

# SYMPOSIUM E

## Integration Challenges in Next-Generation Oxide-Based Nanoelectronics

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\* Invited paper

**8:00 AM \*E1.1**

**Dry Etching of Electronic Oxides.** Stephen J. Pearton, Kyu-Pil Lee, Kelly Ip, David P. Norton and Rajiv K. Singh; Materials Science, Univ. Florida, Gainesville, Florida.

An overview of etching of various electronic oxides in high density plasmas will be given. We will start with some of the plasma chemistries for fluorine-based contact via etching of silicon dioxide and then move to other oxides of interest, including hafnium oxide and tantalum pentoxide for gate dielectrics on silicon, magnesium oxide and scandium oxide for gate dielectrics and field passivation on gallium nitride, zinc oxide for a variety of ultra-violet light-emitter, transparent electronics, spintronics and sensor applications as well as other oxides such as titanium oxide. In many cases there are no readily formed volatile etch products with either fluorine or chlorine plasma chemistries and the only etch mechanism available at room temperature is ion-assisted sputtering of the metal-fluoride or chloride products. We will also give a brief summary of etching of MRAM stacks for non-volatile memory stacks on top of silicon circuitry. In this case, there are two basic classes of etch chemistries. The first is based on chlorine, which can produce high etch rates but attention must be paid to avoiding post-etch corrosion of the feature sidewalls through active in-situ cleaning with hydrogen or oxygen plasmas or post-etch cleaning. The second class of chemistries are non-corrosive to the MRAM stack and include methane/hydrogen or carbon monoxide/ammonia. The drawback with these mixtures are the slow etch rates due to the low degree of chemical enhancement and the consequent mask erosion that occurs when etching deep features.

**8:30 AM E1.2**

**Structure of Sc<sub>2</sub>O<sub>3</sub> Films Epitaxially Grown on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (111).** A. Refik Kortan<sup>1</sup>, Minghui Hong<sup>1,3</sup>, J. Raynien Kwo<sup>2,3</sup>, C. P. Chen<sup>1</sup>, Joseph Mannaerts<sup>1</sup> and Sy-Hwang Liou<sup>4</sup>; <sup>1</sup>Materials Science and Engineering, National Tsing Hua University, Hsin Chu, Taiwan; <sup>2</sup>Physics, National Tsing Hua University, Hsin Chu, Taiwan; <sup>3</sup>Industrial Technology Research Institute, Hsin Chu, Taiwan; <sup>4</sup>Physics, University of Nebraska, Lincoln, Nebraska.

Oxides of some rare-earth and alkaline-earth metals grown on GaN exhibit nice properties and have therefore become the center of attention. For example, thin single crystal Gd<sub>2</sub>O<sub>3</sub> films were found to grow epitaxially on GaN and also to give a low D<sub>it</sub>. The Sc<sub>2</sub>O<sub>3</sub> films grown on GaN<sup>1</sup> have achieved a low D<sub>it</sub> as well as improved the device performance<sup>2</sup>. Previously, Sc<sub>2</sub>O<sub>3</sub> was reported to grow in a cubic crystalline form on GaN, based on a single broad Bragg peak observed in a  $\theta$ -2 $\theta$  x-ray diffraction scan<sup>1</sup>. It is not possible to determine the crystal structure from such limited information. We have grown Sc<sub>2</sub>O<sub>3</sub> on GaN using e-beam evaporation of the oxide from a compacted Sc<sub>2</sub>O<sub>3</sub> powder target in UHV. The Sc<sub>2</sub>O<sub>3</sub> film grows epitaxially in a bixbyite phase on the (0001) surface of the wurzite GaN substrate with its <111> axis aligned parallel to the substrate normal. The film crystal structure was studied in great detail, using x-ray diffraction scans in reciprocal space, in single-crystal geometry setup<sup>3</sup>. The epitaxial growth of the oxide was revealed by both in-situ RHEED and x-ray diffraction. During the course of our studies of growing Sc<sub>2</sub>O<sub>3</sub> films on GaN, it has come to our attention that Sc<sub>2</sub>O<sub>3</sub> grows excellent films on sapphire (Al<sub>2</sub>O<sub>3</sub>) substrate, which have initiated this study. It is very surprising to observe this epitaxial growth considering the large lattice mismatch between Sc<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> crystal lattices. Sapphire (Al<sub>2</sub>O<sub>3</sub>) substrates, two-inch in diameter were heated to over 700C in the UHV chamber to clean the surface, and then the substrate temperature was lowered to 600C for the oxide film growth. RHEED was used to monitor the film growth. Single-crystal x-ray diffraction measurements were carried out on a triple-axis geometry, 4-circle goniometer using a 12 kW rotating anode machine, and Cu-K $\alpha$  radiation. The Sc<sub>2</sub>O<sub>3</sub> film grows epitaxially in bixbyite phase on the rhombohedral (111) surface of the sapphire substrate with its <111> axis aligned parallel to the substrate normal. In-plane orientation of the film, however, goes through a 30-degree rotation with respect to that of the substrate, about the surface normal. Because of this unusual orientational locking, in-plane film growth takes place in two-degenerate orientations. The atomic structure of the epitaxial film is fully relaxed and is of unusually good quality. A strain relaxed film, however, always contains misfit dislocations, which can severely disrupt the long-range order of the film. It is therefore most remarkable that Sc<sub>2</sub>O<sub>3</sub> films on sapphire grow nearly defect free. All the evidence suggests that, the misfit dislocations are confined to a narrow region near the interface and do not extend deep into the film to destroy the atomic order of the Sc<sub>2</sub>O<sub>3</sub> epitaxial film. 1. B. P. Gila et al, Phys. Stat. Sol. (a) 188, 239, 2001. 2. J. Kim et al, Applied Physics Letters, 81, 373, 2002. 3. A. R. Kortan et al, unpublished results, 2002.

**8:45 AM E1.3**

**Highly-Insulating Ultra-Thin SiO<sub>2</sub> Film Grown by Photo-Oxidation.** Atsuyuki Fukano and Hiroyuki Oyanagi; Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

We reported that the high-density SiO<sub>2</sub> film grown by photo-oxidation is promising technique for superior insulating performance.[1] Since, the practical insulation limit of SiO<sub>2</sub> film grown by conventional thermally oxidation technique is dependent on the SiO<sub>x</sub> (sub-oxide) layer thickness which is called "transition layer". It become important to reduce the transition layer and oxygen defect to minimize the thickness of SiO<sub>2</sub> gate dielectric film. We found that the UV photo-oxidation SiO<sub>2</sub> film has a higher density than that of conventional thermally oxidized films and contains negligible thickness of SiO<sub>x</sub> layer. We will report about the wavelength dependence of the physical properties of the film and insulating characteristic of the films grown by photo-oxidation. The SiO<sub>2</sub> samples were grown by photo-oxidation on Si(001) wafer. The wavelength of  $\lambda=126, 172$  and  $222$  nm excimer lamps were used. During the growth, the substrate temperature was maintained not to exceed 500 °C. The oxygen pressure in the growth chamber was held atmospheric level. The density distribution of in-depth profile under the ultra-thin SiO<sub>2</sub> films on silicon substrate was obtained by x-ray reflectivity measurements. It was found that the density of photon-oxidized SiO<sub>2</sub> film is higher than the conventional thermally oxidized film. A striking feature of photo-oxidized SiO<sub>2</sub> films thickness is saturated about 5 nm and the transition layer region is not distinguished using the  $\lambda=126$  nm wavelength radiation by XPS. However, the film growth rate, density and the transition layer thickness were depend on wavelength range of irradiation. In higher photon energy as oxidation which is  $\lambda=126$  nm photon, the SiO<sub>2</sub> density is increased to the same level of silicon (2.23 g/cm<sup>3</sup>) with showing a continuous density across the SiO<sub>2</sub>-Si interface. Since the density and interface layer thickness can be controlled by photon energy, application to gate dielectric SiO<sub>2</sub> film are promising. We show that superior electrical insulating performance is achieved for  $\lambda=126$  and  $172$  nm photo-oxidized SiO<sub>2</sub> films. The breakdown voltage of  $\lambda=126$  nm photo-oxidized SiO<sub>2</sub> was about 45 MV/cm in sharp contrast to 172 nm photo-oxidized film (18 MV/cm) with leakage current less than 10<sup>-4</sup> A/cm<sup>2</sup>. [2] The mechanism of the growth of high density SiO<sub>2</sub> by photo-oxidation will be discussed. Use of UV photo-oxidation technique might be candidate of improving the present limit of silicon dioxide film as a dielectric gate film. [1]A. Fukano and H. Oyanagi, Mat. Res. Soc. Symp. Proc. 751, 61(2003). [2]A. Fukano and H. Oyanagi, J. Appl. Phys. 94, 3345(2003).

**9:00 AM E1.4**

**Improvements to the Si/High-k Interface Layer by the Use of an Etched Back Thermal Oxide.** Joel M. Barnett<sup>1</sup>, Naim Mouden<sup>1,2</sup>, Jim Gutt<sup>1</sup>, Mark Gardner<sup>1,3</sup>, Craig Huffman<sup>1,4</sup>, Prashant Majhi<sup>1,5</sup>, Jeff Peterson<sup>1,6</sup>, Sundar Gopalan<sup>1</sup>, Hong-Jyh Li<sup>1,7</sup>, Byoung Hun Lee<sup>1,2</sup>, Gennadi Bersuker<sup>1</sup>, Peter M. Zeitzoff<sup>1</sup>, George A. Brown<sup>1</sup>, Pat Lysaght<sup>1</sup>, Chadwin D. Young<sup>1</sup>, Robert W. Murto<sup>1,4</sup> and Howard R. Huff<sup>1</sup>; <sup>1</sup>International SEMATECH, Austin, Texas; <sup>2</sup>IBM Assignee, Austin, Texas; <sup>3</sup>AMD Assignee, Austin, Texas; <sup>4</sup>Texas Instruments Assignee, Austin, Texas; <sup>5</sup>Philips Assignee, Austin, Texas; <sup>6</sup>Intel Assignee, Austin, Texas; <sup>7</sup>Infinion Assignee, Austin, Texas.

As transistor sizes continue to shrink, gate oxide thicknesses are scaling below 1.0 nm to increase the gate stack capacitance density. With decreasing gate oxide thickness, however, direct tunneling becomes a major device issue as it contributes to leakage current and, subsequently, to increased standby power consumption. By increasing the permittivity of the gate dielectric, the leakage current can be reduced and the capacitance can still be scaled. Researchers have recently been studying hafnium based high-k dielectrics as an alternative to SiO<sub>2</sub>. However, hafnium films deposited directly on hydrogen terminated silicon surfaces have not achieved electrical performance comparable to that achieved with SiO<sub>2</sub>. In order to achieve sub-nm equivalent oxide thickness (EOT) with high-k dielectrics and still enable the device to meet the requirements of saturation current, transconductance and mobility, the interfacial-layer must be properly optimized. This layer should have a minimal thickness; typically, chemical oxides and thinly grown thermal oxides are used but these can be problematic - the chemical oxide does not appear robust enough and it is very difficult to grow very thin and uniform (0.5nm) thermal oxides. We shall describe a process in which a 2 nm In-Situ-Steam-Generated (ISSG) thermal oxide is grown and then etched back in a controlled manner to achieve both a uniform, robust interface for high-k deposition and significant improvements in device electrical performance compared to previous surface preparation techniques. In particular, utilizing this approach in combination with a HfSiO dielectric film and a TiN gate electrode resulted in EOTs as low as 0.87nm while also demonstrating low

defect density, more tightly distributed gate currents, and better breakdown voltage characteristics as compared to other starting surfaces.

**9:15 AM E1.5**  
**Surface Chemistry of  $\beta$ -diketonate Precursors in Metal Oxide Deposition.** Trinh Tu Van and Jane P Chang; Chemical Engineering, UCLA, Los Angeles, California.

