SYMPOSIUM AA
Structure-Property Relationships of Oxide Surfaces and Interfaces

November 27 – 29, 2000

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*Invited paper
SESSION A1: GRAIN BOUNDARIES IN OXIDES
Chair: Xiaoming Pan and Christian Ekelund
Max-Planck-Institut für Metallforschung, Stuttgart, Germany, 27, 2000
Commonwealth (Sheraton)

8:30 AM A1.1
EFFECTS OF Y AND Zr DOPANTS ON GRAIN BOUNDARY STRUCTURE IN CREEP RESISTANT POLYCRYSTALLINE ALUMINA
G.S. Cegiell, C.M. Wang, J.M. Richman, H.M. Chen, 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 in grain boundaries and not detectable in the creep damage zone. Interpretation of grain size effects has been made from high resolution imaging experiments using TEM. Interpretation of local chemical configurations of the dopant atoms has been used to determine the overall microstructure from electron energy loss spectroscopy. The benefit of the combined experimental and theoretical approaches for characterizations of intercrystal is illustrated. It opens new perspectives in materials science for understanding of microstructural properties of polycrystals and the relations to properties and phenomena.

10:30 AM A1.5
ATOMIC SIMULATION OF A DOMAIN BOUNDARY IN ZrO2
Anthony T. Paxton, Michael W. Finnis, Queen’s University of Belfast, Atomic Simulation Group, Belfast, UNITED KINGDOM.

Tetragonal zirconia (t-ZrO2), a ferroelastic material, readily forms domains with domain boundaries on (001). For example, by compressing a single crystal along [100], the formation and movement of such domain walls have been demonstrated experimentally [1]. We have used atomistic simulations of a domain wall with a self-consistent tight-binding model [2] which correctly reproduces the high temperature tetragonal-cubic phase transition induced 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.

References:

11:00 AM A1.6
HEM OF GRAIN BOUNDARY STRUCTURES IN YTTRIA-STABILIZED CUBIC ZIRCONIA, K.L. Merkle, L.J. Thompson, G.R. Bui 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 MOCD technique. In this manner, nano-crystalline films between 8 and 25 nm thick 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 nano-size structural features of (001) YSZ tilt GBs could be studied by HREM over the whole range of microstrain, using a JEOL 4000EX HREM. Moreover, several well-strutted triple junctions decoupled of amorphous phases could be observed. HREM analysis shows that the cation columns of (001) YSZ GBs form a relatively dense structural arrangement, in contrast to the large open spaces that have been found in fcc stoichiometric oxide, such as NbO. The microstructure of low-angle high-angle GBs will be discussed in view of possible GB relaxation mechanisms, 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 as GBs.

This work was supported by the U.S. Department of Energy under contract W-31-109-ENG-38.

11:15 AM A1.7
ATOMIC SCALE CHARACTERIZATION OF A TEMPERATURE DEPENDENCE TO OXYGEN VACANCY SEGREGATION AT SrTiO3 GRAIN BOUNDARIES. B.E. Klle 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 using their functionality for superconductivity, ferromagnetism, ferroelectricity, magnetic resistance, ionic conductivity and as dielectrics. Although there is an almost innumerable combination of metal cations that can be accompanied by the system, the recent results on perovskites suggests that there should also be a link between the structure that form defects and grain boundaries. To develop a fundamental understanding of the structure-property relationships at grain boundaries in perovskites, we carried out the study of a single model system. In this regard, SrTiO3 serves as the simplest simple model material for perovskites where the alkali properties are very well understood using defect chemistry principles. The correlation between the structural and the local electronic properties of SrTiO3 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 nonmonotonic [tilt gr] tilt grain boundary in order to develop an understanding of the control that the grain boundary phase 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 AMORPHOUS ABRUPT GRAIN BOUNDARIES IN SiO2

Electrostatic force microscopy (EFM) and scanning surface potential microscopy (SSPM) are used to determine the potential distributions above grain boundary - surface junctions in SiO2 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 atomic structure of the grain boundaries and segregation of dopants.

11:45 AM AA1.9
DIRECT IMAGING OF INDIVIDUAL FLUX QUANTA LOCATED AT BOUNDARIES OF YBa2Cu3O7-δ BICRYSTAL FILMS

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 enter these regions, extra energy is needed to move them out, thus the flux-lines are pinned. Unless magnetic flux is larger than the pinning force (Fp ≥ Fc), the penetration 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 µm and magnetic signal resolution of 10^-7 T. From the width of the individual flux lines along the grain boundary which is directly related to Josephson penetration depth, one can determine the critical current density (Jc) that the grain boundary can sustain. In our work, we will show that the spreading of flux-lines increases with increasing misorientation. TEM-SSM images of TiO2 films were either laser ablated or sputtered on seven SiO2 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 Jc 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 Jc with increasing misorientation. The critical current density was found to be a function of 15% for [110] tilt boundaries. The reduction of effective superconducting channel increases with misorientations with the concomitant decrease of Jc.

