SYMPOSIUM U
Materials Science of Novel Oxide-Based Electronics
April 24 – 27, 2000

Chairs

David S. Ginley
PV&EM
Natl Renewable Energy Lab
SERF W102
Golden, CO 80401
303-384-6573

Dennis Newns
Physical Sciences Dept
IBM T.J. Watson Research Ctr
Yorktown Hts, NY 10598
914-945-3551

Hiroshi Kawazoe
R & D Ctr
HOYA
Akishima Tokyo, 196-8510 JAPAN
81-42-546-2775

Andrey Kozyrev
Electrotechnical Univ
St Petersburg, 197376 RUSSIA
812-234-4809

John D. Perkins
Natl Renewable Energy Lab
SERF E100-49
Golden, CO 80401
303-384-6606

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*Invited paper
SESSION U1: APPLICATIONS
Chairs: David S. Ginley and Hiroshi Kawairo
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 new second generation devices which demonstrate a higher transconductance.


9:00 AM #U1.2
SIMULATION OF A SIMPLIFIED DESIGN FOR AN ALL METAL-OXIDE NANOSCALE MOET TRANSITION FIELD EFFECT TRANSISTOR.
Dennis M. News, Prang, C. Ptasnak, 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 (METE). The device uses 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 we treated the source/drain electrodes as unidirectionally 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 a high on-off 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 METE device.

9:15 AM #U1.3
OPTIMIZING FABRICATION OF BURIED OXIDE CHANNEL FIELD EFFECT TRANSISTORS.

The buried oxide channel field effect transistors (BOCFET) recently demonstrated at IBM [1] offer the potential to exceed beyond the limits of silicon technology. In these devices the gate oxide/channel interface quality and gate oxide dielectric strength are critical to the performance. Kawaswaki and coworkers [2] have shown that surface termination has a substantial role in allowing for high gate oxide smoothness in the polysilicon substrates in obtaining perfect stoichiometry of the polyoxide 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 epitaxy process which leads to high quality substrate terminated in titanium. Unfortunately, titanium termination leads to precipitates in the epitaxial growth of the gate oxide. We have examined methods of producing stoichiometric terminal surfaces for BOCFET fabrication. The influence of substrate treatment and temperature on channel conductivity in BOCFET structures will be presented. In addition we have performed studies on optimizing the quality, dielectric constant, and dielectric breakdown potential of gate oxides for BOCFET architecture will be presented.


9:30 AM #U1.4
ELECTRICAL CHARACTERISTICS OF LSCM-DERIVED Sb80.5,Te0.5,Ta2O5 TIN FILMS USING TiO2 BUFFER LAYER FOR METAL/TEgO/HEMT/HIC/INSULATOR FIELD EFFECT TRANSISTOR DEVICES.
Joo-Dong Park, The-Sing Oh, Hong Ik Univ., Dept. of Metallurgical Engineering and Materials Science, Seoul, KOREA.

Using TiO2 buffer layers of 10~200 nm thickness, Sb80.5,Te0.5,Ta2O5 (SBT) thin films of 400 nm thickness were prepared on the Si(100) substrates by Liquid Source Mixed Chemical Deposition (LSCM), and their electrical characteristics were investigated. SBT thin films were used as read out (NDO) MFIS-FET device application. The 400 nm-thick SBT film on Pt/Ti/SiO2/Si(100) substrates exhibited 3P of 8.9 μC/cm2 and Eo of 28 kV/cm at 5 V. CV characteristics of Pt/SBT/TiO2/Si structures exhibit hysteretic loops due to the ferroelectric switching behavior of SBT films, and the maximum capacitance of MFIS structures increased with decreasing the thickness of TiO2 buffer layers. The memory window of 1.3 V was claimed for SBT films on Si substrates using 50 nm-thick TiO2 buffer layer.

9:45 AM #U1.5
STUDY OF Ga2O3-Al2O3 / Sb2O3 interface for GaaS INTERFACE FOR MOSE 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 Ga2O3-Al2O3 (GGG) and ZnO as insulating layers on n-GaAs to provide high resistivity gate dielectric with low Dk. For the first time of oxide, both single crystal GGG and sintered polycrystalline material were used. A stoichiometric mixture of Ga2O3 and Al2O3 was sintered at 1450°C for 12 hrs. to prepare the polycrystalline layer. Steochiometric ZnO 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 x 1020 cm-3. The GGG film thickness was varied from 500 Å to 5000 Å. Pre-treatment of the GaAs substrates involved removal of native oxide in 50% HCl followed by immediate deposition of oxide films. As used metallization was used for ohmic and contact layers. Ohmic 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 modultion of CV. The dielectric constants of the GGG and Al2O3 films were found to be 15.2 and 12.4 respectively while their resistivities were found to be 1014 and 1013 cm respectively.

The CV curves for GGG/ GaAs showed high positive threshold voltages which decreased with increase in oxide thickness with no appreciable change in Dk. From the high frequency (1MHz) CV measurements interface state densities Dk were estimated using Terman’s method. Dk = 1.68 x 1011 eV-1 cm-2 was observed on the GGG (from single crystal) / GaAs interface compared with 3.89 x 1012 eV-1 cm-2 for GGG from bulk / GaAs and 6.9 x 1012 eV-1 cm-2 for ZnO/GaAs GaAs interface. The hysteresis in C-V for GGG/ GaAs was found to be very small while it was larger for ZnO/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 THE ELECTRONIC DEVICES.
T. Venkatesan, University of Maryland, College Park, MD.

In the last decade some of the most exciting materials systems have been studied are the doped antiferromagnets. The high temperature superconducting cuprates and the colossal magnetoresistive magnets are two excellent examples of widely studied systems with a fascinating array of properties and interactions. From the fundamental point of view the key is to look at these systems even in the presence of a stoichiometric, single material phase can exhibit an inhomogeneity with respect to charge distribution, also referred to 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 resistance of the material 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.
Shinobu D. Silliman, Hong Ik Univ., Dept. of Metallurgical Engineering and Materials Science, Seoul, KOREA.

Thin insulating films of aluminum oxide were grown on hydrogen-terminated p-type silicon substrates by Pulsed Laser Deposition (PLD). Stoichiometric Al2O3 targets and an Ar background gas were used in an off-axis growth geometry with no direct laser light between the laser spot and the substrate surface. Capacitance values as high as 1.5 mF/cm2 were measured on films with thicknesses below 40 Å, corresponding to a dielectric constant of 6.5. Forward leakage current densities of 0.5 A/cm2 at -1 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 HYPERTHERMAL SURFACE IONIZATION USING A SCANNING KELVIN PROBE. Uwe Petermeier, Iain D. Balick, Bert Lügel, Konrad M. Dirschel, Robert Gordon Univ., Dept. of Applied Physics, Aberdeen, UNITED KINGDOM.

In order to search for efficient target materials for use in Hyperthermal Surface Ionization (HSI), a new mass spectroscopy ionization technique, we have performed scanning Kelvin probe measurements on low work function [wf] surfaces as part of an ongoing project. HSI relies on high and low work 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-annul cleaning cycles via high resolution wf topographies. Our results indicate oxidized Re for pHSI in terms of ionization efficiency and wf change. The peak wf change of 2.05 eV occurred at 791 K. For the nHSI materials CaK exhibited the best performance with respect to the ionization efficiency indicating a wf of 2.8 eV. We will present data in terms of ionization efficiency using an HSI-TOF system and time stability of the wf.

11:45 AM U1.9
SURFACE INVESTIGATIONS ON SINGLE CRYSTAL ANATASE TiO2 R. Hengeler, L. Kwan, B. Bolliger, M. Erbudak and M. Greveli, EPFL, Lausanne, SWITZERLAND.

In charge separation/injection devices based on nanocrystalline TiO2 films like dye-sensitized solar cells or rocking chair lithium batteries, anatase TiO2 shows superior performance in comparison to the more stable and common polymorph of TiO2, rutile. In contrast to rutile, however, surface investigations that help to elucidate the charge separation processes are missing for anatase due to the lack of a well-defined cleavable crystal. We proceeded in growing suitable and pure single crystals by a chemical transport reaction. The surfaces of these crystals could be characterized by standard physical and electrochemical 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 chemically clean. Furthermore, the discussion of the 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 acetonitrile solutions showed a different lithium insertion behavior for the two surfaces. This is explained by a different structural transperperuency 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 TiO2 films used in solar cells and lithium batteries.

SESSION U2: NEW IDEAS AND MAGNETISM
Chair: Dennis M. Nevis and T. Venky Venkataraman
Monday Afternoon, April 30, 2000
Nob Hill A/B [Marriott]

1:30 PM #U2.1
TRANSPARENT OXIDE NANO PARTICLES FOR ADVANCED ORGANIC/INORGANIC COMPOSITE THIN FILM SENSORS AND EMITTERS. Sue A. Carter, Albon Breeze, University of California, Santa Cruz, CA; Aaron A. Armstrong, Intel Corp., Cambridge, MA; H. Horhold, Friedrich 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/inorganic interface and the composite morphology, I will show that efficient photo- 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 oxide in other novel organo-inorganic based devices, including biosensors, transducers and optical switch.

2:00 PM #U2.2
EPITAXIAL PIEZOELECTRIC HIERARCHICAL STRUCTURES 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(Mg1/3Nb2/3)03-PbTiO3 (PMN-PT) and Pb/Zn1/3Na2/3TiO3-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 form, by thin film methods over 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 thin films of PMN-PT/SrRuO3 single crystal heterostructures by means of metalorganic chemical vapor deposition (MOCVD) and metalorganic chemical solution deposition (MOCSD) and high-temperature epitaxial growth. The SrRuO3 substrate used for growth was of the SrRuO3 (001) orientation by metalorganic chemical epitaxy. The growth was conducted at temperatures of 900 °C with a growth rate of 1 Å/s. The SrRuO3 films show epitaxial growth of PMN-PT/SrRuO3 heterostructures in which the thickness of the PMN-PT layer is about 100 Å and grows epitaxially on the single crystal SrRuO3 thin film bottom electrode. These epitaxial heterostructures lock promising for the fabrication of integrated single crystal piezoelectric devices for the fabrication of integrated single crystal piezoelectric devices for the fabrication of integrated single crystal piezoelectric devices.
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 L-3 PZT composites revealed good performance both as projectors and hydrophones. Ultralene scaled L-3 PZT composites with uniform arrays of 80 nm diameter, 5000 nm long PZT fibers in an epoxy matrix also have been produced. The properties of both PZT composites were investigated.

