

# SYMPOSIUM AA

## Structure-Property Relationships of Oxide Surfaces and Interfaces

November 27 – 29, 2000

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\* Invited paper

## SESSION AA1: GRAIN BOUNDARIES IN OXIDES

Chairs: Xiaoqing Pan and Christian Elsässer  
Monday Morning, November 27, 2000  
Commonwealth (Sheraton)

### 8:30 AM AA1.1

EFFECTS OF Y AND Zr DOPANTS ON GRAIN BOUNDARY STRUCTURE IN CREEP RESISTANT POLYCRYSTALLINE ALUMINA. G.S. Cargill III, C.M. Wang, J.M. Rickman, H.M. Chan, M.P. Harmer, Department of MS&E, Lehigh University, Bethlehem, PA.

Dopants Y and Zr at 100 ppm levels in high purity, micron grain-size polycrystalline alumina are mainly segregated to the alumina grain boundaries and strongly reduce high temperature creep. Information about this segregation has come from high resolution composition mapping experiments by STEM. Information about local structural surroundings of the dopant atoms has come from EXAFS experiments, and information about local bonding of the dopant atoms has come from NEXAFS experiments. Structural models for dopant grain boundary segregation provide a context for these experimental results and for effects of dopant incorporation on grain boundary transport. Recent experimental and theoretical results are discussed in this paper.

### 8:45 AM AA1.2

ATOMIC AND ELECTRONIC STRUCTURE OF SYMMETRIC TILT BOUNDARIES IN ZnO. Fumiyasu Oba, Shigeto R. Nishitani, Hirohiko Adachi, Kyoto Univ, Dept of MS&E, Kyoto, JAPAN; Isao Tanaka, Kyoto Univ, Dept of Energy Science and Technology, Kyoto, JAPAN; Masanori Kohyama, Shingo Tanaka (SWING), Osaka National Research Institute, Dept of Materials Physics, Osaka, JAPAN.

The atomic and electronic structure of the  $[0001] / (\bar{1}\bar{2}30) \Sigma=7$  symmetric tilt boundary in ZnO has been investigated by a first-principles plane-wave pseudopotential method within the local density approximation. Two types of equilibrium geometries are obtained with similar boundary energies. Atomic arrangement has largely reconstructed to vanish dangling-bonds in one configuration, whereas the other shows small bond distortion but has dangling-bonds at the boundary core. The balance between the energies for disturbing the atomic arrangement and vanishing the dangling-bond is therefore significant in determining the boundary energy. The electronic structure of the grain boundaries is discussed with special interests in the relationship with the geometric misalignment. The electronic states in the vicinity of the band gap are not significantly affected by the bond distortion and the presence of the dangling-bonds. Deep electronic states are not recognized in the band gap even for the configuration with dangling-bonds. This behavior is found to be intrinsic to the band structure of ZnO and is quite different from the electronic structure reported for the grain boundaries in other oxides and covalent materials such as Si and SiC. The present results suggest that deep interface states observed for ZnO varistor ceramics can not be explained solely by geometric misalignment at stoichiometric boundaries.

### 9:00 AM \*AA1.3

THE ORIGIN OF ELECTRICAL ACTIVITY AT GRAIN BOUNDARIES IN PEROVSKITES AND RELATED MATERIALS. S.J. Pennycook<sup>1,2</sup>, M. Kim<sup>1,3</sup>, G. Duscher<sup>1,2</sup>, N.D. Browning<sup>3</sup>, K. Sohlberg<sup>1</sup>, S.T. Pantelides<sup>1,2</sup>, <sup>1</sup>Oak Ridge National Lab, Solid State Division, Oak Ridge, TN. <sup>2</sup>Vanderbilt University, Dept of Physics and Astronomy, Nashville, TN. <sup>3</sup>University of Illinois at Chicago, Dept of Physics, Chicago, IL.

A combination of atomic-resolution Z-contrast microscopy, electron energy loss spectroscopy and first-principles theory has been used to investigate the origins of electrical activity at grain boundaries in SrTiO<sub>3</sub>. We show that grain boundaries in SrTiO<sub>3</sub> are intrinsically non-stoichiometric. Total-energy calculations reveal that the introduction of nonstoichiometry into the grain boundaries is energetically favorable and results in structures that are consistent with atomic-resolution Z-contrast micrographs. Electron energy-loss spectra provide direct evidence of oxygen deficiency. These results and calculations for model non-stoichiometric grain boundaries provide an explanation of the microscopic origin of the "double-Schottky barriers" that dominate the electrical behavior of polycrystalline perovskites. The same effects also explain the low critical currents that are observed across grain boundaries in the high-temperature superconductors.

### 9:30 AM \*AA1.4

MICROSCOPIC ANALYSIS OF THE RHOMBOHEDRAL TWIN GRAIN BOUNDARY IN ALUMINA. C. Elsässer, S. Nufer, A.G. Marinopoulos, T. Gemming, W. Kurtz, S. Köstlmeier and M. Rühle, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

An extended structural defect in a technologically important, complex ceramic material was quantitatively analyzed with respect to its atomistic and electronic structure, with very high degrees of accuracy and detail. In a synergistic approach, first-principles local-density-functional calculations, high-resolution transmission electron microscopy and spatially resolved electron energy loss spectroscopy were employed to determine unequivocally the preferred interfacial structure of a rhombohedral twin grain boundary in alumina. The benefit of the combined theoretical and experimental approaches for characterizations of interfaces is illustrated. It opens new perspectives in materials science for the understanding of microscopic structures of polycrystals and the relations to properties and phenomena.

### 10:30 AM \*AA1.5

ATOMISTIC SIMULATION OF A DOMAIN BOUNDARY IN ZrO<sub>2</sub>. Anthony T. Paxton, Michael W. Finnis, Queen's University of Belfast, Atomistic Simulation Group, Belfast, UNITED KINGDOM.

Tetragonal zirconia (*t'*ZrO<sub>2</sub>), a ferroelastic material, readily forms domains with domain boundaries on {011}. For example, by compressing a single crystal along [100], the formation and movement of such domain walls has been demonstrated experimentally[1]. We have made atomistic simulations of a domain wall with a self-consistent tight-binding model[2] which correctly reproduces the high temperature tetragonal-cubic phase transition exhibited by zirconia[3], as well as its low temperature monoclinic phase[4]. We analyse the results of our model, in particular the breadth of the domain wall, in terms of a Ginzburg-Landau theory in which the order parameter measures the degree of tetragonality of the lattice. [1] A. Foitzik, M. Stadtwald-Klenke and M. Rühle, Zeit. Metall. 84, 397-404 (1993). [2] M.W. Finnis, A.T. Paxton, M. Methfessel and M. van Schilfgaarde, Phys. Rev. Lett. 81, 5149-52 (1998). [3] S. Fabris, A.T. Paxton and M.W. Finnis in preparation. [4] S. Fabris, A.T. Paxton and M.W. Finnis Phys. Rev. B, 61, 6617-6630 (2000).

### 11:00 AM AA1.6

HREM OF GRAIN BOUNDARY STRUCTURES IN YTTRIA-STABILIZED CUBIC ZIRCONIA. K.L. Merkle, L.J. Thompson, G.-R. Bai and J.A. Eastman, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Thin films of cubic-phase yttria-stabilized zirconia (YSZ) were synthesized at a deposition temperature of 550°C by the MOCVD technique. In this manner nanocrystalline films between 8 and 25 Mol% of yttria, as determined by EDS, were obtained. High-temperature anneals at 1300°C were used to promote grain growth and production of well-developed grain boundaries (GBs). Since the films typically had a strong [001] texture, the atomic-scale structures of [001] YSZ tilt GBs could be studied by HREM over the whole range of misorientation, using a JEOL 4000EX HREM. Moreover, several well-structured triple junctions devoid of amorphous phases could be observed. HREM analysis shows that the cation columns in YSZ GB cores form a relatively dense structural arrangement, in contrast to the large open spaces that have been found in fcc stoichiometric oxides, such as NiO. The atomicscale structures of low and high-angle GBs will be discussed in view of possible GB relaxation modes, the role of stoichiometry, the necessary restructuring of the oxygen sublattice at GBs, the role of large concentrations of oxygen vacancies in the lattice and near GBs, and the segregation of Y at GBs. This work was supported by the U.S. Department of Energy under contract # W-31-109-ENG-38.

### 11:15 AM AA1.7

ATOMIC SCALE CHARACTERIZATION OF A TEMPERATURE DEPENDENCE TO OXYGEN VACANCY SEGREGATION AT SrTiO<sub>3</sub> GRAIN BOUNDARIES. R.F. Klie and N.D. Browning, Department of Physics, University of Illinois at Chicago, Chicago, IL.

Perovskite oxides have proven themselves to be extremely versatile, exhibiting a broad spectrum of properties and functions. In particular, there is substantial interest in exploiting their functionality for superconductivity, ferromagnetism, ferroelectricity, magneto resistance, ionic conductivity and as dielectrics. Although there is an almost innumerable combination of metal cations that can be accommodated by the system, the fact that they are all perovskites suggests that there should also be a link between the structures that they form at defects and grain boundaries. To develop a fundamental understanding of the structure-property relationships at grain boundaries in perovskites, we can therefore infer much from the study of a single model system. In this regard, SrTiO<sub>3</sub> serves as the ideal simple model material for perovskites where the bulk properties are very well understood using defect chemistry principles. The correlation between the structural and the local electronic properties of SrTiO<sub>3</sub> grain boundaries is obtained by the combination of Z-contrast imaging and electron energy loss spectroscopy (EELS) in

the scanning transmission electron microscope (STEM). We have examined the atomic structure, composition and bonding at a nominally undoped  $58^\circ$  [001] tilt grain-boundary in  $\text{SrTiO}_3$  in order to develop an understanding of the control that the grain boundary plane exerts over the bulk properties. Room temperature and in-situ heating experiments show that there is a segregation of oxygen vacancies to the grain boundary that is increased at elevated temperatures and is independent of the cation arrangement. These measurements provide direct support for recent experimental and theoretical predictions that non-stoichiometry, and in particular oxygen vacancies, are responsible for the widely observed grain boundary properties.

#### 11:30 AM AA1.8

**SURFACE POTENTIAL AT ATOMICALLY ABRUPT GRAIN BOUNDARIES IN  $\text{SrTiO}_3$ .** Dawn A. Bonnell, Sergei V. Kalinin, Dept. Mat. Sci. Eng., University of Pennsylvania, Philadelphia, PA; G. Duscher, Vanderbilt University, Nashville, TN.

Electrostatic force microscopy (EFM) and scanning surface potential microscopy (SSPM) are used to determine the potential distributions above grain boundary - surface junctions in  $\text{SrTiO}_3$  bicrystals. An analytical approach for the quantification of EFM and SSPM images of systems with electric potential inhomogeneity has been developed in order to determine the interface potential from experimental data. The voltage dependencies of the electrostatic force gradient and surface potential verify the solutions. The distance dependencies of force gradient and surface potential were used to quantify the grain boundary potential and the depletion width. Both measurements yield the same properties despite the difference in imaging mechanisms. The interface potential is shown to result from local charge rather than from a local variation in dielectric constant. The relationship between the experimental grain boundary width and force-distance analysis results is discussed. Transport properties of grain boundary were investigated with the in-situ application of external lateral bias normal to grain boundary and quantification of the potential drop across the interface. Z-contrast imaging and electron energy loss spectroscopy were used to investigate the atomistic structure of the grain boundaries and segregation of dopants.

#### 11:45 AM AA1.9

**DIRECT IMAGING OF INDIVIDUAL FLUX QUANTA LOCATED AT BOUNDARIES OF  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  BICRYSTAL FILMS.**

Jack W.H. Tsai\* and Siu-Wai Chan Materials Science Program, HKSM, Columbia University, NY, NY; \*Now at Maxtor Corp., Milpitas, CA; John R. Kirtley, T.J. Watson Research Center, IBM, Yorktown Heights, NY.

When a grain boundary consists of weak-link areas, the superconducting portions of the boundary can serve as magnetic shields (Meissner effect) which divert the penetrating flux-lines into regions of lower order parameter. Once the magnetic flux-lines enters these regions, extra energy is need to move them out, thus the flux-lines are pinned. Unless Magnus force is larger than the pinning force ( $F_L > F_P$ ), the motion of the flux is restricted. The individual trapped flux quanta were imaged using the Scanning SQUID Microscope (SSM) which has a spatial resolution of  $0.1 \mu\text{m}$  and magnetic signal resolution of  $10^{-3} \Phi_0$ . From the width of the individual flux spreading along the grain boundary which is directly related to Josephson penetration depth, one can determine the critical current density ( $J_c$ ) that the grain boundary can sustain. In our work, we will show that the spreading of flux-line increases with increasing misorientation. The YBCO films were either laser ablated or sputtered on seven  $\text{SrTiO}_3$  bicrystal substrates which had specially chosen boundary inclination and misorientation angles. From the SSM images, it can be shown the effective superconducting area reduces with increasing misorientation angles. The  $J_c$  of the boundaries determined by the SSM method was found to agree reasonably well with the previous transport measurements. Our results showed an exponential decrease of  $J_c$  with increasing misorientation. The critical misorientation from our results is at  $30^\circ$  instead of  $15^\circ$  for [001] tilt boundaries. The reduction of effective superconducting channels increases with misorientations with the concomitant decrease of  $J_c$ .

### SESSION AA2: INTERFACES IN COMPOSITES AND MULTILAYERS

Chairs: Robin W. Grimes and Craig A. J. Fisher  
Monday Afternoon, November 27, 2000  
Commonwealth (Sheraton)

#### 1:30 PM \*AA2.1

**SIMULATIONS OF GLASS SURFACES AND INTERFACES.**

Stephen H. Garofalini, Dept. of Ceramic and Materials Engineering, Rutgers University, Piscataway, NJ.

Molecular dynamics computer simulations have been used to study glass surfaces and glass/glass and glass/crystal interfaces. Simulations

of glass/glass interfaces relevant to wafer bonding and chemical mechanical polishing will be presented, with emphasis on the role of water between the surfaces on interface behavior. Two examples of glass/crystal interfaces will also be discussed. One will include the interfaces that form between lithium silicate glasses and layered vanadia crystals applicable to thin film batteries. A charge transfer algorithm was used to alter the charge on the V ions as Li entered the crystal. The effect of crystal orientation on interface behavior and surface relaxation will be presented. In the second case, interfaces formed between the amorphous intergranular phase and alumina crystals in polycrystalline ceramics will be discussed, with emphasis on atomistic structure and segregation.

#### 2:00 PM \*AA2.2

**DEFECT STRUCTURE-PROPERTY RELATIONSHIPS IN PYROCHLORE OXIDES.** Robin Grimes, Licia Minervini, Mohsin Pirzada, Kurt Sickafus, Los Alamos National Laboratory, Materials Science, Los Alamos, NM.

Atomistic simulation calculations based on energy minimization techniques have been used to predict the internal energy changes associated with disorder in an extensive range of  $\text{A}_2\text{B}_2\text{O}_7$  pyrochlore oxides: A=Lu, Yb, Er, Y, Gd, Eu, Sm, Nd, Pr, La, B=Ti, Ru, Mo, Sn, Zn, Pb, Ce. This consistent set of disorder energies is then correlated with the oxygen positional parameter and compared to literature values. The ease to which a material will undergo disorder is also shown to have a strong effect on radiation tolerance and the dielectric constant. In all cases, the results are analysed in terms of contour plots which present the measured quantity as a function of both A and B cation radii: the quantities are disorder energy, oxygen positional parameter, dielectric constant and the activation energy for oxygen ion migration.

#### 2:30 PM AA2.3

**QUANTITATIVE INVESTIGATION OF THIN OXIDE FILMS BY SPECTRUM IMAGING IN A TRANSMISSION ELECTRON MICROSCOPE WITH ENERGY FILTER.** Thomas Walther, Werner Mader, Institut für Anorganische Chemie, Universität Bonn, GERMANY.

A method is described of analysing quantitatively the chemistry (i.e. the chemical composition, the bond symmetry and the oxidation state of cations) of thin planar films in cross-sectional geometry by spectrum imaging in a transmission electron microscope with energy filter. While spectrum imaging was already used by a few research groups in the past, it is shown in this study how experimental data can be evaluated quantitatively without the need for a selective slit aperture, and the spatial resolution is improved considerably so that single atomic planes of crystals can be studied. The systems investigated are planar defects in  $\text{Fe}_2\text{O}_3$ -doped ZnO and  $\text{SrTiO}_3/(\text{La,Ba})\text{MnO}_3$  multilayers. The limits of the technique are determined by the signal-to-noise ratio, specimen drift and electron beam induced reduction of material during the investigation.

#### 2:45 PM AA2.4

**MICROSTRUCTURE OF EPITAXIAL  $\text{BaRuO}_3$  THIN FILMS GROWN ON (001) AND (111)  $\text{SrTiO}_3$ .** W. Tian and X.Q. Pan, Dept. of MS&E, The University of Michigan, Ann Arbor, MI; M.K. Lee and C.B. Eom, Dept. of Mechanical Engineering and Materials Science, Duke University, Durham, NC.

$\text{BaRuO}_3$ , a conductive  $\text{ARuO}_3$  type oxide, exhibits unique hexagonal structure for which there are no analogs in  $\text{SrRuO}_3$  and  $\text{CaRuO}_3$  compounds. Three polymorphs of  $\text{BaRuO}_3$  have been found in bulk compounds, denoted by 9R, 4H and 6R structure. Charted phase diagram reveals 9R phase is stable at ambient temperature and atmosphere, while 4H and 6R phases only exit in regime of the temperature higher than  $1000^\circ\text{C}$  alone with the pressure higher than 2GPa. The 4H and 6R polymorphs were therefore regarded as thermodynamically metastable at ambient atmosphere and temperature. Our transmission electron microscopy (TEM) investigations of epitaxial  $\text{BaRuO}_3$  thin films grown on (001) and (111)  $\text{SrTiO}_3$  revealed the existence of 4H phases. This result demonstrated thin film epitaxy to be a feasible way to form metastable phases. Detailed studies of  $\text{BaRuO}_3$  film microstructured revealed that the films grown on (111)  $\text{SrTiO}_3$  are c-axis oriented, single crystal with an in-plane film substrate orientation relationship of  $[11\bar{2}0]\text{BaRuO}_3//[110]\text{SrTiO}_3$ . In contrast, the thin films grown on (001)  $\text{SrTiO}_3$  substrates consist of four orthogonal crystallographic domains; all are aligned by their (20 $\bar{2}$ ) plane parallel to the surface of the substrate. Additionally, these domains show an anisotropic shape elongated along the  $[\bar{1}210]$  direction, for which the reason is attributed to different lattice mismatches along different directions. It was found that the electrical properties of the thin films depend on the film microstructure.

#### 3:30 PM AA2.5

**ANALYTICAL ELECTRON MICROSCOPY STUDIES OF ACTIVE**

INTERFACES IN ZINC OXIDE VARISTORS. Mattias Elfving, Eva Olsson, Analytical Materials Physics, Department of Materials Science, The Angstrom Laboratory, Uppsala University, Uppsala, SWEDEN.

ZnO varistor materials are polycrystalline ceramics that exhibit extreme non-linear current-voltage characteristics. Their non-ohmic behaviour makes them suitable for overvoltage protection devices. It is the interfaces between ZnO grains that are the key to the non-linear behaviour of the varistor materials. Previous work has shown that the local microstructure determines the breakdown voltage of the individual ZnO/ZnO interface [1]. The pre-breakdown conductivity and the non-linearity in the breakdown region, which are both crucial to the performance of the varistor, are also affected by the height and the width of the potential barriers in the interfaces. In the present work interfaces and adjacent grains in ZnO varistor materials have been characterised using different analytical tools in the transmission electron microscope (TEM). Structural properties of ZnO/ZnO interfaces and triple grain junctions have been studied using imaging and diffraction techniques. The composition of the microstructural constituents and interfaces has been investigated through energy-dispersive X-ray spectrometry (EDS) and energy-filtered TEM (EFTEM). Electron holography has already been shown to be capable of imaging potential barriers in these materials [2]. A more extensive holographic analysis is currently in progress to obtain a detailed picture of these potential barriers.