Over the last decade, an intensive research effort has been directed toward understanding and engineering material properties of metal oxide thin films for next generation of microelectronic and optoelectronic devices. It is apparent that the surface reactions taking place during deposition play an important role in determining the properties of the materials. In this work, we present the results of the adsorption and desorption kinetics of  $\beta$ -diketonate complexes, followed by the deposition kinetics of metal oxides using these precursors with O or H radicals. The  $\beta$ -diketonate complexes are one of the most frequently used metal precursors in applications where low processing temperature is desired. We constructed a UHV reaction chamber that consists of a precursor doser, a coaxial waveguide microwave source for generating H or O radicals, a temperature-controlled substrate holder, and a quartz crystal microbalance (QCM). The  $\beta$ -diketonate complexes chosen for this study are Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) yttrium(III), or Y(TMHD)<sub>3</sub>, and Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) erbium(III), or Er(TMHD)<sub>3</sub>. We used the quadruple mass spectroscopy (QMS) to identify the cracking patterns of these metal precursors. The adsorption and desorption kinetics were investigated by using the temperature-controlled QCM. Combining QMS with temperature programmed desorption (TPD), the composition of the surface species were determined. X-ray photoelectron spectroscopy (XPS) was used to estimate the thickness and composition of the thin oxide films. The adsorption isotherms of Y(TMHD)<sub>3</sub> on the pre-deposited Y<sub>2</sub>O<sub>3</sub> film showed an initial rapid adsorption followed by saturation. The surface coverage increased with increasing substrate temperature, likely due to enhanced surface reaction at higher temperatures. We fitted the adsorption isotherms with the Langmuir-Hinshelwood adsorption model, assuming that the Y(TMHD)<sub>3</sub> precursor chemisorbs on the two nearby empty surface sites during the removal of one bidentate  $\beta$ -diketonate ligand. From these fittings, we found that the Y(TMHD)<sub>3</sub> adsorption rate increased with increasing substrate temperature. In contrast, the desorption rate decreased with increasing temperature. The deposition kinetics of Y<sub>2</sub>O<sub>3</sub> thin films using Y(TMHD)<sub>3</sub> precursor and O radicals were also investigated with the QCM. The deposition rate is found to be relatively independent of temperature for up to 350°C and was verified by thickness measurements from XPS. We also investigated the adsorption and desorption kinetics of Er(TMHD)<sub>3</sub> on the pre-deposited Y<sub>2</sub>O<sub>3</sub> film and similar adsorption and desorption characteristics were observed. Combining the deposition of Er<sub>2</sub>O<sub>3</sub> with every 5-10 layers of deposited Y<sub>2</sub>O<sub>3</sub>, we can synthesize an Er-doped Y<sub>2</sub>O<sub>3</sub> film for potential applications, such as an optical waveguide or amplifier.

**9:30 AM E1.6**  
**Processing and Characterization of Erbium-doped Yttrium Oxide Thin Films.** Trinh Tu Van and Jane P Chang; Chemical Engineering, UCLA, Los Angeles, California.

Yttrium oxide thin film is a material of interest for next generation of microelectronic and optoelectronic devices. In microelectronic applications, it is a promising high dielectric constant material to replace SiO<sub>2</sub> in complementary metal oxide semiconductor (CMOS) field effect transistors. In optoelectronic applications, the Y<sub>2</sub>O<sub>3</sub> thin film has demonstrated superior performance over the conventional SiO<sub>2</sub> when used as a host material for optically active Er<sup>3+</sup> ions. The improved gain of an Er-doped Y<sub>2</sub>O<sub>3</sub> waveguide amplifier arises from the similarities in the crystal structures and lattice constants of Y<sub>2</sub>O<sub>3</sub> and Er<sub>2</sub>O<sub>3</sub>, enabling a higher concentration of Er<sup>3+</sup> ions to be incorporated. In this work, we present the results of the pure and Er-doped Y<sub>2</sub>O<sub>3</sub> thin film deposition, using radical-enhanced atomic layer deposition (RE-ALD). The Y<sub>2</sub>O<sub>3</sub> films were deposited on Si in a UHV reaction chamber by using alternating pulses of Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium(III) precursor, or Y(TMHD)<sub>3</sub>, with O or H radical species. Erbium dopants were incorporated by introducing Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)erbium(III) precursor, or Er(TMHD)<sub>3</sub>, after every five ALD cycles of Y<sub>2</sub>O<sub>3</sub> deposition. The quartz crystal microbalance (QCM) was used to measure the deposition kinetics in situ. X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were used to determine the chemical composition and distribution, crystallinity, surface morphology, and step coverage of the deposited films. Well-controlled RE-ALD of pure Y<sub>2</sub>O<sub>3</sub> and Er-doped Y<sub>2</sub>O<sub>3</sub> were achieved with Y(TMHD)<sub>3</sub> and

Er(TMHD)<sub>3</sub> with either O or H radicals. The Y<sub>2</sub>O<sub>3</sub> deposition rate saturated at 200 to 400°C, yielding an ALD processing window for Y<sub>2</sub>O<sub>3</sub> deposition. The compositional depth profiles obtained from ToF-SIMS analysis indicates that the film composition resembled bulk Y<sub>2</sub>O<sub>3</sub> as the film thickness increased. The XPS analysis shows that stoichiometric Y<sub>2</sub>O<sub>3</sub> films with minimal carbon impurity were obtained with both radicals, though higher carbon levels were consistently observed when H radicals were used. The root mean square surface roughness of the deposited films with either radical is below 5Å, measured by AFM. Fairly conformal deposition of Y<sub>2</sub>O<sub>3</sub> with O radicals was achieved over features with aspect ratio of 4, determined by the cross-sectional SEM images. The cross-sectional SEM images show higher surface coverage of Y<sub>2</sub>O<sub>3</sub> as the surface temperature increased. Radical enhanced deposition is also shown to be a viable technique for doping high concentration of erbium ions in Y<sub>2</sub>O<sub>3</sub> films. The Er-doped Y<sub>2</sub>O<sub>3</sub> film had an Er<sup>3+</sup> concentration of approximately 3-5 at. %, determined XPS. Their optical characterization, conducted with the photoluminescence spectroscopy (PL), will also be addressed.

**9:45 AM E1.7**  
**Structure and electronic structure of Si-SrTiO<sub>3</sub> and Si-LaAlO<sub>3</sub> interfaces.** P W Peacock and John Robertson; Engineering, Cambridge University, Cambridge, United Kingdom.

SrTiO<sub>3</sub> and LaAlO<sub>3</sub> form lattice matched interfaces to Si(100) and are thus interesting functional oxide interfaces. SrTiO<sub>3</sub> reacts with Si and is likely to have a low band offset. On the other hand LaAlO<sub>3</sub> is stable in contact with Si and should have reasonably large band offsets because of its large 5.8 eV band gap. However, the (100) atomic planes in LaAlO<sub>3</sub> (LaO, AlO<sub>2</sub>) are polar unlike in SrTiO<sub>3</sub> and this leads to problems with epitaxy. Various epitaxial atomic configurations of these oxides on Si are constructed, Sr or Ti, La or Al last. Their atomic structures are relaxed to minimise their total energy using the plane wave pseudopotential method, and their band offsets calculated. Half a monolayer of Sr is needed to maintain an insulating configuration for the SrTiO<sub>3</sub>/Si interfaces. In contrast, LaO and AlO<sub>2</sub> terminated interfaces are possible for LaAlO<sub>3</sub>. Varying the termination is found to shift the band offsets.

**10:15 AM \*E1.8**  
**Dual Metal Gate CMOS for High Performance Logic Applications.** Vijay Narayanan<sup>1</sup>, Cyril Cabral<sup>1</sup>, Fenton McFeely<sup>1</sup>, Alessandro Callegari<sup>1</sup>, Sufi Zafar<sup>1</sup>, Paul Jamison<sup>1,2</sup>, Michael Gribelyuk<sup>2</sup>, An Steegen<sup>2</sup>, Victor Ku<sup>2</sup>, Phung Nguyen<sup>2</sup>, Ricky Amos<sup>2</sup>, Jakub Kedzierski<sup>1</sup>, Alexander Vayshenker<sup>2</sup>, Byoung Lee<sup>2</sup>, Supratik Guha<sup>1</sup>, Evgeni Gousev<sup>1</sup>, Matthew Copel<sup>1</sup>, Deborah Neumayer<sup>1</sup>, Rajarao Jammy<sup>1</sup>, Meikei Jeong<sup>1,2</sup> and Wilfried Haensch<sup>1</sup>; <sup>1</sup>IBM T.J. Watson Research Center, Yorktown Heights, New York; <sup>2</sup>IBM Microelectronics Division, Hopewell Junction, New York.

To meet the requirements for scaling high performance logic, it is becoming very apparent that metal gates need to replace doped polysilicon gates to achieve EOTs < 1 nm. However, there are a number of material and integration challenges associated with the introduction of metal gates, including the availability of suitable nFET and pFET workfunction metal electrodes and choice of integration scheme (gate last, conventional or silicide gate). In this presentation, different gate metal electrodes will be reviewed in terms of both their structural and electrical properties on SiON and Hf-based dielectrics. We have concentrated our efforts on developing CVD approaches for metal gate deposition to obviate the well known problems of process damage & conformality (for replacement gate) associated with PVD processes. Focusing on CVD W as a prototypical metal (mid-gap workfunction) we have examined the stability of W/SiON and W/HfO<sub>2</sub> stacks in capacitor and FET structures. The effect of post metal anneals on W gated HfO<sub>2</sub> stacks was examined and correlated with the thermal stability of the gate stack, flatband shifts, changes in EOT and charge trapping. It will also be shown that CVD W gated SiON and HfO<sub>2</sub> stacks show electrical reliability as good - and in some cases better - than poly-Si/SiON gate stacks. Similar data will be presented for other CVD gate electrodes and feasibility of true nFET and pFET functionality will be examined. Finally, some preliminary results on fully silicided gates with NiSi gated HfO<sub>2</sub> will be presented and issues related to the pre-doping of the polysilicon to achieve dual metal gate workfunction will be discussed.

**10:45 AM E1.9**  
**Next generation of thin film transistors based on zinc oxide.** Elvira Maria Correia Fortunato, Ana Pimentel, Guilherme Lavareda, Carlos Nunes de Carvalho, Luis Pereira, Hugo Aguas and Rodrigo Martins; Materials Science, FCT-UNL, Caparica, Portugal.

Transparent electronics are nowadays an emerging technology for the next generation of optoelectronic devices. Oxide semiconductors are very interesting materials because they combine simultaneously

high/low conductivity with high visual transparency and have been widely used in a variety of applications (e.g. antistatic coatings, touch display panels, solar cells, flat panel displays, heaters, defrosters, optical coatings, among others) for more than a half-century.

Transparent oxide semiconductor based transistors have recently been proposed using as active channel intrinsic zinc oxide (ZnO). These transistors present an on-to-off ratio of about 106 and relative low channel mobilities between 1 and 3 cm<sup>2</sup>/Vs. The main advantage of using ZnO deals with the fact that it is possible to growth at/near room temperature high quality polycrystalline zinc oxide, which is a particular advantage for electronic drivers, where the response speed is of major importance. Besides that, since ZnO is a wide band gap material (3.2 eV), it is transparent in the visible region of the spectra and therefore, also less light sensitive. Besides these works Nomura et al. proposed also recently a transparent transistor using as active channel a single crystal of InGaO<sub>3</sub>(ZnO)<sub>5</sub>. The most impressive aspect of this transistor is the high channel mobility of 70 cm<sup>2</sup>/Vs, mainly due to the absence of structural defects and to a low carrier concentration. In this work we report results concerning the fabrication and characterization of a high field-effect mobility ZnO-thin film transistor (ZnO-TFT) deposited at room temperature by rf magnetron sputtering where the gate dielectric is based on silicon oxynitride and the drain and source are based on highly conductive gallium doped zinc oxide (GZO). Moreover, the processing technology used to fabricate this device is relatively simple and it is compatible with inexpensive plastic/flexible substrate technology.

#### 11:00 AM E1.10

**Carrier Concentration Dependence of Ti/Al/Pt/Au Ohmic Contacts to Phosphorus-Doped ZnO Thin Films.** Kelly Ip<sup>1</sup>, Y.W. Heo<sup>1</sup>, K.H. Baik<sup>1</sup>, D.P. Norton<sup>1</sup>, S.J. Pearton<sup>1</sup> and F. Ren<sup>2</sup>; <sup>1</sup>Materials Science and Engineering, University of Florida, Gainesville, Florida; <sup>2</sup>Chemical Engineering, University of Florida, Gainesville, Florida.

The carrier concentration dependence of Ti/Al/Pt/Au ohmic contact resistance on P-doped n-type ZnO thin films is reported. Ti (200 Å)/Al (800 Å)/Pt (400 Å)/Au (800 Å) was deposited by e-beam evaporation on ZnO thin films grown by pulsed laser deposition (PLD) on (0001) sapphire substrates using a ZnO: P<sub>0.02</sub> source. Post-growth annealing from 30 °C to 600 °C resulted in carrier concentrations of 7.5 × 10<sup>15</sup> cm<sup>-3</sup> to 1.5 × 10<sup>20</sup> cm<sup>-3</sup> in the ZnO. After metal deposition, the specific contact resistances were measured at temperatures in the range 30 - 100 °C prior to alloying annealing at 200 °C and at 30-200 °C after this anneal. The lowest specific contact resistance of 8.7 × 10<sup>-7</sup> W-cm<sup>2</sup> for nonalloyed ohmic contacts was achieved in the sample with carrier concentration of 1.5 × 10<sup>20</sup> cm<sup>-3</sup> when measured at 30 °C. In the annealed samples, minimum specific contact resistances of 3.9 × 10<sup>-7</sup> W-cm<sup>2</sup> and 2.2 × 10<sup>-8</sup> W-cm<sup>2</sup> were obtained in samples with carrier concentrations of 6.0 × 10<sup>19</sup> cm<sup>-3</sup> measured at 30 °C and 2.4 × 10<sup>18</sup> cm<sup>-3</sup> measured at 200 °C, respectively. The temperature-dependent measurements suggested that the dominant transport mechanisms were tunneling in the contacts in the most highly doped films and thermionic emission in the more lightly doped films. Auger Electron Spectroscopy detected Ti-O interfacial reaction and intermixing between Al and Pt at 200 °C.