3:30 PM U2.5 THERMAL STABILITY AND SEMICONDUCTING PROPERTIES OF EPITAXIAL La$_2$Sr$_3$MnO$_{10}$ FILMS. K.K. Wong, W.B. Wu, The Hong Kong Polytechnic Univ, Dept of Applied Physics, Hong Kong, KOWLOON, HONG KONG, CHINA.

La$_2$Sr$_3$MnO$_{10}$ (LSMO) perovskite oxide films have been grown on [001] LaAlO$_3$ (LAO) by pulsed laser deposition. The films were deposited in oxygen pressure of 0.1 mTorr to 200 mTorr and under different substrate temperatures. Their structural properties were examined by X-ray diffractometry. Heteropolarization growth was confirmed for films deposited at 650ºC 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 ≤ 60 mTorr. The epitaxial LSMO films have been used as the semi-conducting channel of a ferroelectric field effect transistor. Heteroepitaxial Pb$_{0.52}$Sr$_{0.48}$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 La$_{0.65}$Sr$_{0.35}$Fe$_2$O$_{4+delta}$ FILMS. Haung Chou, M.N. Ono, 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 proton on electrical conductivity and the magnetoresistance [MR] in La$_{0.65}$Sr$_{0.35}$Fe$_2$O$_{4+delta}$ (LSF) films have been investigated. The doses were varied from 1x10$^{11}$ to 2x10$^{12}$ protons/cm$^2$. The point defects by local structures and spin disorder generation drastically enhanced the MR from -0.1% to 0.5% 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 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 La$_{0.75}$Sr$_{0.25}$MnO$_{3}$ FILMS. S.H. Kharev, P. Johnson, Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN.

Sequence of epitaxial La$_{0.75}$Sr$_{0.25}$MnO$_{3}$ (LSMO) films, ranged from 240 to 5 nm, have been prepared by pulsed laser deposition onto [110] SrTiO$_3$ (STO) substrates. Compared with our previous results on LSMO/SrTiO$_3$ (100) films [MRS Spring 99 Proceedings], films on STO (110) substrates exhibit strong anisotropy of electrical resistivity. R. measured in [1-10] direction is comparable with the resistivity of LSMO/SrTiO$_3$/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 approximately in films grown at 500 ºC temperature and 90 mTorr. An almost linear decrease from 3D to 2D case has been observed. For thick films monocrystallinity monotonously decreases with the temperature increase. Films thinner than 200 nm exhibit peak of monocrystallinity 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 [1-11] 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$_2$Ca$_{1-x}$Mn$_x$O$_{4+y}$ Films. D.J. Miller, YK Lin, V. Vlasko-Vlasov, U. Welp, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Structural defects play a large role influence the properties of the CMR materials. In this work, we have studied the effect of grain boundaries on magnetoresistance in La$_2$Ca$_{1-x}$Mn$_x$O$_{4+y}$ thin films. Film bicrystals were prepared by pulsed laser deposition onto bicrystal substrates. In contrast with the epitaxial growth, epitaxially grown films typically observed in bicrystals at 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 magnetic moment 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 is 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 La$_{1-x}$Ca$_x$Mn$_2$O$_{4+y}$ DUE TO ADDITIVES. V. Rawindranath, K.S.P. Phani Kumar, P.V. Suresh, Srimati Thirumalai and M.S. Rama Murthy, Rao, Materials Science Research Centre, and Department of Physics, Indian Institute of Technology, Madras, Chennai, INDIA.

Doped manganite perovskites such as La$_{1-y}$Ca$_y$Mn$_2$O$_{4+y}$ (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. With better understanding it may be possible to exploit the grain boundary properties for device applications. In the present study, polycrystalline La$_{1-y}$Ca$_y$Mn$_2$O$_{4+y}$ (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 into pellets and sintered at 1300ºC 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 the 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 progress in increase the resistivity of these compounds by using in-situ additives such as PtO, PdO, SrO, CeO$_2$, V$_2$O$_5$, etc. 1. A. Gupta et al., Phys. Rev. B 54 (1996) R15629. 2. R. Gross et al. (to appear in JMMM 1999).

4:45 PM U2.10 MAGNETIC AND MAGNETO-OPTIC PROPERTIES OF PULSED LASER DEPOSITED Ce$_{0.3}$Y$_{0.7}$Fe$_{2}$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 Gd$_2$Ga$_5$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 films fabricated at 50 mTorr oxygen pressure exhibit maximum Faraday rotation FR = 0.7 and 1.6 deg/m at 633 nm and 429 nm respectively, the minimum in-plane coercivity He = 35 Oe, and the narrowest full width at half maximum FWHM = 0.06 deg of (444) rocking curve. Analog of the Verdet constant V = FR/AgMs is also found to be dependent on the ambient pressure and reaches the value as high as 1.41x10$^2$ deg/m G at 633 nm, indicating this material is promising for MO applications. Energy dispersion FR spectrum measured in visible region 490 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 AgMs, lower by the same factor. To clarify the role of strain, induced by film/substrate lattice mismatch, and the change of Fe$^{3+}$ and Ce$^{4+}$ valence states, deposition onto the Gd$_3$(Ga$_5$Sc$_{1-x}$)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
Neb Hill A/B (Marriott)

8:15 AM U3.1
FERROELECTRIC THIN FILM BASED TUNABLE MICROWAVE COMPONENTS FOR SATELLITE COMMUNICATIONS: A PROGRESS REVIEW. Felice A. Mirabella, Robert B. Romanchuk, Fred W. Van Keuls, Joseph D. Warren, Carlos S. Assian, NASA-Glenn Research Center, Cleveland, OH; Guru Subramanian, 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 K-band. Thus, the use of ferroelectric technology is evolving from a single, "stand-alone" component, to more ambitious hybrid communication subsystems such as filter/LNA's and resonator/TETs 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, advanced 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 MATERIAL ISSUES IN FERROELECTRIC THIN FILMS. XX Nt, 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$_3$ 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 phonon shows a Pm symmetry, indicating the interaction with a polar continuum of excitation, which is suggested 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 or the transverse field Ising model.

9:15 AM U3.3
PYROELECTRIC COEFFICIENT OPTIMIZATION THROUGH GRAIN SIZE CONTROL IN (Ba,Sr)TiO$_3$ 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$_3$ (BST) thin films being developed for utilization as the active layer in pyroelectric detector arrays have been explored. Thin, epitaxial bilayers of $\text{Ba}_2\text{Sr}_2\text{Ti}_3\text{O}_9$ and $\text{Sr}_2\text{Ru}_2\text{O}_7$ were grown by pulsed laser deposition. $\text{Sr}_2\text{Ru}_2\text{O}_7$ substrates at pulsed laser deposition rate varying from 1 to 20 Hz during BST deposition 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 $\text{Sr}_2\text{Ru}_2\text{O}_7$ deposited at 5 Hz, the pyroelectric coefficient was largest for BST films grown at 5 Hz. While the pyroelectric coefficient was almost identical at low and high repetition rates, the pyroelectric coefficient in this intermediate laser pulse rate was approximately three times larger. High resolution X-ray diffraction, in conjunction with classical and scanning electron microscopy and Rutherford backscattering spectroscopy, were employed in order to elucidate the relation between the electrical properties and the microstructure of these films.

9:30 AM U3.4

We have investigated the materials and dielectric properties of $\text{Ba}_x\text{Sr}_1-x\text{TiO}_3$ thin films with $0 \leq x \leq 0.3$ Mg. Films were deposited via metalorganic deposition technique using barium acetate, strontium acetate, titanium isopropanoxide as precursors to form BST. Acetic acid and 2-methylethanol 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 fired at 300°C for 1 hour to evaporate solvents and organic addends and form an inorganic film. The spin coating 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 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 spectroscopy was employed to access film thickness and composition. The electrical measurements were conducted in the metal-insulator-metal capacitor configuration. Dielectric constant and dielectric permittivity were measured with an HP 4192A impedance analyzer. The films insulating properties, leakage current, were evaluated with 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$_3$ THIN FILMS. Karin M. Roke, Dept of Applied Physics, Yale University, New Haven, CT; Philippe Glazier, 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$_3$ 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 film 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

We have investigated the modulation of superconductivity using a ferroelectric field effect in epitaxial Pb$_2$Zr$_{2-x}$Ti$_x$O$_7$-based superconducting heterostructures. Using the polarization field of the ferroelectric oxide
Electronic properties of Nb-doped SrTiO$_3$, 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 magnitude 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 perovskite 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 dependency of the electronic properties of the junctions. We present existence of intrinsic low permittivity layer at the metal/SrTiO$_3$ junction and suggest structural modulation of SrTiO$_3$ at the interface. This structural model for the intrinsic low permittivity layer is consistent with the experimental findings of the growth of oxide-electrodes in order to suppress the reduction of the permittivity of the dielectric oxide films. In the final topic, photocapacitance spectroscopy of electronic states in the metal/SrTiO$_3$ systems will be described. It is found that the photocapacitance spectroscopy is one of the most effective tools for the deep level characterization of the oxides 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$_3$. Deep levels in Au/SrTiO$_3$ Schottky junctions of the order of $10^2$ to $10^3$ cm$^{-3}$ are characterized and band diagram of the junction will be discussed.

The development of methods for growing highly oriented barium hexaferrite films is of great importance for plane nonreciprocal devices operating at millimeter wavelengths. To date, some work has been the substrate of choice for growing barium hexaferrite films. However, the barium hexaferrite film/substrate combination has significant mismatch in both lattice constants and thermal expansion coefficients, such that thicker films incur large tensile stresses and thus crack and delaminate from the 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 (001) 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 strontium-substituted barium hexaferrite having thicknesses of 0.5 - 2 micrometers were deposited onto (111) MgO substrates by pulsed laser deposition at temperatures of 960°C. X-ray diffraction measurements showed that these films were phase pure and had only (001) diffraction peaks. Magnetometry results on pure barium hexaferrite films showed magnetization values near 4.0 K, lower than those measured in bulk materials. Torque magnetometry measurements showed the films to have excellent anisotropy 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 n-producing 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 tenacity strength of the MgO substrates, as the deposition thick [30 micrometer] non-oriented barium hexaferrite films on (111) MgO has caused the substrates to shatter upon cooling.