1. E. Olsson and G.L. Dunlop, Characterization of individual interfacial barriers in a ZnO varistor material. *Journal of Applied Physics*, 66, 3666-3675 (1989).
2. E. Olsson, P.A. Midgley, J.S. Barnard and J.W. Steeds, Characterisation of potential barriers of ZnO interfaces in a varistor material using electron holography. *Proceedings MRS Fall Meeting 1997*.

#### 3:45 PM AA2.6

INTERFACE ANALYSIS OF OXIDE THIN FILMS USING HIGH ENERGY ION BEAM TECHNIQUES. V. Shutthanandan, S. Thevuthasan, E.M. Adams, S.I. Yi, Y. Gao, S.A. Chambers, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory; S. Maheswaran, School of Science, University of Western Sydney, Nepean, Kingswood, AUSTRALIA; Y.J. Kim, Dept. of Chemical Technology, Tajon National University of Technology, S KOREA.

There is a growing interest in the epitaxial growth of model oxides on various oxide and metal substrates to obtain high-quality surfaces and films. A number of single crystal oxide films on various substrates have been recently synthesized in our laboratory using oxygen-plasma-assisted molecular beam epitaxial growth. In the present work, we have used Rutherford backscattering spectrometry (RBS) and channeling techniques along with nuclear reaction analysis (NRA) to investigate the crystalline quality and interfacial properties of epitaxially grown iron, cerium, titanium and zirconium oxide thin films on number of different substrates. Some of these films exhibit disordering at the interface due to the lattice mismatch. RBS with channeling and NRA is a powerful technique to determine the nature of the interface, elemental diffusion across the interface as a function of temperature, and the location of foreign atoms in the film and the substrate. Ion scattering simulations were performed using VEGAS code to understand the disordering at the interface in some of these films and the results will be discussed along with the experimental data.

#### 4:00 PM AA2.7

ATOMIC FORCE MICROSCOPY STUDIES OF FRACTURE SURFACES FROM OXIDE / POLYMER INTERFACES.

Maura Jenkins, Jeffrey Snodgrass, Dimitrios Pantelidis, Reinhold Dauskardt, John C. Bravman.

Atomic Force Microscopy (AFM) is used to characterize fracture surfaces in silicon oxide/adhesion promoter/polymer systems. Prior X-ray Photoelectron Spectroscopy (XPS) work has been used to identify the species present on each surface, while this study identifies regions of various fracture behavior. Areas which have undergone fast fracture were identified as well as fatigue striations. Finally, these AFM studies are combined with fatigue and chemical data to provide a complete analysis of fracture behavior at these specific interfaces.

#### 4:15 PM AA2.8

STABILIZING NANOMETER-THICK DISORDERED FILMS ON CRYSTALLINE OXIDE SURFACES. Jian Luo and Yet-Ming Chiang, Dept of Materials Science and Engineering, MIT, Cambridge, MA.

Recently, we have observed [J. Juo and Y.-M. Chiang, *J. European Ceram. Soc.*, 19, 697 (1999); J. Juo and Y.-M. Chiang, *Acta Mat.*, in press (2000)] that disordered films of 1-2 nm constant thickness can be stabilized at the surfaces of various two-component oxides. A

model has been developed in which the three key contributions to film stability are the relative surface/interface energies, sign and strength of the dispersion interaction, and the volumetric free energy of amorphization and mixing. In this work we have conducted critical tests of the model with eight systems ( $\text{Bi}_2\text{O}_3\text{-ZnO}$ ,  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3$ ,  $\text{WO}_3\text{-TiO}_2$ ,  $\text{MoO}_3\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-Bi}_2\text{O}_3$ ,  $\text{MoO}_3\text{-TiO}_2$ ,  $\text{V}_2\text{O}_5\text{-TiO}_2$  and  $\text{Bi}_2\text{O}_3\text{-TiO}_2$ ), in which the three key energy terms are systematically varied. The observations are consistent with the model, in terms whether stable surface films appear, and the scaling of film thickness with undercooling, chemical potential, and fusion entropy for the film-forming additive. Transitions in film thickness at critical points are explored. Application of the Gibbs phase rule to these systems is examined. It can be shown that a third (surface) phase of thermodynamically-determined thickness and composition is allowed in a two-component equilibrium system. Correspondingly the film thickness becomes an additional intensive variable, and the composition and stability of the disordered surface phase are markedly different from the bulk liquid. Surface phase separation has also been observed and can be explained by the model. This phenomenon is important in understanding and controlling activated sintering [J. Luo, H. Wang, and Y.-M. Chiang, *J. Am. Ceram. Soc.*, 82, 916 (1999)], supported-oxide catalysts, and nanometer scale surface coatings. Possible applications to silicon-based microelectronics will be discussed. (Research supported by DOE.)

#### 4:30 PM \*AA2.9

MOLECULAR DYNAMICS SIMULATIONS OF ZIRCONIA-ALUMINA INTERFACES. Craig A.J. Fisher, Katsuyuki Matsunaga, Hideaki Matsubara, Japan Fine Ceramics Center, Nagoya, JAPAN.

We have performed molecular dynamics simulations of interfaces between crystals of 8 mol% yttria-stabilized zirconia (8YSZ) and alpha-alumina in an attempt to better understand the behavior of such interfaces in thermal barrier coatings. Atomic interactions were described by a two-body Born-Mayer potential function. Systems containing in excess of 10,000 atoms were constructed based on a Near-Coincidence Site Lattice (NCSL) theory, and equilibrated at 1273 K. The oxide ion conductivity in the zirconia component of the interface system was found to be significantly lower than in a single crystal of 8YSZ, which we attribute to the compressive stresses in the interface zirconia crystal. The structural and energetic characteristics of different interfaces will also be discussed.

#### SESSION AA3: POSTER SESSION

Chairs: C. Barry Carter, Xiaoqing Pan, Kurt E. Sickafus, Harry L. Tuller and Tom Wood  
Monday Evening, November 27, 2000  
8:00 PM

Exhibition Hall D (Hynes)

#### AA3.1

CRYITICAL PHENOMENA AND INTERACTIONS IN NANOCUSTER SYSTEMS. I.P. Suzdalev, V.N. Buravtsev, Yu.V. Maksimov, V.K. Imshennik, S.V. Novichikhin, Institute of Chemical Physics of Russian Academy of Sciences, Moscow, RUSSIA.

The nanocluster measurement range open a great variety ways to obtain new nanomaterials with new unusual properties. For nanoclusters, such fundamental constants as lattice parameters, heat capacity, melting point, electric conductivity etc. change dramatically compared to those in the bulk materials. New optical, magnetic and electronic properties appear in nanosystems, moreover, unusual adsorption and catalytic behavior may arise which reflect some new physical and chemical aspects of surface dynamics. These new properties of the matter are not only introduced by the dimensional effects but also in a stronger form by the extent of cluster-cluster interaction and by peculiarities of cluster organization. In this work we present original models describing nanosystem formation and cluster organization and emphasizing the details of mechanism of cluster-matrix and cluster-cluster interactions. We also consider the role of defectness, in the wide sense of the word, on the nature of the above interactions. The appearance of maximum of defectness at the certain range of cluster sizes is predicted and discussed. For nanoclusters, the conditions for arising of a specific solid-liquid state and peculiar jump-like magnetic phase transition are under thorough discussion. We consider the properties of nanosystems affected by the different ligand surroundings that in one peculiar case take form of polymeric network. The nanosystems where composing clusters directly interact with each other and show either weak or strong interacting ability are also under consideration. For europium and iron oxide nanosystems, the problems of intracluster atomic dynamics affected by cluster-cluster interactions are discussed in view of appearance of peculiar solid-liquid state. For isolated clusters of iron oxide with mean size 1-3 nm located in polymeric network and for

nanosystem with mean size 20-40 nm composed of the above clusters strongly interacting each with other, new structure-dynamic and first order magnetic phase transitions are thoroughly studied. For hydrated cluster system immersed in the polymeric network, an influence of hydrostatic pressure, arising upon freezing, on a shift of critical parameters of magnetic phase transitions is firstly observed and theoretically considered. For the nanosystem composed of iron oxide clusters, upon action of shear stress under high pressure (SSHP) and simultaneous action of the SSHP and SSHP-induced polymerization of acrylamide there were observed and discussed the shifts in critical parameters for the first order magnetic phase transitions in clusters.

#### **AA3.2**

**INTERFACE REACTIONS IN LiNbO<sub>3</sub> BASED OPTOELECTRONICS DEVICES.** Hirotoshi Nagata, Yasuyuki Miyama, Naoki Mitsugi, Kaoru Higuma, Yoshihiro Hashimoto, Futoshi Yamamoto, Yuiji Yamane and Miki Yatsuki, Optoelectronics Research Division, New Technology Research Laboratories, Sumitomo Osaka Cement Co., Ltd., Funabashi, Chiba, JAPAN.

Understanding the interface structures of device constituent materials is important to demonstrate physically the device reliability and quality. In this regard, LiNbO<sub>3</sub> based optoelectronic devices, widely used in recent high-speed optical fiber communication systems, should be investigated on their materials science. For instance, although the SiO<sub>2</sub> buffer layer is usually coated on LiNbO<sub>3</sub> substrate to improve the device RF response, mechanism of their adhesion and bonding strength have not been examined yet. Our cross-sectional TEM observation found an existence of a thin interdiffusion-layer of Nb and Si at the interface of sputtering deposited SiO<sub>2</sub> on x-cut LiNbO<sub>3</sub> wafer. From a fluorocarbon-plasma etched LiNbO<sub>3</sub> surface, a deposition of LiF particles is found and deteriorates the bonding strength of coating layers. The interfacial reaction between the LiNbO<sub>3</sub> (or SiO<sub>2</sub>) and a sacrificial layer such as a Ti film needs to be understood in order to completely remove the layer after the process. The residue of such material sometimes causes a fluctuation in electrical performance of devices. The metallic residue on optical waveguides leads to an increase of optical propagation losses. In order to improve the devices long-term stability, the effectiveness of Si<sub>3</sub>N<sub>4</sub> passivation is also discussed from the viewpoint of the interfacial problems.

#### **AA3.3**

**SURFACE AND INTERFACE TRANSPORT OF DENSE ORIENTED La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-x</sub> THIN FILM ELECTRODES.** Yuemei L. Yang, C.L. Chen, S.Y. Chen, C.W. Chu and A.J. Jacobson, Materials Research Science and Engineering Center, University of Houston, Houston, TX.

Oxygen transport at electrode surfaces of mixed conducting oxides and at electrode/electrolyte interfaces are of fundamental importance to solid oxide fuel cells and oxygen separation membranes. In this work, the 3-probe ac impedance technique was employed to study the oxygen surface exchange kinetics and the interfacial ionic transport in the LSCO/YSZ system, where LSCO = La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-x</sub> and YSZ = yttria-stabilized zirconia. A LSCO working electrode and counter electrode (5000 Å) were prepared by using pulsed laser deposition (PLD) on (100) surfaces of a YSZ single crystal disc. The reference electrode was attached to the side of the electrolyte disc and was typically in equilibrium with dry air as the reference point. Impedance spectra of the working electrode in the frequency range 0.01 to 100000 Hz were recorded as a function of temperature and applied potential (-70 mV to +70 mV). From high to low frequency, the impedance spectra were assigned to contributions from the bulk electrolyte, the interfacial transfer and the surface exchange. An equivalent circuit model corresponding to this assignment was used to fit the impedance spectra, producing relevant time constants and interfacial resistances. Exchange kinetic parameters and activation energies were derived.

#### **AA3.4**

**MICROSCOPIC STRUCTURE AND BONDING AT THE Pd/SrTiO<sub>3</sub> (001) INTERFACE.** Thorsten Ochs, Sibylle Köstlmeier, Christian Elsässer, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

The microscopic structure and energetics of a SrTiO<sub>3</sub> (001) surface covered with thin layers of Pd have been investigated by means of ab-initio electronic-structure calculations. A mixed-basis pseudopotential technique based on the local density functional theory was employed. Supercells containing SrTiO<sub>3</sub> substrate slabs, with either SrO or TiO<sub>2</sub> surface terminations, and Pd films of varying thicknesses were used to model the free (001) surfaces and the (001) heterophase interfaces. Based on the calculated energetics of adhesion for the different interfaces, the microscopic energetics of wetting and layer growth has been analysed. The TiO<sub>2</sub> terminated substrate is energetically favourable for the adhesion of Pd films, with the Pd

atoms bonded on top of the O atoms. The film adhesion is strongest for one (001) layer of fcc Pd and becomes weaker with increasing film thickness.

#### **AA3.5**

**ACTIVATION OF AN Al-Mg-Zn ALLOY BY THE PRESENCE OF PRECIPITATES TO BE USED AS SACRIFICIAL ANODE.** S. Valdez, J.A. Juarez Islas, Instituto de Investigaciones en Materiales (IIM)-UNAM, Circuito Escolar S/N, Cd. Universitaria, MEXICO; J. Genesca, Fac. de Qca., Depto. De Metalurgia-UNAM, Circuito Esoclar S/N, Cd. Universitaria, MEXICO.

In this research, new Al-Mg-Zn-Li alloy sacrificial anode used have been developed and characterised. The interest in the study of Al-Mg-Zn system, due to the presence of precipitates in  $\alpha$ -Al matrix and interdendritic regions which are capable of breaking down passive films and presenting good electrochemical efficiencies. The formation and distribution of fine precipitates phases belonging to the binary Mg-Zn and to the ternary Al-Mg-Zn systems in the aluminium matrix have been promoted as a key factor in achieving a good surface activation of the anode. At the same time, the effect of Li additions on superficial activation of the anode-by means of precipitation of AlLi type compounds was studied. Results of microstructure characterisations showed the presence a solid solution of the  $\alpha$ -Al, and eutectic of Al<sub>2</sub>Mg<sub>3</sub>Zn<sub>3</sub> and precipitates of Mg<sub>7</sub>Zn<sub>3</sub> in interdendritic regions. Electron microscopic observations performed on specimens with and without heat treatments showed in the  $\alpha$  matrix the presence of uniform distribution of precipitates of  $\tau$ -Al<sub>2</sub>Mg<sub>3</sub>Zn<sub>3</sub>, Mg<sub>7</sub>Zn<sub>3</sub> and  $\delta$ -Al-Li type. When the behaviour of aluminium sacrificial anodes is directly related to the electrochemistry of alloys, as correlated the microstructure of the AlMgZnLi alloy with their efficiency and corrosion process, Electrochemical Impedance Spectroscopy measurements were used. For alloys showed a value of 80% of efficiency.

#### **AA3.6**

**ATOMIC FORCE AND ELECTRON MICROSCOPY STUDIES OF TiN DIOXIDE FILMS PREPARED FROM SOLUTIONS WITH HIGH FLUORINE CONTENT.** Dwight R. Acosta, UNAM, Instituto de Fisica, MEXICO; Rebeca Castanedo, CINVESTAV, Querataro, MEXICO; Walter Estrada, Univ Nal. de Ingenieria, PERU.

SnO<sub>2</sub> based gas detectors, despite its high sensitivity, simple construction and low cost which make them one of the favorites among other gas detectors, still suffer poor selectivity which might have to do with behavior of physical surface parameters. In this work we present the variations of electrical resistivity in SnO<sub>2</sub> thin films prepared by spray pyrolysis and doped with fluorine coming from a solution with high fluorine concentration, up to 40% wt. The distribution and concentration of fluorine in thin films were determined from Nuclear Resonance Method measurements. Structural information of films with several fluorine contents was derived using electron microscopy and X rays techniques. The electrical resistance variations in our samples were measured using the conventional Four Point method. Scanning electron microscopy images revealed important surface changes as fluorine content was increased in films and in the starting solution. Atomic Force micrographs reveal detailed variations in grain size and configuration together with surface roughness as the fluorine contents was increased from 4.2 to 20% wt. in the starting solution. Correlations between roughness, grains size and electrical resistance variations and presented related to gas sensitivity properties of detectors based in pure doped SnO<sub>2</sub> thin films.

#### **AA3.7**

**EFFECTS OF DEPOSITION METHOD ON THE PROPERTIES OF W/TiN/SiO<sub>2</sub>/Si MOS SYSTEM.** Dae-Gyu Park, Heung-Jae Cho, Kwan-Yong Lim, Jeong-Tae Kim, Tae-Kyoung Kim, In-Seok Yeo, Jae-Sung Roh and Jin-Won Park, Advanced Process Team, Memory R&D, Hyundai Electronics Industries, Ichon-si, Kyoungki-do, KOREA.

With the scaling the MOSFET gate lengths down to 100 nm regime and gate oxide thickness to below 3 nm, polysilicon (poly-Si) gate depletion, high gate resistance, boron penetration to the channel region, and gate oxide tunnel leakage become critical obstacles to realize high performance transistors. In this paper midgap metal gates W/TiN on thin oxides were investigated, which can be an alternative solution against aforementioned problems. We found that the deposition technique is pivotal in achieving lower defect densities both in bulk oxide and oxide/Si interface. All samples were prepared by oxidizing 8-10 Ohm-cm (100) oriented p-type silicon wafers in wet oxygen at 700-800°C to form 2-6 nm thick SiO<sub>2</sub>. As an electrode barrier, sputtered-TiN films (30 nm) were deposited by reactive sputtering of Ti target in N<sub>2</sub>/Ar ambient under the various sputtering power and temperature. The CVD TiN (30 nm-thick) barriers were also prepared using TiCl<sub>4</sub>, NH<sub>3</sub>, and Ar at 650°C, followed by 70 nm-thick W electrode deposition. MOS capacitors for surface state

measurements and bulk defects were patterned using conventional photolithography and reactive ion etch process. Interface properties of W/TiN/SiO<sub>2</sub>/Si MOS capacitors prepared by CVD technique showed lower interface state density as determined by capacitance-voltage (C-V) and conductance method, whereas those made by sputter process exhibited damaged interface quality near the band edge and bulk defects as well. The trapped oxide charge calculated from hysteresis ( $\rho_2$ ) is  $\sim 1E12$  /cm<sup>2</sup> and the interface state density (Dit) measured by conductance method is  $\sim 2E12$  /eV-cm<sup>2</sup> range. Post-metal anneal (PMA) in sputtered-TiN/SiO<sub>2</sub>/Si structure is inevitable to heal the damages induced by sputtering process. On the other hand, CVD-TiN/SiO<sub>2</sub>/Si MOS capacitors demonstrated non-damaged characteristics as probed by insignificant hysteresis and ideal C-V profiles regardless of PMA. The interface state density of this structure is as low as  $\sim 2E11$  /eV-cm<sup>2</sup> range, which is about an order of magnitude lower Dit value than that of sputter process. Some fundamental MOS characteristics related with deposition technique will be discussed in terms of damage sources such as plasma and metal penetration.

**AA3.8**  
EPITAXIAL STRAIN AS VIABLE ROUTE TO INCREASE T<sub>c</sub> IN CUPRATE SUPERCONDUCTORS. H.-U. Habermeier, X.-J. Chen and P.X. Zhang, Max Planck Institut für Festkörperforschung, Stuttgart, GERMANY.

Epitaxial strain in perovskite-type oxides is known to be an opportunity to systematically modify the ordering temperatures of the electronic system to either superconductivity or ferromagnetism. Locquet has demonstrated that T<sub>c</sub> of LaSrCuO<sub>4</sub> superconductors can nearly be doubled by biaxial epitaxial compressive strain. Razavi and Habermeier showed that in doped Lanthanummagnanites epitaxial strain can induce a metal insulator transition. On the other hand attempts failed to appreciably enhance T<sub>c</sub> of the 123 compounds by epitaxial strain. In this contribution the thickness dependence of T<sub>c</sub> of YBCO thin films deposited on SrTiO<sub>3</sub>, NdGaO<sub>4</sub> and LaSrAlO<sub>4</sub> single crystal substrates will be reanalysed and the reasons for the failure to enhance T<sub>c</sub> are derived from a careful study of the Ramanspectra of ultrathin films. Based on these studies we propose experiments to use epitaxial strain of Hg-1201 thin films in order to enhance T<sub>c</sub>. The analysis includes a theoretical consideration of the role of the apex oxygen bond length to the plane Cu and its pressure dependence. First experimental results will be presented.