SESSION AA2: INTERFACES IN COMPOSITES AND MULTILAYERS
Chair: Robin W. Grimes and Craig A. J. Fisher
Monday Afternoon, November 27, 2000
Commonwealth (Schenectady)

130 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/crystal interfaces relevant to wafer bonding and chemical mechanical polishing will be presented, with emphasis on the role of water at the interface behavior. Two-dimensional models of glass/crystal interfaces will also be discussed. One will include the interfaces of vanadium disilicate glasses and layered vanadium crystal applicable to thin film batteries. A charge transfer algorithm was used to model the charge on the V-O bonds. 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 ceramic will be discussed, with emphasis on atomic structure and segregation.
INTERFACES IN ZINC OXIDE VARISTORS. Mattie 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 extremely high values of voltage/voltage behaviour. The term "varistor" 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 are both crucial to the performance of the varistor, so are affected by the height and the width of the potential barrier 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 grain junctions have been studied using electron holography and diffraction techniques. The composition of the microstructural constituents and interfaces has been investigated through energy-dispersive X-ray spectroscopy (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.


3:45 PM AA2.6 INTERFACE ANALYSIS OF OXIDE THIN FILMS USING HIGH ENERGY ION BEAM TECHNIQUES. Y. Suzuki, S. Thevuthasan, E.M. Adran, S.I. Yi, Y. Gic, S.A. Chambers, Environmental Molecular Sciences Laboratory. Pacific Northwest National Laboratory; S. Matsubara, School of Science, University of Western Sydney, Nepean, Kingswood, AUSTRALIA; Y.J. Kim, Dept. of Chemical Technology, Tajuun 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 spectroscopy (RBS) and channeling techniques along with neutron reaction analysis (NRA) to

investigate the crystalline quality and interface 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 FRAC TURE SURFACES FROM OXIDE / POLYMER INTERFACES. Maura Jenkins, Jeffrey Sengodara, Dimitrios Pantelidis, Reinhold Drauzkard, John C. Brannon.

Atomic Force Microscopy (AFM) is used to characterize fracture surfaces in silicon oxide/silicon dioxide 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 where 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 Gibb's 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 modified differently 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.]

3:40 PM AA2.9 MOLECULAR DYNAMICS SIMULATIONS OF ZIRCONIA-ALUMINA INTERFACES. Craig J. Fishker, Katsuyuki Matsushita, Hidenori Matsubara, Japan Fine Ceramics Center, Nagoya, Japan.

We have performed molecular dynamics simulations of interfaces between crystals of 8 mol% yttria-stabilized zirconia (YSZ) and alpha-alumina in an attempt to better 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 Newtonian 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 YSZ, which we attribute to the compressive stresses in the interface zirconia crystal. The physical and energetic characteristics of different interfaces will also be discussed.

SESSION AA3: POSTER SESSION

Chairs: B. Curry, C. Xiaoqing, P. Kurt E. Wick, H. Terry, and T. Wood

Monday Evening, November 27, 2000

60 Posters

Exhibition Hall D (Hyatt)

AA3.1 CRYSTALLOGRAPHY, PHENOMENA AND INTERACTIONS IN NANOCLUSTER SYSTEMS. I.P. Svitlych, M.V. Barenets, Yu.V. Mikheev, V.K. Matamakov, S.V. Novochiko, 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. New properties of the cluster 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 a polymeric network. The nanosystems where forming clusters directly interact with each other and show either weak or strong interactional ability are also under consideration. The properties of nanosystems affected by iron oxide nanosystems, the problems of intracocrystal 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 1-2 nm located in polymeric network and for

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Nanostructure 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 theoretical consideration for the interaction composed of iron oxide particles, upon action of shear stress under high pressure (SHHP) and simultaneous action of the SHHP and SHSP-induced polymerization of acrylicmide there were observed and discussed the shifts in critical parameters for the first order magnetic phase transitions in clusters.

AA3.2 INTERFACE REACTIONS IN LiNOx BASED OPTOELECTRONICS DEVICES. Hiroshi Nagura, Yasuyuki Miyama, Naoki Mutsugi, Kenichi Higami, Yoshikazu Hoskmito, Toshiyuki Yamamoto, Yutaka Yamane and Miki Yanukai. Optoelectronics Research Division, New Technology Research Laboratories, Sumitomo Osaka Cement Co., Ltd., Funabashi, Chiba, JAPAN.

Understanding the interface structure of device constituent materials is important to demonstrate physically the device reliability and quality. In this regard, LiNOx based optoelectronic devices, developed and used in recent high-speed optical fiber communication systems, should be investigated on their materials science. For instance, although the SiOx buffer layer in usual coated on LiNOx substrate to improve the device 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 Li at the interface of sputter-deposited oxidation on sputter coating LiNOx wafer. From this, in situ observation of LiNOx surface, a deposition of LiF particles is found and deteriorates the bonding strength of coating layers. The interfacial reaction between the LiNOx (or SiOx) and a sacrificial layer such as a Ti film needs to be understood in order to completely remove this 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 Si3N4 passivation is also discussed from the viewpoint of the interfacial problems.