**SESSION U4: FERROELECTRICS II**

**13:50 PM *U4.1 JUNCTION PROPERTIES OF METAL/SrTiO$_3$ SYSTEMS**

Takashi Shimura and Hideo Okashi, Electrotechnical Laboratory, Tsukuba, Ibaraki, JAPAN

Electrical properties of Nb-doped SrTiO$_3$, 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 magnitude 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 perovskite 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 dependency of the electronic properties of the junctions. We present existence of intrinsic low permittivity layer at the metal/SrTiO$_3$ junction and suggest structural modulation of SrTiO$_3$ at the interface. This structural model for the intrinsic low permittivity layer is consistent with the experimental findings of the growth of oxide-electrodes in order to suppress the reduction of the permittivity of the dielectric oxide films. In the final topic, phot.
deposition; SrRuO$_3$ being used as the bottom electrode. The films were observed to be single phase by X-ray diffraction. The thickness of the film varies around 400 nm. Temperature of the film 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. A frequency of 1 kHz was used.  For the EPR measurements, films were decorated with evaporated Ag electrodes. The value of saturation polarization P$_s$ was between 2-25 mC/cm$^2$ and the coercive field E$_c$ varied from 35-154 kV/cm. Growth of films for better values of P$_s$ and E$_c$ is in progress. The variation of the properties of the films with thickness will also be studied in detail.

23:00 PM U4.4

UV RADIATION EFFECTS IN SOL-GEL PROCESSING OF FERROELECTRIC PbTiO$_3$ 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 zinc niobate 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 chemically modifying, or “diluting” agents. In this research, hydrogen peroxide has been used to improve the wetting behavior and stability of precursor solutions. We have used this method to study the wetting behavior of perovskite sol-gel precursors and have found that hydrogen peroxide can improve the wetting behavior of these materials.

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, PFTIR, NMR and FESEM.

24:00 PM U4.5

PERPENDICULAR TASIS ORIENTED FERROELECTRIC NaNbO$_3$ THIN FILMS ON SiO$_2$/Si(001) BY PULSED LASER DEPOSITION. Choong-Ree 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. Perpendicularly oriented at 90$^\circ$ to the SiO$_2$/Si(001) structures, films have been prepared by so-called "polar oriented" SiO$_2$/Si(001) substrates by pulsed laser deposition technique. X-ray diffraction shows multiple-cell crystallization of about 130$^\circ$ with NKN films along the polar axis. The correlation length of NKN grown on a Si substrate is estimated to be larger than that of SiO$_2$ template layers, which suggests a considerable amount of dislocations and grain boundaries in the film. The structural properties of the films are studied by X-ray diffraction in both temperature ranges of 300-700 K.

23:30 PM U4.6

THIN NaNbO$_3$/K$_{0.5}$NbO$_3$ FILMS FOR VARACTOR APPLICATIONS. Choong-Ree Cho, Jung-Hyuck Koh, Alex Grishin, Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN. S. Aladie, P. Petrov, S. Georgiou, 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$_3$ (STO), BaTiO$_3$ (BTO) or solid solutions of these materials. Ba$_5$Ti$_3$O$_{15}$ (BTO) is known to be a ferroelectric at room temperature and has a dielectric constant of 1000-1500. However, it is not stable under high temperature and high electric field conditions. BTO thin films for microwave applications have been reported, but under high electric field conditions, the material is unstable under high electric field conditions. In this paper we will discuss the development of thin film devices and their applications in microwave communications.

4:00 PM U4.7

RETENTION PROPERTIES OF FERROELECTRIC Pb(Zr,Ti)O$_3$ THIN FILMS FOR NANOSTORAGE MEDIA APPLICATIONS. William Jo, Stanford University, Edward L. Gitman Lab, Stanford, CA. J.R. Park, M. Kuk, Oak Ridge National Laboratory, Solid State Division, Oak Ridge, TN; D.C. Kim, LG Corporate Institute of Technology, Devices and Materials Lab, Seoul, Seoul, KOREA.

We report retention characteristics of the c-axis oriented ferroelectric Pb(Zr,Ti)O$_3$ (PZT) thin films on LaNiO$_3$ 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 decayed response and the reverse-poled region reveals a retained characteristic. Decay and retention mechanisms of the phases are explained by charge space redistribution and trapping of defects in the films. Furthermore, an electrical characterization of polarization-voltage loop shows that charge retention is correlated to the imprint nature of the PZT films.

4:15 PM U4.8


Next-generation low-earth-orbiting (LEO) satellite communication systems will require communication channels with much higher data rates and higher frequencies than current systems, as well as satellite tracking capabilities. Piezoelectric Ba$_x$Sr$_{1-x}$TiO$_3$ (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 promising needs is for broadband satellite communications systems, and can be used as a beam steerable antenna at the user terminal. The objective of this work is to develop BST thin films targeted toward the development of an extremely high-frequency, tunable, beam steerable antenna. BST films were deposited on single-crystal MgO substrates using in situ pulsed laser deposition. The film compositions had Ba/Sr compositions of 40/60/40, and were either 300 nm or 1200 nm thick. The film microstructures were characterized using high-resolution x-ray diffraction, high-resolution x-ray diffraction, ellipsometry, and ultraviolet Raman spectroscopy. The Raman spectra show that the film structure is completely retained via dilutions at the film/substrate interface. Ellipsometry measurements show that the film thickness has a much larger impact than the film composition. The extinction coefficients of the 300 nm films 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)$_2$TiO$_5$ (BST) AND (Ba,Sr)$_2$Ti$_2$O$_5$MgO COMPOSITE THIN FILMS FOR TUNABLE DEVICES. C.M. Carlson, T.V. Rivkin, P.A. Poiril, J.D. Perkins, D.S. Ginley, L.C. Sengupta, L. Chu, Z. Zhang, Y. Zha, S. Sengupta, A. Kozhevnikov, V. Osadchy, A. Pnueli, A. Golosov, M. Sugakov, D. Kalinin, National Renewable Energy Laboratory, Golden, CO; Tannex Microwave, Inc., Columbia, MD; 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 results and the results of other measurements of the film strain during pulsed laser deposition and post-anneal for very high quality epitaxial films and a novel approach using Ba,Sr$_2$Ti$_2$O$_5$BTO thin films to improve the properties. We also report on the performance of tunable microwave devices made from these films. We deposited thin films of pure BST and BST-MgO substrates (Appl. Phys. Lett., 79, 927, [1998], Appl. Phys. Lett., 75, 208 [1999]). We report on perfectly c-axis oriented NKN thin films prepared by magnetron sputtering of the substoichiometric, Sr$_2$RuO$_3$ (SRO) target and 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 devices at GHz range frequency, frequency stability and fatigue against tuning electric field will be discussed.
4:45 PM U4 10
BARIUM STRONTIUM TITANATE (BST) THIN FILMS FOR HIGH FREQUENCY TUNABLE DEVICES. P.K. Basaven, S.K. Streiffer, O. Auclerc, Argonne National Laboratory, Materials Science Division, Argonne, IL; D. Knaflic, R.A. Erick and J. Giuriatti, Argonne National Laboratory, Energy Technologies Division, Argonne, IL.

BARIUM STRONTIUM TITANATE (BST) thin films have been studied for high frequency applications as tunable capacitors for resonant circuits and ho.

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

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


In the SIS (Semiconductor-Insulator-Semiconductor) solar cell, the insulator plays the main role in the device performances. It should be very thin (below 4 nm thickness) and also compact, to form the desired tunneling 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 oxidized in a furnace at a temperature of 550°C, using a mixture of oxygen and nitrogen gases. This process is very slow, so it 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 a better 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 data obtained from the chemical and physical 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 M ODE S. GROWTH INDUCTED LINEAR DEFECTS AND VORTEX PINNING ANISOTROPY IN YBa2Cu3O7-x FILMS. V.I. Svetstonikov, V. A. Komlik, V. S. Flis, and V.M. Piat, Institute for Metal Physics, Kyiv, UKRAINE; C.L. Snedl and M. Suecker, 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 single crystal substrates. Pure epitaxial BST films exhibit peak dielectric constants ε_r > 6000 with a change in dielectric constant of ∼45% with an applied dC of ∼7V/μm, but had a loss tangent tan δ > 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 100% tuning of the dielectric constant with a loss tangent of only 0.03 at 10 GHz.

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Li stoichiometry and Mn oxidation state play a key role on the electrochemical properties of Li,MnO2 films. The ultraviolet-assisted pulsed laser deposition (UVPD) technique we used to deposit Li,Mn2O4 films on Si and stainless steel grids. By changing the deposition temperature and carrier gas flow, films having short range 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 as anode and reference electrode and the grown Li,MnO2 film as cathode. The results of 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 low capacity fading even at high discharge rates (100-500 microA), good coulombic efficiency and recharging 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/PI LMS. V. Huang, H. Lin, W. Chen, C. Chung, H.K. Choy, The Hong Kong Polytechnic University, Dept. of Applied Physics and Materials Research Centre, Hong Kong, CHINA.

Lanthanum nickel oxide (LNO) is a conducting ceramic which has potential to be used as interlayer electrodes in multilayer ceramic actuators. Thicker LNO films have been formed by incorporating multiple LNO powder (annealed at 700°C for 10h) 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 cermet ceramic composite film was investigated by 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 maximum temperature of this can also be decreased from 600°C to 500°C due to a seeding effect introduced by the nanoscale.
U5.5 PREPARATION AND CHARACTERIZATION OF LiCoO₂ THIN FILMS ON POROUS Ni/Nb CATHODES FOR MCFC BY COMPLEX SOL- GEL PROCESS (CSGP) W. Lubba, A. Deptula, B. Sartowska, T. Olek, A. G. Chmielowski, Institute of Nuclear Chemistry and Technology; W. Piech, Poland; M. Cirelli, A. Scocanni; E. Simonetti, L. Giorghi, A. Moreno, ENEA-CRF-Casaccia, ITALY.

NiO cathodes are most frequently used in Molen Carbon 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 LiCoO₂ thin films on Ni/NiO in order to protect the cathode body against dissolution. Sol-gel dipping technique was selected. For preparation of starting slurry Complex Sol-Gel Process (CSGP) has been applied. The starting slurries have been prepared by adding appropriate amounts of solutions of Co₂⁺ and Ni²⁺ with acetic acid and then aging with aqueous ammonia to pH=8. Cathode plates of various dimensions (several to several hundreds cm²) have been dipped in these slurries 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 sintered at 160°C for 24h, then at 300°C for 2h, and calcined (using low heating rate 1°C/min) at 1400°C. Heat treatment should be carried out under pressure of inert ceramic plates in order to avoid cracking. The presence of LiCoO₂ 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 μm and depended strongly on concentration, viscosity, and growth withdrawal rate. It has been found, in a 300 hours test in molten carbonate, that covering of Ni/NiO cathode bodies completely dissolves Ni in molten K/Li electrolyte. Also dissolution of LiCoO₂ coating was not observed. In contrast separate prepared LiCoO₂ powders exhibit small solubility (several ppm of Co). After several hundreds hours treatment in molten electrolyte SEM observation show not even minor changes in microstructures and morphology of covered cathodes. Characterization of covered cathodes in MFC working conditions are currently studied.