#### 11:15 AM E1.11

**Comparison of Digital versus Continuous Growth Techniques for MgCaO Dielectric on GaN.** Andrea Hope Onstine<sup>1</sup>, A. Herrero<sup>1</sup>, B. P. Gila<sup>1</sup>, D. Stodilka<sup>1</sup>, J. LaRoche<sup>2</sup>, C. R. Abernathy<sup>1</sup>, F. Ren<sup>2</sup> and S. J. Pearton<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of Florida, Gainesville, Florida; <sup>2</sup>Chemical Engineering, University of Florida, Gainesville, Florida.

Fabrication of high-performance metal oxide semiconductor field effect transistors (MOSFETs) on gallium nitride will require both good interfacial electrical characteristics and good thermal stability. While amorphous dielectrics such as silicon dioxide have demonstrated promising results their low dielectric constants argue against their use in high-power wide bandgap devices. In this talk we will discuss the growth and utility of crystalline ternary oxides based on magnesium oxide, MgO, as gate dielectric materials for GaN. Deposition of these materials by gas-source molecular beam epitaxy from elemental metals and an oxygen plasma has been found to produce epitaxial interfacial layers with excellent surface morphologies as evidenced by SEM and AFM. Oxide/GaN diodes fabricated using this approach show low densities of interface traps, ~1-4x10<sup>11</sup> eV<sup>-1</sup> cm<sup>-2</sup>, as measured by the AC conductance method. Utilizing a gated diode configuration, these oxides have produced the first demonstration of inversion in a GaN heterostructure. However, further improvements in interface electrical characteristics along with good thermal stability will require a reduction in the interfacial mismatch between the oxides and the GaN. One possible material to fill this gap is MgCaO. Two different growth techniques have been tried to grow this oxide. One is the continuous method where the shutters are open for the entire growth run. The other is the digital alloy method where there is a sequence of

opening and closing of the source metal shutters during the growth. The digital approach was found to produce significant improvement in the compositional uniformity as determined by Auger electron spectroscopy (AES) and surface morphology as shown by atomic force microscopy (AFM). Neither growth method showed evidence of phase separation in the resultant films. X-ray diffraction shows a change in lattice parameter with the addition of calcium, which reduces the lattice mismatch to GaN. Electrical and structural characterization of the oxide/GaN interface as a function of oxide composition will also be presented. The authors gratefully acknowledge the support from ONR contract No. N00014-98-0204 (H.B. Dietrich) and AFOSR Contract No. F49602-02-1-0366 (G.L. Witt) for this work.

#### 11:30 AM E1.12

**Fundamental Study and Oxide Reliability of the MBE Grown Ga<sub>2-x</sub>Gd<sub>x</sub>O<sub>3</sub> Dielectrics for Compound Semiconductor MOSFETs.** J. Kwo<sup>1</sup>, M. Hong<sup>2</sup>, J. P. Mannaerts<sup>2</sup>, Y D Wu<sup>2</sup>, Q Y Lee<sup>2</sup>, B Yang<sup>3</sup> and T Gustafsson<sup>4</sup>; <sup>1</sup>Physics, National Tsing Hua University, Hsin Chu, Taiwan; <sup>2</sup>Materials Science and Engineering, National Tsing Hua University, Hsin Chu, Taiwan; <sup>3</sup>Agere Systems, Allentown, Pennsylvania; <sup>4</sup>Physics, Rutgers University, Piscataway, New Jersey.

The GaAs based MOSFETs are expected to outperform Si based devices in high speed and high power applications due to the large electron mobility and the semi-insulating substrates of GaAs. However, the lack of an insulating oxide of low interfacial defects for effective GaAs passivation has hampered the progress of developing this device over thirty five years. Recently our discovery of a mixed oxide dielectric Ga<sub>2-x</sub>Gd<sub>x</sub>O<sub>3</sub> (κ=12) and a pure oxide of Gd<sub>2</sub>O<sub>3</sub> (κ=14) formed inversion and accumulation channels on the GaAs surface with a low interfacial density of states, D<sub>it</sub> of mid 10<sup>10</sup> cm<sup>-2</sup> eV<sup>-1</sup>, and later led to the first demonstration of p- and n-inversion channel MOSFETs and CMOS circuits. X-ray coherent Bragg rod analysis of the interface indicated that the unusual epitaxial structure of ultrathin Gd<sub>2</sub>O<sub>3</sub> layer conforming to underlying (2x4) GaAs (100) surface may hold the key for achieving the low D<sub>it</sub>. In this work we have successfully extended this novel dielectrics Ga<sub>2-x</sub>Gd<sub>x</sub>O<sub>3</sub> to several compound semiconductors including AlGaAs, InGaAs, and InP, and demonstrate the formation of low leakage, insulating barrier on their (100) surfaces. Fundamental studies of the MOS diodes consisting of Au/Ga<sub>2-x</sub>Gd<sub>x</sub>O<sub>3</sub> mostly on InGaAs are reported, including the crystal-chemical and electrical properties in order to address the oxide reliability issue. An atomically abrupt interface between the gate dielectric/GaAs interface was achieved by our MBE growth, as indicated by the medium energy ion scattering. Systematic post annealing studies of varying temperature and gas species were carried out to improve the dielectric performance as measured by C-V, such as the reduction of undesirable feature of frequency dispersion, voltage hysteresis, and the D<sub>it</sub> value. For instance, He gas anneal anneals at 450-650C was performed to densify the oxide and to heal the growth induced defects. We observed notable frequency dispersion reduction due to removal of the slow-moving charge carriers after the 600C He anneal, accompanied with marked improvement of D<sub>it</sub> from the initial 10<sup>12</sup> to mid 10<sup>10</sup> at 100K Hz. The forming gas anneals at 375C was found to reduce the voltage hysteresis to below 0.2V. We show that these results are essential to device process optimization, and to further establish a viable GaAs MOSFET technology.

#### 11:45 AM E1.13

**Fin Sidewall Microroughness Measurement by AFM.** Carolyn F. H. Gondran<sup>1</sup>, Emily Morales<sup>1</sup>, Angela Guerry<sup>1</sup>, Weize Xiong<sup>2</sup>, C. Rinn Cleavelin<sup>3</sup>, Rick Wise<sup>3</sup>, Sriram Balasubramanian<sup>4</sup> and Tsu-Jae King<sup>4</sup>; <sup>1</sup>International SEMATECH, Austin, Texas; <sup>2</sup>X - Chips Technologies Incorporated, Austin, Texas; <sup>3</sup>Texas Instruments Incorporated, Dallas, Texas; <sup>4</sup>University of California Berkeley, Berkeley, California.

As bulk-Si CMOS quickly approaches its scaling limits, new avenues are being pursued to allow continued improvement in device performance. The use of new transistor designs such as multi-gated MOSFETs is one promising option. The preferred approach to building multi-gated devices uses a 3-dimensional channel structure or Fin. Such FinFET devices have received much attention due to their relative ease of integration with existing planar processes. The introduction of non-planar device designs such as Fin structures ushers in new characterization challenges along with a host of new manufacturing challenges. For example, in FinFET devices, the sidewalls of etched Si features would be used as the channel surfaces. Carrier mobility and gate dielectric quality are both strongly influenced by the roughness of this surface. It is critical for good FinFET device performance to develop and qualify a Fin sidewall smoothing process that produces a surface as smooth as epi or polished Si. Thus the development of a method to quantitatively measure the Fin sidewall surface microroughness is required. In this paper, such a methodology is presented; along with microroughness

data demonstrating the ability to measure meaningful differences for surfaces that have seen different surface smoothing treatments. This sidewall roughness measurement method must be sensitive enough to measure short-wavelength microroughness in the sub-Angstrom ( $\text{\AA}$ ) RMS roughness range. These requirements rule out the use of automated CD-mode atomic force microscope (AFM) metrology. A well-isolated Digital Instruments Dimensions 5000 AFM is used. To measure sidewall roughness, without the use of a dual-direction-sensing CD-mode AFM, the sample must be cleaved and mounted such that the surface of interest is exposed on the top of the sample. Because film heights are expected to be in the sub-100nm range, it is also critical that the AFM tip have access to the entire sidewall. Shadowing of the lower sidewall, due to the AFM probe geometry is avoided by mounting the sample at an angle complementary to the AFM tip angle. Focused ion beam (FIB) milling is used during sample preparation to control the size of the step from the edge of the sample to the sidewall. The FIB mill is also extremely helpful in marking the area of interest.

SESSION E2: Complex Oxide Heterostructures  
Chairs: Dhananjay Kumar and Leonard Uitenham  
Wednesday Afternoon, April 14, 2004  
Room 2000 (Moscone West)

### 1:30 PM \*E2.1

**Domain Matching Epitaxy: A New Paradigm for Epitaxial Growth of Oxides.** Jagdish Narayan, Materials Sc and Eng., N. C. State, Raleigh, North Carolina.

This talk focuses on epitaxial growth of oxides (such as ZnO and its alloys, PZT, NdNiO<sub>3</sub>, YBa<sub>2</sub>Cu<sub>3</sub>O) on silicon and sapphire substrates having a large misfit with the oxide films. We demonstrate that epitaxial growth occurs via domain matching epitaxy (DME), where integral multiples of lattice planes match across the film-substrate interface. The residual misfit beyond the integral matching is accommodated via domain variation, where two domains alternate with a certain frequency to attain a zero misfit. The planar matching could be different in different directions. Thus, epitaxy in this new paradigm is defined as the film having a fixed orientation with respect to the substrate rather than having the same orientation. If the critical thickness is less than one to two monolayers, most of the misfit dislocations get set from the beginning, resulting in a complete relaxation of the film. If the initial growth is two-dimensional, most of the dislocations are confined near the interface and the rest of the film can be grown virtually strain-free. We illustrate DME with atomic-level details using high resolution cross-section TEM and in-situ X-ray diffraction techniques, and discuss properties and applications of new systems. (1) J. Narayan and B. C. Larson, J. Appl. Phys. 93, 278(2003).

### 2:00 PM E2.2

**BaTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices grown on LaNiO<sub>3</sub>-coated SrTiO<sub>3</sub> substrates by RF sputtering and their dielectric properties.** Hsin-Yi Lee, C. -H. Hsu, Y. -W. Hsieh and Keng S. Liang; Research Division, National Synchrotron Radiation Research Center, Hsinchu, Taiwan.

BaTiO<sub>3</sub> (BTO) and SrTiO<sub>3</sub> (STO) artificial superlattices were grown on LaNiO<sub>3</sub> (LNO) coated SrTiO<sub>3</sub> (001) substrates by a computer-controlled triple-gun RF magnetron sputtering system. The superlattices consist of BTO and STO sublayers of 4nm thick (10 unit cells) and the films contain 20 periods of BTO/STO bilayers. The LNO interfacial layer was prepared at 500°C with thickness of 80nm. The growth of superlattices was systematically studied by varying the substrate temperature between 400 and 650°C. The formation of superlattices structure was examined by synchrotron x-ray scattering. From the x-ray measurements, the optimum condition for growing epitaxial BTO/STO superlattices was determined. Films prepared under such condition are found to exhibit a dielectric constant ( $\epsilon$  300) twice that of the single-phase BTO ( $\epsilon$  155) or STO ( $\epsilon$  150) films. The obtained dissipation factors of the superlattice films are found to be quite low ( $\tan \delta < 0.02$ ). Our work demonstrates a new approach by RF sputtering to fabricate dielectric thin films with artificial superlattice structures.

### 2:15 PM E2.3

**Bulk-like ferroelectric and piezoelectric properties of transferred-BaTiO<sub>3</sub> single crystal thin films.** Young-Bae Park, Jennifer L. Ruglovsky, Matthew J. Dicken and Harry A. Atwater; Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California.