AA3.3 SURFACE AND INTERFACE TRANSPORT OF DENSE ORIENTED Ln3Sb5O17 THIN FILM ELECTRODES. Yasmeen L. Yang, C.L. Chen, S.Y. Chen, C.W. Chu and A.J. Jacobson, Materials Research 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 ionic and electronic conductivity of dense ionic conducting Ln3Sb5O17 in the LSCO/YSZ system, where LSCO = Ln2O3·5Sb2O5·4O. The reference electrode was attached to the side of the electrolyte disk and was typically in equilibrium with dry air as the reference point. Impedance spectra of the working electrode in the frequency range 8 Hz to 10000 Hz were recorded as a function of temperature and applied potential (-70 mV to 470 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/SrTiO3 (001) INTERFACE. Theoren Ochi, Sillykel Kraichmaner, Christian Schachter and Jochen Schuch, Technische Universität-Dresden-Forschungszentrum-Institut für Metallforschung, Stuttgart, GERMANY.

The microscopic structure and energetics of a SrTiO3 (001) surface covered with a thin layer 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 SrTiO2 substrate slabs, with 20 or 30 A SrTiO3 surface terminations, and Pd films of varying thicknesses were used to model the free (001) surfaces and the (001) heterojunction interfaces. Based on the calculated energetics of adhesion for the different interfaces, the microscopic energetics of wetting and layer growth were analyzed. The SrTiO3 terminated substrate is energetically favorable for the adsorption 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.


In this research, new Al-Mg-Zn-Zn alloy sacrificial mode used have been developed and characterized. The interest in the study of Al-Mg-Zn system, due to the presence of precipitates in Al-Mg-Zn and intermetallic regions which are capable of breaking down passive films and presenting good electrochemical efficiencies. The formation and distribution of precipitates phases belong to the binary Mg-Zn and to the ternary Al-Mg-Zn systems in the aluminum 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 characterization show the presence a solid solution of the α-Al, and eutectic of α-Al3Mg6Zn3 and precipitates of Mg5Zn2 in intermetallic regions. Electronic microscopic observations performed on specimens with and without heat treatments showed in the α-Al matrix the presence of uniform distribution of precipitates of α-Al3Mg6Zn3, MgZn2, and Al3Li type. When the behavior of aluminum sacrificial anodes is directly related to the electrodeposition of aluminum alloys as corrodend microstructure of the AlMgZn2 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. Arcton, UNAM Instituto de Física, MEXICO; Rebec Castanedo, CINVESTAV, Querétaro, MEXICO; Walter Estrada, Univ. Nal. de Ingeniería, PERU.

SnO2 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 SnO2 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 ray 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, shape and surface roughness as fluorine content was increased from 4.2 to 20% wt. in the starting solution. Correlation between roughness, grains size and electrical resistance variations and presented related to gas sensitivity properties of detectors based in pure doped SnO2 thin films.

AA3.7 EFFECTS OF DEPOSITION METHOD ON THE PROPERTIES OF W/Ti/SiO2/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-ni, Kyungsando, KOREA.

With the scaling the MOSFET gate lengths down to 100 nm regime and gate oxide thickness to below 3 nm, poly-silicon (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/Ti 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 Si/Si interface. All samples were prepared by oxidizing 8-10 Ohm-cm (100) oriented p-type silicon wafers in wet oxygen at 700-800C to 20-500 nm thick Pd. As oxide barrier, sputtered TiN films (30 nm) were deposited by reactive sputtering of Ti target in N2/Ar ambient under the various sputtering power and temperature. The CVD TiN (30 nm thick) barriers were also deposited using TiCl4 (Ar) plasma growth and 50 nm TiN film. The 50 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\textsubscript{2} and Si/MOS capacitors were compared. A threshold voltage lower than the interface state density, as determined by capacitance-voltage (C-V) characteristics, indicates the presence of interface states.

Post-mortem analysis of (PMA) in superconductors of TiN/SiO\textsubscript{2}/Si structure is done using transmission electron microscopy, and the results are compared with the literature. On the other hand, CVD/TiN/SiO\textsubscript{2}/Si MOS capacitors demonstrated non-damaged characteristics as probed by insignificant hysteresis and ideality C-V profiles regardless of PMMA. The interface state density of this structure is at least as low as $\sim 2 \times 10^{12}$ eV/cm$^2$ range, which is about an order of magnitude lower than that of PMA. Some fundamental MOS characteristics related with deposition technique will be discussed in terms of damage sources such as plasma and metal penetration.

A3.3.8 EPITAXIAL STRAIN AS VISIBLE ROUTE TO INCREASE $T_c$ IN CUPRATE SUPERCONDUCTORS. H.-U. Habermeier, X.J. Chen, and P.X. Zhang, Max Planck Institute für Festkörperphysik, 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. Recent years have seen an increasing interest in $T_c$ of Ca$\textit{A}$CuO$_4$ superconductors can nearly be doubled by biaxial epitaxial compressive strain. Rauszy and Habermeier showed that in doped Lanthanum nickelates epitaxial strain can induce a metallic transition. On the other hand, attempts to further increase $T_c$ of the 123 compounds by epitaxial strain. In this contribution the thickness dependence of $T_c$ of Bi$\textit{Sr}_{2}$Ca$_{2}$Cu$_{2}$O$_{8}$ thin films deposited on SrTiO$_{3}$, NiGaO$_{3}$ and LaSrAlO$_{4}$ single crystal substrates will be presented and the reasons for the failure to enhance $T_c$ are derived from a careful study of the Raman spectra of urhanna thin films. Based on these studies our propose experiments to use thin films of Bi$\textit{Sr}_{2}$Ca$_{2}$Cu$_{2}$O$_{8}$ thin films in order to enhance $T_c$. The analysis includes a theoretical consideration of the role of the apex oxygen bond length to the plane Cu and its pressure dependence. The first experimental results will be presented.