U5.6 EFFECTS OF THE FINAL HEAT-TREATMENT CONDITIONS ON MICROSTRUCTURES OF YBa₂Cu₃O₆₋ₓ SUPERCONDUCTING FILMS FORMED ON LaAlO₃(001) SUBSTRATES BY THE DIPPING-PYROLYSIS PROCESS. Junako Shibata, Tsukasa Hirayama, Japan Fine Ceramics Center, Nagoya, JAPAN; Kansai University, Yamanashi, Supercriticality Research Laboratory, ISCE, Nagoya, JAPAN; Yukihiro Itoh, 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 YBa₂Cu₃O₇-x films with hole concentrations excess 10¹²/cm² 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 YBa₂Cu₃O₆₋ₓ (Yb123) films formed on LaAlO₃(001) substrates. First, we prepared precursor films by spin-coating the LAO substrates with a solution containing metal nitrates of Yb, Ba, and Cu in toluene, and then by heating the substrates at 425°C in air. Subsequently, these precursor films were heated under various conditions of heating rate and holding time at 500°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 microscopy, JEM-2100, working at 200 kV. The film, prepared by using the precursor films at 20°C/min to 500°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 1h was also polycrystalline, in contrast, the film formed by heating at the same rate and by holding for 1h was c-axis oriented Yb123 film. In conclusion, rapid heating at the final heat-treatment is necessary for 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 SELLENIDE SINGLE CRYSTALS. Yu. A. Zagosniko, N.O. Kovelenko, T.S. Teplyatska, O.A. Fedorenko, P.V. Marychenko, 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. Determination of the rates of the oxidation processes depends 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 films 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 the optical characteristics of oxide coatings obtained on different surfaces of the semiconductor samples. Examined are the mechanical strength and laser damage threshold (wavelength ±1.0 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 "insets" 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 photomaxima of oxidation on the surface of ZnSe. The oxide films are characterized by lower values of optical absorption (wavelength ±1.0 micrometers), higher transmission within 2.5 - 12.0 micrometers spectral range and higher adhesion. The method of photomaxima allows to make strong, homogeneous thermostable high-quality ZnO coatings. The obtained heterostructures of ZnSe/ZnO type possess high thermal and mechanical stability and optical (in the IR region) properties. Presented are the results of practical use of such heterostructures as photoreactors, varistors, antireflection IR optical elements.

U5.8 Abstrat Withdrawn.

U5.9 INFLUENCE OF LOW TEMPERATURE-GROWN GaAs ON LATERAL THERMAL OXIDATION OF Al₀.₉₆Ga₀.₉₂ As. J.C. Ferrer and Z. Lifshitz-Weber, Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley CA. H. Reese and E. He, 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 Al₀.₉₆Ga₀.₉₂ As layers grown by molecular beam epitaxy. Samples with LT GaAs layers placed below the oxidized Al₀.₉₆Ga₀.₉₂ As and reference samples without LT GaAs are compared. The effect of addition of a SiN cap layer is also discussed. Results show that reference samples, with and without a cap layer, tend to accumulate As in the oxide interface with the surroundings layer. Numerous small voids are found at the oxide/GaAs interface that does not occur in the sample with a current density of the 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 samples by diffusion toward the layer, providing a mechanism for enhanced As migration.

U5.10 FABRICATION OF Bi₂Sr₂CaCu₂O₉ SUPERCONDUCTOR THICK FILMS ON Cu SUBSTRATES. Sang-Chul Han, The-Hyun Sung, Young-Hee Han, Jun-Seung Lee, Sung-Joon Kim, Korea Electric Power Research Inst, Power System Lab, Taejon, KOREA.

Well oriented Bi₂Sr₂CaCu₂O₉ (B2212) superconductor thick films were formed successfully on Cu tapes by liquid reaction between Cu-free precursors and Cu targets. Cu-free Bi₂Sr₂CaCu₂O₉ powder mixtures were screen-printed on Cu tapes and heat-treated at 850±5°C for several minutes in air. Cu-free precursors were composed of Bi₂Sr₂CuO₉ (x=1.2-2). In order to obtain the optimum heat-treatment condition, we studied on our previous publication on the superconducting properties of B2212 films and the reaction mechanism of their rapid formation. Microstructures and phases of films were analyzed by XRD and optical microscopy. 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-2212 phase and liquid and grow in preferred orientations. It was confirmed that the column-like phase from the colony diagram of the Bi2O3/SeO2/C6O2/2-O3Oy system corresponded to the observed result.

**US.11 GROWTH MORPHOLOGY AND ELECTRONIC STRUCTURE OF ULTRA-THIN TaOx FILMS ON Ag(100).** Carl A. Ventris, Jr, Marc M. Howard, and John T. Robinson, University of California, Los Angeles, CA; Heike Geiser, Xiushan Huang, and Olaf Hauk, University of California, Los Angeles, CA; C. C. Clark, Jr, and Philip T. Yang, University of California, Los Angeles, CA.  
As device sizes in integrated circuits continue to shrink, high dielectric constant metal oxides such as TaOx are being replace to SiO2 for use in storage capacitors and as gate dielectrics. Despite the widespread use of TaOx 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 TaOx films on the Ag(100) substrate using LEED and synchrotron-based, angle-resolved, photoelectron spectroscopy. The Ag(100) substrate was chosen to prevent the formation of a mixed interface oxide (e.g., Ta2O5/SiO2 interface for growth on Si). In addition, the Ag(100) substrate has a relatively close lattice match with TaOx, and the metallic Ag substrate allows characterization of the insulting TaOx films without sample charging. TaOx films were grown by thermal evaporation of Ta in an oxygen atmosphere of 10^−6 Torr. Growth on a Ag(100) surface held at room temperature results in an amorphous TaOx overlayer. Subsequent annealing of these films to 600°C for 10 min results in a LEED pattern that has been assigned to a 3-domain epitaxial TiO2 overlayer structure. Photoemission measurements of these films show the onset of Ta-O emission at 4 eV below the Fermi level. The formation of either TaOx or TaOx2 on Ag(100) is observed provided the LEED for deposition onto a Ag(100) substrate held at temperatures above 200°C. This indicates that the Ta is either forming large islands or going sub-surface at these elevated temperatures.

**US.12 MICRO PATTERN OF TiO2 THIN FILM FORMATION BY DIRECT SYNTHESIS FROM AQUEOUS SOLUTION AND TRANSCRIPTION OF RESIST PATTERN.** Takeshi Yano, Yoshitaka Uchiyama, Hiroshi Inoue, 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 possibility to making films with wide area 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 microelectronic devices such as DRAM, FRAM, and so on. We prepared a glass plate printed micro pattern on the surface by commercial organic photore sist material. The glass plate was soaked as the substrate in ammonium hexafluorosilicate solution, in which the chemical equilibrium holds as in reaction (1)

\[ \text{TfO}^2_- + 3\text{H}_2\text{O} = \text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ + \cdots \]  
We added boric acid to the solution. The fluoride ions are consumed by reaction (2),

\[ \text{BO}_3^3^- + 4\text{H}^+ + 6\text{F}^- + \text{H}_2\text{O} = \text{TiO}_2 + \text{B(OH)}_4^- + 3\text{F}^- + \text{H}_3\text{BO}_3 \]  
then the chemical equilibrium in reaction (1) is shifted from left in order to form TiOx. 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 amorphous TiOx were observed. Then the substrate was soaked in acetone with ultrasonic vibration. The resist material was dissolved off with TiOx film on. Micro pattern of TiO2 thin film transcribing the resist pattern with line width of 1 μm was obtained.

**US.13 REACTED LEAD MAGNESIUM NIOBATE EPITAXIAL THIN FILMS FOR FERROELECTRIC AND PIEZOELECTRIC APPLICATIONS.** P.K. Bauron, S.K. Streiff, G.R. Bai, O. Ancello, Materials Science Division, Argonne National Laboratory, Argonne, IL; S. Stemmer, Department of Physics, University of Illinois at Chicago, Chicago, IL; K. Ghosh, C. Thompson, Department of Physics, Northern Illinois University, DeKalb, IL; and Matierics 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 metallocorganic chemical vapor deposition at 700°C on SrRuO3/SrTiO3 substrates. The zero-bias dielectric constant and loss are 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 constant 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.

**US.14 HYDROTHERMAL PREPARATION OF BaTi3ZrO7 THIN FILMS FROM Ti-Zr METAL ALLOYS ON Si SUBSTRATES.** Chang-Tai Xin, V.M. Hazemidha and R.A. Zaree, Universidad de Chile, Facultad de Ciencias Fisicas y Matemáticas, Departamento de Física, Santiago, CHILE.  
Hydrothermal preparation of BaTi3ZrO7 thin films from sputtered Ti-Zr metallic alloys was achieved on silicon substrates. A Ti-Zr 66:34 a/o alloy target was used in the sputtering source. X-ray diffraction indicated that a 4 hour hydrothermal treatment in 0.5 M Ba(OH)2 aqueous solution was enough to fully react a 55 nm Ti-Zr alloy 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 BaTi3ZrO7 films were different for the different preparation conditions. This showed that the Ti/Zr ratio in the prepared BaTi3ZrO7 films were different from that in the sputtered Ti-Zr alloy film. Preliminary capacitive measurement revealed that a dielectric constant ~200 for the hydrothermal 300 nm BaTi3ZrO7 films. The low dielectric constant value could be due to the poor density of the hydrothermal films. The formation mechanism will be discussed.

