The temperature and bias stability of the dielectric and insulating properties were also analyzed.

**5:00 PM U9.11**

**REACTIVE SPUTTERING OF ZINC OXIDE FOR PIEZO-ELECTRIC APPLICATIONS.** Glen R. Kowach, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

The deposition and characterization of zinc oxide (ZnO) thin films by reactive RF magnetron sputtering will be discussed with an emphasis on processing conditions. The films were characterized using X-ray diffraction, spectroscopic ellipsometry, field-emission scanning electron microscopy, electrical property measurements, Raman spectroscopy, and dispersive atomic force microscopy. X-ray diffraction spectra indicate that the films deposited at high temperatures are crystalline and c-axis oriented normal to the substrate. The film crystallinity and orientation are found to increase with increasing substrate temperature during deposition with the best texture (rocking curve 1.52° FWHM) obtained at a temperature of 700°C. The FESEM images show that all the films are dense and relatively smooth. However, a strong dependence of film microstructure on substrate type, roughness and texture was revealed. A textured film of platinum promotes nucleation thereby improving crystallinity and texture in the sputtered ZnO film. Resistivity was correlated to the substrate temperature during deposition, such that resistivities on the order of 10<sup>10</sup> Ω-cm were obtained at temperatures below 500°C. In addition, the piezoelectric constant was determined to match the bulk value for ZnO.