**AA3.9**  
METAL-INSULATOR TRANSITION IN LaSrMnO THIN FILMS INDUCED BY EPITAXIAL STRAIN. H.-U. Habermeier, F.R. Razavi, R.P. Praus, G.M. Gross, A. Vigliante.

Pseudomorphically grown perovskite-type thin films can exhibit appreciable interfacial biaxial strain either compressive or tensile, depending on the lattice mismatch of substrate and film, respectively. Tensile stress causes the shift of the Curie temperature to lower values and an increase of the resistivity in LaCaMnO thin films in addition to modifications of the magnetisation curve especially in the range of the Rayleigh law and the approach to saturation. In this contribution, the results of structural, transport and magnetic properties of films under tensile stress of LaCaMnO films are discussed from the point of view of epitaxial stress. Additionally, recent results will be presented showing a film thickness dependent transition from an insulating to a ferromagnetic metallic state in La-Sr-Mn-O thin films of different compositions. The films have been prepared by PLD and analysed by XRD, TEM, transport and Ramanscattering investigations. A generalised picture of the strain generation and relaxation emerges and will be discussed.

**AA3.10**  
THE BEHAVIOR OF ULTRATHIN ALUMINA FILMS UNDER STM-INDUCED HIGH ELECTRIC FIELDS: DIELECTRIC BREAKDOWN AND PRE-BREAKDOWN BEHAVIOR. Chengyu Niu, Noel Magtoto, Jeffrey A. Kelber, Department of Chemistry, University of North Texas, Denton, TX.

An STM tip has been used to induce localized dielectric breakdown and pre-breakdown pit formation in 7 Å thick alumina films grown on Ni<sub>3</sub>Al(111) substrates under UHV conditions. Breakdown is induced by increasing the STM tip bias voltage with the feedback loop on to inhibit tip/sample physical interaction. Breakdown is marked by a precipitous retreat of the tip from the surface ( $\sim 15$  nm or more) due to the breakdown of the insulating nature of the substrate. Breakdown is also marked by the formation of features  $\sim 100$  nm in diameter and up to  $\sim 20$  nm in apparent height, as imaged in constant current mode. Constant height measurements, however, show that these features are mainly due to electronic effects rather than mass transport. Breakdown is observed to occur at a field threshold of  $11 \pm 1$  MV/cm, in good agreement with extrapolations of macroscopic capacitance measurements on thicker films. Pulsing below breakdown

thresholds induces pits (0.3 nm deep  $\times$  50 nm wide) at the oxide/substrate interface. Both pit depth and diameter can be increased by repeated pulsing of the sample bias voltage. Once a pit is formed, the breakdown threshold within the pit is  $\sim 75\%$  of the breakdown threshold outside the pit. The mechanisms of pit formation and breakdown will be discussed, as well as the relevance of such mechanisms to both corrosion and the operation of CMOS and magnetoresistance devices.

**AA3.11**  
OXIDES INFLUENCE ON ELECTRICAL PROPERTIES OF Si AND A<sub>2</sub>B<sub>6</sub> MATERIALS. A. Andrukhiv, Komatsu Silicon America Inc., Hillsboro, OR; G. Khlyap, M. Andrukhiv, State Pedagogical University, Drogobych, UKRAINE; V. Belosertseva, State Politechnical University, Kharkov, UKRAINE.

Oxygen is known as an inevitable impurity almost for all semiconductor compounds, so studies of its influence on different characteristics (mechanical, electrical, etc.) of various devices is seemed to be essential, especially in aspect of possible numerical modeling of these properties crucial for active elements based on epitaxial layers (p-Si<B>/p-Si quasi-heterojunction grown by CVD technique) and on some A<sub>2</sub>B<sub>6</sub> (in particular CdTe) thin film structures. The structural investigations were shown that in case of silicon quasi-heterojunctions (I-V and C-V measurements results allowed to make such a conclusion) SiO<sub>2</sub> layer formed at the interface Si<B>-substrate/Si-film was appeared as a distinctive generator of surface electron states forming the potential barrier with height fluctuations. In the case of cadmium telluride films grown on glass-ceramics substrate by vacuum deposition in closed-space system with significantly nanoscale inhomogeneous film surface SEM/TEM and Auger analysis were demonstrated oxygen to precipitate on microinhomogeneities forming CdO/CdTe quasi-3D dimensional microheterojunctions. The work proposes the main results of electrical properties numerical modeling and calculation of energy band diagrams of the examined structures.

**AA3.12**  
INFLUENCE OF OXIDATION ON BORON SEGREGATION TO GRAIN BOUNDARIES OF IN-SITU FRACTURED Ni<sub>3</sub>Al ALLOYS. G. Palasantzas, S.A. Koch, D.T.L. van Agterveld, J.Th. M. De Hosson, Department of Applied Physics, Materials Science Center, University of Groningen, Groningen, THE NETHERLANDS.

A common theme in all studies of B-segregation to grain-boundaries in Ni<sub>3</sub>Al alloys is the fact that B segregates more strongly to grain-boundaries than to free surfaces, while segregation was observed onto sputtered surfaces annealed below 800°C. However, despite the vast number of studies in this alloy system, no precise attention has been paid to the dynamics of B segregation on intergranularly fractured surfaces in the absence of any annealing and/or sputtering treatments, as well as influences associated with surface/subsurface oxidation after prolonged exposure even under UHV conditions. In this work Scanning electron/Auger studies are performed on in-situ fractured B-doped hypo-stoichiometric alloys. Auger measurements on the surface of exposed grain boundaries immediately after intergranular fracture showed a very small amount or total absence of B, while B segregated to the grain boundaries after several hours exposure to the ambient system ultra-high vacuum environment at room temperature. Moreover, whenever S was present on grain boundaries both the O and B content was low, and drastically increasing upon S removal by Ar-sputtering. The B segregation appeared to be driven by an electronic nature mechanism related to Ni enrichment and O supplied from the environment resulting in a dynamic state of B.

**AA3.13**  
DIRECT OBSERVATION OF SILVER DOUBLE ATOMIC LAYER IN Al-Cu-Mg-(Ag) ALLOYS INTERFACE. X. Fan, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; C.R. Hutchinson, G.J. Shiflet, Department of MS&E, University of Virginia, Charlottesville, VA; S.J. Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

Alloys based on the Al-Cu-Mg-(Ag) system are expected to be a promising candidate for elevated temperature aerospace applications with its superior creep properties at temperatures up to 200°C due to the new Omega phase on the {111} slip planes of the Al matrix. The function and exact location of Ag are still under debate. Here we show the atomic resolution structure of Ag segregation at the omega/matrix interface by Z-contrast scanning transmission electron microscopy imaging technique. The first sample examined was aged at 200°C. The atomic resolution Z-contrast image shows at least two atomic layers of Ag at the interface of an Omega plate and Al-matrix. The Ag concentration profile across the plate is confirmed by electron energy loss spectroscopy. In the image of the second samples aged at 300°C, atomic steps formed at interface with Ag seen along the

terrace of the growth ledge but not along the riser, indicating further growth of the omega phase is possible by diffusion of Cu and Al through the ledges. The heights of ledges are ranging from one to several atomic layers. In all cases, a double layer of enhanced intensity was found in contrast to the single monolayer of Ag and Mg previously found from other techniques. There is no enhanced intensity at the end of the Omega plates or other phase. Samples aged at 200°C appeared to possess very few thickening ledges.

#### AA3.14

**INFLUENCE OF Fe ON THE MORPHOLOGY OF SPINEL IN THE SYSTEM MgO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>.** O.V. Kharissova, U. Ortiz, M. Hinojosa, FIME UANL, San Nicolas de los Garza, N.L., MEXICO.

The investigation of the morphology of crystalline solid surfaces is of practical and general interest because many processes such as sintering, the growth of epitaxial films and catalytic reactions are intimately connected with surfaces. In this work we study the surface morphology of the spinel as produced in the system MgO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> at 1400° for 15 h in a conventional furnace. The spinel was analyzed by scanning electron microscopy (SEM), X-ray spectrometry (EDX), and atomic force microscopy (AFM). The AFM images were recorded in the contact mode. Images scanned at different magnifications show flat terraces and steps. Experimental observations were made on the nature and distribution of the observed polygonal microstructure.

#### AA3.15

**PHYSICO-CHEMICAL CHARACTERIZATION OF CONVERSION COATINGS GROWN ON ALUMINUM IN CHROMATE SOLUTIONS.** Liana Anicai, Nicoletta Mallandrino, Monica Santamaria, Francesco Di Quarto, Palermo University, Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Palermo, ITALY; Valerie Laget, Rudolph Buchheit, Ohio State University, Department of Materials Science and Engineering, OH.

Chromate conversion coatings (CCCs) are usually applied on Al and Al-alloys in order to improve the corrosion resistance and/or the adhesion of paints. The use of chromate poses several problems due to its toxicity and suspected carcinogenicity. In order to tailor new, environmentally friendly and corrosion resistant coatings, it is necessary to understand the physico-chemical properties and corrosion protection mechanisms of CCCs. In spite of numerous research efforts aimed to characterize CCCs, the chemical composition is not well defined. Additionally, the mechanisms of CCC formation and failure in corrosion protection are not well understood. While previous studies have shown CCCs to be comprised of an amorphous Cr(III) film containing Cr(VI), the electronic properties of these coatings have not been yet investigated. In situ characterization of electronic properties is essential in understanding the corrosion behavior of passivating layers and the accelerating role of redox couples, such as ferro/ferricyanide, in the growth of the conversion layer. The objective of the present study is to characterize CCCs using both ex situ (XANES and AUGER spectroscopy) and in situ (Photocurrent Spectroscopy, PCS) techniques. The detailed PCS study of CCC grown has revealed the formation of p-type semiconducting layers having optical band gap values that depend on preparation conditions and electrochemical history. The energetics of the semiconductor/electrolyte interface has been derived by determining the flat band potential of the junction and the optical band gap of the coating surface. The XANES and AUGER spectroscopy data and the PCS study are in agreement with the formation of a Cr(III)-Cr(VI) mixed valency oxy-hydroxide layer on Al surface in chromate conversion bath. A first evaluation of the chemical composition of the CCC based on all three of these techniques will be presented.

#### AA3.16

**THE INTERFACIAL REACTION PRODUCTS AND MECHANICAL PROPERTIES WITH OXIDIZED LAYER THICKNESS OF SiC PARTICLE IN 2014Al/SiC COMPOSITE.** Jong-Hoon Jeong, Youngman Kim, Chonnam National Univ, Dept of Metallurgical Engineering, Kwangju, KOREA; Jae-Chul Lee, Korea Institute of Science and Technology, Dept of MS&E, Seoul, KOREA.

Metal matrix composites (MMCs) are known to be widely applicable for the parts of transportation devices such as automobiles and aircrafts. Especially Al matrix composites using SiC particles as a reinforcement are spotlighted because of low cost, superior specific modulus, specific strength, wear resistance and high temperature stabilities. But Al<sub>4</sub>C<sub>3</sub> formed by interfacial reaction between Al and SiC weakens the interfacial bonding strength. It also was known to be unstable in the water-soluble atmosphere. In this study, the passive oxidation of SiC powder is used as protective layer against the reaction between matrix Al and SiC particle. The oxidized layer thickness of reinforcement is changed with holding time during 1,2,4,6hr at 1100°. And, 15Vol% SiC particulate reinforced 2014Al composite was fabricated by vacuum hot pressing (VHP) and

subsequent extrusion. We investigated the changes in interfacial reaction product of the composites and mechanical properties such as interfacial bonding strength, tensile strength in terms of the oxidized layer thickness of reinforcement.

#### AA3.17

**ANALYSIS OF SEGREGATION BEHAVIOUR OF GRAIN BOUNDARIES IN SAPPHIRE BY ANALYTICAL AND HIGH-RESOLUTION TEM.** Stefan Nufer, Thomas Gemming, Wolfgang Kurtz, and Manfred Rühle, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

Segregation of yttrium on grain boundaries (GBs) in Sapphire changes the mechanical properties. However, the segregation behaviour of different GB structures is still not understood. Therefore, bicrystals were produced (with and without Y addition) with "special" symmetrical tilt GBs ( $\Sigma 3$ ,  $\Sigma 7$ ,  $\Sigma 11$ ,  $\Sigma 13$ ). The segregation behaviour of these "special" GBs is compared with observations at "general" GBs (symmetrical 24° and asymmetrical  $\Sigma 7$  (0001)<sub>1</sub>/(20 $\bar{2}$ 3)<sub>2</sub>). In order to avoid contamination of the GB by impurities, the bicrystals were produced by diffusion bonding under ultra high vacuum [1]. The deviation from the ideal coincident site lattice orientation [2] is for all "special" GBs less than 0.14°. For the "special" GBs, prior to the bonding process a nominally 2 nm thick layer of Y was sputtered on the bonding planes, whereas for the "general" GB Y was introduced by GB diffusion.

To achieve a better accuracy, the Cliff-Lorimer factor k for Y in Sapphire was determined experimentally by reference measurements in YAG (Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>; k = 4.58), YAM (Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub>; k = 4.49), and YAP (YAlO<sub>3</sub>; k = 4.42), resulting in a mean value of k = 4.5.

At the Y-free  $\Sigma 7$ -bicrystal we found a faceted GB caused by the miscut of the bonding surface. Two kinds of facets were observed: symmetrical (1012) and (0001)<sub>1</sub>/(20 $\bar{2}$ 3)<sub>2</sub>. At the atomical sharp (0001)<sub>1</sub>/(20 $\bar{2}$ 3)<sub>2</sub> facets Si, Ti, and Ca were detected. Within the detection limit (0.3 atoms/nm<sup>2</sup>) no segregation of Si, Ca or Ti was found at the symmetrical GB.

At this stage of investigations it seems that "special" GBs are no good hosts for impurities.

[1] H.F. Fischmeister et al., Rev. Sci. Inst. **64** (1993) 234.

[2] H. Grimmer et al., Phil. Mag. A **61** (1990) 493.

[3] G. Cliff and G.W. Lorimer, Microsc. **103** (1975) 203.

#### AA3.18

**INFLUENCE OF INTERNAL p-n JUNCTIONS ON THE ELECTROCHEMICAL PROPERTIES OF CuO-TiO<sub>2</sub> COMPOSITE MATERIALS IN AQUEOUS SOLUTION.** Y. Massiani and P. Knauth, Laboratoire des Matériaux Divisés, Revêtements, Electroceramiques (MADIREL), Université de Provence-CNRS, Marseille, FRANCE.

Interfaces between semiconductor compounds with different majority carrier are the basis of electronics. Homo- and heterojunction properties are well investigated, but the majority of experimental studies were made on single interfaces, including p-n junctions. We are investigating composite materials of ionic conductors, mixed conductors and insulators. This kind of sample presents a large interface density with a distribution of interface properties. In this study, we prepared composites of p-type copper(II) oxide CuO and nanocrystalline n-type titanium dioxide TiO<sub>2</sub>. A novel preparation route was developed by mixing and room temperature compression of TiO<sub>2</sub> with CuBr followed by annealing in air at 350°C. Under these circumstances, CuBr is completely oxidized into CuO and transient defects due to the previous compression are eliminated, without risks of formation of ternary compounds. The electrochemical properties of the composite in an inert aqueous electrolyte under argon can be interpreted by the presence of a surface layer of TiO<sub>2</sub> nanoparticles. Their carrier density is low, because the n-type TiO<sub>2</sub> nanocrystals can be depleted of electrons by the presence of highly doped p-type CuO.

#### AA3.19

**ORIGIN OF VOIDS AT THE INTERFACE OF WAFER BONDED SAPPHIRE ON SAPPHIRE.** Stephan Senz, Pascal Kopperschmidt and N.D. Zakharov, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

Two sapphire (Al<sub>2</sub>O<sub>3</sub>, r-cut) wafers were bonded at room temperature. The bonding energy increased during heating up to 1100°C. The interface was investigated by plane-view and cross-section TEM. The bonding strength after heating to 1100°C is similar to the bulk bonding strength. A high density of voids at the bonded interface was observed. The voids are elongated along the interface in a pancake shape. The surfaces are low index planes. The volume inside the voids is higher than expected from a model, where a hydrophobic initial bonding is assumed. The strength of initial bonding and the free volume at the interface can be understood, if the sapphire surfaces are covered by several monolayers of water during initial bonding. During annealing the water diffuses out along the

bonded interface and a free volume remains. These results will be compared to investigations of other bonded interfaces, like GaAs/GaAs and Si/Si.

#### **AA3.20**

**MISFIT ACCOMMODATION MECHANISMS AT MOVING REACTION FRONTS DURING THE INITIAL GROWTH STAGE OF  $\text{La}_2\text{Zr}_2\text{O}_7$ -BASED PYROCHLORE THIN FILMS ON YSZ(100).** C.J. Lu, S. Senz and D. Hesse, Max-Planck Institute of Microstructure Physics, Weinberg, Halle, GERMANY.

$\text{La}_2\text{Zr}_2\text{O}_7$ -based pyrochlore (LZO) thin films were grown on  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2(100)$  (YSZ) single crystals by reaction (at  $1100^\circ\text{C}$  in vacuum) between the crystals and  $\text{La}_2\text{O}_3$  vapour, which was produced by e-beam evaporation. The initial stage of film growth is studied by using X-ray diffraction, atomic force microscopy and transmission electron microscopy (TEM). The atomic structure of LZO-YSZ reaction fronts is also investigated by cross-sectional high resolution TEM. Film growth begins with isolated square islands, which later coalesce forming a continuous film. The islands generally nucleate at the surface steps of YSZ crystals and they are well oriented to YSZ in the very beginning of the reaction. Above a certain size (100 nm), however, they always show a characteristic domain structure. Each island typically consists of four domains which are tilted by a small angle off the exact cube-to-cube orientation around four different  $\langle 110 \rangle$  axes. These domains arise from the large positive lattice mismatch between LZO and YSZ (5.0%). This lattice mismatch leads to a network of interfacial edge dislocations, with their Burgers vectors pointing out of the plane of the reaction front. The Burgers vector component perpendicular to the interface leads to a slight tilt of the LZO lattice with respect to the YSZ lattice. It has also been found that the nucleation, shape and domain structure of LZO islands strongly depend on the surface steps and defects of YSZ substrates. Interestingly, a hole is present at the centre of each island and sometimes more than four domains are formed in one island.

#### **AA3.21**

**SPIN POLARIZED INJECTION INTO A D-WAVE SUPER-CONDUCTOR.** Z.Y. Chen, Amlan Biswas, Igor Zutic, T. Wu, S.B. Ogale, R.L. Greene and T. Venkatesan.

High quality  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO)/ $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) and  $\text{LaNiO}_3$  (LNO)/ $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) interfaces have been prepared by PLD technique. Using a simple and unique testing device structure, we are able to obtain transport properties across these interfaces, and their temperature, magnetic field and surface roughness dependence. The results show evidence for Andreev bound states induced zero conductance peaks, in both normal metal / YBCO and LNO/YBCO interface. Further, these peaks are completely suppressed by spin polarized injection at LSMO/YBCO interface at low temperature. However, they persist at high temperature because of the well known fact that the surface polarization of colossal magnetic material (CMR) drops rapidly with temperature. This phenomenon can be used as an indicator of surface spin polarization. It also has potential for practical applications such as a spin detector and spin filter.

#### **AA3.22**

**POLARIZATION AND LOCAL POTENTIAL AT LATERALLY BIASED PTCR INTERFACES.** Sergei V. Kalinin, Dawn A. Bonnell, Dept. Mat. Sci. Eng., University of Pennsylvania, Philadelphia, PA.