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 strain causes the shift of the Curie temperature to lower values and an increase in the magnetic activity in the film. Compressive strain in thin films gives rise to modifications of the magnetic structure specially in the range of the Neel temperature and the approach to saturation. In this contribution, the results of structural, magnetic and magnetic properties of films under tensile stress of LaCaMnO$_{3}$ films are discussed from the point of view of epitaxial strain. Additionally, recent results will be presented showing a film thickness dependent transition from an insulating to a ferromagnetic one in LaSrMnO$_{4}$ thin films of different compositions. The films have been prepared by PLD and analysed by XRD, TEM, transport and Raman scattering investigations. A generalised picture of the strain generation and relaxation emerges and will be discussed.

A3.3.10 THE BEHAVIOR OF ULTRATHIN ALUMINA FILMS UNDER STEM-INDUCED HIGH ELECTRIC FIELDS. DIELECTRIC BREAKDOWN AND PRE-BREAKDOWN BEHAVIOR. Chengyu Niu, Noel Mistry, Jeffery A. Keller, Department of Chemistry, University of North Texas, Denton, TX.

An STEM tip has been used to induce localized dielectric breakdown and pre-breakdown pit formation in $\lambda$ thick aluminium films grown on Ni$_3$Al(111) substrates under UHV conditions. Breakdown is induced by increasing the STEM 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 (~15 nm or more) due to the breakdown of the tip/sample interface and by the appearance of a dark spot. Breakdown is observed to occur at a field threshold of $1 \pm 1$ MV/cm, in good agreement with extrapolations of microscopic capacitance measurements on thicker films. Puking below breakdown thresholds induces pits (10 nm deep x 50 nm wide) at the oxide/substrate interface. Both pit depth and diameter can be increased by repeated pulse with STEM. Once a pit is formed, the breakdown threshold within the pit is ~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 current erosion and the operation of CMOS and magnetoresistive devices.

A3.3.11 OXIDES INFLUENCE ON ELECTRICAL PROPERTIES OF Si AND Al$_2$O$_3$ MATERIALS. A. Andrusik, Komatsu Silicon America Inc., Hillsboro, OR; G. Kiby, M. Andrusik, State Pedagogical University, Drugofi, UKRAINE; V. Belosvestna, 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 the said materials is seemed to be essential, especially in aspect of possible numerical modeling of these properties crucial for active elements based on epitaxial layers ($p$-$Si$/$p$-$Si$ quasi-heterojunctions grown by CVD technique) and on some $A$/$B$O$_3$ (in particular $Gd$O$_3$) thin film structures. The structural investigations were done in case of silicon quasi-heterojunctions (LV and C-V measurements allowed to make such a conclusion). SiO$_2$ layer formed at the interface Si$-$SiO$_x$-$Si$ film was appeared as a distinctive generator of surface electronic states forming the potential barrier with height fluctuations. In the case of calcium telluride films grown on glass ceramics substrate by vacuum deposition in closed-space system with significantly large scale surface surface TEM/STEM and Auger analysis were demonstrated oxygen to precipitate on microinhomogeneities forming CdO/GdFe quasi-3D dimensional microstructures. The work proposes the main results of electrical properties numerical modeling and calculation of energy band diagrams of the examined structures.

A3.3.12 INFLUENCE OF OXIDATION ON BORON SEGREGATION TO GRAIN BOUNDARIES OF IN-SITU FRACTURED Ni$_3$Al ALLOYS. G. Pahlavanzad, S.A. Koch, D.T.L. van Acker, J.Th. M. De Rooz, Department of Materials Science Center, University of Groningen, Groningen, THE NETHERLANDS.

A common theme in all studies of B segregation to grain boundaries in Ni$_3$Al alloys is the fact that B segregates more strongly to grain boundaries than to free surfaces, while segregation is observed onto sputtered surfaces annealed below $800\degree$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 intergranular 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, a number of experiments are performed on in situ fractured B-doped hypoeutectic aluminides. 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 of exposure to the ambient ultrahigh 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 S supplied from the environment resulting in a dynamic state of B.

A3.3.13 DIRECT OBSERVATION OF SILVER DOUBLE ATOMIC LAYER IN Al-Cu-Mg-(Ag) ALLOYS INTERFACE. N. Faj, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN. C.R. Hutton, G.J. Shiftlet, Department of MSE, 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 $200\degree$C due to the eutectic Omega phase of Cu-Mg in Al-Cu-Mg-(Ag) alloys. More specifically, our function and exact location of Ag are still under debate. Here we show the atomic resolution structure of Ag segregation on the omegamatrix interface by the means of Z-contrast scanning transmission electron microscopy imaging technique. The first sample examined was aged at $200\degree$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. This Ag concentration profile across the plate is confirmed by electron energy loss spectroscopy. In the image of the second samples aged at $300\degree$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 Ca and Al through the layers of the riser. At higher values of ledge density, several atomic layers are observed in all cases, showing an enhanced intensity of the omega phase. Samples aged at 1000°C appeared to possess very thin ledges.