We have characterized the ferroelectric/piezoelectric properties for layer transferred single crystal BaTiO<sub>3</sub> thin films with heteroepitaxial and polycrystalline ferroelectric thin films grown by MBE, MOCVD

and sol-gel. We observed a striking bulk-like ferroelectric domain structure in single crystal films. We also found that  $d_{33} = 90 \text{ pm/V}$  compared to 10-20 pm/V range of MOCVD and solgel films. Bulk single crystal BaTiO<sub>3</sub> was processed by crystal ion slicing method with high dose H and He ion implantation. The ion implantation energy was 20 115 keV and dose ranged from  $5 \times 10^{16}$  to  $1 \times 10^{17}/\text{cm}^2$  for H<sup>+</sup> and energy was 30 200 keV with dose of  $1 \times 10^{17}/\text{cm}^2$  for He<sup>+</sup>, respectively. After substrate cleaning, BaTiO<sub>3</sub> was bonded to various substrates (Si, Si<sub>3</sub>N<sub>4</sub>, Pt and Al). Single crystal BaTiO<sub>3</sub> layers with the area of  $5 \times 5 \text{ mm}^2$  were transferred onto Si<sub>3</sub>N<sub>4</sub> or Pt substrates. Transferred layers exhibited single crystalline structure with tetragonal structure. Film stoichiometry does not change compared to bulk BaTiO<sub>3</sub> but it exhibited stacking faults and polarization change. RMS surface roughness of transferred layer is ranged below 17 nm. Ferroelectric domain size was ranged from 5 to 20 nm and showed typical ferroelectric domain switching behavior. Various composition and textured Pb<sub>x</sub>Ba<sub>1-x</sub>TiO<sub>3</sub> (PBT) films were grown by solgel, MOCVD and MBE. In a sol-gel system, solution with Pb-acetate trihydrate: Ba-acetate: Ti-isopropoxide dissolved in ethylene glycol was spin coated onto the biaxially textured MgO templates and Pt substrates at 4000 rpm, pyrolyzed at 450°C for 3 minutes, and then calcined at 600°C for 2 hours. PBT was also grown using metallorganic chemical vapor deposition (MOCVD). The Ba, Pb, and Ti precursors are Ba(tmhd)<sub>2</sub>, Pb(tmhd)<sub>2</sub>, Ti(OPri)<sub>2</sub>(tmhd)<sub>2</sub>. Molecular beam epitaxy (MBE) was performed at 700°C by co-evaporation of Pb, Ba and Ti. The oxygen source was introduced with O<sub>2</sub> partial pressure of  $6 \times 10^{-5}$  torr. AFM was used to characterize surface roughness and measured the grain size. Piezoresponse force microscopy (PFM) was used to investigate the domain structure and switching property. The piezoelectric constant,  $d_{33}$ , was evaluated by calibrating the force-distance curve in AFM and lock-in amplifying technique. Raman spectroscopy was used for local vibrational structure and chemical disorder. Microstructural analysis was performed using TEM. For the oxide layer stoichiometry and binding configuration, RBS and XPS analyses were performed.

### 2:30 PM E2.4

**Growth of single phase c-axis aligned La<sub>1.2</sub>Ca<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> films on SrTiO<sub>3</sub> (001).** Ashutosh Tiwari and J. Narayan; NC state university, raleigh, North Carolina.

We have developed a method to grow single phase, c-axis aligned thin films of La<sub>1.2</sub>Ca<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> on SrTiO<sub>3</sub>(001) substrates using a pulsed laser deposition process. In this method, constraint of epitaxy is utilized to stabilize the Ruddlesdon-Popper (RP) phase of La<sub>1.2</sub>Ca<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub>. It has been shown that the oxygen ambient pressure and the rate of deposition are the two most important factors affecting the microstructure as well as overall phase purity of the material. Films, prepared by this method, have been characterized using x-ray diffraction, transmission electron microscopy and electrical resistivity measurements.

### 2:45 PM E2.5

**Comparison of Sol-Gel Derived and Pulsed Laser Deposited Epitaxial La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> Films for IR Bolometer Applications.** Rickard Bengtsson<sup>1</sup>, Alexander M Grishin<sup>1</sup>, Sergey I Khartsev<sup>1</sup>, Annika Pohl<sup>2</sup> and Gunnar Westin<sup>2</sup>; <sup>1</sup>Condensed Matter Physics, Royal Institute of Technology, Stockholm-Kista, Sweden; <sup>2</sup>Material Chemistry, Uppsala University, Uppsala, Sweden.

To date, most perovskites engineered towards applications are grown by pulsed laser deposition (PLD) which is not an industrially viable technique since there is almost no possibility of large area deposition. Sol-gel derived thin films do not suffer this drawback and represent a cheap and fast route to industry scale production. High quality sol-gel derived, epitaxial La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> (LCMO) have been demonstrated, but a comparison of transport, quality of epitaxy and surface morphology to PLD-grown films is to the best of our knowledge lacking. We present results on the characterization of both pulsed laser deposited and a novel all-alkoxide sol-gel derived LCMO on LaAlO<sub>3</sub> single crystals with and without post-annealing. Different out-of-plane lattice parameters are found for the as prepared films, and scanning electron microscopy shows a more porous structure for sol-gel films as compared to PLD. These differences are removed by post-annealing at 1000 °C. Transport measurements show maximum temperature coefficient of resistivity (TCR) of 8.2 %/K @ 258 K (PLD) and 6.1 %/K @ 241 K (sol-gel) and colossal magnetoresistance (CMR) of 35 % @ 263 K (PLD) and 32 % @ 246 K (sol-gel). To conclude, all-alkoxide sol-gel derived LCMO/LaAlO<sub>3</sub> film structures can compete with PLD in terms of structure and transport, making sol-gel a prime candidate for future industrial manganite thin film production. Differences in microstructure and oxygen content can be largely eliminated by post-annealing, which results in sol-gel film of remarkable epitaxial quality.

### 3:30 PM \*E2.6

**Electronic properties of charged interfaces with a perovskite**

oxide SrTiO<sub>3</sub>. Isao Inoue, Kazunori Ueno, Hidenori Takagi, Toshikazu Yamada, Hiroshi Sato, Akihiro Odagawa, Hiroshi Akoh, Hiroyuki Yamada, Masashi Kawasaki and Yoshinori Tokura; Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

SrTiO<sub>3</sub> is widely used as one of the most important bulk substrates for epitaxial syntheses of oxide thin films. Thus, to establish a method of the field-effect doping to SrTiO<sub>3</sub> is believed to open the door of unexplored field, where various kinds of functional oxides epitaxially grown on the SrTiO<sub>3</sub> substrate constitute the base of the electronic devices such as the field effect transistors (FET). We have had two complementary approaches to fabricate FET with a SrTiO<sub>3</sub> channel. One effort was spent on the so-called dry process: a method of the device fabrication which uses stencil masks made of thin metal plates. The other effort was done on the so-called wet process: a widely used process in contemporary semiconductor-device production lines. The dry process produced an exemplary FET device of SrTiO<sub>3</sub> showing a spectacular saturation of the drain current and large on-off ratio over 100, though the temperature dependence of the field-effect mobility was an activation-type and thus the device did not work below 150K. Hence the low temperature behaviours below 30K were explored on the wet-process device. Since the carriers are frozen out at low temperatures, the Schottky barriers at the channel/electrodes interface becomes so high to make an injection of carriers from the electrodes difficult. However, since the mobility is so high at the low temperature, once the carrier injection was bulldozed in any methods, the conduction at the channel becomes extremely enhanced. The resulting metallic state at 1.9K showed peculiar characteristics accompanied by a hysteresis reflecting the electronic inhomogeneity of the system; a research along the line is now in progress, and the details will be given in the talk.

#### 4:00 PM E2.7

**Persistent electronic conduction in 12CaO·7Al<sub>2</sub>O<sub>3</sub> thin films produced by Ar ion implantation: selective kick-out effect leads to electride thin films.** masashi miyakawa<sup>1</sup>, Katsuro Hayashi<sup>1</sup>, Yoshitake Toda<sup>1,2</sup>, Toshio Kamiya<sup>1,2</sup>, Masahiro Hirano<sup>1</sup> and Hideo Hosono<sup>1,2</sup>; <sup>1</sup>Hosono Transparent Electro-Active Materials Project, Japan Science and Technology Corporation, Kawasaki, Japan; <sup>2</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

We have found that novel functions in 12CaO·7Al<sub>2</sub>O<sub>3</sub> (C12A7) originating from nano-porous structure and clathrated anions, such as strong oxidation and light-induced electronic conduction [1,2]. These properties arise from the unique crystal structure of C12A7 that is composed of a positively charged [Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>]<sup>4+</sup> framework containing twelve crystallographic cages and two extra O<sup>2-</sup> ions (referred as free O<sup>2-</sup> ion) occupying two different cages. These free O<sup>2-</sup> ions can be substituted with O<sup>-</sup> or H<sup>-</sup> ions, which lead to the appearance of the above novel properties. The free O<sup>2-</sup> ions are also replaceable with electrons through chemical reductions by the Ca-treatment [3]. The resultant material represented by C12A7:e<sup>-</sup> is a first demonstration of thermally and chemically stable electride. It is expected to show non-traditional properties based on the cooperative motion of high-density semi-delocalized electrons and flexible framework. However, fabrication process of the C12A7 electride utilizing the strong reductive chemical reaction is limited to the bulk samples, and it is hardly applicable to polycrystalline (p-) thin films. Hence, in this work, we have examined an alternative technique based on physical processes. Ion implantation was applied to prepare C12A7:e<sup>-</sup>, intending to directly kick out the free O<sup>2-</sup> ions from the cages through nuclear collision. Hot Ar<sup>+</sup> ions implantation into p-C12A7 films with a fluence higher than 1x10<sup>17</sup> cm<sup>-2</sup> extruded the free O<sup>2-</sup> ions from the films by the kick-out effects, which left electrons in the cages and produced high concentration F<sup>+</sup>-like centers (1.4x10<sup>21</sup> cm<sup>-3</sup>). On the other hand, with the fluence less than 1x10<sup>17</sup> cm<sup>-2</sup>, the resulting films were transparent and insulating, while it shows ultraviolet light-induced coloration and conduction, indicating H<sup>-</sup> ions were loaded in the cages presumably due to the conversion from preexisted OH<sup>-</sup> ions to the H<sup>-</sup> ions. The concentration of the induced F<sup>+</sup>-like centers was proportional to calculated displacements per atom (dpa) value. However, the generation efficiency was larger in the higher fluence region (1x10<sup>18</sup> cm<sup>-3</sup>/dpa) compared to that in the lower region (e.g. 0.3x10<sup>18</sup> cm<sup>-3</sup>/dpa). [1] K.Hayashi, M.Hirano, S.Matsuishi, and H.Hosono, *J. Am. Chem. Soc.* **124**, 738(2002). [2] K.Hayashi, S.Matsuishi, T.Kamiya, M.Hirano, and H.Hosono, *Nature* **419**, 462(2002). [3] S.Matsuishi, Y.Toda, M.Miyakawa, K.Hayashi, T.Kamiya, M.Hirano, I.Tanaka, and H.Hosono, *Science* **301**, 626(2003).

#### 4:15 PM E2.8

**Synthesis and Optical Properties of Novel Wide-Gap Layered Oxychalcogenide, La<sub>2</sub>CdO<sub>2</sub>Se<sub>2</sub>.** Hidenori Hiramatsu<sup>1</sup>, Kazushige Ueda<sup>2</sup>, Toshio Kamiya<sup>1,2</sup>, Hiromichi Ohta<sup>1</sup>, Masahiro Hirano<sup>1</sup> and

Hideo Hosono<sup>1,2</sup>; <sup>1</sup>Hosono Transparent Electro-Active Materials Project, ERATO, Japan Science and Technology Agency, Kawasaki, Japan; <sup>2</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Wide-gap semiconductors have attracted much interest for various optoelectronic applications that utilize high optical transparency in the ultraviolet (UV) - visible region and high electrical conductivity. However, most of wide-gap materials are insulators or n-type semiconductors although p-type semiconductors are necessary to develop active optoelectronic devices. We have reported that Cu-based layered oxychalcogenides, LnCuOCh (Ln = lanthanide, Ch = chalcogen), are wide-gap p-type semiconductors and that an exciton, an electron-hole pair, is stable even at room temperature [1]. Besides, although LnCuOCh are promising as active layers in the UV - blue light-emitting diode (LED) [2], it is difficult to fabricate good LED structures because there is no n-type semiconductor with a similar crystal structure. Therefore, we have surveyed n-type oxychalcogenides having a crystal structure similar to LnCuOCh. We found that La<sub>2</sub>CdO<sub>2</sub>Se<sub>2</sub> was a candidate for a n-type conductor because the conduction band may be formed by extended Cd 5s orbitals. In this paper, single-phase powder and heteroepitaxial thin films of La<sub>2</sub>CdO<sub>2</sub>Se<sub>2</sub> were prepared, and their structural and optical properties were examined. It has not exhibited good electrical conduction, however, stable excitons were observed also in the Cd-based layered oxychalcogenide. Synthesis of La<sub>2</sub>CdO<sub>2</sub>Se<sub>2</sub> and its crystal structure were reported by Baranov et al. [3], however, their sample was not single-phase. La<sub>2</sub>CdO<sub>2</sub>Se<sub>2</sub> also has a layered structure, composed of alternate stacking of (La<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> and (CdSe<sub>2</sub>)<sup>2-</sup> layers along the c-axis, which is similar to that of LnCuOCh. We succeeded to prepare single-phase La<sub>2</sub>CdO<sub>2</sub>Se<sub>2</sub>, and heteroepitaxial films were prepared by a reactive solid-phase epitaxy technique [4]. Using the single-phase heteroepitaxial thin films, it was found that La<sub>2</sub>CdO<sub>2</sub>Se<sub>2</sub> has the widest band gap energy of 3.3 eV among the layered oxychalcogenides reported so far. Sharp UV photoluminescence bands due to free and bound excitons were clearly observed along with optical absorption peaks by the free exciton. The excitons are stable enough at room temperature, indicating that the excitons have a large binding energy similar to those of LnCuOCh. Comparison with LnCuOCh and CdSe-based artificial superlattices revealed that the carriers are confined in the naturally-formed two-dimensional crystal structure. [1] K. Ueda et al., *Appl. Phys. Lett.* **77**, 2701 (2000); *Appl. Phys. Lett.* **78**, 2333 (2001); *Chem. Mater.* **15**, 3692 (2003). [2] H. Hiramatsu et al., *Appl. Phys. Lett.* **81**, 598 (2002); *Appl. Phys. Lett.* **82**, 1048 (2003); *J. Appl. Phys.* **94**, 5805 (2003). [3] I. Yu. Baranov et al., *Russ. J. Inorg. Chem.* **41**, 1819 (1996). [4] H. Ohta et al., *Adv. Funct. Mater.* **13**, 139 (2003).