**US.15 PREPARATION OF THICK PZT FILMS BY TAPE CASTING TECHNIQUES.** Ralph Nonning, Norbert Bendzko, Helmut Schmidt, INM Institut für Neue Materialien, Department of Chemistry and Technology of Non-Isotropic Inorganic Materials, Saarbrücken, GERMANY.  
For the production of thick PZT films / nanocrystalline PZT powders an aqueous precursor system based on a mixture of PbO, Zr- and Ti-hydrosol was synthesized and precipitated by using an organic base. The resulting mixture was treated in an autoclave system at 250°C to crystalize the PZT powder in a pure perovskite phase. The PZT powder based on this process has a density of 7.8 g/cm3 (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 m²/g. Green PZT-films in the range of 3 to 20 μm have been prepared by single- and double-sided tape casting. These films are 100% dense and crack-free, and the PZT powders were transferred to the surface of Si and Pt wafers. After sintering at 1000°C the PZT films are dense, crack-free and pure perovskite phase.

**US.16 PHASE TRANSFORMATIONS IN SOL-GEL PZT THIN FILMS.** D.P. Esaki, 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 solgel components containing the proper chemistry are deposited upon pinhole-free 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 C the films transform with time to the cubic and then the perovskite crystal structure. Additionally, these films have been exposed to samples formed outside of the TEM to ensure
effects of vacuum annealing are minimal. Finally, a similar study using films with 20 nm of platinum deposited on the initial manganese perovskite film was used to determine if the underlying platinum is responsible for the phase transformations observed through x-ray diffraction of films on platinum substrates.


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 Xpert Materials Research Diffractometer System (Philips MRD) equipped with parabolic mirror optics collimating the incident and diffracted beams. XRD was used to characterize perovskite Pb(Zr,Ti)O_3 (PZT) films of various compositions (x = 0.5), grown hydrothermally on (100) oriented SrTiO_3 substrates. Films synthesized under mild hydrothermal conditions form continuous epitaxial, textured polycrystalline layers, or discontinuous pseudocubic crystal "shards". Conventional x-2θ scans were conducted to determine the exact position of the (200) film peak. Vegard's Law is applied to calculate the expected peak location as a function of the compositional value of x in the PZT for film compositions with x > 0.5, a series of overlapping tetragonal and rhombohedral film peaks was observed, indicating that the 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° for smooth epitaxial layers. Pole figure texture measurements of the [111] film planes showed four-fold symmetry in the smooth epitaxial film. Textured polycrystalline film 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 La_0.25Sr_0.75MnO_3 BY GRAIN BOUNDARY MODIFICATION. V. Ramakrishnan, May Sheeh Pholky and M.S. Ramakrishna Rao, Materials Science Centre and M.G. Institute of Technology, Madras, Chennai, INDIA.

Doping studies in colossal magnetoresistance (CMR) manganese perovskites such as La_0.25Sr_0.75MnO_3 where Mn = Ca, Sr, Bi, Pb etc. throw light on the understanding of the underlying physical mechanisms that would pave way to envisage device applications. Giant magnetoresistive (CMR) 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. On the other hand, very large MR ratios could be realized in CMR manganese oxides 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. Presence of grain boundaries in polycrystalline bulk CMR compounds result in higher MR ratios over a large temperature range around the Curie temperature (T_C). In the present study, grain boundary modifications of La_0.25Sr_0.75MnO_3 and Y-doped La_0.25Mn_0.75O_3 have been attempted. La_0.25Mn_0.75O_3 (x = 0.15, 0.2) and La_0.25Y_0.05Sr_0.75MnO_3 (x = 0.05, 0.075, 0.175, 0.3, 0.4 and 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 at temperatures close to RT using insulating additives like PbO, SiO_2, ZnO, CrO_3 etc. Preliminary studies showed a 25% MR in pure La_0.25Sr_0.75MnO_3 at RT. Further work is underway to increase the resistivity of this compound using the above mentioned additives. This work has been supported by the PLD technique. CMR manganeseites with considerable changes in MR at RT are the potential candidates for device applications like magnetic proximity switches and sensors.

References:

U5.19 ELECTRIC AND MAGNETIC PROPERTIES OF NON-STOICHIOMETRIC Fe_{2-x}Ti_xO_3 FILMS. Hisashi Fujii, Tatsuya Yano, Masato Suda, Makoto Nakemishi, Jun Takada, Okayama University, Department of Applied Chemistry, Okayama, JAPAN; Mitsuo Sasaki, Kenji Kawanami, Naito Institute of Materials Chemical Research, Tsukuba, JAPAN.

Fe_{2-x}Ti_xO_3, a solid solution between Fe_2O_3 and FeTiO_3, is a half-metallic ferromagnet with Curie temperature of 250-600 K. Electric and magnetic properties of Fe_{2-x}Ti_xO_3 are very sensitive to the cation arrangement in the octahedral interstices of a hcp oxygen lattice. The ferromagnetism appears only when the octahedral cation sites are ordered into two non-equivalent layers along the c-axis, one is a Ti^{2+}-rich layer and another is a Fe^{3+}-rich layer. Moreover the formation of mixed valence states between Fe^{3+} and Fe^{4+} in the Fe^{2+}-rich layer gives an anisotropic electrical conductivity along the c plane. We have already succeeded to prepare well-crystallized epitaxial Fe_{2-x}Ti_xO_3 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 Fe_2O_3 films. We will report here the results of nonstoichiometry on electric and magnetic properties of Fe_{2-x}Ti_xO_3 films. Sample films were prepared on Al_2O_3(1000) single crystal substrates by two ways. One is a 02-reactive MBE system with an analysis chamber of in situ x-ray photoelectron spectroscopy (XPS), and another is an O2-reactive magnetron sputtering system with high temperature oven. High purity Fe and Ti targets were evaporated separately and sputtered individually to control the Fe/Ti deposition ratio. Total evaporation rate and thickness were about 0.1 mm/s and 200 nm for both films, respectively. The substrate temperature of MBE films was fixed to 723 K, while that of sputtered films was kept at 1273 K. The deposited films were examined by energy dispersive x-ray spectroscopy (EDX), x-ray diffraction (XRD), magnetization (MS), conversion electron Mössbauer spectroscopy (CEMS) and dc Hall measurements.

U5.20 THE GROWTH OF La-(Sr-Ca)-Mn-O FILMS BY RF SPITTER SPREADING. Haung Chau, 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. Kuo, Cheng 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 SrTiO_3 (001) have been grown by the on- and off-axis RF sputtering. It was found that the film properties were more sensitive to the deposition conditions. In the off-axis geometric growth, the strong back sputtering effect of negative ion gas changed the composition of the films and so did the metal-insulator transition temperature (T_C) and the magnetoresistance (MR). The total sputter 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 these films will be presented.

U5.21 NEW STRUCTURE MODEL FOR LITHIUM NICKEL BATTERIES. Marín Ángeles 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 Li_0.25Na_0.75O have been grown for the first time. They have led to establish a novel structure type which is a superstructure of known rhombohedral LiNIO_2. It is a structure that is formed by an arrangement of Li and Ni in various proportions that will also be given. The new structure consists in a close packing of cubic anions in which the cations occupy half of the octahedral holes, giving rise along the c direction to a sequence of layers containing Li and Ni in various proportions. Since the magnetic behavior of polycrystalline 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

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

Charged ion conductivity, electrophoretic and electrical breakdown effects are evidenced for the crystal properties of solids, in the electric properties of crystalline (CS) [1] and organic (OS) [2] solids. This approach allows one to describe the insulator-metal-semiconductor transition (IMST) through the increase of crystal work-hardening [WH] which depends on 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 strain correlation between the mechanical [WH], structural (orientations), and electronic properties of solids. The same features of the motion of deformation units in CS [6] and OS [7] confirm the universality of WH-effects in CS and OS. The change of resistivity in strained (due to hydraulic pressures, inhomogeneous phases, macroscopic stresses, etc.) samples closely varies with the hardening of soft crystals and the softening of hardened samples [8]. The sharp increase of WH at low temperatures means the sudden decrease in electrical resistivity (the IMST), the higher WH of crystalline permits the higher transitions in temperature of low-temperature WH can be observed in the insulator-superconductor transition and vice versa. The remarkable finding of this work is the scaling of mechanical [4-11] and electrical parameters of superconductors in different scales of observation, which confirms the new approach to IMST.

References:

U5.23

PROPERTIES OF A NOVEL AMORPHOUS TRANSPARENT CONDUCTIVE OXIDE. In GaO$_2$(ZnO)$_n$. Masahiro Orita, Hirokichi Ohba, Masahiro Hirose, Hideo Hosono, Hosono TEAM Project, ERATO, JST, Kawasaki, JAPAN; Hiroaki Tanji, Hiroshi Kawase, R&D Center, HOYA, Tokyo, JAPAN.

Amorphous thin films of InGaO$_2$(ZnO)$_n$ were prepared by a pulsed laser deposition method in which a quartz substrate was used at room temperature. It was found that this composite system is a novel 4d-type amorphous transparent conducting oxide (TCO), which can be excited as a sol-gel glass. The structure of the film was confirmed as an amorphous in terms of XRD and TEM measurements. Compositional ratio of ZnO to GaO$_2$ in the films analyzed by means of XRF was sensitive both to KeV laser power and to oxygen pressure, that is, the ratio increased with an increase in laser power or in oxygen pressure. For laser power of 80 mJ/cm$^2$ and oxygen pressure of 0.8 Pa, the electrical resistivity varied from 1 x 10$^{-3}$ ohm-cm to 4 x 10$^{-5}$ ohm-cm by increasing the m values from 1 to 4. Optical band gap (Eq) obtained from optical absorption spectra 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$_2$ THIN FILMS BY SOL-GEL METHOD FOR CO-SENSING. Carmen Canoalvi, Norberto Chicioni, Francesca Morroni, Roberto Scorti, Univ. Milano-Bicocca, Dept. Scienze dei Materiali, Milano, ITALY.

SnO$_2$ 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 InGaO$_2$(ZnO)$_n$ to SnO$_2$ to be observed in the kind of gas is to be detected, improves the sensitivity 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 properties of a homogeneous distribution of the metal affect the electric response amplitude and reproducibility. Previous works suggested that also the intimacy of the metal-semiconductor contact plays an important role to improve the electronic properties between the gases and the metal/oxide system. Aim of this work was to obtain films of Pt- and Ru-dispersed SnO$_2$ by a sol-gel method which allows the simultaneous deposition of tin (tetrachlorotitanate) and metal (Pt or Ru) nanocrystalline precursors and a more intimate metal-semiconductor contact. Films of 100-150 nm of thickness were produced by spin-coating technique on silicon or silicon substrates and were morphologically characterized by Scanning Electron Microscopy and Atomic Force Microscopy. The sensing properties of the metal-dispersed SnO$_2$ films were tested by measuring the variations of resistance and selectivity in reducing CO. X-ray Photoelectron Spectroscopy and Electron Paramagnetic Resonance were used to detail the surface centers and detect the responsible for the material functionality and the change in the oxidation state of the loaded metal. Correlations between the film electronic 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.