**A3.14**

**INFLUENCE OF Fe ON THE MORPHOLOGY OF SPINEL IN THE SYSTEM MgO-Al₂O₃-Fe₂O₃**

O.V. Khruslov, U. Ortiz, M. Moroz, and M. Silva

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 surface morphologies. In this work, we studied the surface morphology of the spinel MgO-Al₂O₃-Fe₂O₃ at 1400°C 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 fine terraces and steps. Experimental observations were made on the nature and distribution of the observed polynuclear structure.

**A3.15**

**PHYSICOCHEMICAL CHARACTERIZATION OF CONVERSION COATING DEPOSITED ON ALUMINUM IN CHLORATE SOLUTIONS**

Liana Amari, Nicoletta Muladzani, Monica Santarina, Francesco Di Quarto, Palermo University, Dipartimento di Ingegneria Chimica dei Materiali, Palermo, ITALY.

Valerie Liag, Rudolph Bucher, Giessen University, Department of Materials Science and Engineering, GI.

Chromate conversion coatings (CCCs) are usually applied on Al and Al alloys in order to improve the corrosion resistance of surfaces for the attachment 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 chemical and thermodynamic properties of the conversion protection mechanisms of CCCs. In spite of numerous research efforts aimed to characterize CCCs, the chemical composition is not well defined. Additionally, the mechanism of CCC formation and failure in corrosion protection are not well understood. While previous studies have shown CCCs to be comprised of an amorphous CrIII 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 (X-ray diffraction, photoelectron spectroscopy, PCS) techniques. The detailed PCS study of CCC growth 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 determined by deriving 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 reveal the formation of a CrIII mixed valency layer on the surface of an ion beam sputtered TiO₂-VI mixed valency ox-hydroxide layer on Al surface in chromate conversion bath. A first evaluation of the chemical composition of the CCC based on all of these techniques will be presented.

**A3.16**

**THE INTERFACIAL REACTION PRODUCTS AND MECHANICAL PROPERTIES WITH OXIDIZED LAYER THICKNESS OF SC Composite Interfaces**

Yong-Gun Jeung, Young-Min Kim, Chang-Moon Kwon, and 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 MSE, 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 reinforcement are spotlighted because of their low density, superior specific modulus, specific strength, wear resistance and high temperature stability. But Al₂O₃ formed by interfacial reaction between Al and SiC weakens the interfacial bonding strength. It was also known to be unstable in the water-soluble atmosphere. In this study, the passive oxidation of SiC powder was used as protective agent against the reaction between matrix Al and SiC particles. The oxidized layer thickness of reinforcement is changed with holding time during 1,2,4,6,9,12 h at 1100°C. The reinforced SC particles 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 indentation hardness and failure strength in terms of the oxidized layer thickness.

**A3.17**

**ANALYSIS OF SEGREGATION BEHAVIOUR OF GRAIN BOUNDARIES IN SAPPHIRE BY ANALYTICAL AND HIGH-RESOLUTION TEM**

Stefan Naef, Thomas Gammer, Wolfgang Kutz, and Manfred Riekel, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

Segregation of yttrium on grain boundaries (GBs) in Sapphire changes the mechanical properties. However, the segregation behavior of different GB structures is still not understood. Therefore, birefringence were produced (with and without Y addition) with "special" asymmetrical tilt GBs (23, 27, 211, 231). The segregation behavior of "special" GBs were compared with observations at "general" GBs (symmetrical 24° and asymmetrical 29° (0001) l/(2012)).

In order to avoid contamination of the GB by impurities, the birefringence 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 Chiff-Lorimer factor k for Y in Sapphire was determined experimentally by reference measurements in YAG (Y₃Al₅O₁₂; k = 4.58), YAM (Y₃Al₅O₁₄, k = 4.49), and YAP (Y₃Al₅O₁₄, k = 4.42), resulting in a mean value of k = 4.5.

At the Y-free 2ZB-crystal we found a faceted GB caused by the miscut of the bonding surface. Two kinds of facets were observed: symmetrical (T012) and (0001)l/(2012)l. At the nominal sharp (0001)l/(2012)l were observed. Within the detection limit (0.3 nm/nm²) 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 barriers for impurities.


**A3.18**

**INFLUENCE OF INTERIOR p-N JUNCTIONS ON THE ELECTROCHEMICAL PROPERTIES OF CuO·TiO₂ COMPOSITE MATERIALS IN AQUEOUS SOLUTION**

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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 ion conductors, mixed electronic and ionic conductors. This kind of sample presents a large interface density with a distribution of interfaces per unit area. In this study, we prepared composites of p-type copper (II) oxide CuO and n-type all n-type titanium dioxide TiO₂. A novel preparation route was developed by mixing and room temperature compression of TiO₂ with CuO followed by sintering at 850°C. Under these circumstances, CuO 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 TiO₂ nanoparticles. Their carrier density is low, because the n-type TiO₂ nanoparticles can be depleted of electrons by the presence of highly doped p-type CuO.