#### 4:30 PM E2.9

**Carrier transport of extended and localized states in InGaO<sub>3</sub>(ZnO)<sub>5</sub>.** Kenji Nomura<sup>1,2</sup>, Hiromichi Ohta<sup>2</sup>, Kazushige Ueda<sup>1</sup>, Toshio Kamiya<sup>1,2</sup>, Masahiro Hirano<sup>2</sup> and Hideo Hosono<sup>1,2</sup>; <sup>1</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; <sup>2</sup>Hosono Transparent Electro-Active Materials Project, JST, Kawasaki, Japan.

Several optoelectronic devices have been developed based on transparent oxide semiconductors (TOSs), which include ultraviolet light emitting diode (UV-LED) and transparent field-effect transistor (TFET). Recently we reported that TFETs fabricated in single-crystalline InGaO<sub>3</sub>(ZnO)<sub>5</sub> film showed good performances such as normally-off characteristics and a large field-effect mobility of ~ 80 cm<sup>2</sup>(Vs)<sup>-1</sup> [1]. It is important to know carrier transport mechanisms in order to design and attain high performance devices. However, as it is difficult to control carrier concentration down to intrinsic level in many TOSs, intrinsic carrier transport properties would be masked by the high-density carriers. In addition, it had not been possible to obtain single-crystalline films of InGaO<sub>3</sub>(ZnO)<sub>m</sub> (m=integer) homologous compounds. In this work, we have investigated carrier transport in InGaO<sub>3</sub>(ZnO)<sub>5</sub> using single-crystalline films. Unlike other well-known semiconductors such as Si and ZnO, carrier mobility decrease with increasing carrier concentration, insulator-metal transition was observed around the carrier concentration of 10<sup>18</sup> cm<sup>-3</sup>. This would be explained by Anderson localization originating from random distribution of Ga<sup>3+</sup> and Zn<sup>2+</sup> ions. Crystal structure of InGaO<sub>3</sub>(ZnO)<sub>5</sub> is characterized by a periodic layered structure composed of InO<sub>2</sub><sup>-</sup> and GaO(ZnO)<sub>5</sub><sup>+</sup> layers stacked along the (0001) and Ga<sup>3+</sup> and Zn<sup>2+</sup> ions randomly take trigonal bipyramidal and tetrahedral sites, respectively, in the GaO(ZnO)<sub>5</sub><sup>+</sup> layer. Single-crystalline films were fabricated by reactive solid-phase epitaxy [2]. Polycrystalline films were also deposited by conventional pulsed-laser deposition for comparison. Carrier concentration was varied from ~10<sup>14</sup> to 10<sup>19</sup> cm<sup>-3</sup> by reduction under H<sub>2</sub> gas atmosphere at 550 ~ 650 °C. Current-voltage characteristics and Hall effect measurements were performed at temperatures from 20 K to 300 K. Single-crystalline films exhibited different behavior:

variable-range hopping is observed in carrier concentration ( $10^{16}$  cm<sup>-3</sup> films while carrier transport changes to a thermally-activated mechanism, and finally to degenerate conduction at carrier concentrations  $10^{18}$  cm<sup>-3</sup> accompanying with a rapid increase in room temperature Hall mobility from ( $1$  to  $\sim 10$  cm<sup>2</sup>(Vs)<sup>-1</sup>). This behavior is not due to extrinsic effects such due to domain/grain boundaries since polycrystalline films exhibited completely different behavior that is explained by grain-boundary barrier-controlled transport. The above results imply that shallow localized states are formed in the vicinity of conduction band, which would originate from random distribution of Ga<sup>3+</sup> and Zn<sup>2+</sup> ions in the GaO(ZnO)<sub>5</sub><sup>+</sup> layer. [1]K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, and H. Hosono, *Science* **300**, 1269 (2003). [2]H. Ohta, K. Nomura, M. Orita, M. Hirano, K. Ueda, T. Suzuki, Y. Ikuhara and H. Hosono, *Adv. Funct. Mater.*, **13**, 139 (2003).

#### 4:45 PM E2.10

##### Photo-induced magnetism of Pr<sub>0.65</sub>Ca<sub>0.35</sub>MnO<sub>3</sub> in powder and thin films. Otagiri Takanobu<sup>1</sup>, Masato Arai<sup>1</sup>, Masakazu

Kodaira<sup>1</sup>, Osami Yanagisawa<sup>2</sup> and Mitsuru Izumi<sup>1</sup>; <sup>1</sup>Tokyo University of Marine Science and Technology, Laboratory of Applied Physics, Koto-ku, Tokyo, Japan; <sup>2</sup>Maritime Technology, Yuge National College of Maritime Technology, Yuge, Ehime, Japan.

Intensively, application of the photo-induced magnetism in perovskite manganese oxide for the photo-magnetic advanced device are in full progress. The photo-induced magnetism was originally found in Pr<sub>0.65</sub>Ca<sub>0.35</sub>MnO<sub>3</sub> powder sample by the ESR and x-ray diffraction studies. However, mechanism of the photo-induced magnetism was under cover for long time. Now, D.C. magnetization measurement under a near infrared pulse laser irradiation with photon energy  $h\nu$  of 1.17 eV, laser average power of 10  $\mu$ W, and pulse repetition rate of 1 MHz reveal the mechanism of photo-induced magnetism. The D.C. magnetization prominently increases (approximately 7 %) under the laser irradiation, especially around 90 K which is near to the canted antiferromagnet - antiferromagnet (CAF - AF) transition. It is worth to notice that a peak for the CAF - AF transition in the temperature dependence of D.C. magnetization under the laser irradiation does not show any shift. This fact indicates the photo-induced magnetism is not due to thermal heating of the laser irradiation. The result is consistent with the ESR and x-ray diffraction studies and indicates that the canted antiferromagnet - ferromagnet transition is caused associating with the charge-order - charge-delocalize transition (insulator - metal transition) by the laser irradiation. As the second step for development, Pr<sub>0.65</sub>Ca<sub>0.35</sub>MnO<sub>3</sub> thin films were prepared by the off-axis RF magnetron sputtering deposition in which target and sample holder are perpendicular, which is respected less resputtering for deposited thin films. The LaAlO<sub>3</sub> (LAO) (001) substrate that lattice constant is close to the Pr<sub>0.65</sub>Ca<sub>0.35</sub>MnO<sub>3</sub> one provides better texture than the SrTiO<sub>3</sub> (STO) (001) substrate. Preparing at high deposition temperature provides better texture of the thin film. An annealing process at 1000°C in O<sub>2</sub> gas enhances the quality of thin films. The off-axis geometry provides better texture of the thin film than the on-axis geometry in which target and sample holder is parallel since peak intensity increases prominently in x-ray diffraction profile at room temperature. The peak for the CAF - AF transition in the temperature dependence of D.C. magnetization of the thin film prepared with off-axis geometry is situated at 90 K and near to powder sample at 90 K than one prepared with on-axis geometry at 80 K. The ESR profile for the thin film prepared with the off-axis geometry is much similar to one prepared with the on-axis geometry. There are striking feature in the temperature dependence of D.C. magnetization and the ESR profile for the thin film under the near infrared laser irradiation. The detail of this effect will be reported in the meeting.

SESSION E3: Magnetic Oxide Nanostructures

Chair: Supratik Guha

Thursday Morning, April 15, 2004

Room 2000 (Moscone West)

#### 8:30 AM \*E3.1

##### Integration of Semiconductor Devices with Oxide Electronics.

Hiroshi Fujioka, <sup>1</sup>Department of Applied Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo, Japan; <sup>2</sup>Kanagawa Academy of Science and Technology, Takatsu, Kawasaki, Kanagawa, Japan.

We have investigated a possibility for integration of semiconductor devices with oxide electronics using heteroepitaxial growths of semiconductors on oxide substrates. For this purpose, we developed a UHV cluster process system which consists of a solid source MBE chamber for III-V compound semiconductors, an e-beam MBE chamber for Si, two PLD chambers for oxides and nitrides, and XPS.[1-4] We grew typical semiconductors (GaAs, Si, and GaN) on

various single crystalline oxides such as STO, LSAT, NGO, LGO, MnZn ferrite, LiNbO<sub>3</sub>, YSZ, and MnO. Characterization of the semiconductor films was performed with in-situ RHEED, semi-in-situ XPS, AFM, high resolution XRD, synchrotron radiation surface diffraction, photoluminescence, and X-ray reflectivity measurements. We have found that it is indeed possible to grow the typical semiconductors on these substrates. However, their crystalline quality was poor mainly due to the oxidation reactions of semiconductors at the early stage of the film growths. To solve this problem, we have tried to insert an AlN buffer layer, which does not have oxygen atoms as components, at the semiconductor/oxide interface. We have found that the use of the AlN buffer layer improves the crystalline quality and the surface morphology dramatically. XPS and X-ray reflectivity measurements have revealed that the out-diffusion of atoms from the substrates into the semiconductor films is also suppressed by the use of the AlN buffer layers. Strong near-band-edge photoluminescence has been also observed from GaN grown on these substrates. These results indicate that the present technique makes it possible to integrate conventional single-crystalline semiconductor devices with the electronic, magnetic, and optical oxide devices. [1] H. Fujioka, J. Ohta, H. Katada, T. Ikeda, Y. Noguchi, and M. Oshima, *Journal of Crystal Growth*, **229**, 137 (2001). [2] J. Ohta, H. Fujioka, S. Ito, and M. Oshima, *Applied Physics Letters*, **81**, 2373 (2002). [3] J. Ohta, H. Fujioka, M. Oshima, K. Fujiwara, and A. Ishii, *Applied Physics Letters* **83**, 3075 (2003). [4] J. Ohta, H. Fujioka, and M. Oshima, *Applied Physics Letters*, **83**, 3060 (2003).

#### 9:00 AM E3.2

##### Epitaxial La<sub>0.67</sub>(Sr,Ca)0.33MnO<sub>3</sub> Films on Si for IR Bolometer Applications. Alexander M Grishin<sup>1</sup>, Sergey I

Khartsev<sup>1</sup>, Joo-Hyung Kim<sup>1</sup> and Jun Lu<sup>2</sup>; <sup>1</sup>Condensed Matter Physics, Royal Institute of Technology, Stockholm-Kista, Sweden; <sup>2</sup>Materials Science, Uppsala University, Uppsala, Sweden.

La<sub>0.67</sub>(Sr,Ca)0.33MnO<sub>3</sub> (LSCMO) films have been grown by a pulsed laser deposition technique on Si(001) substrates buffered with Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>/CeO<sub>2</sub>/YSZ heteroepitaxial layers. X-ray diffraction showed cube-on-cube growth of an epitaxial Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>/CeO<sub>2</sub>/YSZ/Si heterostructure whereas the LSCMO layer growth in the "diagonal-on-side" manner on top of the Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> template. Out-of-plane and in-plane lattice parameters have been calculated to determine mismatch strain in the multilayer stack. High resolution TEM images have revealed sharp interfaces between the template layers and LSCMO film as well as rare misfit dislocations on the CeO<sub>2</sub>/YSZ interface. There were no traces for the interdiffusion. Temperature coefficient of resistivity (TCR) is the main material parameter for bolometer applications. The maximum TCR = 4.4%/K and colossal magnetoresistance 2.9%/K have been reached at 294 K. This was achieved due to successive improvement of c-axis orientation of the layers: Full widths at half-maximum 0.65, 0.58, 0.65, 1.13, and 0.18 degrees in LSCMO/BTO/CeO<sub>2</sub>/YSZ/Si stack, respectively. As a prototype of an uncooled bolometer, heteroepitaxial CMR structure on Si demonstrates, at 294 K, the noise equivalent temperature difference of 1.2  $\mu$ K/(Hz)<sup>1/2</sup>@30Hz.