U5.25

THE PREPARATION AND PROPERTIES OF CADMIUM OXIDE FILMS PRODUCED BY METALORGANIC CHEMICAL VAPOR DEPOSITION. Xiuwen Li, Daoyang 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 reactive sputtering, sputter pyrolysis, and activated reactive evaporation. However, no production has been done by metalorgancs 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 a n-type semiconductor with band gap of 2.4 eV. The highest mobility ever achieved was 100 cm$^2$/V·s by K. Gurumurugan and others with de 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 100 mbar and substrate temperature range of 100 to 300°C. The surface roughness and the texture of CdO films changed with deposition temperature. Without any extrinsic doping, the carrier concentration of CVD produced CdO could reach to low of 10$^{20}$ cm$^{-3}$. As carrier concentration decreasing, the Hall mobility increased from less than 10 to 220 cm$^2$/V·s, which was about twice height as it ever reached previously. The optical data indicated that the total band gap increased from 2.27 eV because of the band gap narrowing. Four coefficients method measurement confirmed that, with the increasing of carrier concentration, the increment of energy band gap was about 1 eV.

U5.26

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

Homogeneous ultrafine mono/multi-element oxide powders are the key to produce high-performance electronic materials. It is well known that many biomaterials such as bone, shell 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 responsive and non-toxic reactive natural precursors. The properties of inorganic oxide film are promising, it's self-standing, can withstand temperature to 1000°C.

U5.27

FABRICATION OF MgIn$_2$O$_4$ THIN FILMS WITH LOW RESISTIVITY ON MgO(100) SURFACE BY PLD METHOD. 343
Magnesium indium oxide (MIO) is one of the recently discovered n-type conducting transparent oxides. MIO films were deposited on Mo substrates by using a ceramic target by PLD under two different conditions in atmosphere: one was deposited under an oxygen pressure of 0.2 Pa to introduce electron carriers from oxygen vacancies. Another was fabricated by using an oxygen radial source to suppress formation of the oxygen vacancies under high oxygen partial pressure. Prase 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 highly grown on the substrates and their properties were reproducible. The highest conductivity was obtained for the films fabricated under the reducing atmosphere: 4500 S cm⁻¹. The carrier density, Hall mobility and Burstein-Moss shift observed for the thin film were, respectively, 2.1x10¹⁷ cm⁻³, 14 cm² V⁻¹s⁻¹ and 0.6eV.

SESSION 6E: TRANSPARENT CONDUCTORS I

Chair: Sue Anne Carter and Jeremy Levy

Wednesday Morning, April 26, 2000
Nob Hill A/B (Marriott)

8:30 AM #6E.1 FUNDAMENTAL ADVANCES IN TRANSPARENT CONDUCTING OXIDES. Timothy J. Kota, Xinmin Li and David L. Young

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 optical-electro-properties will be required to meet these demands. Research and development efforts in the field are aimed at developing more effective and optical properties that are consistent with higher electron mobility by means of intrinsic and extrinsic properties. This is to end, we investigated the properties of several TCOs including cadmium oxide, tin oxide, indium oxide, indium tin oxide and zinc stannate. All of these may be fabricated by chemical vapor deposition (CVD) and we have the capability to fabricate the aluminum oxide in the cadmium oxide, tin oxide, indium 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 MIEssafar, Raman and UV-visible/NIR spectroscopy. 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 conditions, as well as doping. We have found that the advantages of the TCOs in the cadmium oxide, tin oxide, indium oxide, indium tin oxide and zinc stannate are greater than those in the other materials, and they may add together to the oxygen relaxation times. In the case of cadmium oxide, there is also an increase and the lower effective mass is a much more sensitive response of the fundamental. Several techniques have been developed for TCOs that will be required in more demanding applications next century.
scattering in the ZnO:Al and neutral impurity scattering in the undoped material. Preliminary data shows zinc stannate, with a carrier concentration of 8 x 10^16 cm^-3, to have an effective mass of 0.19 m0.

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 Kizyuma-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 Miedecke energy while n-type doping using Al, Ga, In or P species decreases the Miedecke energy. We proposed that codoping using N acceptors and p-doping agents, Al or 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-majority states for Li-doped ZnO, in contrast with the case of Ndoped 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 codoping for ZnO:Li based on the above findings.

References:

11:00 AM # U6.6

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

Double oxides with delafosse structure are candidate materials for preparing transparent p- and n-type conductive oxides and fabricating a transparent p-n heterojunction in the same crystal structure. CuAlO2, CuGaO2 and AgInO2 with delafosse structure were recently found to show both optical transparency and electrical conductivity on the bases of our working hypotheses. CuAlO2 and CuGaO2 show p-type electrical conductivity and AgInO2 show 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 heterojunction that the materials were deposited by the same method. The electrical conductivity of CuAlO2 thin films was 0.3 S cm^-1 at room temperature. An optical energy band gap was roughly evaluated as the absorption edge in the infrared region and the value was approximately 3.5 eV. CuGaO2 thin films deposited by PLD were highly oriented to (001). Their conductivity was 4 x 10^-11 S cm^-1. Optical band gap of CuGaO2 thin films was ~3.4 eV. No intentional doping was carried out on CuAlO2 and CuGaO2. Though CuAlO2 and CuGaO2 were prepared by ordinary solid state reaction, direct preparation of AgInO2 by same method was unsuccessful. AgInO2 was prepared by cation exchange reaction using NaInO2 and AgNO3. In addition, because non-doped AgInO2 sintered was almost insulating, we carried out intentional doping by using Sn doped NaInO2 for cation exchange reaction. Increase of electrical conductivity of sintered was successful by doping. AgInO2 thin films fabricated by PLD using these as target. Optical band gap was ~4.4 eV. The electrical conductivity of Sn 5% doped AgInO2 thin films at 300K was 7 x 10^-10 S cm^-1 and no remarkable temperature dependence was observed. The carrier concentration and the Hall mobility were 3.5 x 10^13 cm^-3 and 1.4 cm^2 V^-1 s^-1, respectively.

11:30 AM # U6.7


Recent results have shown that CuAlO2 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 CuAlO2 phase diagram. We report a novel technique for making CuAlO2 thin films. Thin film precursors of CuAlO2 were deposited on sapphire (001) substrates by radio frequency sputtering and by pulsed laser deposition (PLD). Subsequent annealing at 1150°C in a closed crucible containing NaAlO2 and CuO yielded nearly phase-pure, pinhole-free textured CuAlO2 films. The films were p-type and transparent with a gap of 3.5 eV, but typical carrier concentrations were low, on the order of 10^15 cm^-3 to 10^16 cm^-3. Oxygen anneals at 1150°C or 1 atm of O2 raised the carrier concentration to 10^17 cm^-3 in some samples. In order to increase the carrier concentration further, we were testing chemical substitution on the metal sublattice. Initial experiments were done with Mg, either by direct solid-state synthesis for bulk materials or by ion implanted deposition of MgO during the PLD growth of thin films. At Mg molar concentrations of 2% or less, the bulk material was phase-pure CuAlO2 by x-ray diffraction, but was mixed phase CuO on CuAlO2 and CuO grain size concentration was reduced to 5%. The ion-implanted MgO/CuAlO2 films crystallized to CuAlO2 after the 1050°C anneal, in contrast to non-Mg-containing films which form the CuAl2O4 phase at this temperature.

11:45 AM # U6.8

INFRARED-TRANSPARENT ELECTRICALLY-COURLU CONDUCTIVE CuAlO2, DEPOSITED BY REACTIVE MAGNETRON SPUTTERING. Linda F. Johnson, Mark B. Moran, Randell R. Kolega and Daniel C. Harris, Naval Air Warfare Center, Weapons Division, Naval Aviational Science and Technology Office, China Lake, CA; Edler Shaw, Sean Technologies, Inc., Woodside, WA; Mehmet Sarikaya, University of Washington, Dept of Materials Science and Engineering, Seattle, WA.

Thin films of CuAlO2 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 electronic properties and chemical structure of the CuAlO2 films. FTIR absorption bands at 1470 and 1395 cm^-1 are present only in films that exhibit enhanced electrical conductivity. When these bands are absent, the CuAlO2 films have high values of resistivity. It is possible that the enhanced conductivity of sputter-deposited CuAlO2 films could be a result of the overlapping d-orbitals on neighboring Cu^+ ions in the plane perpendicular to the c-axis of the delafosse unit cell. Overlapping d-orbitals also explain why the sputter-deposited CuAlO2 films absorb strongly in the visible. Another possibility is that the 1470 and 1395 cm^-1 bands involve complicated vibrational modes of the entire Cu-O-Al-O-Cu sequence along the c-axis of the delafosse unit cell. The fact that the frequencies of these bands are about twice those of the major phonon frequencies in Cu2O and Al2O3 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 cm^-1 could accelerate the development of CuAlO2 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 CuAlO2 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 (HRM) and electron energy loss spectroscopy (EELS) indicate that the CuAlO2 films consists of islands of cubic-copper crystallites in a Cu-Al-O matrix.

SESSION U7: TRANSPARENT CONDUCTORS II

NOVEL CHARACTERIZATION

Chairs: Robert W. Schwartz and Dave H.A. Blank
Wednesday Afternoon, April 26, 2000

Nor HB A/B (Marriott)

1:30 PM U7.1

A STUDY OF THE AMORPHOUS-TO-CRYSTALLINE PHASE TRANSFORMATION AND POTENTIAL TECHNOLOGICAL APPLICATIONS IN INDIVIDUAL IODINE: A C-TYPE RARE EARTH DEFECT STRUCTURE, David C. Prince, Daniel Spirceanu, Eric Chason, Brown University, Division of Engineering, Providence, RI.