**A3.19**

**ORIGIN OF VOIDS AT THE INTERFACE OF WAFER BONDED SAPPHIRE ON SAPPHIRE**

Stephan Sezn, Pascal Kopferman, and N.D. Zhukhovıc, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

Two Sapphire (Al₂O₃, 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 may be the reason, if 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
MISCELLANEOUS MECHANISMS AT MOVING
REACTION FRONT DURING THE INITIAL GROWTH STAGE
OF La$_2$Zr$_2$O$_7$-BIASED PYROCHLORITE THIN FILMS ON YSZ(100).
C.J. Lu, S. Senn and D. Hesse, Max-Planck Institute of
Microstructure Physics, Weinberg, Halle, GERMANY.
La$_2$Zr$_2$O$_7$-biased pyrochlore (LZO) thin films were grown on Y$_2$O$_3$
 stabilized ZrO$_2$(100) (YSZ) single crystals by reaction [at 1100°C in vacuum]
between the crystals and La$_2$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 front are investigated by the 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 crystal and they are well oriented to YSZ in
the very beginning of the reaction. Above a certain size (100 nm),
evertheless, they always show a characteristic domain structure. Each
island typically consists of four domains which are tilted by a small
angle off the exact cubic-to-tetragonal orientation around four different
<110> 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
vectors of the edge dislocations are perpendicular to the islands.
The Burgers vector components parallel to the interface leads to an
additional 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 center of each island and
sometimes more than four domains are formed in one island.

AA3.21
SPLIT POLARIZED INJECTION INTO A D-WAVE SUPERTUN-CONDUCTOR.
High quality La$_2$Sr$_{1-x}$Mn$_x$O$_3$ (LSMO)/YBa$_2$Cu$_3$O$_{7-y}$ (YBCO) and
LaNiO$_3$ (LNO)/YBa$_2$Cu$_3$O$_{7-y}$ (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 Andrei 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 (CMM)
drops rapidly with temperature. This phenomenon can be used as an
indication of surface 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,
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)
BiFeO$_3$, 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
groins can be studied 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 piezoelectric potential and potential drops across
grain boundaries were quantified and compared to Ginzburg, Devonshire and
Hewitt- -Joner 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-Jusaimi, T.F.
Wang and T.P. Snoke, 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$_2$ 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 theoretically
grown Si-SiO$_2$ 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 Burck et al.
[1]. Our models result in a valence band offset in agreement with
experimentally observed values. These models result in a chemically
and structurally non-uniform interface. However, if this
micrograph is on a scale of a few atomic layers, the interface will
appear smooth in a TEM image.


AA3.25
DEGRADATION IN SURFACE EXCHANGE RATES DUE TO
SURFACE ENRICHMENT OF STRONTIUM AND CHROMIUM IN
MIXED CONDUCTING Lao$_{x}$Sr$_{0.5-x}$Cr$_{0.5}$Fe$_{0.5}$O$_{3}$-δ,
P.A. van der Heide, A.R. Verma, S. Wang, A.J. Jacobson, University of
Houston, Materials Research Science and Engineering Center,
Houston, TX.
The La$_{x}$Sr$_{0.5}$Cr$_{0.5}$Fe$_{0.5}$O$_{3}$-δ 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 surface exchange coefficients.
Conductivity reduction measurements, however, indicate a
degradation in the longterm oxygen transport kinetics, or more
precisely the surface exchange kinetics of this material. Since bulk
transport properties were not affected, 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 photoelectron peaks.

AA3.26
ABRupt ELECTRICAL EFFECTS IN ZINC OXIDE GRAIN
BOUNDARIES VERIFIED BY ELECTRON AND ION SCANNING
MICROSCOPY. Martin Ellingsen, Michael E. Gaevski, Eva Olson,
Analytical Materials Physics, The Angstrom Laboratory, Dept. of
Materials Science, Upplands, Sweden, ANDENIV, 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 electron beam across grain
boundaries, were compared with computer simulations made using
three well known models of electron hole generation functions:
linear 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 types of indicated 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
magnitude assuming the presence of a double barrier at the individual
grain boundary were analysed. Several origins of the barrier asymmetry under zero bias voltage conditions are discussed.

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contrast profiles with application to silicon. Journal of Applied
Physics, 84(10), 5475-5481 (1998).
2 F. Greuter, and G. Blatter, Electrical properties of grain boundary domains in polycrystalline compound semiconductors.

**AA3.27**
**MICROSTRUCTURAL CHANGES OF INDIUM TIN OXIDE (ITO)**

THIN FILMS AS A FUNCTION OF RESISTANCE BY TEM

Yun Tae Chae, Chingamo Sung, University of Massachusetts Lowell,
Dept of Chemical and Nuclear Engineering, MA; G.M. Ying, ITO Division, Samsung Electro, Gemini, KOREA.