#### 9:15 AM E3.3

##### Pulsed laser deposition of manganites films with in situ reflection high energy electron diffraction from non-stoichiometric targets. Antonello Tebano,

Giuseppe Balestrino, Massimo Angeloni, Norberto Boggio and Pier Gianni Medaglia; COHERENTIA-INFM, Ing. Meccanica, Universita Roma Tor Vergata, Roma, Italy.

Pulsed laser deposition (PLD) has been shown to be a powerful technique for the deposition of thin films and heterostructures of complex oxides. Furthermore, the in-situ use of reflection high energy electron diffraction (RHEED) can allow to control the thickness of the deposited layers at the level of a single unit cell, which is a crucial requirement for many practical applications such as tunnel devices. However, the in-situ use of RHEED requires a sufficiently low growth oxygen pressure (typically < 10<sup>-4</sup> mbar). Under these gas pressure conditions the ablation process from multi-element targets can result in segregation effects among the different elements: heavy species are more focused along the jet axis (perpendicular to the substrate surface) than light species. This segregation effect has immediate consequences on the composition of the deposited film. This effect is of particular relevance if the component species are very different in atomic weight, which is the case of manganite targets. As a result the physical properties of deposited films can be severely affected. Here we show that stoichiometric films with excellent transport and magnetic properties can be grown, at low oxygen pressure with in-situ RHEED, using targets whose stoichiometry has been adjusted to compensate the segregation effects. This approach can be very useful for the PLD deposition of manganites based heterostructures where the control of the deposited layer at a level of a single unit cell is mandatory.

### 9:30 AM E3.4

#### Structural and Electrical Properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ Thin Films for Tunable Microwave Applications.

Sriraj G Manavalan<sup>1,2</sup>, A.K. Sikder<sup>3</sup>, Ashok Kumar<sup>2,3</sup> and T.

Weller<sup>1</sup>; <sup>1</sup>Department of Electrical Engineering, University of South Florida, Tampa, Florida; <sup>2</sup>Nanomaterials and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; <sup>3</sup>Department of Mechanical Engineering, University of South Florida, Tampa, Florida.

The dependence of dielectric permittivity on the applied electric field and high dielectric constant makes barium strontium titanate (BST) as a promising ferroelectric material for applications in tunable microwave devices like filters, phase shifters and resonators. High tunability and low dielectric loss are desired for tunable microwave devices. The primary objective of this research is to optimize the tunability and dielectric loss of BST thin films at microwave frequencies with different deposition and annealing conditions.  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  thin films were grown on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates by both pulsed laser deposition (PLD) and sputtering technique. Platinum was deposited on top of the BST films using lithography technique in order to make the top electrode. The electrical measurements were achieved in the parallel plate capacitor configuration with Pt as the top and bottom electrode. The microstructure and phase analysis of the BST films were performed using X-ray diffraction (XRD) method. XRD results show that the BST(110) peak is the most intense and the BST(100), (200) and (211) peaks are less intense. The diffraction patterns are attributed to cubic (perovskite) crystal system. The analysis of surface morphology is done using atomic force and scanning electron microscopy. Results of structural and surface analysis, tunability and loss tangent as a function of deposition temperature, oxygen pressure and annealing temperature will be discussed. The optimized structural and dielectric properties of thin films deposited using both the techniques will also be compared.

### 9:45 AM E3.5

#### Preparation of epitaxial perovskite manganese oxide thin films by an excimer laser metal organic deposition (ELMOD) process at low temperature. Tetsuo Tsuchiya<sup>1</sup>, Tsutomu

Yoshitake<sup>2</sup>, Yuichi Shimakawa<sup>2</sup>, Iwao Yamaguchi<sup>1</sup>, Takaaki Manabe<sup>1</sup>, Toshiya Kumagai<sup>1</sup>, Yoshimi Kubo<sup>2</sup> and Susumu Mizuta<sup>1</sup>; <sup>1</sup>National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; <sup>2</sup>Fundamental Research Laboratories, NEC Corporation, Tsukuba, Japan.

Perovskite manganese oxides materials such as  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSMO) have attracted a great deal of attention due to their electrical and magnetic properties. However, the fabrication of LSMO films is required for the heat treatment at higher than 800 degrees, it is difficult to fabricate them in a Si devices. In this paper, to lower the fabrication temperature, we examined the preparation of LSMO films on LAO and STO substrates using an excimer laser metal organic deposition (ELMOD) process. Metal(La,Sr,Mn)-naphthethenate solutions was spin-coated onto single-crystal LAO (001) and STO(001) substrates at 4000rpm. The MO coated films were dried at 200 degrees in air, were then heated and kept in the constant temperature range of 400, and 500 degrees for 10min, and then irradiated by an ArF excimer laser while being heated. The obtained films were characterized by the IR, XRD ( $\Theta$ -2  $\Theta$ scans, and pole-figure analysis), SEM, AFM and DC four-probe method. In the case of using a STO substrate, (00C) oriented LSMO films were obtained by the ArF laser irradiation in the fluence ranges from 50 to 90mJ/cm<sup>2</sup> at 500 degrees. On the other hand, in the case of using a LAO substrate, (00C) oriented LSMO films were obtained by the ArF laser irradiation in the fluence ranges from 100 to 130mJ/cm<sup>2</sup> at 500 degrees. Both their (00C) oriented films on the STO and the LAO substrates were found to be epitaxially grown based on XRD pole figure measurements. In the case of using a conventional pyrolysis process, epitaxial LSMO films were obtained above 800 degrees on a STO and LAO substrates. Thus, the ELMOD process was found to be effective for lowering the fabrication temperature. Also, the temperature dependence of the resistance and TCR (temperature coefficient of resistance) of the LSMO films prepared by the ELMOD at different conditions was investigated from 310K to 100K. As a result, the resistance of LSMO film 80nm in thickness that was irradiated by the ArF laser at a fluence of 100mJ/cm<sup>2</sup> for 60min showed metallic temperature dependence, and the maximum temperature coefficient of resistance (TCR) of the film was 3.4% at 265K. The detailed experiment results will be described in presented paper. This study was supported by the Industrial Technology Research Grant Program in 2003 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

### 10:30 AM E3.6

#### Preparations and Evaluations of Magnetoelectric Thin Films for Josephson Field Effect Transistor. Nobuyuki Iwata, Koji

Matsuo, Noriaki Otuska and Hiroshi Yamamoto; Electronics & Computer Science, College of Science and Technology, Nihon University, Chiba, Japan.

Since the discovery of high T<sub>c</sub> superconducting oxides, various kinds of superconducting three-terminal devices have been developed. However, the change of I<sub>c</sub> and/or T<sub>c</sub> are not so large. In order to achieve the large modulation of I<sub>c</sub> and/or T<sub>c</sub>, we proposed a novel Josephson field effect transistor (JFET) by adopting the magnetoelectric (ME) materials as a gate insulator. We named it Josephson ME field effect transistor (JMEET). Magnetoelectric materials are characterized by the appearance of induced magnetization with electric field applied, and the appearance of induced electric polarization with magnetic field applied. In JMEET device large I<sub>c</sub> modulation was expected as the induced magnetic field, controlled by electric field, penetrated through the Josephson junction. We chose an antiferromagnetic insulator, Cr<sub>2</sub>O<sub>3</sub>, which is a representative among ME materials. Induced magnetic field was calculated at 42 gauss, assuming that the electric field of 1 MV/cm was applied to single crystalline Cr<sub>2</sub>O<sub>3</sub> along the c-direction at room temperature. Josephson junctions are generated by self-assembled grain boundaries due to large lattice mismatch between YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> (YBCO) and MgO substrate. Thin films of Cr<sub>2</sub>O<sub>3</sub> were grown on ITO substrates by off-axis RF magnetron sputtering method without substrate heating. Target was sintered Cr<sub>2</sub>O<sub>3</sub>. The sputtering gas pressure and RF power were 2.0 Pa (100% Ar) and 100W. The YBCO thin films were grown on MgO substrates by off-axis DC-RF magnetron sputtering method. MgO substrates were annealed in air at 1000 degree C for 4 h in advance. Temperature at the side of the substrate holder was 800 degree C. Sintered YBCO target was sputtered with RF power of 50W and DC current of 0.3A. Sputtering atmosphere was 26 Pa with the flow rate of 45 cc in Ar and O<sub>2</sub> (Ar : O<sub>2</sub> = 1 : 1). From the I-V characteristic of the Cr<sub>2</sub>O<sub>3</sub> thin film, leakage current was 5.2\*10<sup>-3</sup> A/cm<sup>2</sup> at 0.28 MV/cm. Below 0.3 MV/cm, grown Cr<sub>2</sub>O<sub>3</sub> worked as a gate insulator. Induced magnetic field calculated at 0.3 MV/cm was 1.26 gauss at the junction area, assuming that the linear magnetoelectric susceptibility of Cr<sub>2</sub>O<sub>3</sub> was 10<sup>-6</sup> and the area ratio of Josephson junctions to superconducting grains was 1/100. Such the value was sufficient to modulate the I<sub>c</sub> down to zero. The YBCO thin films with thickness of 50 nm and 200 nm showed the T<sub>c</sub> of 77 K and 92 K, respectively. Grain boundaries with the depth of about 35 nm were observed. The ME field effect to the Josephson junctions will be discussed.

### 10:45 AM E3.7

#### Evaluation of AlO<sub>x</sub> in Co/AlO<sub>x</sub>/Co spin tunneling junctions by XPS. Yuki Otaka, Hideo Kaiju, Mao Nishiyama, Naoki Sakaguchi and Kazuo Shiiki; Department of Applied Physics and Physico-Informatics, Keio University, Yokohama, Japan.

Properties of spin tunneling junctions depend on their insulator, so it is very important to investigate oxidation states of the insulator. In this study, oxidation states of AlO<sub>x</sub> in Co/AlO<sub>x</sub>/Co spin tunneling junctions were studied using X-ray photoelectron spectroscopy. Co/AlO<sub>x</sub>/Co spin tunneling junctions were fabricated on glass substrates by ion-beam mask sputtering. The Al layers were deposited in various thicknesses and were oxidized in pure O<sub>2</sub> gas for 24 hours. Co/AlO<sub>x</sub> bilayers simultaneously fabricated were measured by XPS. We have determined the thickness of the AlO<sub>x</sub> layer and the residual Al layer from the Co 2p peak and the metallic and oxidic Al 2p peaks. The photoelectron inelastic mean free paths were calculated from TPP-2M formula[1]. The thicker the Al layer is deposited, the more the unoxidized Al remains. TMR ratio of junctions increased as the unoxidized Al decreased, and this result is qualitatively in agreement with the LMTO calculation result. However, TMR ratio becomes small when the deposited Al layer is very thin. It is confirmed that this is due to the leakage current. The O/Al ratio of AlO<sub>x</sub> layer is about 1.9, which means existence of higher order oxides than Al<sub>2</sub>O<sub>3</sub>. XPS depth profiles showed that the unoxidized Al remains mostly near the interface with Co when the deposited Al layer is thin. Furthermore, two peaks appear in metallic Al depth profiles as deposited Al layer thickness becomes thick. It is thought that two different oxidation states exist from this result. [1] S. Tanuma, C. J. Powell, D. R. Penn: Surf. Interface. Anal., **11**, 57 (1988) **17**, 911 (1988).

### 11:00 AM \*E3.8

#### Combinatorial Integrations of Oxide Field Effect Transistors. Akira Ohtomo<sup>1</sup> and Masashi Kawasaki<sup>1,2</sup>; <sup>1</sup>Institute for Materials Research, Tohoku University, Sendai, Japan; <sup>2</sup>COMET, National Institute for Materials Science, Tsukuba, Japan.

Oxide electronics is of increasing interest due to a broad range of intriguing physical properties inaccessible by conventional semiconductors. In the last decade, there has been remarkable progress making novel devices such as high-T<sub>c</sub> Josephson junctions, perovskite manganite tunneling magnetoresistance junctions, and ZnO ultraviolet lasers with an aid of advanced oxide epitaxy technique.