Variable temperature Atomic Force Microscopy (AFM), Scanning Surface Potential Microscopy (SSPM) and Piezoresponse Imaging (PRI) are used to directly measure potential and polarization variations at positive temperature coefficient of resistance (PTCR)  $\text{BaTiO}_3$  interfaces. SSPM image contrast is comprised of contributions due to chemical inhomogeneities on the surface and charged grain boundaries; potential variations due to local polarization were not detected. The polarization distribution within grains can be visualized by PRI. Dynamic interface behavior is examined by in-situ measurements with laterally applied local bias. No potential steps at the grain boundaries were detected under ambient conditions. Imaging at elevated temperatures revealed potential drops on electroactive grain boundaries. The temperature dependencies of piezoresponse and potential drops across grain boundaries were quantified and compared to Ginzburg-Devonshire and Heywang - Jonker theories. The dependencies of potential drop across grain boundaries and potential profile width on external bias was investigated. Possibilities for the extraction of potential and current distributions from SSPM data are discussed.

#### **AA3.23**

**INTERACTION BETWEEN PLANAR DEFECTS AND OXYGEN IMPURITIES IN Si THIN FILMS.** Yanfa Yan, M.M. Al-Jassim, T.H. Wang and T.F. Ciszek, National Renewable Energy Lab, Golden, CO.

The structure of planar defects in rapid deposited polycrystalline Si

thin films was determined using high-resolution transmission electron microscopy. The interactions between these defects and oxygen atoms were studied by first-principles total energy calculations. We found that extrinsic stacking faults attract oxygen impurities, forming possible silicon oxides, while intrinsic stacking faults repel oxygen impurities. The lamellar twins, however, have very little interaction with oxygen impurities. These results and their implications will be discussed.

#### **AA3.24**

**THE ATOMIC STRUCTURE OF THE Si-SiO<sub>2</sub> INTERFACE AND ITS RELATION TO TEM IMAGING OF THE INTERFACE.** Peter Fejes, Digital DNA Laboratories, Motorola, Inc., Mesa, AZ; Alexander A. Demkov, Physical Sciences Research Laboratories, Motorola, Inc., Tempe, AZ.

We combine *ab-initio* calculations, image modeling and high resolution TEM to infer the atomic structure of the thermally grown Si-SiO<sub>2</sub> interface and its effect on the valence band offset. The theoretical structural models assume diffusion driven growth of the buried oxide in contrast to those recently discussed by Buzcko *et al.* [1]. Our models result in a valence band offset in good agreement with experimentally observed values. These models result in a chemically and structurally non-uniform interface. However, if this microroughness is on a scale of a few atomic layers, the interface will appear smooth in a TEM image.

[1] R. Buzcko, S.J. Pennycook, and S.T. Pantelides, Physical Review Letters **84**, **943**, (2000).

#### **AA3.25**

**DEGRADATION IN SURFACE EXCHANGE RATES DUE TO SURFACE ENRICHMENT OF STRONTIUM AND CHROMIUM IN MIXED CONDUCTING  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ .** P.A.W. van der Heide, A.K. Verma, S. Wang, A.J. Jacobson, University of Houston, Materials Research Science and Engineering Center, Houston, TX.

The  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  perovskite type oxide is one of many new oxides that are presently being synthesized at MRSEC with the aim of using them ion transport membranes. Such materials should exhibit among other things, high O surface exchange coefficients. Conductivity relaxation measurements, however, indicate a degradation in the long-term oxygen transport kinetics, or more precisely the surface exchange kinetics of this material. Since bulk transport properties were not effected, angle resolved X-ray photoelectron spectroscopy (XPS) was used to examine whether segregation may be responsible. Indeed, Cr and Sr surface enrichment was observed along with oxidation of Cr. This was revealed through (a) compositional analysis of the outer most atomic layers and (b) shifts in the positions of the Cr and Sr photo-electron peaks.

#### **AA3.26**

**ASYMMETRIC ELECTRICAL EFFECTS IN ZINC OXIDE GRAIN BOUNDARIES VERIFIED BY ELECTRON AND ION SCANNING MICROSCOPY.** Mattias Elfving, Mikhail E. Gaevski, Eva Olsson, Analytical Materials Physics, The Angström Laboratory, Dept. of Materials Science, Uppsala, SWEDEN; Anders Kvist, Microscopy and Microanalysis, Dept. of Experimental Physics, Chalmers, Göteborg, SWEDEN.

3D-investigations of electrically active grain boundaries in ZnO varistor material have been performed using electron beam induced current (EBIC) contrast in the scanning electron microscope (SEM) with nano-meter spatial resolution. To study the depth dependence of the EBIC signal, the accelerating voltage was varied from 2 kV to 30 kV. Subsequent cross section preparation using a focused ion beam workstation allowed the tilt angle for certain grain boundaries to be determined with a precision better than one degree. Experimental EBIC profiles, obtained by scanning the e-beam across grain boundary, were compared with computer simulations made using three well known models of electron-hole generation functions: pear-shaped, spherically-symmetrical Gaussian and their linear combination [1]. The effect of grain boundary alignment, below the sample surface, on the EBIC signal was separated from the influence of the depletion region geometry. The entire width of the depletion region was estimated to be less than 100 nm. Differences in the depletion region width between the two sides of individual grain boundaries was observed experimentally at zero bias voltage. The dependence of this asymmetry on the value of applied bias voltage was also studied. Various combinations of tilting angle and asymmetry assuming the presence of a double Schottky barrier at the individual grain boundary [2] were analysed. Several origins of the barrier asymmetry under zero bias voltage conditions are discussed. References:

1. R. Corkish, T. Puzzer, A.B. Sproul, and K.L. Luke, Quantitative interpretation of electron-beam-induced current grain boundary contrast profiles with application to silicon. Journal of Applied

Physics, 84(10), 5473-5481 (1998).

2. F. Greuter, and G. Blatter, Electrical properties of grain boundaries in polycrystalline compound semiconductors. *Semiconductor Science and Technology*, 5, 111-137 (1990).

#### **AA3.27**

**MICROSTRUCTURAL CHANGES OF INDIUM TlN OXIDE (ITO) THIN FILMS AS A FUNCTION OF RESISTANCE BY TEM.**

Tam Yau Chan, Changmo Sung, University of Massachusetts Lowell, Dept of Chemical and Nuclear Engineering, MA; G.M. Yang, ITO Division, Samsung Corning, Gumi, KOREA.

A set of Indium tin oxide (ITO) thin films with different thickness was prepared by dual magnetron sputtering technique on the two layers substrate (250 $\mu$ m SiO<sub>2</sub> layer and glass substrate). The electronic properties of ITO thin films are highly dependent on the deposition parameters. In this work, cross sectional and plan view ITO samples are going to be studied by Transmission Electron Microscopy (TEM) and the composition of ITO thin film is examined by EDXS. We want to find out the relation of ITO thin film thickness and resistance, and the grain size in plan-view observation.

#### **AA3.28**

**GRAIN SIZE DEPENDENT CONDUCTIVITY IN MIXED IONIC/ELECTRONIC CONDUCTIVE CERIUM OXIDE.**

Andreas Tschöpe, Rainer Birringer, Universität des Saarlandes, Technische Physik, Saarbrücken, GERMANY.

Variation of the grain size of polycrystalline cerium oxide in the micro- and nanometer regime and the impact on electrical conductivity was investigated. At a temperature of 500°C and high oxygen partial pressure, a transition from extrinsic ionic to redox controlled electronic conductivity upon reduction of grain size was observed. The electronic conductivity of nanocrystalline ceria was larger than the intrinsic electronic conductivity of pure single crystalline ceria and was increasing with decreasing grain size. A theoretical model based on space charge theory was developed, which explicitly takes into account the opposite sign of the two mobile charge carriers, i.e. electrons and oxygen vacancies, and their segregation in space charge layers. Calculations of the size dependent electrical conductivity will be presented and compared with experimental results. The impact of space charge layers on surface reduction and stoichiometry will also be discussed.

#### **AA3.29**

**INFLUENCES OF DEFECT SEGREGATIONS ON THE POTENTIAL BARRIER FORMATION IN Nb-DOPED SrTiO<sub>3</sub> GRAIN BOUNDARY LAYER.** Seong-Ho Kim, Jung-Ho Moon, Kun-II Park and Yoonho Kim, Multifunctional Ceramics Center, Korea Institute of Science and Technology, Cheongryang, Seoul, KOREA.

The origins of defect formations have been investigated in Nb-doped SrTiO<sub>3</sub> single crystal and ceramics using electrochemical methods. In particular, impedance spectroscopy was applied to determine thermal activation energies for the conduction of Nb-doped SrTiO<sub>3</sub> grains and grain boundaries. From results, it was suggested that the activation energy, 0.8 eV, measured in grains was originated from oxygen vacancies and the activation energy, 1.3 eV, in grain boundaries was from strontium vacancies. Direct observations using a high-resolution transmission electron microscopy (HR-TEM) and an energy dispersive spectroscopy (EDS) revealed that Nb-doped SrTiO<sub>3</sub> ceramics were composed of well-developed crystalline grains whose boundaries have a facet structure. And it was found that the strontium vacancies were segregated near grain boundary layers. The space charge formations originated from the defect segregations were believed to be responsible for a potential barrier in grain boundaries. On the basis of the kinetic process of the defects and the observed electrical behavior in time and temperature domains, the effects of the space charge segregation on the electrical properties of grain boundaries were also studied.

#### **AA3.30**

**FIRST PRINCIPLES CALCULATIONS OF ZrO<sub>2</sub>/Ni INTERFACES.**

Katsuyuki Matsunaga, Masanori Kohyama, Singo Tanaka, Dept. of Materials Physics, Osaka National Research Institute, Ikeda, Osaka, JAPAN; Hideaki Matsubara, Japan Fine Ceramics Center, Nagoya, JAPAN.

It is very important to understand atomic structures and properties of ceramic / metal interfaces for practical applications such as coating systems. In this study, we performed ab initio calculations of ceramic / metal interfaces using a plane-wave basis set and norm-conserving pseudopotentials. Special attention was paid to systems including zirconia (ZrO<sub>2</sub>) and nickel (Ni), such as may be found in thermal barrier coatings and solid oxide fuel cells. We first constructed the norm-conserving pseudopotentials for Zr, O and Ni from first principles. We found that the calculated lattice constants and bulk moduli of cubic ZrO<sub>2</sub> and fcc Ni are in good agreement with

experiment. Secondly, we calculated atomic and electronic structures at interfaces between the cubic ZrO<sub>2</sub> (001) plane and fcc Ni (001) plane, and analyzed bonding characteristics at the interface. This study was supported by the Proposal-Based New Industry Creative Type Technology RD Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

#### **AA3.31**

**GRAIN AND GRAIN BOUNDARY ANALYSIS OF NANO-CRYSTALLINE TUNGSTEN TRIOXIDE USING HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM) AND ELECTRON ENERGY LOSS SPECTROSCOPY (EELS).**

A. Hoel, E. Olsson, L.B. Kish, M. Saunders, Department of Materials Science, The Angström Laboratory, Uppsala University, Uppsala, SWEDEN.

Tungsten trioxide (WO<sub>3</sub>) is a very versatile material. It is widely used in different thin film technologies, for example as the electrochromic film in smart windows and as the active layer in chemical sensors. In this work, tungsten trioxide nanoparticles were produced using an advanced gas evaporation unit where the tungsten was oxidized in low pressure ambient air. The tungsten trioxide particles were formed via vapor condensation and deposited on glass substrates by gas deposition technique to avoid coagulation effects. The nanocrystalline films showed resonance and negative capacitance effects in the impedance spectrum. The fabrication conditions and the film thickness had a large influence on the characteristics. The degree of sintering and the crystallinity of the different particles were studied using high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS). Particular attention has been paid to the grain boundaries in the films.

#### **AA3.32**

**SEGREGATION OF FISSION PRODUCTS TO SURFACES OF UO<sub>2</sub>.**

Chris Stanek, Robin Grimes, Imperial College, Dept of Materials, London, UNITED KINGDOM; Mark Bradford, British Energy, Gloucestershire, UNITED KINGDOM.

In order to predict the release rates of fission products from UO<sub>2</sub> nuclear fuel, it is necessary to determine the energetics associated with their segregation from the bulk to surfaces. Segregation is determined by calculating the total energy of a simulation repeat unit which includes a fission product, as a function of the distance of the fission product from the surface. We have investigated the possibility that specific fission products segregate preferentially to certain surfaces. In particular, Zr<sup>4+</sup> and Ce<sup>4+</sup> segregate to the (100) surface, while Ba<sup>2+</sup> and Sr<sup>2+</sup> segregate to the (111) surface. Kr<sup>0</sup> and Xe<sup>0</sup> are presently under investigation. Two issues make these calculations more complex. First, charged defects need to be compensated by oxygen vacancies. For example, divalent Ba<sup>2+</sup> and Sr<sup>2+</sup> substituting on uranium sites are compensated by a single oxygen vacancy, while zero-valent Kr<sup>0</sup> and Xe<sup>0</sup>, similarly substituting on uranium sites, are compensated by two oxygen vacancies. Second, certain surfaces, such as the (100), are inherently unstable, but can be stabilized by oxygen vacancies. Arrangements of these defects lead to complex defect structures which have several geometric configurations and must be duly considered.

#### **AA3.33**

**ELLIPSOmetry AS A SENSITIVE TECHNIQUE TO PROBE OXIDE FILM-SUBSTRATE INTERFACES: ALUMINA ON SILICON{100}.**

M.P. Singh and S.A. Shivashankar, K. Chattopadhyay, Materials Research Centre, Indian Institute of Science, Bangalore, INDIA; G. Raghavan, Indira Gandhi Centre for Atomic Research, Kalpakkam, INDIA.

An attempt has been made to study the film-substrate interface, which is an open problem in thin film science and technology field, by using a sensitive, non-conventional tool. Because of the prospective use of alumina as the gate oxide in MOSFET devices, we have chosen to study alumina films grown on silicon. Film-substrate interfaces of as-grown alumina on Si{100} have been studied systematically using spectroscopic ellipsometry, supported by cross-sectional SEM, and SIMS. The alumina films used in the present study were deposited by low-pressure metalorganic chemical vapor deposition (MOCVD) using aluminum acetylacetonate {Al(acac)<sub>3</sub>} as the precursor. Ellipsometric data were recorded in the wavelength range of 300-1000 nm. The  $\epsilon_1, \epsilon_2$  versus wavelength data obtained for films grown at 600°C, 700°C, and 800°C were modeled to fit a substrate/interface/film "sandwich". The experimental results reveal (as may be expected) that the nature of the substrate-film interface depends strongly on the growth temperature. The simulated  $\epsilon_1, \epsilon_2$  patterns are in excellent agreement with observed spectroscopic data, which reveal both sharp interfaces and diffuse ones with voids. The use of aluminum acetylacetonate as CVD precursor results in the presence of carbon in the films. Theoretical simulation was able to account for the ellipsometry data by invoking the presence of "free" carbon in the alumina films. For example, the observed variation in the index of refraction of the films

as a function of growth temperature can be explained in this manner. The nature of films-substrate interface was also examined using cross-sectional SEM, which reveals columnar growth. The SIMS analysis corroborates the presence of carbon in thin films. The distribution of carbon in the alumina matrix and at the interface was profiled using SIMS.

**AA3.34**  
INTERDIFFUSION EFFECTS ON THE MAGNETIC PROPERTIES OF EPITAXIAL COBALT FERRITE THIN FILMS. G. Hu, Y. Suzuki, Dept. of Materials Science and Engineering, Cornell University, Ithaca, NY; V.G. Harris, Naval Research Laboratory, Washington, DC.

Epitaxial cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) thin films were grown on  $\text{CoCr}_2\text{O}_4$  buffered  $\text{MgAl}_2\text{O}_4$  substrates by pulsed laser deposition. Post deposition annealing in air at  $1000^\circ\text{C}$  changed the sign and magnitude of the magnetic anisotropy. Interdiffusion between the film and buffer layer, as a result of annealing, was directly observed by Rutherford backscattering spectroscopy and electron microprobe measurements. Due to the chemical and structural similarity between  $\text{CoFe}_2\text{O}_4$  and  $\text{CoCr}_2\text{O}_4$ , there was no phase change but cation redistribution among the interstitial sites during the annealing process, as observed in extended x-ray absorption fine structure and electron energy loss spectroscopy (EELS). By varying the annealing time, we observed an evolution of the in-plane magnetic anisotropy, which can be attributed to an increasing magnetic contribution from the interdiffusion layer. For films grown on bare  $\text{MgO}$  substrates, the interdiffusion between film and underlying substrate resulted in phase segregation, as verified by a combination of annular darkfield images and EELS analyses from scanning transmission electron microscope. These observations were consistent with magnetic measurements of annealed films grown on  $\text{MgO}$ .

**AA3.35**  
OXIDE MONOLAYER PASSIVATION OF POLAR AND NONPOLAR SURFACES OF  $\alpha$ -SiC. Eva Rauls, Zoltán Hajnal, Thomas Frauenheim, Univ Paderborn, Dept of Theoretical Physics, GERMANY; Péter Deák, Budapest Univ of Technology and Economics, Dept of Atomic Physics, HUNGARY.

Oxide interface quality, among others, is one of the major issues in SiC electronics. Although the native oxide of SiC is the same as that of Si, its interface quality is still orders of magnitude worse! Microscopic modelling of Si-SiO<sub>2</sub> interfaces has only recently provided some enlightening views of interface structure and formation dynamics. Since hexagonal SiC surfaces are not only chemically, but also topologically different from Si, a direct transfer of the experience in Si oxidation to SiC is not possible. Therefore we present density functional based theoretical investigations of the structure and energetics of polar, as well as nonpolar 4H- and 6H-SiC surfaces. Monolayer coverage of a surface is certainly very important in the initial phase of the oxidation process. The existence of such a stable monolayer on the SiC (0001) surface has recently been shown by electron microscopy and complementary theoretical simulations. Si-O-Si chain element connected to the Si terminated SiC surface by additional O atoms can be identified as characteristic feature of this structure. However, it leaves one third of the dangling bonds unsaturated, thus the surface chemically active. On the other hand, systematic Si-O adstructure construction on both (11 $\bar{2}$ 0) and (10 $\bar{1}$ 0) nonpolar SiC surfaces yields interfaces without unsaturated bonds, and provide a well-defined, passivated, abrupt interface between SiC and the oxide monolayer. Furthermore, the SiO<sub>2</sub> decorated SiC (11 $\bar{2}$ 0) surface, besides being chemically inert, also represents a low-strain, atomically smooth interface between SiC and its oxide. Our results may stimulate further research towards the use of these surfaces in SiC device applications.

**AA3.36**  
AMORPHIZATION OF CRYSTALLINE ORTHOBORIC ACID ON A VITREOUS B<sub>2</sub>O<sub>3</sub> SUBSTRATE. Eric McCalla, Ralf Brüning, Mount Allison Univ, Dept of Physics, Sackville, NB, CANADA.

Crystals of orthoboric acid form readily when vitreous boron oxide is exposed to humid air. Crystals grow with a preferred orientation such that planar sheets of B(OH)<sub>3</sub> molecules are aligned parallel to the surface of the vitreous substrate. These samples are studied by time resolved, *in situ* x-ray diffraction measurements. After the space above the sample is evacuated following a controlled exposure to air, it is found that crystal peaks disappear altogether and only an amorphous scattering pattern remains. Thus the B(OH)<sub>3</sub> crystal phase on an anhydrous B<sub>2</sub>O<sub>3</sub> glass substrate decays in favor of the glass with dissolved water. During the decay the remaining crystalline material changes its orientation so that the B(OH)<sub>3</sub> layers become perpendicular to the substrate. To interpret these data, the B<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O binary system is investigated to determine how much water the vitreous phase can contain before orthoboric acid is formed,

and to find the relative amounts of the amorphous and orthoboric acid phases for samples with higher water content. An amorphization process similar to the one considered here, occurring at the interface of crystalline metallic phases, has been studied extensively.

[1] In the present case outdiffusion of water, rather than interdiffusion of one of the elements, drives the process.

K.S. Samwer, H.J. Fecht and W.L. Johnson, in H. Beck and H.J. Güntherodt (eds.) *Glassy Metals 3*, (Springer, Berlin, 1994).