A set of Indium tin oxide (ITO) thin films with different thickness were prepared by dual magnetron sputtering technique on the two layers substrate (250μm SiO₂ 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 EDSX. We want to find out the relation of ITO thin film thickness and resistivity, and the grain size in plan-view observation.

**AA3.28**
**GRAIN SIZE DEPENDENT CONDUCTIVITY IN MIXED IONIC/ELECTRONIC CONDUCTIVE CERIUM OXIDE.**

Andrew Schäfer, Rainer Biringger, Universität des Saarlandes, Technische Physik, Saarbrücken, GERMANY.

Variation of the grain size of polycrystalline cerium oxide in the macro- 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 ion to redox controlled electronic conductivity upon reduction of grain size was observed. The electronic conductivity of cerium oxide 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 oxygen vacancies on the grain boundaries on surface reduction and stoichiometry will also be discussed.

**AA3.29**
**INFLUENCES OF DEFECT SEGREGATIONS ON THE POTENTIAL BARRIER FORMATION IN Nb-DOPED SrTiO₃ GRAIN BOUNDARY LAYER.**

Seong-Ho Kim, Jung-Ho Moon, Kuns-II Park and Yoonho Kim, Multifunctional Ceramics Center, Korea Institute of Science and Technology, Cheonggyeong, Seoul, KOREA.

The origins of defect formations have been investigated in Nb-doped SrTiO₃ single crystal and ceramics using electrochemical methods. In particular, impedance spectroscopy was applied to determine thermal activation energies for the conduction of Nb-doped SrTiO₃ grains and grain boundaries. From results, it was suggested that the activation energy, 0.8 eV, measured in grains is originated from oxygen vacancies and the activation energy, 1.2 eV, in grain boundary was from from strontium vacancies. Direct observations using a high-resolution transmission electron microscopy (HR-TEM) and an energy dispersive spectroscopy (EDS) revealed that the Nb-doped SrTiO₃ ceramics were composed of the nearly single crystalline grains whose boundaries have a faceted 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 space charge segregation on the electrical properties of grain boundaries were also studied.

**AA3.30**
**FIRST PRINCIPLES CALCULATIONS OF ZrO₂-Ni INTERFACES.**

Kazuyuki Matsunaga, Masanori Koyanagi, Sangu Tanaka, Dept. of Materials Physics, Osaka National Research Institute, Ikeda, Osaka, JAPAN; Hideki 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 housing systems. In this study, we performed ab-initio calculations of ceramic / metal interfaces using a plane-wave basis set and norm-conserving pseudopotential method. Special attention was paid to systems including zirconia (ZrO₂) 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 then calculated the calculated bulk moduli and bulk moduli of cubic ZrO₂ and for Ni and are in good agreement with the experiment. Secondly, we calculated atomic and electronic structures at interfaces between the cubic ZrO₂ (001) plane and for Ni (001) plane and analyzed bonding characterisitcs. This study was supported by the Proposals-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. Heel, E. Olson, L.B. Kish, M. Saunders, Department of Materials Science, Angström Laboratory, Uppsala University, Uppsala, SWEEDEN.

Tungsten trioxide (WO₃) is a very versatile material. It is widely used in transparent thin film technology for example as the active layer in amorphous silicon solar cells.

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 high mechanical and high capacitance efficiency in the impedance spectrum. The fabrication conditions and the film thickness has 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 FISSURE PRODUCTS TO SURFACES OF UO₂.**

Chris Sneeke, 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 UO₂ nuclear fuel, it is necessary to determine the energies 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 and Cr segregate to the (111) surface, while Ru and Sr segregate to the (111) surface. In particular, Zr and Cr segregate preferentially to certain surfaces. In particular, Zr and Cr segregate to the (111) surface, while Ru and Sr segregate.
as a function of growth temperature can be explained in this manner. The nature of film-substrate interface was also examined using cross-sectional transmission electron microscopy (TEM). The STEM 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. Ha. Y. Suzuki, Dept. of Metallurgical Science and Engineering, Tohoku University, Sendai, Japan; V.G. Harris, Naval Research Laboratory, Washington, D.C.

Epitaxial cobalt ferrite (CoFe₂O₄) thin films were grown on CoCr₂O₄ buffered MgAl₂O₄ substrates by pulsed laser deposition. Post deposition annealing in air at 1000°C changed the sign and magnitude of the magnetization. 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 CoFe₂O₄ and CoCr₂O₄, 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 MgO substrates, the interdiffusion between film and underlying substrate resulted in phase segregation, mainly by a combination of amorphous field-induced images and EELS analyses from scanning transmission electron microscope. These observations were consistent with magnetic measurements of annealed films grown on MgO.