Despite significant research going into these advantages, oxygen nonstoichiometry and lower materials purity ( $< 4N$ ) limits current capability of carrier doping control comparable to that of semiconductor electronics. In this context, we have been studying field effect doping instead of the substitutional chemical doping, also aiming at new class of field effect transistors (FETs) for wide-gap oxide semiconductors such as ZnO and SrTiO<sub>3</sub>. Here, major confronted issue is the difficulty in controlling electronic properties at the heterointerfaces between electronically and chemically dissimilar materials, especially at the interfaces between channels and insulators. This issue can be efficiently studied by using combinatorial approach, where various heterostructures are simultaneously integrated in one chip by pulsed laser depositions of multi targets with use of *in-situ* mobile stencil masks. We have tested dozens of materials for buffer layers between gate insulators and ZnO channel to discover CaHfO<sub>3</sub> as a robust buffer for achieving high-mobility polycrystalline ZnO FET ( $> 7 \text{ cm}^2/\text{Vs}$ ).<sup>1</sup> In the latter case, FETs having LaAlO<sub>3</sub>/SrTiO<sub>3</sub> epitaxial heterostructure have been investigated. Using combinatorial approach, carrier generation arising from valence mismatch across the interface could be controlled by inserting fractional atomic layer of SrO between LaAlO<sub>3</sub> layer and TiO<sub>2</sub>-terminated SrTiO<sub>3</sub> substrate.<sup>2</sup> Metallic conductivity has been observed in the electron-accumulated channel at temperatures down to 100 K. <sup>1</sup> J. Nishii *et al.* Jpn. J. Appl. Phys, **42** L347 (2003). <sup>2</sup> J. Nishimura *et al.* submitted to Appl. Phys. Lett.

### 11:30 AM E3.9

**High mobility nanocrystalline indium doped zinc oxide deposited at room temperature by rf magnetron sputtering.**  
Elvira Maria Correia Fortunato, Ana Pimentel, Alexandra Goncalves, Antonio Marques and Rodrigo Martins; Materials Science, FCT-UNL, Caparica, Portugal.

Transparent Conductive Oxides (TCO) has been study for more than a half of century and is still under investigation in several laboratories around the world. One of the major issues related to these materials are the increase on the electrical conductivity and also the increase on the optical transmittance, especially in the visible part of the spectra. Nevertheless the obtained values for optical transmittance around 90% are difficult to increase, because we are close to the theoretical optical limits of these oxides. The other possibility is by reducing the electrical conductivity ( $s$ ). Concerning this point and since  $s = qNm$ , the only way to achieve such goal is by increasing the carrier concentration ( $N$ ) or the electron mobility ( $m$ ). The carrier concentration is limited to the maximum solid solubility of the dopant, while the electron mobility depends more on the structural defects, grain size and also on the dopant concentration. In this paper we present results of indium-doped zinc oxide deposited at room temperature by rf magnetron sputtering, with electron mobility as high as  $60 \text{ cm}^2/\text{Vs}$ . The films present a resistivity as low as  $5 \times 10^{-4} \text{ Wcm}$  with an optical transmittance of 85%. Concerning the structural properties exhibited by these films, they present an amorphous-like diffraction pattern, while the surface morphology is very smooth and uniform, which is a very important property for ensuring long life time in display devices.

### 11:45 AM E3.10

**Magnetic and transport properties of Fe<sub>3</sub>O<sub>4</sub> nanostructures.**  
Li Hongliang<sup>1,2</sup> and Wu Yihong<sup>1,2</sup>; <sup>1</sup>Data Storage Institute, DSI Building, 5 Engineering Drive 1, Singapore 117608, Singapore, Singapore; <sup>2</sup>Department of Electrical and computer engineering, national university of singapore, singapore, Singapore.

Recently, magnetite (Fe<sub>3</sub>O<sub>4</sub>) has been extensively studied due to its half-metallic property and possible applications in spintronic devices. We report the magnetic and transport properties of Fe<sub>3</sub>O<sub>4</sub> films grown by molecular beam epitaxy with molecular oxygen on sapphire (0001) substrates. The magnetic and transport properties of thin film magnetite are investigated using X-ray diffraction, VSM, AFM and SQUID. The thin film exhibit a negative magnetoresistance resulting from the field-dependent hopping rate of electron from Fe<sup>2+</sup> and Fe<sup>3+</sup> which is enhanced due to the alignment of their moment by an applied magnetic field. At the same time, the magnetic and electric transport properties of one-dimension Fe<sub>3</sub>O<sub>4</sub> nanowires with different diameters have also been studied for the first time. Until now, one-dimensional half-metal structure has rarely been studied. We report that a new method of half-metal nanowires fabrication based on Fe<sub>3</sub>O<sub>4</sub> thin film. Firstly, Nickel nanowires fabricated with electrodeposition is placed on Fe<sub>3</sub>O<sub>4</sub> thin film as hard mask; Then, the thin film is etched out with ion milling until all the Fe<sub>3</sub>O<sub>4</sub> disappears except for the place covered by Ni nanowire; Thirdly, four-probe electrodes is fabricated with laser writer; Because the Ni nanowire is about 200nm, the Fe<sub>3</sub>O<sub>4</sub> is about 300nm; Based on this nanowire, we continue to etch the nanowire using FIB. Now we can get different diameter nanowires as thin as about 50nm. The nanowires also exhibit a negative magnetoresistance, which decreases with decreasing the diameter. However, unusual electric transport was found in the nanowire current-voltage curves,

which may result from the Fe<sub>2</sub>O<sub>3</sub> impurity phase or reduced dimensions

## SESSION E4: Functional Nanostructures

Chair: Alexander Grishin

Thursday Afternoon, April 15, 2004

Room 2000 (Moscone West)

### 1:30 PM \*E4.1

**Atomic Scale Interface Characterization.** Maria Varela<sup>1</sup>, Andrew Lupini<sup>1</sup>, Jacobo Santamaria<sup>3</sup>, Vanessa Pena<sup>3</sup>, Z Sefrioui<sup>3</sup>, Alberto Franceschetti<sup>2,1</sup>, Sokrates Pantelides<sup>2,1</sup> and Stephen Pennycook<sup>1,2</sup>; <sup>1</sup>Oak Ridge National Lab, Oak Ridge, Tennessee; <sup>2</sup>Vanderbilt University, Nashville, Tennessee; <sup>3</sup>Universidad Complutense de Madrid, Madrid, Spain.

Integration of the many promising oxide materials is a challenging issue for future device development. It requires understanding and tuning of the interfacial atomic and electronic structure to achieve the desired macroscopic properties. The scanning transmission electron microscope is ideally suited to this task, providing Z-contrast imaging and electron energy loss spectroscopy (EELS) at atomic resolution. With the recent introduction of aberration-correction, images now show greatly improved contrast and signal to noise ratio, sufficient to allow sensitivity down to the single atom level in both imaging and spectroscopy. Examples will be shown of charge-ordered stripes and grain boundaries in manganites, where EELS shows not only composition but also the local magnetic state of the Mn. Interfaces between superconducting and insulating or magnetic oxides in superlattice device structures have also been probed by EELS, and significant differences in hole concentration profiles are seen.

### 2:00 PM E4.2

**Nanoetching of metallic perovskites using STM.** Oystein Dahl<sup>1</sup>, Svein Hallsteinsen<sup>2</sup>, Jostein Grepstad<sup>1</sup>, Anne Borg<sup>2</sup> and Thomas Tybell<sup>1</sup>; <sup>1</sup>Department of Physical Electronics, Norwegian University of Science and Technology, Trondheim, Norway; <sup>2</sup>Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway.

In the present work we use scanning tunneling microscopy (STM) to modify the surface structure of epitaxial SrRuO<sub>3</sub> thin films. The goal is to create templates for direct growth of laterally confined complex oxide nanostructures. Point and line etching experiments were carried out both in air, using Pt-Ir tips, and in UHV, using tungsten tips. We present extensive data on the effect of writing voltage, tunneling current and pulse length applied in this etching. In UHV and at small bias voltages, no change was observed beyond the formation of small mounds on the SrRuO<sub>3</sub> surface. For voltages in excess of 4V, etched structures were found along with these mounds. Moreover, well-defined line etching was achieved with a typical depth of approximately one unit cell. Experiments in air showed increased sensitivity to the etching parameters, as compared in UHV, e.g. the threshold voltage for effective etching was reduced from 4V to 2.5V. Controlled line etching was demonstrated, as for etching in UHV. The experiments demonstrate that an STM can be used for patterning of epitaxial thin films of SrRuO<sub>3</sub>, and structures as small as 5nm were obtained routinely. These results are encouraging for the development of nanoscale-engineered templates.

### 2:15 PM E4.3

**Control Growth of Well-aligned ZnO Nanowire Arrays and ZnO Nanoribbons with a Simple Double-tube System.**  
Geng Chunya, Liu Yingkai, Yao Yuan, Zapien Juan Antonio, Lee Chun Sing, Lifshitz Yeshayahu and Lee Shuit Tong; Department of Physics and Material Science, City University of Hong Kong, Hong Kong, Hong Kong.

Arrays of well-aligned single-crystal zinc oxide (ZnO) nanowires of uniform diameter and length have been synthesized on (100) silicon substrate via a simple horizontal double-tube system. ZnO nanoribbons can also be obtained with this system by adjusting the experimental parameters, such as mixing oxygen into the carrying gas. Double-tube structure makes the reaction vapor environment form a local balance and steady state, also benefits the high concentration and low flow rate of reaction vapor, which are not available in traditional chemical vapor transport and condensation method, while quite necessary to synthesize the aligned nanowire arrays and nanoribbons. X-ray diffraction and transmission electron microscopy (TEM) characterizations showed the single-crystal hexagonal wurtzite structure. Raman spectra revealed phonon quantum confinement effect. Photoluminescence exhibited strong ultra-violet emission at 3.29 eV under 355 nm excitation and green emission at 2.21 eV under 514.5 nm excitation. The growth mechanisms of different ZnO nanostructures are discussed. The present growth technique would be of particular interest in the current silicon-technology-based

optoelectronic devices.

### 2:30 PM E4.4

**Guided control of  $\text{Cu}_2\text{O}$  nanodot self-assembly on  $\text{SrTiO}_3$  (100).** Yingge Du<sup>1</sup>, Surajit Atha<sup>1</sup>, Robert Hull<sup>1</sup>, James Groves<sup>1</sup>, Igor Lyubnitsky<sup>2</sup> and Donald Baer<sup>2</sup>; <sup>1</sup>Material Science and Engineering, University of Virginia, Charlottesville, Virginia; <sup>2</sup>Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington.

A method has been developed for specifying the growth location of  $\text{Cu}_2\text{O}$  nanodots on  $\text{SrTiO}_3$  (100) substrates. Growth location has been specified by using a focused ion beam (FIB) to modify microscopic or nanoscopic regions of the  $\text{SrTiO}_3$  substrate prior to  $\text{Cu}_2\text{O}$  deposition. Deposition onto the modified regions under carefully selected process conditions has generated nanodot growth at the edge of microscopic FIB-induced features or on top of nanoscopic FIB-induced features. For this work, an array of evenly spaced FIB implants was first patterned into several regions of each substrate. Within each region, the FIB implants were identical in Ga<sup>+</sup> energy and dosage and implant diameter and spacing. After FIB surface modification and subsequent in-situ substrate cleaning,  $\text{Cu}_2\text{O}$  nanodots were synthesized on the patterned  $\text{SrTiO}_3$  substrates using oxygen plasma assisted molecular beam epitaxy. The substrates and nanodots were characterized using atomic force microscopy at various stages of the process; in-situ X-ray photoelectron spectroscopy and Auger electron spectroscopy analysis demonstrated that the final phase of the nanodots was  $\text{Cu}_2\text{O}$ . Quantitative methods have been employed to confirm the relationship between FIB implant region and  $\text{Cu}_2\text{O}$  nanodot growth location. The technological implications of these research results appear to be significant. The photocatalytic decomposition of water on  $\text{Cu}_2\text{O}$  under visible light irradiation has been reported in the literature. Such breakdown could be an efficient, clean means of producing hydrogen for fuel cells. If the  $\text{Cu}_2\text{O}$  is located in the form of islands on a carefully selected substrate, e.g.  $\text{SrTiO}_3$ , then the efficiency of the photochemical process can be greatly enhanced. By patterning metal oxide islands in a dense, patterned array, the efficiency of engineered devices can be increased. Additionally, the ability to define metal oxide nanodot growth location has broad implications for incorporating such nanostructures into next generation nanoelectronic and spintronic devices.

### 2:45 PM E4.5

**Integration of Magnetoresistive  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  Oxide Thin Films with Silicon.** D. Kumar<sup>1</sup>, J. Sankar<sup>1</sup>, J. Narayan<sup>2</sup>; <sup>1</sup>Center for Advanced Materials and Smart Structures, North Carolina A & T State University; <sup>2</sup>Department of Materials Science and Engineering, North Carolina State University.

The huge magnetoresistance of perovskite based manganites has a serious drawback due to the need of large magnetic fields to obtain such large changes of the resistance. This fact is an important handicap since many of their potential applications require a good response in the low field regime. The difficulty in growing the colossal magnetoresistive films on technologically important Si substrates, which arises due to lattice mismatch and chemical reaction between the film and substrate, has also prevented a direct integration of manganite materials based memory devices with existing Si-based microelectronic devices. It is in this context that we have tried to deposit  $(\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3)$  LCMO films on Si substrates by means of a multilayered thin film buffer layer. The multilayered thin film buffer layer consists of TiN, MgO, and  $\text{SrTiO}_3$  (STO) layers. The selection of this combination of multilayered buffers layers was inspired due to the following reasons: (i) TiN can be grown epitaxially at low temperatures on Si substrates by domain matching; four lattice constants of TiN are well matched with three of Si (see Table I), (ii) TiN has good lattice match with MgO, which in turn, has good lattice match with STO and LCMO. MgO and STO layers are used as intermediate layers between LCMO and TiN in order to control oxidation and lattice mismatch between the top and bottom layer, (iii) TiN provides a good diffusion barrier and templates for subsequent epitaxial layers, and (iv) integration of CMR with Si can become possible as TiN is highly metallic. Our results have shown that LCMO films on buffered Si substrates are indeed epitaxial and possess good magnetotransport properties.