**AA3.37**  
Abstract Withdrawn.

**AA3.38**  
MICROSTRUCTURE OF SPUTTER DEPOSITED TiO<sub>2</sub>/SiO<sub>2</sub> MULTILAYER OPTICAL COATINGS. E. Mateeva, J.J. Moore, Dept of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO; P. Sutter, Department of Physics, Colorado School of Mines, Golden, CO.

The main requirements for the materials forming a TiO<sub>2</sub>/SiO<sub>2</sub> multilayer optical filter are structural and optical stability. The aim of the present work was to relate the observed structural properties to the optical stability of the filters. The TiO<sub>2</sub>/SiO<sub>2</sub> multilayer optical filters were deposited by d.c. magnetron reactive sputtering at room temperature (RT). The multilayers were annealed at low temperatures (RT -  $320^\circ\text{C}$ ) to study the changes in microstructure. Cross-sectional transmission electron microscopy (XTEM) was used to investigate the microstructure of TiO<sub>2</sub>/SiO<sub>2</sub> multilayers. The transmission of the multilayers was measured after environmental exposure over extended time periods. The transmission edge of the multilayers grown at RT was found to gradually shift with environmental exposure. In contrast the transmission edge of the annealed multilayers was found to shift during annealing but to remain stable after environmental exposure. The XTEM investigations show that while the SiO<sub>2</sub> layers in the TiO<sub>2</sub>/SiO<sub>2</sub> multilayer grown at RT are homogeneous the TiO<sub>2</sub> layers consist of nanocolumns with axes parallel to the growth direction and intercolumnar regions consisting of voids or non-stoichiometric oxide. These regions with voids most probably act as channels for water absorption that leads to the change in transmission of the filters. In the case of the annealed multilayers the optical stability was found to be due to densification of the materials forming the TiO<sub>2</sub>/SiO<sub>2</sub> multilayer and transition to polycrystalline anatase phase in the TiO<sub>2</sub> layers.

**AA3.39**  
NON-STOICHIOMETRY OF NANOCRYSTALLINE CUBIC ZIRCONIA THIN FILMS. Igor Kosacki, Toshio Suzuki and Harlan U. Anderson, Electronic Materials Applied Research Center, University of Missouri-Rolla, Rolla, MO.

Since the enhanced properties of nanocrystalline materials are attributed to grain boundary and size-dependent defect equilibria, it is important to determine the relationship between the stoichiometry and microstructure. This can be achieved for oxides by the measurements of the electrical conductivity as a function of oxygen activity and temperature. In the present work, the results obtained on a study of the influence of microstructure and type of acceptor on the electrical transport of nanocrystalline ZrO<sub>2</sub>:16%M (M=Y; Sc) thin films are reported. The results show that the ionic conductivity of 20nm grain sized ZrO<sub>2</sub>:Y and ZrO<sub>2</sub>:Sc thin films is enhanced above one order of magnitude (at  $900^\circ\text{C}$ ) compared with microcrystalline specimens. In addition it has been observed that the stoichiometry is also dependent upon the type of acceptor. The electronic conductivity of ZrO<sub>2</sub>:Sc is about 4 orders of magnitude higher than observed for ZrO<sub>2</sub>:Y, which suggests a reduction of the enthalpy of oxygen vacancy formation in Sc-doped specimen. The results showed that the electrical properties of nanocrystalline oxides are indeed dependent upon the microstructure and it is possible to control these properties by establishing their relationships to defect equilibria and type of dopant.

**AA3.40**  
DISORDER-ORDER TRANSITION IN MESOSCOPIC SILICA THIN FILMS. N. Yao, A.Y. Ku, N. Nakagawa, T. Lee, D.A. Saville and I.A. Aksay, Princeton Materials Institute and Department of Chemical Engineering, Princeton University, Princeton, NJ.

Electron microscopy has been used to study the mesoscopic (nanometer-level) and microscopic (micron-level) structural evolution of mesoscopic silica thin films grown at the air-water interface under dilute, acidic (pH < 2) conditions. Transmission electron microscope observations reveal that the film begins with a disordered (amorphous) structure. Over time, mesoscopically ordered regions (hexagonally packed cylindrical channels) nucleate and grow within the film. Scanning electron microscopy reveals microscopic structural features such as ribbons, protrusions, domain boundaries, microindentations, and pits. Our work shows that mesoscopic order develops within the film through a "disorder to order transition." Our

observations also clarify the role of the air-water interface in confining film growth to two dimensions during the initial stages. We note that a two-dimensional (in plane) to three-dimensional (unconstrained) growth transition occurs when the film exceeds a critical thickness. We extend the current understanding of the structural evolution of the film by providing a detailed mechanism for the development of mesoscopic order and microscopic features and consider the possibility of a universal growth mechanism for films and particles.

**AA3.41**  
RELATIONSHIPS BETWEEN FILM CHEMISTRY, STRUCTURE, AND MECHANICAL PROPERTIES IN TITANIUM OXIDES. M. Pang, D.E. Eakins, M.G. Norton and D.F. Bahr, Mechanical and Materials Engineering, Washington State University, Pullman, WA.

Titanium oxides grown anodically on titanium metal exhibit vastly different mechanical properties when the film growth rate is varied. These mechanical property variations, from extremely soft to hard as measured using nanoindentation techniques, are shown to be linked to the film structure. Crystal structures were examined using thin film x-ray diffraction and TEM, film thickness and composition were analyzed with both XPS and RBS. The strength of the oxide films tended to increase as the films were grown more quickly, corresponding to films which contained a high amorphous content. Films which were grown slowly, and consisted of substantial fractions of rutile and anatase, were softer than the original titanium surface. This softening is likely due to defect structures present in these films, leading to large numbers of sites where a localized stress field generated via nanoindentation can cause either fracture or grain boundary sliding. The growth rate is shown to impact the interface between the exterior oxide and the metal, with RBS spectra of films grown at faster rates showing a smaller region of non-stoichiometric oxide present in between an outer titanium dioxide film and the underlying metal.

**AA3.42**  
INTERFACIAL EFFECTS IN VO<sub>2</sub>/Al/Si(100) THIN FILM HETEROSTRUCTURES. K. Dovidenko, S. Beasor, A. Topol, H. Efsthadiadis, S. Oktyabrsky and A.E. Kaloyeros, NYS Center for Advanced Thin Film Technology, University at Albany-SUNY, Albany, NY; S. Shokhor and S. Naar, CopyTele Inc., Melville, NY.

Vanadium dioxide is a promising candidate material for use in various electronic and opto-electronic applications that are based on temperature-induced metal-insulator transitions. However, the existence of a wide range of vanadium oxide crystalline phases results in significant technological challenges since only one particular phase, namely VO<sub>2</sub>, does exhibit the desired phase transition. In order to fully address key material and process challenges pertaining to the reliable and reproducible development of the target VO<sub>2</sub> system, VO<sub>2</sub>/Al thin film heterostructures were fabricated on Si(100) by a combination of PVD and CVD methods. Detailed chemical and structural characterization of the resulting heterostructures was carried out using Rutherford Backscattering, Auger Electron Spectroscopy, Nuclear Reaction Analysis, X-Ray Diffraction, Scanning Electron Microscopy, and Transmission Electron Microscopy (TEM). These studies compared the structural, physical, and chemical properties of two types of 20-30 nm thick VO<sub>x</sub> layers: one which exhibited a metal-insulator phase transition, and another which failed to undergo a temperature-induced transition. Interfacial study done by high-resolution TEM in combination with energy dispersive x-ray analysis and electron energy loss spectroscopy showed the existence of an aluminum oxide interfacial layer between VO<sub>2</sub> and Al for the samples with metal-insulator phase transition. The presence of more than one V-O phase with smooth VO<sub>x</sub>/Al interface was established for the structures exhibiting no phase transition. Pertinent details of compositional/structural studies are presented, along with a discussion of their correlation to observed physical properties.

**AA3.43**  
INFLUENCE OF PREGATE CLEANING AND OXIDATION PROCESSES ON THE GATE OXIDE PERFORMANCE. X. Duan, MIT, Dept of Materials Science and Engineering, Cambridge, MA and National Semiconductor, South Portland, ME; S. Ruby, J. Barret, K. Kisslinger and L. Mayes; National Semiconductor, South Portland, ME.

The Si(100)/SiO<sub>2</sub> interface is attracting new interest as gate dielectrics in MOS devices become ultrathin. A systematic investigation of the kinetics of silicon etching and oxidation in pregate cleaning and SiO<sub>2</sub> growth processes has been performed. Using the High-Resolution Transmission Electron Microscopy (HRTEM) technique, we have observed Si/SiO<sub>2</sub> interface at an atomic level. We have found a direct experimental relationship between the pregate cleaning scheme, Si/SiO<sub>2</sub> interface morphology, and electrical properties of gate oxides. When H<sub>2</sub>O<sub>2</sub>:NH<sub>4</sub>OH > 1.6, the roughness of the Si/SiO<sub>2</sub> interface was dramatically improved, which, in turn, increased the gate break down voltage to an ideal value of VBD=7 V.

We have observed the preferential growth of SiO<sub>2</sub> along certain Si directions during the early stages of thermal SiO<sub>2</sub> growth on Si(100). The effect of the initial condition of Si surface on the preferential growth of SiO<sub>2</sub> layer has been studied. The experimental results will be compared with our modeling in this talk.

**AA3.44**  
EPITAXY OF PEROVSKITE PZT FILMS GROWN UNDER HYDROTHERMAL CONDITIONS. K. Mikulka-Bolen, P. Pinceloup, M. Oledzka, W. Suchanek, W. Mayo, R. Riman, Rutgers Univ, Dept of Ceramic and Materials Engineering, Piscataway, NJ; T. Ryan, Philips Analytical, Natick, MA; V. Kogan, Philips Analytical, Almelo, NETHERLANDS; L. McCandlish, Ceramaré Corp, Highland Park, NJ.

The degree of crystal perfection obtainable in epitaxial perovskite films does not yet approach that of epitaxial semiconductor films, regardless of the oxide synthesis method. The reasons for this discrepancy may be related to substrate defects, lattice mismatch, crystal structure or synthesis factors. The influence of variations in hydrothermal synthesis conditions and substrate quality on film microstructure, orientation and composition was investigated to identify factors that limit the crystal quality of perovskite films. Epitaxial PZT [Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub>] films (x>0.5) were synthesized on (100) oriented SrTiO<sub>3</sub> substrates at temperatures from 150 to 300°C. Conventional powder XRD ( $\theta$ -2 $\theta$ ) scans were used to confirm that the epitaxial films were single-phase perovskite PZT. XRD texture measurements were used to compare the orientation and crystal quality of films grown under different hydrothermal conditions. Continuous epitaxial layers were observed to be transparent under SEM, with the surface either atomically smooth or dominated by a screw dislocation-type morphology. Textured polycrystalline layers were observed to be opaque under SEM, and sometimes contained areas of transparent, tilted pseudocubic crystals. XRD reciprocal space mapping was used to determine the quality of epitaxy from the broadening of intense symmetric (200) and (400) and asymmetric (013) reflections in reciprocal space. The XRD measurements were correlated with RBS data on film thickness and composition. Films less than about 100 nm in thickness showed the best epitaxial crystal quality, with rocking curve FWHM values as low as 0.08°. Films thicker than 100 nm showed a series of overlapping peaks, indicating that the film composition and lattice parameter may vary normal to the film-substrate interface to minimize lattice mismatch. Thicker films also showed broader rocking curve widths, indicating that epitaxial quality decreased as film thickness increased above 100 nm. Current research focuses on improving epitaxial crystal quality at the film-substrate interface.

**AA3.45**  
EFFECT OF SUBSTRATE SURFACE STRUCTURE AND DEPOSITION CONDITIONS IN THE MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF TiN OXIDE THIN FILMS. Juan E. Dominguez, Li Fu, Xiaoqing Pan, Univ of Michigan, Dept of Materials Science and Engineering, Ann Arbor, MI; Paul Van Rompay, Zhiyu Zhang, Peter Pronko, Center for Ultrafast Optical Science and Department of EECS, University of Michigan, Ann Arbor, MI.

Tin oxide (SnO<sub>2</sub>) films were deposited on sapphire and silicon substrates at temperatures ranging from room temperature to 700°C. The effect of electrical discharge and background oxygen on the thin film microstructure and electrical properties was studied. The microstructure of the films was characterized by transmission electron microscopy and x-ray diffraction. SnO<sub>2</sub> films fabricated consist of different textures in microstructures which depend on the deposition conditions and substrate surface structures. For instance, films deposited on the (10 $\bar{1}$ 2) sapphire (r-cut) are amorphous if deposited at room temperature, whereas films deposited at 700°C were epitaxial and single crystal. Discharge and oxygen pressure had a strong effect on the ion/neutral ratio of the ablated plasma plume of SnO<sub>2</sub>. Annealing in air had an effect in the change of film microstructure. Gas sensitivity of these films and their relationships to microstructures will also be presented.

**AA3.46**  
A COMBINED THEORETICAL AND EXPERIMENTAL STUDY OF GRAIN BOUNDARIES IN STRONTIUM TITANATE. S. Hutt, S. Köstlmeier, T. Gemming, C. Elsässer and M. Rühle, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

A novel technique was developed which allows the reproducible preparation of accurately orientated grain boundaries in SrTiO<sub>3</sub> bicrystals by diffusion bonding. The resulting atomistic interface structures were analysed by high-resolution transmission-electron-microscopy. For a theoretical understanding of grain boundary structures and properties, ab-initio local-density-functional calculations with a mixed-basis pseudopotential method were carried out for the structurally simplest bicrystal with a  $\Sigma$  3 (111)

symmetrical twin grain boundary. A low grain boundary energy of  $0.52 \text{ J/m}^2$  was obtained. Minor structural relaxations compared to a purely geometrical coincidence-site-lattice model appear close to the interface both in theory and experiment. Although a rather small slab model with periodic boundary conditions was employed in the calculations, the calculated interface structure agrees well with the experimentally observed one. An analysis of the calculated local electronic structures shows that the perturbation induced by the grain boundary is localized in the near vicinity of the grain boundary plane without far extension into the bulk region. Based on the present results obtained with the small slab model, no evidence can be derived for a build-up of a space-charge layer at the undoped  $\Sigma 3$  (111) grain boundary.

#### **AA3.47**

**CHARACTERIZATION OF OXIDE LAYERS OF BULK  $\text{Si}_{1-x}\text{Ge}_x$ .** W. Suzukake, S. Nemoto, T. Iida, Y. Takanashi, S. Sakuragi\*, Science University of Tokyo, Dept of Materials Science and Technology, Chiba, JAPAN. \*Union Material Inc, Ibaraki, JAPAN.

Silicon germanium ( $\text{Si}_{1-x}\text{Ge}_x$ ) alloys are important as a material not only for microelectronic devices but also for thermoelectric devices to be used in energy conversion. Recently,  $\text{Si}_{1-x}\text{Ge}_x$  alloy has also attracted much attention as a solar cell material with the high conversion efficiency (A43%) which is considered to be caused by carrier multiplication due to Auger mechanism. However, since the surface recombination velocity of these alloys is very large, the stable surface passivation layer is required to achieve such a high efficiency. So far, although many studies have been made on the thermal oxidation layer of  $\text{Si}_{1-x}\text{Ge}_x$ , little is known about not only its formation mechanism but also its bulk property. In this paper, we have investigated in detail the oxidation mechanism for oxidation layers which are fabricated on a single bulk crystal of  $\text{Si}_{1-x}\text{Ge}_x$  by using such conventional methods as dry, wet, and anodic oxidations; the crystals used were grown by vertical Bridgman (VB) method. The samples used in this experiment have the Ge mole fraction ( $x$ ) of 0.6, at which Auger process is predominant. Dry and wet oxidations were performed at 600-800 C for 1-10 h, and anodic oxidation at room temperature for 1 h. The samples were characterized by X-ray photoelectron spectroscopy (XPS) to determine the chemical state of Si and Ge. It was revealed that the composition of dry-oxidized layer significantly differs from that of wet-oxidized layer. For the dry-oxidized sample, the composition of oxidized layer was only  $\text{GeO}_2$  near the surface, but it changed from  $\text{GeO}_2$  to  $\text{SiO}_2$  with increasing the depth. On the contrary, for the wet-oxidized sample, a mixture of  $\text{GeO}_2$  and  $\text{SiO}_2$  was observed over the whole oxide layer. The anodic-oxidized layer has a similar composition to that of the wet-oxidized layer. In the case of the dry oxidation, oxidation mechanism can be explained by lower formation free energy of  $\text{SiO}_2$  than  $\text{GeO}_2$  and higher diffusion velocity of Ge in the oxide.

#### **AA3.48**

**CARRIER CONTROL OF DOPED  $\text{SrTiO}_3$  SINGLE CRYSTAL FILMS GROWN UNDER LAYER-BY-LAYER GROWTH MODE.** Akira Ohtomo, Harold Y. Hwang, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Perovskite oxides show many novel properties, such as high temperature superconductivity and colossal magnetoresistance, which have attracted attention due to new possibilities in micro- and opto-electronics based on artificial heterostructures. Modern epitaxial growth techniques of oxides such as pulsed laser deposition have been developed to approach the degree of atomic control found in MBE of conventional compound semiconductors. Among the transition metal oxides,  $\text{SrTiO}_3$  is important because of its electrical properties (semiconducting, superconducting, and dielectric), and an important substrate material. However, controllable carrier doping of epitaxial  $\text{SrTiO}_3$  thin films has not yet been fully established. We have studied the growth and electrical properties of layer-by-layer grown doped  $\text{SrTiO}_3$  films, and report the range and conditions for controlled carrier doping.

#### **AA3.49**

**ORDERING AND CONDUCTIVITY IN YTTRIA STABILIZED ZIRCONIA FROM FIRST PRINCIPLES.** Alexander Bogicevic, Christopher Wolverton, Gary Crosbie, Ford Research Laboratory, Dearborn, MI; Anton van der Ven, Gerbrand Ceder, MIT, Cambridge, MA; David Raczkowski, UC Davis, CA; E.B. Stechel, Ford Research Laboratory, Dearborn, MI.

Atomistic insight into the defect chemistry of electrolyte materials and their interfaces with electrodes paves the way for design of electrochemical devices with increased power density and better aging characteristics. Here we report a finite-temperature first-principles study of the structure and ionic conductivity of yttria doped zirconia. The ordering problem on the coupled cation (Zr/Y) and anion (O ion/vacancy) sublattices is studied with Monte Carlo simulations

based on a 3D Ising-like model built on a sizeable database of gradient-corrected density functional calculations. Strong long-ranged interactions between the two sublattices are found to render pyrochlores highly unstable, and produce a highly competitive ordered structure in the Zr-rich end of the phase diagram, in addition to the known  $\text{Zr}_3\text{Y}_4\text{O}_{12}$  ordered vacancy compound. The effects of structure on ion mobility are investigated using the nudged elastic band method, and implications for ionic conductivity upon aging are assessed.

#### **SESSION AA4: METAL-OXIDE INTERFACES**

Chairs: C. Barry Carter and J. T. De Hosson  
Tuesday Morning, November 28, 2000  
Commonwealth (Sheraton)

#### **8:30 AM \*AA4.1**

**INFLUENCE OF MISFIT AND INTERFACIAL BINDING ENERGY ON THE SHAPE OF OXIDE PRECIPITATES IN METALS.** B.J. Kooi and J. Th. M. De Hosson, Department of Applied Physics, Materials Science Centre and Netherlands Institute for Metals Research, University of Groningen, Groningen, NETHERLANDS.