The iodine oxide crystal structure (biotite) is based on the arrangement of two types of non-equivalent In6O16 structural units to form a 48 atom unit cell. In the crystalline form, slightly disordered metric iodine 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 hot sensitized polymer substrates in an amorphous structure that crystallizes at remarkably low temperatures (<150°C) relative to the iodine oxide melting point (1910°C) which is 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 semi-conductor in the amorphous state to a metal-like degenerate state in the crystalline form. The attendant change in carrier density and mobility determines the conductivity and the plasma absorption edge of iodine oxide.
These critical properties provide an ideal tool for studying the a/o-formation that we have used to show that the a/o-formation of PVC microspheres is a result of the structural relaxation followed by crystallization. We have studied the a/o-formation in electron-beam deposited indium oxide using isothermal annealing (110 to 350°C) combined with in situ reactivity, in situ conductivity, TEM, glancing incidence angle x-ray diffraction, and in situ x-ray curvature measurements. From these measurements we have determined that the structural relaxation of the amorphous structure occurs via a process that is thermally activated (Ea = 1.3 eV) and has a kinetic dimensionality (Arrhenius 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 of approximately 20 MPa. Subsequent crystallization occurs with a surprising increase in molar volume and a kinetic dimensionality of approximately 3 which is consistent with 3-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/o-formation in indium oxide.

2:00 PM U7.2
ROOM TEMPERATURE GROWTH OF INDUM TIN OXIDE FILMS BY ULTRAVIOLET-ASSISTED PULSED LASER DEPOSITION

The properties of indium tin oxide thick 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 365 nm (5% of the energy) which did not affect the molecular oxygen and form oxide 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 of water. 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). 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 exhibit 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 ohm cm were routinely grown by the UVPLD technique.

2:15 PM U7.3
ELECTRICAL AND OPTICAL PROPERTIES OF Tb-DOPED SnO2 THIN FILMS PREPARED BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION ON GLASS SUBSTRATE. Sang Woo Lee, Hyung Chen, University of Illinois at Urbana-Champaign, Dept of Materials Science and Engineering, Materials Research Laboratory, Urbana, CHampaign, IL 61801

Undoped and Tb-doped SnO2 thin films have been deposited on glass substrates using metal organic chemical vapour 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, Tb 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 × 10-4 to 2 × 10-4 Ω cm depending upon the Tb contents and the minimum resistivity was observed with two stages with minimum 3.8% at Tb concentration of 5% and average optical transmittance in the visible spectrum was about 89%. The role of Tb 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 Tb doping in the thin films.

2:30 PM U7.4
MAJOR VARIABLES AFFECTING THE CONDUCTIVITY IN A FIXED-FRAME METAL OXIDE. Flavia 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 TiO2 nanoporous ceramic materials prepared by firing serpentine obtained via a sol-gel route are potential candidates for use as the electrolyte in proton exchange membranes (PEMs) for PEM electrolysis. In this work we have studied conductivity of a fixed-frame (constant pore structure and surface area) nanoporous TiO2 as a function of relative humidity (RH), temperature, surface acidity, number of surface sites and surface doping with phosphate. The effect of RH was studied by samples rehydrated by exposure to water vapor or by subjecting to solutions with pHe values of 1.5, 2.5 and 4.0. For the vapor-rehydrated samples a drastic increase in conductivity with RH is observed (from 4.0 × 10^-4 S/cm at 23% RH to 1.34 × 10^-3 S/cm at 81% RH). The effect obtained from samples rehydrated by solutions shows that there is also an increase, but to a lesser extent (from 6.46 × 10^-4 S/cm at 33% RH to 1.45 × 10^-3 S/cm at 81% RH for rehydration at pH 1.5). Conductivity was also studied as a function of total water content (25°C) and the relationship between adsorption isotherms and it was found that, for constant water content, higher conductivities were observed in the samples rehydrated at lower pH. As an example, at a water content of 66 molecules/fm², 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 30% from the vapor-rehydrated sample to the sample treated at pH 1.5.

2:45 PM U7.5
OXYGEN TONS DIFFUSIVITY IN DOPED TIN DIOXIDE THIN FILMS. Nick Y. Shklovskii, 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. D⁰, which is measured in experiments, can be converted into individual diffusivity in D⁰ and Do (in some factor, depending on units). The diffusion of the oxygen ions in tin dioxide is characterized by a small size of the oxygen ions and a relatively large oxygen vacancies concentration. The role of oxygen vacancies in the diffusion process is important.

3:15 PM U7.6
NANOSCALE OPTICAL PROBES OF OPTOELECTRONIC OXIDE MATERIALS. Jeremy Levy, Charles Hubert, Oleg Tirkkonen, 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 photorefractive effects in ferroelectric thin films such as Ba9Sr1xTiO3. They include: quasi-static electric field, temperature dependent confocal scanning optical microscopy (CSOM), and spatterless near-field scanning optical microscopy (ANSOM). For ferroelectric thin films, the electro-optic coefficient is proportional to the free charge, and micro-nanometer optical microscopy can image the ferroelectric contribution to dielectric loss. Microwave frequency measurements show a remarkable dependence of the local dielectric loss on electric field bias. This phenomenon 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 light insight into the optical and electronic properties of thin film materials.

This work is supported by ONR N00014-88-1-0011, NSF DMR-9710725, and NSF IMR-982984.

3:45 PM U7.7
SPIN-POLARIZED TUNNELING IN OXIDE FERROMAGNETS. Daniel Wodarz and T.H. Geballe, Stanford University, Dept of Applied Physics, Stanford, CA

We have developed the ability to grow reproducible La0.67Sr0.33

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MnO$_3$/SrTiO$_3$/Al tunnel junctions with high quality gap characteristics for spin-transport measurements. A VIn$_2$/O$_3$-counter-electrode was required to prevent uncontrolled 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 $P = 4-7\%$, for a variety of deposition conditions.

**SESSION U8/J6 JOINT SESSION
LASER-BASED DEPOSITION OF OXIDES**

Chair: 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. Croun 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 problems, and re-evaporation of volatile components. Unfortunately, most high quality PLD grown films 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. This short wavelength UV radiation 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 UV-PLD 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
EPITOXY OF OXIDES ON DISSIMILAR SUBSTRATES USING PULSED-LASER DEPOSITION. David Norton, Chan Park, Yong Lee, John Bau, Stephan Penev, Carolyn Ems 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 or metals 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 enabled and complex. One must consider both the kinetics of film growth on a dissimilar material, as well as the thermodynamic and kinetic nature of the film/oxide interface.

In this talk, we will discuss the role of film kinetics, thermodynamics, and microstructure in the formation of epitaxial oxide interfaces on semiconductors and metals using pulsed-laser deposition. The specific oxides discussed include CrO$_2$ or Si$_3$N$_4$ on (001) Si. Reflection high energy electron diffraction is used to characterize the oxidation of cerium 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 characterize the epitaxial relationship between the film and crystalline substrate.

This research was sponsored by the U.S. Department of Energy under contract No. DE-AC05-86OR22194 with Lockheed Martin Energy Research Corp.

**9:15 AM - U8.3/J6.3

The fabrication of La$_{2-x}$Ca$_x$MnO$_7$ (LCMO) thin films on silicon (Si) substrates is very important from the point of view of integrating conventional magnetic-sensitve films into microelectronics. In particular, Si is 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.
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 been regarded as an attractive material because of its low electrical resistivity and its excellent mechanical stability and reliability when subjected to high temperatures. By suitably changing the growth parameters during pulsed laser deposition, TiN films with resistances as low as 250 \( \Omega \) cm were obtained. In order to achieve epitaxial growth of LCMO films, MgO and SrTiO\(_3\) films were used as intermediate layers between LCMO and TiN layers. The structural characteristics of single layered and multi-layered structures were carried out using x-ray diffraction, transmission electron microscopy, and photo-acoustic 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 magnetic spectrometer. 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 LSCO in terms of paramagnetic-to-ferrimagnetic 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 US/4/6.4
PREPARATION OF PZT-YBCO HETEROSTRUCTURE ON YSZ COATED SI BY KGF LASER ABALATION Kenji Ebara, Fumihiko Matsumi, Tomoki Hagiwara, Kumamoto University, Department of Electrical and Computer Engineering, Kumamoto, Japan; Jagdish Narayan, North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC, J.F. Muth, C.W. Teng, R.M. Kolb, North Carolina State University, Department of Electrical and Computer Engineering, Raleigh, NC.

KGF excimer laser ablation technique is applied to fabricate the ferroelectric Pb\(_{0.2}\)Zr\(_{0.8}\)Ti\(_{0.5}\)O\(_{3}\) (PZT) capacitor on Si(100) substrate. The YBa\(_2\)Cu\(_3\)O\(_{7}\) (YBCO) bottom electrode was deposited on the Si substrate by pulsed laser deposition. The film was annealed at 550 \( ^\circ \)C for 20 min under vacuum of 1x10\(^{-6}\) Torr. The XPS measurement indicates the formation of Ti-O bonds. The interface between the YBCO and PZT is found to be well defined. The PZT/YBCO/YSZ/Si capacitor shows the ferroelectric properties of the remanent polarization 25 \( \mu \)C/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\(^{10}\) cycles for the decrease to 10 \( \mu \)C/cm\(^2\) polarization. A detailed discussion on the interface structure and properties will be presented.

9:45 AM US/4/6.5
PULSED LASER DEPOSITION OF EPITAXIAL SE\(_{0.4}\)V\(_{0.6}\)O\(_{3}\) FILMS ON (100)LaAlO\(_3\) AND (100)Si P.W. Yip and K.H. Wong, Dept. of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, Kowloon, Hong Kong, China.

Thin films of SE\(_{0.4}\)V\(_{0.6}\)O\(_{3}\) have been grown on (100)LaAlO\(_3\) and (100)Si buffered (100)Si substrates by pulsed laser deposition. The films were deposited in temperature range of 450 \( ^\circ \)C 750 \( ^\circ \)C and under ambient oxygen pressure between 10\(^{-3}\) 10\(^{-6}\) Torr. Their structural properties were characterized using a four-circle x-ray diffractometer. High quality thin films were obtained at high growth temperature (above 600 \( ^\circ \)C) without post annealing. Heteroepitaxial relationship of c = 100 >Se0.4V0.6O3 // c = 100 >LaAlO3 and c = 100 >Se0.4V0.6O3 // c = 110 >Si was obtained. The in situ x-ray diffraction, transmission microscopy, and photoelectron spectroscopic studies of the films support the view that the surface is mainly pentagonal. Charge transport measurements show that the films from semiconducting to highly conducting for different growth conditions. Resistance of a few micro-ohm cm was recorded for some of the epitaxial thin films.