### 3:30 PM E4.6

**Optical Characteristics of Indium Doped Zinc Oxide Nanorods Grown By Vapor Transport Process.** Joodong Park<sup>1</sup> and Rajiv K Singh<sup>1,2</sup>; <sup>1</sup>Department of Materials Science and Engineering, University of Florida, Gainesville, Florida; <sup>2</sup>Microelectronics Research Center, University of Texas, Austin, Texas.

In situ In-doped ZnO nanorods for applications in nanoscale electronic and optoelectronic devices were synthesized using vapor

transport process at growth temperature ranging from 800 °C to 1050 °C. This process was based on the thermal decomposition and condensation of oxide nanoparticle sources in reducing atmosphere. Using this method, well-aligned single crystalline In-doped ZnO nanorods were successfully synthesized on silicon substrates. Structural and optical properties of as-grown and annealed In-doped ZnO nanorods were investigated in this research. From the observations using field emission scanning electron microscope and transmission electron microscope, single crystalline In-doped ZnO nanorods were grown via vapor-solid (VS) growth mechanism with the diameter ranging from 40 nm to 150 nm and the length up to several micrometers. XRD measurements showed that the In-doped ZnO nanorods exhibited wurtzite hexagonal structures with a preferred growth orientation of <0002> direction. Photoluminescence (PL) spectra of In-doped ZnO nanorods were dominated by near-band-edge emission with negligible deep-level emission.

### 3:45 PM E4.7

**Properties of SrZrO<sub>3</sub> nanowires deposited on rippled SrRuO<sub>3</sub> thin films.** E. Vasco, S. Karthaeuser, Regina Dittmann, J. Q. He, C. L. Jia, K. Szot and R. Waser; Institut fuer Festkoerperforschung, Forschungszentrum Juelich, Juelich, Germany.

The growth mode of epitaxial SrRuO<sub>3</sub> (SRO) thin films pulsed-laser deposited on vicinal SrTiO<sub>3</sub> is expediently modified through a substrate treatment in order to create nanopatterned (rippled) films by self-organization in a step-flow inhibited regime. The so-deposited SrRuO<sub>3</sub> films are used as templates to fabricate arrays of epitaxial nanowires of Cr-doped SrZrO<sub>3</sub> (SZO) which is a promising candidate for resistive switching non-volatile memories [1]. The samples were studied by AFM, x-ray diffraction, RBS and HTREM. AFM-measurements with a conducting tip allow to identify SZO during its first growth stages on basis of the difference between the electrical conductivities of SZO and SRO. Thus, the correlation between the topographic and conducting images corresponding to the same area displays the formation of regular SZO nanowires separated by deep and narrow boundaries that extend up to the conductive buffer layer [2]. HRTEM images reveal the epitaxial nature of the nanowires and RBS investigations prove their stoichiometry. Finally, switching properties of the nanopatterned SZO are investigated by AFM with a conducting tip. [1] A. Beck, J. G. Bednorz, Ch. Gerber, C. Rossel, and D. Widmer, Appl. Phys. Lett. 77, 139 (2000) [2] E. Vasco, S. Karthaeuser, R. Dittmann, J.Q. He, C.L. Jia, K. Szot, and R. Waser, submitted to Appl. Phys. Lett.

### 4:00 PM E4.8

**Fabrication and Characterization of Integrated Piezoelectric Actuator Devices using Highly Textured Lead Barium Titanate Thin Films.** Jennifer Lynn Ruglovsky<sup>1</sup>, Alexandros

Papavasiliou<sup>2</sup>, Matthew Dicken<sup>1</sup>, Mohamed El-Naggar<sup>3</sup>, David Boyd<sup>3</sup>, Stacey Boland<sup>4</sup>, Youngbae Park<sup>1</sup>, David Goodwin<sup>2</sup>, Sossina Haile<sup>3</sup>, Kaushik Bhattacharya<sup>2</sup> and Harry Atwater<sup>1</sup>; <sup>1</sup>Applied Physics, California Institute of Technology, Pasadena, California; <sup>2</sup>Lawrence Livermore National Laboratory, Livermore, California; <sup>3</sup>Mechanical Engineering, California Institute of Technology, Pasadena, California; <sup>4</sup>Materials Science, California Institute of Technology, Pasadena, California.

Traditionally, ferroelectric thin films have polycrystalline microstructures that may affect time-dependent fatigue, piezoelectric coefficients and other microstructure-dependent properties important to ferroelectric device applications, which has motivated investigation of methods to fabricate functional oxide films with high quality, textured ferroelectric active layers. We have fabricated thin film actuator based on 90° domain wall switching, which has potential for high work/volume ratios, high frequency of operation, large displacements, and linear response[1]. The active thin films in these piezoelectric actuators are biaxially-textured  $\text{Pb}_x\text{Ba}_{1-x}\text{TiO}_3$  films formed via epitaxy on biaxially-textured MgO template on amorphous  $\text{Si}_3\text{N}_4$ [2]. Several device structures including membrane, bridge and cantilever structures were fabricated on a single substrate, with features defined by standard photolithography methods. The  $\text{Si}_3\text{N}_4$  was deposited over the entire substrate via CVD. The biaxially-textured MgO was highly textured and showed in-plane distribution of 15 degrees and out-of-plane 8 degrees.  $\text{Pb}_x\text{Ba}_{1-x}\text{TiO}_3$  films were deposited via two methods: metallorganic chemical vapor deposition ( $x=0.9$ ) and sol-gel ( $x=0.5$ ) film synthesis. The  $\text{Pb}_x\text{Ba}_{1-x}\text{TiO}_3$  inherits the texture of the MgO template. Both blanket and interdigitated electrodes allow in- and out-of-plane application of electric field for measurements of film actuation. Device areas of 0.25, 2, and 4 mm<sup>2</sup> are defined as the substrate is back-etched to release the ferroelectric layer structure. The  $\text{Pb}_x\text{Ba}_{1-x}\text{TiO}_3$  films deposited by sol-gel and chemical vapor deposition both exhibited grain-scale domain morphology and microstructure-dependent domain switching, as evidenced by piezoresponse force microscopy. This grain-scale microstructure of the films - ie. texture, grain size, Ba/Pb ratios - will be related to domain

structure and also to the piezoelectric performance of the macroscopic device. Ferroelectric properties of substrate supported, partially supported, and released films will be compared. Finally, quantitative actuation displacements as a function of device size will be presented. [1] Burescu et al, APL 77, (2000) 1698-1700 [2] Brewer et al, APL 80, (2002) 3388

#### 4:15 PM E4.9

**Electron field-emission from nanoporous crystalline electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$  and application to field-emission display device.** Yoshitake Toda<sup>1,2</sup>, Satoru Matsuishi<sup>1,2</sup>, Katsuro Hayashi<sup>2</sup>, Kazushige Ueda<sup>1</sup>, Toshio Kamiya<sup>1,2</sup>, Masahiro Hirano<sup>2</sup> and Hideo Hosono<sup>1,2</sup>; <sup>1</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; <sup>2</sup>Hosono Transparent Electro-Active Materials, Japan Science and Technology Agency, Kawasaki, Kanagawa, Japan.

We report efficient electron emission from a newly-found electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$  with a small apparent work function of 0.6 eV and the room temperature operation of field-emission display (FED) devices. The electron emission properties are discussed in relation with the crystal and electronic structures.  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  (C12A7) is a nano-porous crystal, having twelve positively-charged cages with 0.4 nm in diameter in a unit cell. It may clathrate various active anion species such as  $\text{O}^{2-}$ ,  $\text{O}^-$  and  $\text{H}^-$  in the cages and exhibits unique properties such as photo-induced insulator-to-conductor transition<sup>1</sup>. It is also possible to introduce electrons, which thereby forms the new inorganic electride  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$ <sup>2</sup>. As the electrons are loosely confined in the cages at a high density of  $10^{21} \text{ cm}^{-3}$ , we expect that it is promising for cold electron emitter.

$[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$  single crystal was prepared by a Ca-treatment method<sup>2</sup>. Field emission was measured at  $6 \times 10^{-5} \text{ Pa}$  using a mirror-polished surface to examine the fundamental material properties. The distance between the emitter surface and an extraction electrode was adjusted precisely to be 0.05 mm using a 0.05-mm-thick mica plate with a hole 6 mm in diameter. It was observed that electron emission is controlled by thermionic emission at low extraction voltages, while Fowler-Nordheim (FN) field-emission dominates at voltages higher than 1500 V. The work function was estimated from the thermionic and FN emission models, both of which provide a value of 0.6 eV. The electronic structure was also investigated by UPS, which gives a larger work function value of 3.7 eV. We tentatively consider that the discrepancy in the work function arises from surface band-bending. In FED devices, sodium salicylate or ZnO:Zn were used for phosphor, and emitter surfaces were roughened to earn emission current. These devices display bright light emission clearly visible in typical ambient light at extraction voltages > 800 V. <sup>1</sup> Hayashi K. et al., Nature 419, 462-465 (2002) <sup>2</sup> Matsuishi S. et al., Science 301, 626-629 (2003).

#### 4:30 PM E4.10

**Two-dimensional electronic structures in layered oxychalcogenide semiconductors,  $\text{LaCuOCh}$  (Ch=S, Se, Te) and  $\text{La}_2\text{O}_2\text{CdSe}_2$ .** Toshio Kamiya<sup>1,2</sup>, Kazushige Ueda<sup>1</sup>, Hidenori Hiramatsu<sup>2</sup>, Hiromichi Ohta<sup>2</sup>, Masahiro Hirano<sup>2</sup> and Hideo Hosono<sup>1,2</sup>; <sup>1</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; <sup>2</sup>Hosono Transparent Electro-Active Materials, ERATO, Japan Science and Technology Agency, Kawasaki, Japan.

Low-dimensional systems have been studied intensively because novel properties are expected originating from quantum confinement or size effects. Such systems have been fabricated artificially so far, e.g. by alternate stacking of thin layers using molecular-beam epitaxy. We have proposed an alternative idea to utilize nanostructures naturally-formed in periodic crystal structures of materials. Oxychalcogenides  $\text{LaCuOCh}$  (Ch=S, Se, Te) are such systems, where  $(\text{La}_2\text{O}_2)^{2+}$  and  $(\text{Cu}_2\text{Ch}_2)^{2-}$  layers are stacked alternately along the c-axis, forming layered periodic structures. They exhibit exceptional electronic and optical properties such as p-type degenerated conduction (1) and sharp blue-light emission originating from room-temperature excitons (2), which are thought to relate with the two-dimensional layered structure. In this paper, we report the electronic structures of  $\text{LaCuOCh}$  calculated by an ab-initio method. Electronic structure of another layered oxychalcogenide  $\text{La}_2\text{O}_2\text{CdSe}_2$  was also examined for comparison.  $\text{LaCuOCh}$  and  $\text{La}_2\text{O}_2\text{CdSe}_2$  epitaxial films were prepared on MgO (001) by reactive solid-phase epitaxial (3). Optical absorption spectra were measured to examine electronic structures experimentally. Electronic structures and optical dielectric functions were calculated with the Wien2k code (4) using PBE96 GGA functional. Relativistic calculations were performed to incorporate spin-orbit interaction. The optical absorption spectra displayed step-wise structures with sharp absorption peaks almost on the step edges for  $\text{LaCuOCh}$ . The energy split between the lowest two absorption peaks increases as Ch is changed from S to Se, and to Te. The energy split calculated were 8 meV, 100 meV and 290 meV for S,

Se and Te, respectively, which are in good agreement with the observation and indicate that the energy split originates from the spin-orbit interaction in the Ch anions. Simulated optical absorption spectra explained well the structures of the observed spectra. Projected density of state and electron density map suggested that holes are confined in the  $(\text{Cu}_2\text{Ch}_2)^{2-}$  layer, resulting in the two-dimensional feature of the optical absorption spectra. Details will be reported at the conference in comparison with  $\text{La}_2\text{CdO}_2\text{Se}_2$ . (1) H. Hiramatsu et al., Appl. Phys. Lett. 82, 1048 (2003). (2) H. Hiramatsu et al., J. Appl. Phys. 94, 5805 (2003). (3) H. Hiramatsu et al., Crystal Growth & Design (2003) accepted. (4) P. Blaha et al. WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Techn. Universit?t Wien, Austria), 2001, ISBN 3-9501031-2.