Transmission electron microscopy revealed  $\text{Mn}_3\text{O}_4$  precipitates with two types of dominant shapes in Pd-3at.%Mn that was internally oxidized in air at  $1000^\circ\text{C}$ . One type is octahedrally shaped and bounded by {111} planes of the  $\text{Mn}_3\text{O}_4$ . These observations were compared with earlier observations in the Ag/ $\text{Mn}_3\text{O}_4$  system and the octahedrons show a relatively larger truncation by (002) in Pd than in Ag. Further, a second type of precipitate shape, comprising about 1/3 of all the precipitates in Pd, was not observed in Ag. It corresponds to a plate-like structure, showing an orientation relation where the tetragonal axes of  $\text{Mn}_3\text{O}_4$  are parallel to the cube axes of Pd, with as habit plane normal the c-axis of  $\text{Mn}_3\text{O}_4$ . The conclusions of the present analysis based on HRTEM observations and calculations based on anisotropic linear elasticity of interface dislocations are: (i) anisotropy in interface energy for the oxide is substantial due to the ionic nature of the oxide, giving well defined shapes associated with the Wulff construction; (ii) the influence of misfit energy on the precipitate shape as bounded by semi-coherent interfaces is important only if sufficient anisotropy in mismatch is present and if the matrix is sufficiently stiff; (iii) the stronger coupling strength due to electronic binding effects across the interface in Pd compared to Ag is responsible for the formation of the dislocation network structures at larger misfit. The general conclusion is therefore that the final shape is determined by the competition between misfit and interfacial-binding energy.

#### **9:00 AM AA4.2**

**FIRST PRINCIPLES SIMULATION OF ADHESION AT Al/METAL OXIDE INTERFACES.** Donald J. Siegel, University of Illinois at Urbana-Champaign, Department of Physics, Urbana, IL; Louis G. Hector, Jr., ALCOA Technical Center, Surface Technology Division, ALCOA Center, PA; James B. Adams, Arizona State University, Department of Chemical, Bio, and Materials Engineering, Tempe, AZ.

We have performed the first set of *ab initio* calculations aimed at uncovering the influence of the oxide cations on adhesion at three related Al(111)/metal-oxide(0001) interfaces. We have focused on the isostructural corundum-type oxides— $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ —since they appear frequently in industrial applications ranging from microelectronics to Al manufacturing. In order to accurately predict the lowest-energy interface geometries we have considered both metal- and oxygen-terminations for the oxide interfacial layer and have sampled three distinct adsorption sites. The influence of the oxide cations has been determined by comparing the results for adhesion energy, interfacial structure, and bonding type across the three different systems.

#### **9:15 AM AA4.3**

**CLASSICAL INTERATOMIC POTENTIAL FOR Nb-ALUMINA INTERFACES.** K. Albe, R.S. Averback, University of Illinois at Urbana-Champaign, Urbana, IL; R. Benedek, D.N. Seidman, Northwestern University, Evanston, IL.

To model the atomic structure of an oxide-metal interface, one requires in principle an interatomic potential that can describe disparate bonding and coordination environments, e.g., the metallic bonding in the bulk metal and the ionic-covalent bonding in the bulk oxide, as well as the bonding at the interface, which may have aspects of metallic, covalent and ionic character. The absence of a demonstrated framework that meets all of these requirements has led workers to consider ad-hoc potentials whose periodicities match those of the real system, but are otherwise not tailored to the actual chemical bonding of the constituents (A. Levay et al., Acta mater. 47 (1999) 4143). A more realistic alternative is to adopt the modified embedded atom method (MEAM) potential, which has previously

been applied to Al-alumina interfaces (J. E. Angelo and M.I. Baskes, Interface Sci. 4 (1996) 47). The MEAM functional form has the capability to describe diverse bonding and coordination environments. In the present work, we apply the MEAM to Nb-alumina, a prototype interface for which a great deal of experimental (and first-principles theoretical) data exist to test the validity of the model. Preliminary tests of the potential are described, and possible approaches to improve the treatment are discussed.

Work supported by the U.S. Department of Energy at NW by grant no. DEFG02-96ER45597 and at UIUC through the University of California under subcontract No. B341494.

#### 9:30 AM AA4.4

ATOMISTIC STUDY OF STRUCTURAL CORRELATIONS AT A MODEL LIQUID-SOLID INTERFACE. Adham Hashibon, Joan Adler, Technion-Israel Institute of Technology, Dept. of Physics, Haifa, ISRAEL; Wayne D. Kaplan, Technion-Israel Institute of Technology, Department of Materials Engineering, Haifa, ISRAEL.

Metal-ceramic interfaces play a prominent role in a variety of technological applications that range from electronic devices to protective coatings and high-temperature structural components. The functionality of these systems depends crucially on their macroscopic properties such as fracture, yield, and electrical conductivity. These properties are strongly correlated with microscopic details of the metal-ceramic interface, such as bonding, chemistry, diffusion, and structure. Correlating macroscopic properties to the structure and chemistry of interfaces is one of the most intriguing topics in materials science.

Atomistic simulations, such as Molecular Dynamics or Monte Carlo permit the controlled study of these systems at the atomistic level for a large number of atoms and for large structures. However, the main limitation to such simulations is the lack of appropriate interatomic potential schemes which can model both metallic and ionic bonding across the interface. Nevertheless, simplified models can be used to obtain basic qualitative insights into the problem.

In this study we explore structural correlations at a metal-ceramic interface with Molecular Dynamics simulations of a model aluminium system with the Ercolessi-Adams potential and up to 4320 atoms. Several rows of substrate atoms are pinned to equilibrium crystalline positions to mimic a rigid ceramic substrate, and the remaining aluminium atoms form a liquid metal whose atoms are free to move. The density profile and inplane structure at the interface are investigated for different interface crystallographic orientations and temperatures. An exponential decay of the density profile was observed,  $\rho(x) \sim e^{-\kappa x}$ , leading to the definition of  $\kappa$  as a quantitative measure of the ordering at the liquid-solid interface. We find a direct correlation between the amount of ordering in the liquid phase and the underlying substrate structure.

#### 9:45 AM AA4.5

ATOMISTIC SIMULATION AND DENSITY FUNCTIONAL ANALYSIS OF Ni(111)-ZrO<sub>2</sub>(100)(CUBIC) AND NiO(111)-Ni(111)-ZrO<sub>2</sub>(100)(CUBIC) INTERFACE. Chang-xin Guo<sup>1</sup>, Donald E. Ellis<sup>1</sup>, Luke Brewer<sup>2</sup>, Vinayak P. Dravid<sup>2</sup>, Northwestern Univ. <sup>1</sup>Dept of Physics. <sup>2</sup>MS&E Dept, Evanston, IL.

The atomic arrangement and electronic structure in the vicinity of Ni(111)-ZrO<sub>2</sub>(100)(Cubic) and NiO(111)-Ni(111)-ZrO<sub>2</sub>(100)(Cubic) interfaces have been studied by atomistic simulation and by first-principles Density Functional theory. "Depth profiling" is carried out in both methodologies, to determine modifications of cohesive energy and electron distribution of atomic layers from the interface plane. The energy profiling results show the interface consists of only a few atomic layers. Simulation results and electron density analyses are in good agreement with High Resolution Spatially Resolved Electron Microscopy data.

Supported by USDOE and NSF

#### 10:30 AM \*AA4.6

WETTING, SEGREGATION, AND RECONSTRUCTION AT METAL-OXIDE INTERFACES. Wayne D. Kaplan and George Levi, Technion-Israel Institute of Technology, Dept of Materials Engineering, Haifa, ISRAEL.

Wetting experiments between metals and ceramics provide important technological and scientific information on interface energy and adhesion between dissimilar materials. The classical approach to characterize wetting is via the sessile drop experiment and contact angle analysis. However, to fully understand the process of wetting, characterization of the interface structure and chemistry is required. This presentation will compare two basic metal-ceramic systems: liquid Al on sapphire and liquid Ni on sapphire. Sessile drop experiments were conducted to study high temperature wetting as a function of temperature and oxygen partial pressure. After cooling, the structure and chemistry of the metal-ceramic interfaces were investigated using conventional and high resolution electron

microscopy techniques. For experiments requiring chemical analysis at very high spatial resolution, energy dispersive spectroscopy (EDS) and parallel electron energy loss spectroscopy (PEELS) were conducted on a VG HB501 dedicated scanning transmission electron microscopy (STEM) at the Max-Planck Institute in Stuttgart, Germany. At oxygen partial pressures above the equilibrium values, non-equilibrium wetting of Al on sapphire is characterized by dissolution of the substrate at the liquid-solid-vapor interface, and by epitaxial deposition of sapphire at the liquid-solid interface. The driving force for sapphire dissolution is the local change of curvature at the triple junction, which can also be viewed as the sine of the contact angle in Youngs equation. High spatial resolution EDS analysis showed the presence of a relative large quantity of Al in Ni in contradiction with the Ni-Al-O equilibrium phase diagram. Use of the spatial difference technique indicated the existence of an Al excess (segregated) at the Ni-sapphire interface. This implies a process of dissolution of the sapphire during wetting by Ni, followed by the formation of more than a monolayer of pure Al in between the Ni and sapphire. The driving force for dissolution and segregation will be discussed.

#### 11:00 AM AA4.7

COMPARISON OF TERMINATION PLANES ON INTERFACIAL ENERGIES OF Ni(111)/ZrO<sub>2</sub>(100) BOUNDARIES: AB-INITIO CALCULATIONS. Yong Ma, Susan B. Sinnott, Elizabeth C. Dickey, University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY.

Interfaces between metals and metal-oxides occur in a variety of technologically important material systems such as those found in electronic, catalysis or thermal protection systems. In this talk we report on the interfacial and adhesion energies of Ni(111)/ZrO<sub>2</sub>(100) interfaces that have been calculated using density functional theory within the generalized gradient approximation, thus providing one of the first calculations of interfacial energies for an incoherent, polar metal-ceramic interface. Geometric optimization of both oxygen-terminated and zirconium-terminated interfaces have been performed. The calculations predict that the effect of termination is significant and a detailed comparison is made between the calculated interfacial and adhesion energies for both termination systems. Comparisons between the theoretical results and experimental observations will be made.

#### 11:15 AM AA4.8

SEMIEMPIRICAL CORRELATIONS BETWEEN OPTICAL BAND GAP OF OXIDES AND HYDROXIDES AND ELECTRO-NEGATIVITY OF THEIR CONSTITUENTS. F. Di Quarto, M. Santamaria, S. Piazza, C. Sunseri, Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, Palermo, ITALY.

In a recent paper [1] we proposed a quantitative correlation between the optical band gap of pure crystalline oxides and the difference of electronegativity of the oxide constituents. According to our results, two different interpolating lines were obtained for sp-metal and transitional d-metal oxides, with the noticeable exception of NiO laying on the sp-metal oxide interpolating line. The fitting equations for the two cases were:  $E_g$  (eV) = 1.35 ( $X_M - X_O$ )<sup>2</sup> - 1.49 for d-metal oxides and  $E_g$  (eV) = 2.17 ( $X_M - X_O$ )<sup>2</sup> - 2.71 for sp-metal oxides where  $X_M$  and  $X_O$  represent the Pauling electronegativities of the metal and oxygen respectively. In that paper it was also suggested that these correlations could be extended to ternary oxides, A<sub>a</sub>B<sub>b</sub>O<sub>c</sub>, containing only d,d-metal oxides or sp,sp-metal oxides by substituting to the metal electronegativity,  $X_M$ , the arithmetic mean for the cationic group,  $\bar{X}_c$ . The rather limited number of investigated systems, at our disposal, hampered the possibility to check the existence of such a similar correlation in the case of metal hydroxides. As a consequence of recent efforts on the study of photo-electrochemical behaviour of different sp and d-metal passive films and by taking into account some older experimental results we propose the existence of a correlation between the optical band gap and the difference of electronegativity between the cation and the average value of the OH group  $\bar{X}_{a,n}$ =2.85. It will be shown that the proposed correlations seems to hold both for mixed d,d-metal oxides and for hydroxides films electrochemically formed. The possibility to use such correlations in a quantitative way for the in situ analysis of corrosion films will be highlighted by taking into consideration also the possibility to extend such correlations to the more complex sp,d-metal mixed oxides.

References:

- [1] F. Di Quarto, C. Sunseri, S. Piazza and M.C. Romano, J. Phys. Chem. B, 101, 2519 (1997).
- [2] M. Santamaria, D. Huerta, S. Piazza, C. Sunseri and F. Di Quarto, Extended Abstracts of the 194th Electrochemical Society Meeting, Boston (1998); idem, J. of Electrochem. Soc., 147(4), 1366-1375, (2000).

**11:30 AM AA4.9**

A SUB NANOSCALE STUDY OF SEGREGATION AT CdO/Ag(Au) HETEROPHASE INTERFACES. Jason T. Sebastian, Olof C. Hellman, David N. Seidman, Northwestern Univ, Dept of Materials Science and Engineering, Evanston, IL.

Three-dimensional atom-probe (3DAP) allows for the atom-by-atom reconstruction of a small volume (typically 10 nm x 10 nm x 100 nm) of a material with respect to both position and chemical identity. It is, therefore, ideally suited for the study of solute segregation at internal heterophase interfaces. We present recent results of a 3DAP study of solute segregation at ceramic/metal (C/M) heterophase interfaces prepared by internal oxidation. In particular, results on the CdO/Ag(Au) (where Au is the segregating species) system are presented. In the 3DAP atomic reconstructions, the interfaces of the nanometer-size CdO ceramic particles are delineated as isoconcentration surfaces. The distribution of the segregating species (i.e., Au) as a function of distance to the isoconcentration surfaces is determined via the proximity histogram (proxigram) method. The Gibbsian excess of solute at the C/M interfaces is calculated, where possible, from the experimental data. Trends in the measured value of the Gibbsian excess as a function of segregation annealing treatment are discussed.

Research supported by the U.S. Department of Energy. J.T.S. was supported by a Department of Defense National Defense Science and Engineering Graduate Fellowship. O.C.H. was supported by the National Science Foundation.

**11:45 AM AA4.10**

TIME DEPENDENT DEBONDING OF ALUMINUM/ALUMINA INTERFACES UNDER CYCLIC AND STATIC LOADING. J.J. Kruzic, J.M. McNaney, R.M. Cannon and R.O. Ritchie, Materials Sciences Division, Lawrence Berkeley National Laboratory, and Department of Materials Science and Engineering, University of California, Berkeley, CA.

The structural integrity of oxide/metal interfaces is important in many applications, including composite materials, coatings, microelectronic packaging, and material joining. While most attention has focused on the debonding of oxide/metal interfaces by conducting strength and fracture toughness tests, very few investigations have looked at time dependant failure of interfaces under cyclic or static loading. Tests have been conducted on sandwich specimens consisting of 1-100  $\mu\text{m}$  thick aluminum layers bonded between both polycrystalline and single crystal aluminum oxide to determine cyclic fatigue-crack growth, as well as static loaded moisture-assisted crack-growth, properties of aluminum/alumina interfaces. Under cyclic loading, growth was observed to predominantly occur by interfacial debonding, but also was observed to make excursions into the alumina. Static loading in a moist environment also caused interfacial cracks to deviate into the alumina or arrest. Due to the poor crack growth resistance of the alumina, cracks leaving the interface propagated at faster rates than those at the interface. Trends in crack trajectories and crack growth rates are explained in terms of the degree of plastic constraint in the aluminum layer, the modulus mismatch, and the effects of environmental mechanisms.

**SESSION AA5: SURFACES**

Chairs: Tom Wood and I-Wei Chen  
Tuesday Afternoon, November 28, 2000  
Commonwealth (Sheraton)

**1:30 PM \*AA5.1**

UNDERSTANDING METAL OXIDE SURFACES AT THE ATOMIC SCALE. Ulrike Diebold, Dept of Physics, Tulane University, New Orleans, LA.

The reactivity of metal oxides is strongly affected by local deviations of surface structure and stoichiometry. Scanning probe techniques, with their capability to investigate oxide surfaces at the atomic scale, are ideal tools to further our understanding of this relationship. We have performed Scanning Tunneling Microscopy measurements of several transition metal oxides (titanium dioxide, iron oxide, zinc oxide), both clean and covered with adsorbates. In this talk, we will bring some examples on the role of first-principle, total-energy calculations in interpreting and understanding these results.

**2:00 PM AA5.2**

STRUCTURE-PROPERTY RELATIONSHIPS FOR SMALL MOLECULE ADSORPTION ON TiO<sub>2</sub> AND SrTiO<sub>3</sub> SURFACES. Kim F. Ferris, Li-Qiong Wang, Pacific Northwest National Laboratory, Materials Resources, Richland, WA.

Interactions of water and HCOOH with stoichiometric and defective TiO<sub>2</sub> (100), TiO<sub>2</sub> (110), and SrTiO<sub>3</sub>(100) surfaces have been studied

using TPD measurements and electronic structure calculations to develop a structure-property relationship for metal-oxide surfaces. Two key structural parameters have been identified; the accessibility of surface oxygen atoms and the basicity of these acceptor sites. The lack of bridging oxygen atoms on TiO<sub>2</sub>-terminated SrTiO<sub>3</sub> (100) surfaces results in different adsorption and desorption properties for H<sub>2</sub>O on SrTiO<sub>3</sub> as compared to the TiO<sub>2</sub> (100) and (110) surfaces. Preliminary results for formate interaction with SrTiO<sub>3</sub>(100) indicate strong adsorption consistent with experimental results, but in a distinctly different geometric arrangement due to absence of bridging oxygens present for the TiO<sub>2</sub> surfaces. Stepped SrTiO<sub>3</sub> (100) surfaces have accessible oxygen sites for adsorbates, and are predicted to have increased reactivity for H<sub>2</sub>O, CH<sub>3</sub>OH, and HCOOH. Further results will be discussed in terms of potential reaction mechanisms and correlations with ongoing experimental studies.

This work was supported by the U.S. Department of Energy, Office of Science, Material Sciences Division, under contract DE-AC06-76RLO 1830.

**2:15 PM AA5.3**

CALCULATIONS OF SURFACE RELAXATIONS FOR PEROVSKITE SURFACES. Eugene Heifets, Materials Simulation Center, California Institute of Technology, Pasadena, CA; Eugene A. Kotomin, Dept of Physics, University of Osnabruck, Osnabrueck, GERMANY and Institute of Solid State Physics, Riga, LATVIA.

We present and discuss results of the calculations of the surface relaxation for SrTiO<sub>3</sub>, BaTiO<sub>3</sub> and KNbO<sub>3</sub> perovskite crystals. By means of semi-empirical shell model, the positions of atoms in 16 near-surface layers placed atop a slab of rigid ions are optimized. This permit us determination of a surface rumpling and surface-induced dipole moments for different terminations of the (100) and (110) surfaces. We demonstrate that our results for the (100) surfaces are in good agreement with ab initio plane wave pseudopotential calculations (with a few relaxed planes) and LEED experiments. For the (110) BaTiO<sub>3</sub> and SrTiO<sub>3</sub> surfaces O-termination is predicted to be lowest in energy whereas the KNbO<sub>3</sub> (110) O-terminated surface is found to be unstable with respect to a strong reconstruction leading to a K termination. The latter conclusion is confirmed by ab initio LCAO calculations.

**2:30 PM AA5.4**

IN-SITU SYNCHROTRON X-RAY SCATTERING DETERMINATION OF SURFACE STRUCTURE OF PbTiO<sub>3</sub> IN THE METAL-ORGANIC CHEMICAL VAPOR DEPOSITION ENVIRONMENT. G.B. Stephenson<sup>a</sup>, A. Munkholm<sup>b</sup>, M.V. Ramana Murty<sup>a</sup>, O. Auciello<sup>a</sup>, S.K. Streiffer<sup>c</sup>, C. Thompson<sup>a,c</sup>, J.A. Eastman<sup>a</sup>, G.-R. Bai<sup>a</sup>. <sup>a</sup>Materials Science Div., Argonne National Laboratory, Argonne, IL. <sup>b</sup>Chemistry Div., Argonne National Laboratory, Argonne, IL. <sup>c</sup>Dept. of Physics, Northern Illinois University, Dekalb, IL.