10:30 AM US/4/6.6
IMPOSED LAYER-BY-LAYER GROWTH OF COMPLEX OXIDES WITH PULSED LASER DEPOSITION M.J. Black, G.H. Rijnders and H. 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 new layer may only occur after the previous layer is completed. We introduced a growth method, based on a periodic sequence of steps: isolation of the amount of material needed to complete one monolayer followed by an interval in which no deposition takes place and the film can relax. This makes it possible to grow in a layer-by-layer fashion in a growth regime (temperature, pressure) where it will not relax. We present the results obtained for heteroepitaxial growth on SrTiO\(_3\) 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 US/4/6.7
GROWTH OF ZnO/MgZnO MULTIPLE QUANTUM WELL STRUCTURES 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. Kolb, North Carolina State University, Department of Electrical and Computer Engineering, Raleigh, NC.

We have recently grown \( \text{Mg}_2\text{Zn}_{1-x}\text{O} \) alloy single crystal films on c-plane sapphire by pulsed laser deposition (PLD). The bandgap of these alloys was varied up to 4.97 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 new possibilities for optoelectronic devices such as truly solid blind detectors and uv lasers. In further pursuit of this material system, we have grown ZnO/Mg\(_{24}\)Zn\(_{76}\)O\(_{46}\) 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 characteristic of these superlattices was performed by high resolution transmission electron microscopy, transmission measurements and photoluminescence. Photoluminescence 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 \( \pm 0.5 \) eV between ZnO and MgZnO. The PLD has been successfully achieved to grow these ultra thin layers with sharp interfaces. This work has a potential for fabricating highly efficient optoelectronic devices based on ZnO.


11:15 AM US/4/6.8
SINGLE QUANTUM WELL STRUCTURE OF MgZnO/ZnO/MgZnO ON C-PLANE SAPPHIRE Supa. Choopun, Dae Chulk, Wei Yang, R.D. Vugstede, B.S. Ogale, R.F. Sharma and T. Venkatesan, CSR, Dept of Physics, Univ of Maryland, College Park, MD.

The single quantum well structures of Mg\(_{24}\)Zn\(_{76}\)O\(_{46}\)/ZnO/Mg\(_{24}\)Zn\(_{76}\)O\(_{46}\) 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 for the magnesium oxide for different growth conditions. The one-dimensional confinement model and the conduction band quantized-energy as a function of well thickness was achieved. Our quantized-energy and the well width as a function of band offset, growth conditions, interface roughness, quantum size effect on Mg\(_{24}\)Zn\(_{76}\)O\(_{46}\)/ZnO/Mg\(_{24}\)Zn\(_{76}\)O\(_{46}\) quantum wells will be discussed.

11:30 AM US/4/6.9
DEVELOPMENT OF LSCO AND LNO OXIDE ELECTRODES FOR SENSOR PROTECTION DEVICES. Main Chonwongson, Kelly Budin, Malek 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 protective schemes for sensors that operate in the 3-5 \( \mu \)m and 8-12 \( \mu \)m ranges. One such protective device currently under development is an electrostatic shutter, which is driven into an closed condition for protection against high energy pulses. For the fabrication of this device, electrodes must be developed that possess a sheet resistance of 300 500 \( \Omega /\text{sq} \) and which have a transparency, ideally, of at least 80\%. We are evaluating the suitability of \((\text{La},\text{Sr})\)CoO\(_3\) (LSCO) and \( \text{LaNiO}_3 \) 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 were deposited by pulsed laser deposition and MgO substrates by sputtering or sputtering deposition followed by annealing at temperatures as high as 1100 \( ^\circ \)C. Crystallization into the perovskite structure has been studied by x-ray diffraction and optical
properties have been studied by standard FTR techniques. As expected, both the conductivity and transparency of the films are highly dependent on the best treatment conditions. For the solution deposited films, best treatment conditions 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 coefficients of the LSCO materials indicate that they may approach 150,000 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 μΩ-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 electrooptical 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 EPIAXIAL ZnO FILMS
Y.R. Ryn, 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 effects of the growth process. The films are studied by atomic force microscopy (AFM), x-ray diffraction (XRD), and photoinducemissence (PL). Optical qualities for textured ZnO films are remarkably good, comparable with those for high-quality epitaxial ZnO. Detailed examination of these films shows that ZnO films are very strong and narrow bound exciton peaks. These results will be discussed.

SESSION U9: ALTERNATIVE DEPOSITION APPROACHES
Chair: Timothy J. Coutts and Hiroshi Kawanabe
Thursday Afternoon, April 27, 2000
Nob. Hill (Marrriott)

1:30 PM U9.1
DEVELOPMENT OF NEW VOLATILE Cd PRECURSORS FOR THE GROWTH OF Cd-O CONTAINING OXIDE THIN FILMS VIA MOCVD
Jason R. Babcock, Anshum 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 (Cd₂SnO₄) via metal-organic chemical vapor deposition (MOCVD), a volatile Cd precursor was desired. β-diketonates of various ligands were studied by x-ray diffraction (XRD) and photoluminescence (PL). Optical qualities for textured ZnO films are remarkably good, comparable with those for high-quality epitaxial ZnO. Detailed examination of these films shows that ZnO films are very strong and narrow bound exciton peaks. These results will be discussed.

1:30 PM U9.2
DEVELOPMENT OF NEW VOLATILE Cd PRECURSORS FOR THE GROWTH OF LANTHANIDE OXIDE THIN FILMS VIA MOCVD
Nikki L. Edleman, John A. Bolot, Anshum 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. Chung, Northwestern University, Dept of Materials Science and Engineering and The Materials Research Center, Evanston, IL; Michael P. Chudzik, Carl R. Kanneurff, Northwestern University, Dept of Electrical and Computer Engineering and The Materials Research Center, Evanston, IL.

A proven method of oxalic acid 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 react 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 the subsequent film growth. A current concentration is on lanthanide-containing materials. Lanthanides are of interest as photocatalyst components in magnetic devices, oxide fuel cell catalysts, superconductors, and oxide buffer layers in semiconductor and superconducting device multilayers. The classic lanthanide MOCVD precursors, fluorinated or non-fluorinated β-diketonates, are prone to extensive decomposition and oligomerization or in the fluorinated case are incompatible with certain substrates. Hence, 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 (Ln = Gd, Er) is completely saturated by three tridentate β-diketonate ligands. The alkyl substituents at the ketone, imine, and ether sites of the ligand are synthetically tunable for tuning precursor volatility and morphology. Results of a full synthetic study of the new complexes will be outlined. The complexes have been fully characterized by NMR, elemental analysis, single-crystal x-ray diffraction, mass spectrometry,
2:45 PM U9.5
HYBRID BEAM DEPOSITION (HBD) TECHNIQUE FOR GROWTH OF METAL OXIDE FILMS. Yang H. Ryu, Henry W. White, Univ. of Missouri, Dept. of Physics & Astronomy, Columbia, MO.

We introduce hybrid beam deposition (HBD) as a novel growth technique. This pulsed laser deposition/pulsed laser ablation/beam epitaxy (PLD/PLAE/MBE) and chemical vapor deposition (CVD). The flux density of available reactive oxygen for ZnO film growth can be effectively increased by using a (ZnO) plasma created by combined laser ablation and oxygen at low flow rates between the plasma and ZnO target 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 SrBi2Nb2O9 FILMS. J. Lestieri, M.A. Zurbuchen, Y. Jin, 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 SrBi2Nb2O9 [-Sr2Bi2O7]2+ sheets. The superior ferroelectric resistance even after significant ferroelectric cycling. This advantage is particularly evident in SrBi2Nb2O9 films excellent candidates for ferroelectric memory. It has been shown that it is the highly anisotropic crystal structure of this material which makes it superior to other perovskite-based ferroelectrics. A study was performed to observe the material's properties, structure, and ferroelectric properties of SrBi2Nb2O9 A films as a function of orientation of these epitaxial thin films as an insulator to quantify the anisotropy. Growth evolution, defects, interfaces, anisotropic electrical properties, and substrate influence on orientation, microstructure, and morphology are emphasized. Electrical characterization, TEM, AFM, and 4-circle X-ray diffraction will be presented.

4:30 PM U9.9
PREPARATION AND CHARACTERIZATION OF EPITAXIAL Bi2WO6 THIN FILMS PREPARED BY SOL-GEL PROCESS. Chikako Kodama, Keishi Nishio, Tsutomu Nagashima, Yachi 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 (Bi2WO6: BWO), one of the bismuth layer-structured ferroelectrics (BiSLF), on SrTiO3 (STO) single crystal substrates by a spin coating process. BLSF are expected to apply for ferroelectric random access memories (FAMRA). A homogeneous solvent solution was prepared with tungsten hexachloride and bismuth 2-ethylhexanoate as raw materials, and 2-butoxyethanol and formamide as solvents. The coating thin films were sintered at temperatures from 500°C to 800°C for 1h in air. BWO crystalized at temperature above 500°C. Any crystal phase was not observed in the thin films except for (011) phase of BWO in the XRD patterns using a 2θ-scanning diffraction method. Structural characterization of BWO thin films shows increasing heat treatment temperature up to 600°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 crystallographic relationship of the film and the substrate shows that the thin films are oriented on the BWO (001) // STO (001), BWO[110] // STO[010]. This relationship would be expected from the a and b lattice constant of BWO nearly equal to 2/3 times that of STO.

4:45 PM U9.10

The development of future generation of DRAMs will require the introduction of new materials with higher dielectric constant than the conventional SiO2 or silicon oxide/nitride based systems. Among the dielectric materials under consideration, tantalum pentoxide is a promising insulating material for DRAM capacitance. The high dielectric constant and low dielectric loss materials are also attractive for microwave applications. TaOx thin films have potential for numerous microwave electronic applications such as gate dielectric of MIS devices, optical waveguides, electrooptic high-speed display devices, and surface acoustic wave devices. For successful integration into microelectronic circuits, reliable TaOx thin films are desired. The properties of Ta2O5 thin films have been reported to be strongly dependent on the fabrication method, nature of substrate and electrode materials, and post-deposition annealing treatment. An understanding of process-structure-property correlation is important for design and compare various thin film studies reported in literature and exploit Ta2O5 thin films for devices. In this paper, we
report on the systematic study of structural, optical, dielectric, and insulating properties of amorphous and crystalline Ta2O5 thin films fabricated by metalorganic solution deposition (MOSD) technique. Ta2O5 thin films were fabricated on Pt-coated Si, n-type 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 Ta2O5 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 P.M. U9.11
REACTIVE SPUTTERING OF ZINC OXIDE FOR PIEZO-
ELECTRIC APPLICATIONS. Glen R. Kovach, 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 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 10¹⁰ Ω·cm were obtained at temperatures below 500°C. In addition, the piezoelectric constant was determined to match the bulk value for ZnO.