We report *in-situ* measurements of the atomic-scale surface structure of PbTiO<sub>3</sub> (001) in the metal-organic chemical vapor deposition (MOCVD) environment using synchrotron x-ray scattering at the Advanced Photon Source. Coherently-strained epitaxial films of PbTiO<sub>3</sub> were grown *in situ* on SrTiO<sub>3</sub> (001) substrates by MOCVD using tetraethyl lead (TEL), titanium isopropoxide, and O<sub>2</sub> as precursors. Annealing the films at 775°C in O<sub>2</sub> with or without TEL present produced surfaces having different reconstructions ("PbO-rich" or "TiO<sub>2</sub>-rich", respectively). The PbO-rich surface is well ordered with a c(2x2) symmetry. A surface structure consisting of a bilayer of PbO is consistent with the x-ray data. The TiO<sub>2</sub>-rich surface is poorly ordered with (n x 1) symmetry, where n is 2, 4 or 6 depending upon annealing history. The influence of initial surface structure upon film growth will be discussed.

This work is supported by the U.S. Dept. of Energy, BES-DMS, under contract W-31-109-ENG-38, and by the State of Illinois, under HECA.

**2:45 PM AA5.5**

INVESTIGATION OF THE MAGNITUDE OF THE CHEMICAL DRIVING FORCE REQUIRED TO FORM SPACE CHARGE NANODOMAINS IN RELAXOR FERROELECTRICS. C.M. Bishop, A.N. Soukhovjak, W.C. Carter, Y.-M. Chiang, Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA; R.M. Cannon, University of California Berkeley, Lawrence Berkeley Lab, Berkeley, CA.

Experimental evidence in annealed lead-based B-site relaxor perovskites, e.g. PMN, indicates that space charge domains are not stable (M.A. Akbas and P.K. Davies, J. Am. Cer. Soc. 83, 119, 2000). However, composition maps measured by EDX indicate that chemical segregation in the form of nanometer sized domains may be present in A-site relaxors, namely alkaline bismuth titanates. In this system, such chemical segregation should be accompanied by a space charge. We develop a model that determines the magnitude of chemical

driving force required to create a space charge modulation of a given size and compare this result to reasonable chemical driving forces.

### 3:30 PM \*AA5.6

NEAR SURFACE FERROELECTRICITY-AFM CHARACTERIZATION AND MODELING. Xiaoping Li, Alexander Mamchik, L-Wei Chen, Univ of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA.

Near surface ferroelectricity can be induced and imaged using an AFM tip that has a large electrical field highly localized near the tip. This electrical field can be adequately modeled by a conducting sphere in or near contact with a dielectric surface. The electrical field causes ferroelectric switching without any nucleation barrier. Upon tip removal, the stability of the domain is determined by domain wall energy, depolarization energy, interfacial friction or coercive field, and possibly a chemical free energy in the case of ferroelectric/antiferroelectric transition. These theoretical aspects and their manifestation in various AFM writing and imaging modes have been systematically investigated using several ferroelectric, anti-ferroelectric, and dielectric oxide thin films and ceramics.

### 4:00 PM AA5.7

TIME EVOLUTION OF THE METASTABLE SURFACE STRUCTURE OF KTAO<sub>3</sub>(001) STUDIED BY HELIUM ATOM SCATTERING. E.A. Akhadov, J.A. Li, T.W. Trelenberg, J.G. Skofronick, S.A. Safron, D.H. Van Winkle, Florida State University, Tallahassee, FL; F. Flaherty, Valdosta State University, Valdosta, GA; L.A. Boatner, Oak Ridge National Laboratory, Oak Ridge, TN.

As a probe for surface structure and dynamics, helium atom scattering (HAS) is often a preferred method, especially for insulating surfaces where the neutral helium does not cause charging of the surface as can occur with charged probes. The thrust of this abstract is to report the use of HAS to examine the structure of the (001) surface of the cubic perovskite KTAO<sub>3</sub>, produced by cleaving *in situ* in a UHV scattering chamber. Measurements taken immediately after cleaving indicate metastable satellite peaks with intensities greater than that of specular peak and with comparable width. Over the period of one to two hours (if the sample is kept at 190 K), the satellite peaks decrease to nearly zero while the specular grows, providing what appears to be normal angular distribution from a (1×1) surface. A model of the initially cleaved surface, consisting of KO and TaO<sub>2</sub> islands and terraces of equal areas, respectively, separated by steps of one-half the bulk unit cell lattice spacing (2.0 Å) is presented which agrees with the initial observations.

### 4:15 PM AA5.8

EXUDATING SILICATE LIQUID FROM POLYCRYSTALLINE ALUMINA. N. Ravishankar and C. Barry Carter, Department of Chemical Engineering and Materials Science, University of Minnesota Minneapolis, MN.

Aluminosilicates are the most common liquids that form during liquid-phase sintering of alumina. While the presence of the liquid enhances mass transport and aids in faster sintering, the liquids remain as an intergranular glassy phase in the microstructure. This is usually detrimental to the high-temperature mechanical behavior of the ceramic. It has been shown that it is possible to exude this liquid from the bicrystal boundaries in alumina. The influence of crystallography is brought out using this geometry. However, from a practical point of view, it is important to study the feasibility of exudation of the liquid from a polycrystalline compact. The present study is aimed at understanding the exudation behavior of anorthite liquid from polycrystalline alumina. To minimize the effect of dopants and impurities, lucalox has been chosen. Lucalox is infiltrated with liquid anorthite for different times. The infiltration results in a compact where glass is present along most grain boundaries. The back side of the sample is polished and the compact is annealed at different temperatures for a range of times. On cooling the sample, it is seen that many of the surfaces have droplets of the silicate present on them. The liquid exudes out of the grain boundaries in the polycrystalline compact and wets the surface at the annealing temperature. The results are discussed in terms of the wetting behavior of the boundaries and the free surface.

### 4:30 PM AA5.9

DETERMINATION OF SPHEROSILOXANE CLUSTER BINDING TO Si(001) BY SCANNING TUNNELING MICROSCOPY. K.S. Schneider, M.M. Banaszak Holl, Chemistry Department, University of Michigan, Ann Arbor, MI; Z. Zhang, B.G. Orr, Physics Department, University of Michigan, Ann Arbor, MI; U.C. Pernisz, Dow Corning Corp., Midland, MI.

The silicon-silicon dioxide interface has been at the heart of the microelectronics industry for the past 30 years. As a means to study a well characterizable ultra-thin oxide layer we have examined the

adsorption of H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> clusters bound to a Si(100)-2x1 surface. Atomically resolved STM images of these clusters bound to the Si(100)-2x1 surface have been obtained. We are able to identify the binding mechanism as activation of a single Si-H bond and monovortex binding to the Si substrate. Filled and empty states images show good agreement with calculations for the HOMO and LUMO states of the clusters. These results will be discussed in the light of recent numerical calculations and XPS studies.

### 4:45 PM AA5.10

ELECTRONIC STRUCTURE OF TITANIUM OXIDE CRYSTAL SURFACE WITH LITHIUM ATOM ON THE SURFACE. Mitsutake Oshikiri, National Research Institute for Metals, Physical Property Division, Tsukuba, Ibaraki, JAPAN; Ferdi Aryasetiawan, Joint Research Center for Atom Technology - Angstrom Technology Partnership, Theory Research Group, Tsukuba, Ibaraki, JAPAN.

Titanium oxide is well known as a photo catalyst and the function can be drastically controlled by doping. Since titanium oxide is an inexpensive and lightweight material which has favorable sites for Li insertion in its structure, it is also promising to be used as cathode material for the lithium ion secondary batteries. Standing on such background, we have investigated the electronic structure of titanium oxide surface with lithium atom on the surface from first principles. In this work, the energy levels derived from 3d of Ti and 2s of Li are mainly discussed. Not only density functional approach within the local density approximation but also GW approach has been tried to investigate the unoccupied state of the system. We have used the LMTO method with the atomic sphere approximation. A few sheets of titanium oxide layers and open space of more than several angstroms were used as the surface model. The electronic structures of the bulk titanium oxide in the rutile structure, the (001) surface of it and the surface with lithium atom are compared and the structure dependence of electronic structure will be discussed.

## SESSION AA6: OXIDE THIN FILM EPITAXY

Chairs: Harry L. Tuller and Darrell G. Schlom  
Wednesday Morning, November 29, 2000  
Commonwealth (Sheraton)

### 8:30 AM \*AA6.1

ATOMIC LAYER CONTROL OF EPITAXIAL SrRuO<sub>3</sub>-SrTiO<sub>3</sub>-SrRuO<sub>3</sub> HETEROSTRUCTURES USING IN-SITU HIGH PRESSURE RHEED FOR SPIN-POLARIZED PERPENDICULAR TRANSPORT. C.B. Eom, J.H. Choi, J.S. Noh, University of Wisconsin-Madison, Department of MS&E, Madison, WI; G.J.H.M. Rijnders, H. Rogalla, D.H.A. Blank, University of Twente, Department of Applied Physics, Enschede, THE NETHERLANDS; W. Tian, X. Pan, University of Michigan, Department of MS&E, Ann Arbor, MI; J.Z. Sun, IBM T.J. Watson Research Center, Yorktown Heights, NY.

Atomic scale control of epitaxy and interfaces in complex oxide heterostructures is very important for the fabrication of novel devices and the understanding of solid state phenomena. We have grown SrRuO<sub>3</sub>-SrTiO<sub>3</sub>-SrRuO<sub>3</sub> Atomic scale control of epitaxy and the interfaces in complex oxide heterostructures is very important for the fabrication of novel devices and the understanding of solid state phenomena. We have grown SrRuO<sub>3</sub>-SrTiO<sub>3</sub>-SrRuO<sub>3</sub> epitaxial heterostructures on perfect TiO<sub>2</sub>- terminated (001) SrTiO<sub>3</sub> substrates using pulsed laser deposition including in-situ high pressure RHEED. SrRuO<sub>3</sub> is an ideal system to study the heteroepitaxial growth mechanism of various perovskite thin films and to fabricate high quality multilayered devices. SrRuO<sub>3</sub> is a negatively spin polarized ferromagnetic oxide with a lattice parameter of 3.93 Å, i.e., a lattice mismatch with (001) SrTiO<sub>3</sub> substrates of 0.64%. Our RHEED intensity data and AFM images suggest that the SrRuO<sub>3</sub> films on SrTiO<sub>3</sub> substrate grow in the step-flow mode with a transition from 2-dimensional layer-by-layer mode into step-flow mode after covering one monolayer of SrRuO<sub>3</sub>. The origin of the growth mode transition can be attributed to a change in mobility of ad-atoms and switching of a surface termination layer from the substrate into the film. In contrast, the SrTiO<sub>3</sub> barrier layer on SrRuO<sub>3</sub> bottom electrode grow in the two-dimensional layer-by-layer mode. Transmission electron microscopy images of a cross-sectional SrRuO<sub>3</sub>- 6 unit cell SrTiO<sub>3</sub>-SrRuO<sub>3</sub> heterostructure show that the trilayer is single domain with atomically sharp interfaces between SrRuO<sub>3</sub> and SrTiO<sub>3</sub>. Such an atomic scale control of the interfaces and barrier layers in ferromagnetic oxide (FM-I-FM) trilayer junctions allows for quantitative studies of spin-polarized transport across the ferromagnetic oxide (FM-I-FM) trilayer junction interface, which will also be discussed.

### 9:00 AM \*AA6.2

KINETIC MONTE CARLO STUDIES OF OXIDE MOCVD.

David J. Srolovitz, Chaitanya S. Deo, Princeton University, Princeton Materials Institute and Dept. of Mechanical & Aerospace Eng., Princeton, NJ.

A simple model of metallorganic chemical vapor deposition of single crystal oxides is developed that includes deposition and etching of multiple species and surface diffusion. The model is implemented within a three-dimensional kinetic Monte Carlo simulation. We examine growth on a variety of different surfaces (homoepitaxial, elemental and disordered) with different crystallographic orientations as a function of temperature, pressure and ordering tendency. The simulations are used to predict, film structure, growth rates, surface roughness, terrace size, domain size, and the short range order parameter. Depending on conditions, the films can grow either in a step growth mode or via nucleation on terraces. Growth on elemental and disordered substrates leads to the formation of anti-phase boundaries (APBs). Quantitative predictions of growth rates requires accurate kinetic parameters. Several approaches for obtains these parameters will be discussed.

#### 9:30 AM AA6.3

QUANTUM CHEMICAL MOLECULAR DYNAMICS STUDY ON EPITAXIAL CRYSTAL GROWTH PROCESSES. Momoji Kubo, Yusaku Inaba, Ken Suzuki, Seiichi Takami, Akira Miyamoto, Tohoku Univ., Dept. of Materials Chemistry, Sendai, JAPAN; Akira Imamura, Hiroshima Kokusai Gakuin Univ., Dept. of Mathematics, Hiroshima, JAPAN; Masashi Kawasaki, Tokyo Inst. of Technol., Dept. of Innovative and Engineering Materials, Yokohama, JAPAN; Mamoru Yoshimoto, Tokyo Inst. of Technol., Materials and Structures Laboratory, Yokohama, JAPAN; Hideomi Koinuma, CREST-JST and Tokyo Inst. of Technol., Materials and Structures Laboratory, Yokohama, JAPAN.

Novel technology on the artificial construction of atomically defined metal oxide layers has been desired in relation to electronic, magnetic, and optical devices. Hence, the atomistic understanding of the epitaxial growth processes of metal oxide surfaces is desired to fabricate atomically controlled structure that exhibits unexplored and interesting physical properties. However, experimentally it is impossible to clarify the atomistic mechanism of the epitaxial growth process of metal oxide electronics materials. Previously we developed an atomistic crystal growth molecular dynamics simulator MOMODY and successfully applied it to the homoepitaxial growth processes of MgO(001), SrTiO<sub>3</sub>(001), and ZnO(0001) surfaces [1-4]. However, the above classical molecular dynamics approach could not reproduce surface chemical reactions and electron transfer during the epitaxial growth processes since empirical interatomic potential is used. Hence, in the present study we developed a new atomistic crystal growth simulator MOMODY/Colors based on our accelerated quantum chemical molecular dynamics methodology. To the best of our knowledge, this is a first simulator to clarify the surface reaction dynamics, low-dimensional structure fabrication, and electron transfer during the epitaxial growth processes. Moreover, we applied it to various epitaxial growth processes on metal oxide surfaces and some new findings which can not be elucidated by experiments were obtained.

[1] M. Kubo, Y. Oumi, R. Miura, A. Stirling, A. Miyamoto, M. Kawasaki, M. Yoshimoto, and H. Koinuma, Phys. Rev. B 56 (1997) 13535.

[2] M. Kubo, Y. Oumi, R. Miura, A. Stirling, A. Miyamoto, M. Kawasaki, M. Yoshimoto, and H. Koinuma, J. Chem. Phys. 109 (1998) 8601.

[3] M. Kubo, Y. Oumi, H. Takaba, A. Chatterjee, and A. Miyamoto, J. Phys. Chem. B 103 (1999) 1876.

[4] M. Kubo, Y. Oumi, H. Takaba, A. Chatterjee, A. Miyamoto, M. Kawasaki, M. Yoshimoto, and H. Koinuma, Phys. Rev. B, in press.

#### 9:45 AM AA6.4

GROWTH STUDIES OF PEROVSKITE HETEROSTRUCTURES USING IN-SITU HIGH PRESSURE RHEED, AFM AND TEM. Dave H.A. Blank, Guus Rijnders, Horst Rogalla, Low Temperature Division, MESA Research Institute, University of Twente, Enschede, THE NETHERLANDS; and Junghoon Choi, Chang-Beom Eom, Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC.

The control of interfaces, domain structure and defects in perovskite hetero-structures is the key-issue in junction fabrication processes. In order to fabricate thin films and heterostructures of these complex oxides with atomically smooth surfaces and sharp interfaces, well-controlled layer-by-layer growth is required. In-situ monitoring the film growth with reflection high energy electron diffraction (RHEED) is desirable for the proposed research. We have grown SrRuO<sub>3</sub>-SrTiO<sub>3</sub>-SrRuO<sub>3</sub> trilayers on well-defined (001) SrTiO<sub>3</sub> substrates using pulsed laser deposition. In this contribution we will discuss the initial growth of the SrRuO<sub>3</sub> layers. In-situ high-pressure RHEED studies and AFM and TEM analyses show a transition from

2D-nucleation and growth to stepflow growth within the first few unit cell layers. This transition depends on the miscut angle and termination of the substrate as well as the deposition rate. Additionally, this change in growth mode during the deposition of other perovskites will be discussed.

#### 10:30 AM \*AA6.5

THE INTERRELATIONSHIP BETWEEN INTERFACES AND THE STRUCTURAL CUSTOMIZATION ON THE NANOMETER SCALE OF OXIDE FILMS, SUPERLATTICES, AND NEW COMPOUNDS. D.G. Schlom, M.A. Zurbuchen, J.H. Haeni, J. Lettieri, C.D. Theis, J. Yeh, A.H. Carim, Penn State Univ, Dept of Materials Science and Engineering, University Park, PA; W. Tian, J.C. Jiang, X.Q. Pan, Dept of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI; J. Im, O. Auciello, A.R. Krauss, S.K. Streiffer, Argonne National Laboratory, Materials Science Division, Argonne, IL; G.W. Brown, M.E. Hawley, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM.

In this talk we will describe some of the interrelationships between interfaces (chemistry, faceting, roughness) and the customized synthesis of perovskite and layered-perovskite films, including new compounds and metastable superlattices. Structural and chemical characterization of interfaces will be presented including high-resolution TEM, AFM, STM, TOF-ISARS, and *in situ* RHEED. The importance of the interface between the film and its underlying substrate will be highlighted. Examples of the terminating layer of the substrate and initial layer of the film at the substrate/film interface and the terminating layer of the film at the film/vacuum interface will be given. Defects resulting from interfacial mismatch will be described, including out-of-phase boundaries, lattice-matched intergrowths, and dislocations with a screw component. The latter result in a spiral growth mode and undesired surface roughness that frustrates the controlled synthesis of new compounds via the sequential deposition of elemental constituents in monolayer pulses. The specific perovskites and layered perovskites in which the interfaces have been characterized are Aurivillius phases (SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>, SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, and Bi<sub>4</sub>(Pb,Sr)<sub>n-3</sub>Ti<sub>n</sub>O<sub>3n3</sub>), Ruddlesden-Popper phases (Sr<sub>n1</sub>Ti<sub>n</sub>O<sub>3n1</sub> and Sr<sub>n1</sub>Ru<sub>n</sub>O<sub>3n1</sub>), and metastable superlattices (PbTiO<sub>3</sub> / SrTiO<sub>3</sub> and BaTiO<sub>3</sub> / SrTiO<sub>3</sub>) grown by reactive molecular beam epitaxy (MBE) and pulsed laser deposition (PLD).

#### 11:00 AM AA6.6

EPITAXIAL GROWTH OF ZnO AND MgZnO ON SILICON.

W. Yang†, R.D. Vispute, S. Choopun, R.P. Sharma and T.

Venkatesan† CSR, Dept of Physics, Univ of Maryland, College Park, MD. †also with Electrical and Computer Engineering Dept, Univ of Maryland, College Park, MD.

Epitaxial growth of ZnO and MgZnO on Si substrates is important for optoelectronic integrated circuits(OEIC), owing to the combination of wide band gap optical materials and well-established Si technology. In this paper, we investigate the epitaxial growth of ZnO/MgZnO on Si using pulsed laser deposition (PLD), with various buffer layers such as yttrium stabilized zirconia (YSZ), SrTiO<sub>2</sub> (STO), CeO<sub>2</sub> and MgO. The morphology and structural properties of ZnO/MgZnO films have been investigated in details using x-ray diffraction (XRD), atomic force spectrometry (AFM), scanning electron microscopy (SEM) and Rutherford backscattering spectroscopy (RBS). Optical properties have been studied by photoluminescence (PL) at room temperature and 77K. Ultra-violet (UV) and visible transmission spectroscopy has also been carried out for absorption and band gap measurements. The carrier concentration and Hall mobility have been measured by the van der Pauw method. Dependence of buffer layer material and growth conditions on the film quality will be discussed in details. By choosing appropriate buffer material and optimizing the PLD conditions, high quality ZnO/MgZnO epilayers have been obtained. Visible blind ZnO and MgZnO UV detectors with high gain and low cut-off wavelength have been successfully fabricated on Si.

#### 11:15 AM AA6.7

THE INTEGRATION OF TANTALUM OXIDE WITH TITANIUM NITRIDE, TANTALUM NITRIDE, AND RUTHENIUM ELECTRODES FOR METAL-INSULATOR-METAL CAPACITOR APPLICATIONS. R.S. Urdahl, P.K. Narwankar, S.A. Athreya, A.K. Sinensky, Applied Materials, Santa Clara, CA.

The capacitance and leakage current densities of planar thin-film tantalum oxide capacitors are measured as a function of dielectric thickness, annealing conditions, and electrode material. Depth-profile Auger spectroscopy and transmission electron microscopy are used to evaluate the extent of electrode oxidation at the tantalum oxide/titanium nitride and tantalum oxide/tantalum nitride interfaces. Variations in the Ta:N ratio for reactively sputtered tantalum nitride electrodes are correlated to the electrical performance of the capacitors and interpreted in terms of relative

oxy-nitride formation. The C-V behavior of tantalum oxide on TiN is measured as a function of film thickness, and the linearity coefficients are compared to those obtained from silicon dioxide and silicon nitride dielectrics.

#### 11:30 AM **AA6.8**

**BAND DISCONTINUITIES AND INTERFACIAL STRUCTURE AT EPITAXIAL STO/Si HETEROJUNCTIONS.** S.A. Chambers, Y. Liang, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, WA; Z. Yu, R. Droopad, J. Ramdani, K. Eisenbeiser, Physical Sciences Research Laboratories, Motorola Labs, Tempe, AZ.

Epitaxial oxides with high dielectric constants are being aggressively investigated as potential new gate oxides for next-generation CMOS devices. Strontium titanate (STO) is an attractive candidate because it is well lattice matched to Si. In addition, its equivalent dielectric layer thickness is more than ten times less than that of STO. Thus, the gate oxide layer thickness can be ten times larger when silicon dioxide is replaced with STO, and yet the capacitance is the same. Despite these attractive properties, the band offsets at the STO/Si(001) interface have not been determined experimentally, and the relationship between band offset and interface structure is completely unknown. We have used photoemission methods to directly measure the valence and conduction band offsets at STO/Si(001) interfaces, as prepared by molecular beam epitaxy with no interfacial oxide. Within experimental error, the measured values are the same for growth on n- and p-Si, with the entire band discontinuity occurring at the valence band edge. In addition, band bending is much larger at the p-Si heterojunction than at the n-type heterojunction. Previously published threshold voltage behavior for these epitaxial interfaces can now be understood in light of the present results. We are also initiating an investigation of the band offset as a function of interface structure. The interface structure is being modified by heating specimens consisting of thin ( $\sim 20\text{\AA}$ ) epitaxial STO films on Si(001) in an oxygen plasma within the MBE chamber, but after growth. Activated oxygen indiffusion creates an interfacial oxide layer that can in principle alter the band offset. Results from these experiments will also be presented.

#### 11:45 AM **AA6.9**

**ATOMIC-SCALE STUDY OF THE INTERFACE OF CRYSTALLINE OXIDES EPITAXY ON SILICON.** Shupan Gan, David E. McCready, Daniel J. Gaspar, Theva Thevuthasan, and Yong Liang, Pacific Northwest National Laboratory, Richland, WA.

Crystalline oxides such as SrTiO<sub>3</sub> (STO) are important alternative gate oxides to SiO<sub>2</sub> in the existing Si-based CMOS technology. A great challenge for the growth of high quality single-crystal oxides on Si is avoiding the oxidation of Si and subsequent formation of amorphous SiO<sub>2</sub>. The key to achieve this is to produce a robust interfacial template layer that stabilizes in oxygen environment at high temperatures. Herein we studied the structure of STO-Si interface in situ by scanning tunneling microscopy/spectroscopy (STM/STS) combined with x-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED). It was found that the strontium-covered surfaces exhibit a series of reconstructions such as (1x2), (3x2), (1x5), and (1x7) depending on the surface strontium coverage. Furthermore, these phases showed distinct difference in reactivity with oxygen. For instance, upon exposure to oxygen, the (3x2) structure was converted to a (1x1) surface while the (1x2) surface remained intact. For the growth of oxides, the (2x1) structure was found to provide the most stable interface, as evidenced by a uniform layer in angular-dependent XPS results. Additionally, we used time-of-flight second ion mass spectrometry (TOF-SIMS), x-ray diffraction (XRD), and Rutherford backscattering (RBS) to investigate the interfacial chemistry and film structure. By combining these techniques, we correlated the interface structures with film properties, which allowed us to identify suitable interfacial templates for optimized growth.

### SESSION AA7: STRUCTURE-PROPERTY RELATIONSHIPS

Chairs: Kurt E. Sickafus and Gregory S. Rohrer  
Wednesday Afternoon, November 29, 2000  
Commonwealth (Sheraton)

#### 1:30 PM **\*AA7.1**

**COMPUTER SIMULATION AND EXPERIMENTAL STUDY OF ADSORPTION ON SILICATE GLASS SURFACES.** Carlo G. Pantano, Victor A. Bakaez, Tamara Bakaez and William A. Steele, Department of MS&E, The Pennsylvania State University, University Park, PA.

We have used the grand canonical Monte Carlo method to simulate isotherms of adsorption for Ar, CO<sub>2</sub>, and H<sub>2</sub>O on model surfaces of

silica and sodium-silicate glasses. The model surfaces were obtained through molecular dynamics simulations, and differed in both composition and thermal history. We found that annealing of the model surfaces exerts a significant effect on the simulated adsorption isotherms for the dipolar molecules CO<sub>2</sub> and H<sub>2</sub>O. It was found that coordination defects and distorted silica tetrahedra, defined by their dipole and quadrupole moments, give rise to hydrophilic adsorption sites on the surface. Upon annealing with an optimum cooling rate, these defects can be eliminated and a hydrophobic silica surface can be obtained. The experimentally determined isotherms were acquired on glass fibers using inverse gas chromatography. The combined use of experimental and simulated isotherms not only provides a way to validate the modelled surfaces, but also provides direct information about the fundamental origin of heterogeneous adsorption for silica and multicomponent silicate glass surfaces. The pure silica surfaces, and even multicomponent silicates, are found to be homogeneous with respect to non-polar adsorbates such as hexane, but heterogeneous in the case of alcohols. In general, the heterogeneity in adsorption is due to local variations in the surface electrostatic field. The strongest adsorption sites are associated with non-bridging oxygens and tri-coordinated oxygens. These results are of interest for relating nanoscale characteristics of glass surfaces to macroscopic properties such as wetting and adhesion.

#### 2:00 PM **AA7.2**

**KINETIC PROPERTIES OF HEAVILY DONOR-DOPED STRONTIUM TITANATE WITH REGARD TO OXYGEN SENSOR APPLICATIONS.** Wolfgang Menesklou, Karl Heinz Hårdt, Ellen Ivers-Tiffèe, Universität Karlsruhe (TH), Institut für Werkstoffe der Elektrotechnik, GERMANY; A. Cengiz Palanduz, Harry L. Tuller, MIT, Dept. of Materials Science and Engineering, Cambridge, MA.

The electrical and kinetic properties of ceramic and single crystal samples of heavily donor-doped strontium titanate are examined as a function of oxygen partial pressure, temperature and donor content. Porous ceramics, used as oxygen sensors, show an n-type conductivity behaviour with surprisingly short response times, in contrast to single crystals, which display a very slow response. We demonstrate that the fast kinetics of porous donor-doped strontium titanate is dominated by the surface, and can not be correlated with the behaviour of the bulk, which is responsible for the long term stability.

#### 2:15 PM **AA7.3**

**MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF DOPED TIN OXIDE THIN FILMS.** X.Q. Pan, J.E. Dominguez, L. Fu, Univ of Michigan, Dept of MS&E, Ann Arbor, MI.

Tin oxide thin films are widely used as gas sensors. The mechanism for gas sensitivity depends on the chemisorption characteristics of the oxide surface and on the electronic characteristics of the film. The electronic properties can be influenced by metal doping and the film microstructure. In this paper tin oxide thin films doped with rare earth and transition metals were deposited on sapphire substrates with different surface crystallographic orientations by pulsed laser deposition. The microstructure of the films was characterized using transmission electron microscopy and X-ray diffraction. The microstructure of films are controlled by the lattice mismatch across the substrate-film interfaces. The response of the films to reducing gases was measured in a gas reactor at high temperature. The electrical properties of the films were determined by Hall effect measurements within the gas reactor. The electron activation energy increases with increasing acceptor dopant ionic radius. A model correlating the microstructure to the electrical properties was developed.

#### 2:30 PM **\*AA7.4**

**THE ANISOTROPY OF THE SURFACE ENERGY AND PHOTO-CHEMICAL PROPERTIES OF STRONTIUM AND BARIUM TITANATE.** Jennifer L. Giocondi and Gregory S. Rohrer, Carnegie Mellon University, Pittsburgh, PA.

Heterogeneous photochemical reactions can occur on ceramic surfaces when the absorption of light with an energy greater than the band gap creates electrons and holes that, instead of recombining, become trapped on the surface and react with adsorbed surface species. To develop a surface structure-property relation for photochemical reactions on titanates, we have determined the relative photochemical reactivity and surface energy of strontium titanate and barium titanate as a function of orientation. Surfaces for analysis were prepared by polishing and thermally etching polycrystalline specimens (with a 20 micron grain size) in air. The surface orientations of selected grains in the sample were then determined from backscattered electron diffraction patterns recorded in a scanning electron microscope. To make a local measurement of the photochemical activity of each grain, we used a well established probe reaction (the reduction of aqueous Ag(I) to Ag(0)) that deposits metallic silver on the surface as a reaction product. The amount of

silver deposited on each grain's surface during a given reaction, which is determined from atomic force microscopy (AFM) images, is taken to be a quantitative indicator of that grain's relative photochemical reactivity. We have also used observations of the surface facet structures to estimate the relative surface energy as a function of orientation. The relative photochemical reactivity can then be correlated to the grain's surface orientation and/or the relative area of each facet on the surface. On strontium titanate, surfaces vicinal to (100) reduced the greatest amount of Ag. However, the photochemical properties of barium titanate are dominated by the ferroelectric domain structure. The influence of the domain orientation on the relative rate of the photochemical reaction will be described.

### 3:30 PM AA7.5

**GAS SENSING PROPERTIES OF NANOCRYSTALLINE WO<sub>3</sub> FILMS MADE BY ADVANCED REACTIVE GAS DEPOSITION.** J.L. Solis, A. Hoel, L.B. Kish, S. Saukko\*, C.G. Granqvist, and V. Lantto\*, Dept of Materials Science, The Angström Laboratory, Uppsala University, Uppsala, SWEDEN. \*Microelectronics and Materials Physics Laboratories, University of Oulu, Oulu, FINLAND.

Nanocrystalline materials have been used in semiconductor gas sensors due to their large surface area and some other useful sensing properties. The semiconductor gas sensor changes its conductance when the composition of the surrounding atmosphere changes. Tungsten oxide, WO<sub>3</sub>, is a very interesting semiconductor oxide in the field of gas-sensing applications. We have produced nanocrystalline WO<sub>3</sub> films by advanced reactive gas deposition. Synthetic air was used instead of an inert gas for both the cooling and reaction purposes. Before the introduction of 13 mbar of synthetic air into the evaporation chamber, the chambers were evacuated to  $3 \times 10^{-2}$  Torr. The starting material, which was a tungsten pellet, was installed in the evaporation chamber where the heating and oxidation of the tungsten occurs. Tungsten oxide forms on the surface of the starting material. There is a pressure difference between the evaporation and deposition chambers. The formed particles are carried through a transfer pipe with the gas flow and are ejected out of a nozzle into the deposition chamber for the deposition on a substrate. Tungsten oxide nanoparticles were deposited onto alumina substrates with a preprinted gold electrodes and Pt-heating resistor. The obtained films consisted of nanocrystalline WO<sub>3</sub> with a tetragonal crystal structure and a mean grain size of around 6 nm. The gas-sensing properties of the films were studied. After an initial activation, the nanocrystalline WO<sub>3</sub> films showed unique and excellent sensing properties at room temperature upon exposure to low concentrations of H<sub>2</sub>S in air. The optimum thickness of the WO<sub>3</sub> films was around 15 nm. A main drawback of conventional semiconductor gas sensors is that they work only at elevated temperatures and, therefore, require heating power for their operation. The nanocrystalline WO<sub>3</sub> films were insensitive at room temperature to many other tested gases, such as CO, NO, NO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>.

### 3:45 PM AA7.6

**NANOPOROUS CERIA FILMS PREPARED FROM COLLOIDAL SUSPENSION.** Vladimir Petrovsky, Brian Gorman, Harlan U. Anderson, Tatiana Petrovsky, University Missouri-Rolla, EMARC, Rolla, MO.

Nanoporous ceria films are of interest for such applications as high surface area catalyst supports, interface layers for gas separation membranes on porous substrates, interlayers in the fuel cells, etc. Ceria films were prepared by spin coating from water colloidal suspension of 50nm ceria particles. Special components were used to stabilize solution, to improve wetting and adhesion. Silicon and sapphire were used as the substrates. The resulting film thickness ranged from 500nm to 1000nm. No cracking or separation from the substrate took place over the temperature region under investigation (up to 1000°C). The XRD analysis was used to determine the composition of the films and to investigate the changes in the grain size and strength at the sintering process. The quality of the depositions was evaluated by SEM and AFM. Roughness of the surface was measured by a mechanical profilograph to characterize the planarization effect. The resulting films were optically smooth, which gives the possibility of the ellipsometrical and spectrophotometrical measurements and the characterization of the optical properties of the coatings. These data were used to calculate the changes of the thickness and refractive index of the films by the sintering process as well as optical absorption and scattering on the grains. The density of the films, which was initially about 50%, was increased up to 85% by sintering at 1000°C. The changes in the scattering are connected with the grain size grow and are in good correlation with the SEM results. The differences in the absorption are connected with the densification of the film without any sufficient changes in the optical properties of the grains.

### 4:00 PM AA7.7

**MICROSTRUCTURAL EVOLUTION AND ELECTRICAL PROP-**

**ERTIES OF TiN OXIDE THIN FILMS.** J.E. Dominguez, Q. Ding, L. Fu, X.Q. Pan, Univ of Michigan, Dept of MS&E, Ann Arbor, MI.

The sensitivity of semiconductive tin oxide (SnO<sub>2</sub>) to reducing gases is determined by the electrical conductivity change in the material. This change in conductivity strongly depends on the layer thickness of electron depletion near the oxide film surface. In this paper we study the effect of the film thickness and microstructure on the electrical properties and gas sensing performance. Pure SnO<sub>2</sub> thin films varying in thickness from 15 nm to 100 nm were deposited on sapphire substrates with different surface crystallographic orientations by pulsed laser deposition. Films grown on the (10 $\bar{1}$ 2) sapphire (r-cut) are epitaxial, single crystal, with a (101) out of plane orientation. High resolution TEM shows crystallographic defects such as crystallographic shear planes and misfit dislocations in single crystal films. Films grown on the (0001) sapphire substrates are polycrystalline with (200) texture. Gas sensitivity was measured in a gas reactor at high temperature. Sensitivity to reducing gases increases with decreasing thickness. In-situ Hall measurements were used to determine the extent of the depletion layer and the influence of thickness on gas sensitivity. A model relating the different factors to gas sensitivity is proposed.

### 4:15 PM AA7.8

**DESIGN AND MODELING OF A SELECTIVE COMPOSITE GAS SENSOR.** Brian Chwieroth, Nancy Savage, Bruce Patton, Prabir Dutta, Center for Industrial Sensors and Measurements, The Ohio State University, Columbus, OH.

Mixtures of anatase and rutile TiO<sub>2</sub> can provide an n-type/p-type composite with attractive gas sensing properties for high temperature industrial environments. We have developed the Polychromatic Percolation Model (PPM) to facilitate the development of a gas sensor selective to carbon monoxide and methane. The PPM characterizes conduction as a percolative phenomenon through resistive grain interfaces using a five component extension to McLachlan's General Effective Medium (GEM) equation. We find that the sensor response (n-type or p-type) to a reducing gas follows the least resistive intergranular path, and depends on the n-type/p-type composition, the sintering, and the relative sizes and shapes of the grains. By comparing the fractional interface contacts with their respective percolation thresholds, we can accurately calculate the composition and microstructure at which the response of the CO/CH<sub>4</sub> anatase/rutile composite sensor shifts from n-type to p-type. Using the PPM, we predict the preparation requirements necessary to design a selective composite sensor.

### 4:30 PM AA7.9

**GRAIN BOUNDARY EFFECTS ON THERMAL CONDUCTIVITY IN YTTRIA-STABILIZED ZIRCONIA BY MOLECULAR-DYNAMICS SIMULATION.** P.K. Schelling, S.R. Phillpot and D. Wolf, Argonne National Laboratory, Argonne, IL.

Lattice defects such as grain boundaries are known to be important scattering centers for phonons. We report results of molecular-dynamics simulations of the thermal conductivity in perfect crystals and across grain boundaries. By heating and cooling two well-separated regions, we directly impose a temperature gradient in a manner similar to experiment. The energy added and removed from the hot and cold regions respectively is then used to compute the energy current through the system, from which the thermal conductivity is calculated. Predictions for the grain-size dependence of the thermal conductivity are made and compared with recent experimental results. Work Supported by the U.S. Department of Energy, Office of Science, under Contract W-31-109-Eng-38.

### 4:45 PM AA7.10

**Al DOPED Ta<sub>2</sub>O<sub>5</sub> THIN FILMS FOR MICROELECTRONIC APPLICATIONS.** P.C. Joshi, M.W. Cole, C.W. Hubbard, E. Ngo, U.S. Army Research Laboratory, Weapons and Materials Research Directorate, APG, MD.

Ta<sub>2</sub>O<sub>5</sub> thin films are attractive for numerous microelectronic applications such as gate dielectric of metal-insulator-semiconductor devices, optical waveguides, electroluminescent display devices, and surface acoustic wave (SAW) devices. Ta<sub>2</sub>O<sub>5</sub> is one of the most promising insulator materials for DRAM cell capacitors. The high dielectric constant and low dielectric loss materials are also attractive for microwave applications. For successful integration into microelectronic devices, extremely reliable Ta<sub>2</sub>O<sub>5</sub> thin films are desired. Ta<sub>2</sub>O<sub>5</sub> based composites have been investigated to improve the dielectric and insulating properties of tantalum oxide. In this paper, we report on the systematic study of structural, dielectric, and insulating properties of Al doped Ta<sub>2</sub>O<sub>5</sub> thin films fabricated by metalorganic solution deposition (MOSD) technique. The Al doped Ta<sub>2</sub>O<sub>5</sub> thin films were fabricated by spin-coating technique using

room temperature processed carboxylate-alkoxide precursor solution. The structure of the films was analyzed by x-ray diffraction (XRD). The surface morphology of the films was examined by field emission scanning electron microscope (FESEM) and atomic force microscope (AFM) using tapping mode with amplitude modulation. The film/substrate interfacial characteristics were examined by RBS technique. The electrical measurements were conducted on films in MIM and MIS configurations. The effects of Al content and the post-deposition annealing temperature on the dielectric and insulating properties were analyzed. The effects of the applied bias and the measurement temperature on the dielectric and insulating properties were also analyzed to establish the stability and reliability of Al doped Ta<sub>2</sub>O<sub>5</sub> thin films. Thin films with 0.9 Ta<sub>2</sub>O<sub>5</sub>-0.1Al<sub>2</sub>O<sub>3</sub> composition exhibited improved dielectric and insulating properties compared to Ta<sub>2</sub>O<sub>5</sub> thin films. The high dielectric constant, low dielectric loss, low leakage current density, and good temperature and bias stability suggest the suitability of Al doped Ta<sub>2</sub>O<sub>5</sub> thin films as capacitor dielectric layer for DRAMs and integrated electronic applications.