**AA3.35**

**OXIDE MONOLAYER PASSIVATION OF POLAR AND NONPOLAR SURFACES OF α-SiC.** Eva Bashein, Zoltan Hajnal, Thomas Friesekein, Univ. Paderborn, Dept. of Theoretical Physics, GERMANY; Péter Dér, 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/SiO₂ 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 Hterminated surfaces 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 in characteristic feature of this structure. However, it leaves one third of the dangling bonds ununsaturated, thus the surface chemically active. On the other hand, we analyze the surface structure on both (1120) and (1010) nonpolar SiC surfaces yields interfaces without unsaturated bonds, and provides a passivation layer between SiC and the oxide monolayer. Furthermore, the SiO₂ decorated SiC (1120) 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 ORTHOBOUCIC ACID ON A VITREOUS B₂O₃ 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. Crystall growth with a preferred orientation such that plate sheets of B(OH)₃ 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 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)₃ crystal phase on an amorphous B₂O₃ glass substrate decays in favor of the glass with dissolved water. During the decay the remaining crystalline material changes its orientation to that of the B(OH)₃ layers become perpendicular to the substrate. B₂O₃·H₂O 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 orthobic 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.


**AA3.37**

Abstract Withdrawn.

**AA3.38**

**MULTILAYER STRUCTURE OF SPUTTER DEPOSITED TiO₂/SiO₂ MULTILAYER OPTICAL COATINGS.** E. Meetsva, J.J. Moore, Dept. of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO; P. Sitter, Department of Physics, Colorado School of Mines, Golden, CO.

The main requirements for the materials forming a TiO₂/SiO₂ multilayer optical filter are structural and optical stability. The aim of the present work was to realize the observed structural properties to the optical stability of the filters. The TiO₂/SiO₂ multilayer optical filters were deposited by d.c. magnetron reactive sputtering at room temperature (RT). The multilayers were annealed at low temperatures (RT + 320°C) to study the changes in microstructure. Cross-sectional transmission electron microscopy (XTEM) was used to investigate the microstructure of TiO₂/SiO₂ multilayers. The transmission of the multilayers was measured after environmental exposure over extended time periods. The microstructure of the multilayers 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 SiO₂ layers in the TiO₂/SiO₂ multilayer grown at RT are homogeneous the TiO₂ layers consist of nanoclusters 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 oxygen 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 TiO₂/SiO₂ multilayer and transition to polycrystalline amorphous phase in the TiO₂ layers.

**AA3.39**

**NON-STOICHIOMETRY OF NANOCRYSTALLINE CUBIC ZIRCONIA THIN FILMS.** Igor Kosnul, Toruho Suzuki and Harun 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 has mostly been done by thermodynamic calculations. Since then, a number of microstructural features, such as columnar growth, have been observed for the films. The microstructural features of the ZrO₂ thin films are reported. The results show that the ionic conductivity of ZrO₂ thin films is enhanced above one order of magnitude (at 300°C) compared with nanocrystalline specimens. In addition it has been observed that the stoichiometry is also dependent upon the type of acceptor. The electronic conductivity of ZrO₂ is about 4 orders of magnitude higher that observed for ZrO₂-Y, which suggests a reduction of the enthalpy of oxygen vacancy formation in Sr-doped specimens. 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. Yag, A.Y. Ku, N. Nakagawa, T. Lee, D.A. Steffe and I.A. Akam, 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 microscopy observations reveal that the films form an 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 misoriented, prismatic, domain boundaries, and micro-domains, 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 (2D) to three-dimensional (3D) film 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.

**AA3.44**


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 reason 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 [Pt(Zr,Ti)O3] films (x=0.5) were synthesized on (001) oriented SrTiO3 substrates at temperatures from 150°C to 300°C. Conventional powder XRD (6-2θ) 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. Consequent epitaxial layers were observed to be transparent under SEM, with the surface either nominally smooth or dominated by a screw dislocation-type morphostructure. Textured polycrystalline layers were observed to be opaque under SEM, and sometimes contained anisotropic, tilted pseudocubic crystallites. XRD pole figure and space mapping was used to determine the degree 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 filmsubstrate 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.** J. E. Domingues, J. P. Liu, X. Qian, Ann Arbor, MI; J. C. Harlow, Ann Arbor, MI; P. Van Duyne, Z. Zhil, Z. Zhu, A. Kroto, Center for Ultrafast Optical Science and Department of ECECS, University of Michigan, Ann Arbor, MI.

TiN oxide [Ti2O3] 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. TiN oxide films fabricated consist of different textures in microstructures which depend on the deposition conditions and substrate surface structures. For instance, films deposited on the (102) sapphire [001] surface 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 activated plasma plume of TiN oxide. Anodizing in air had an effect in the change of film structure. 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. Hatt, S. Kaske, T. Geum, C. Eichhorn, and M. Rühle, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

A novel technique was developed which allows the reproducible preparation of accurately oriented grain boundaries in SrTiO3 bicrystals by diffusion bonding. The resulting atomic structure was analyzed by high-resolution transmission electron microscopy. For a theoretical understanding of grain boundary structure, a-site local densities of electronic states were calculated. Combined with a molecular dynamics technique, the results were well described with a model based on the assumption that the boundary formation is an equilibrium process.
symmetrical twin grain boundary. A low grain boundary energy of 0.52 J/m² was obtained. Minor structural relaxations compared to a purely geometric 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 electronic structures shows that the perturbation induced by the grain boundary is localized in the vicinity of the grain boundary plane without any extension into the bulk region. Based on the present results obtained with the slab model, it can be derived for a build-up of a space-charge layer at the un toddled Σ 3 (111) grain boundary.

AA3.47
CHARACTERIZATION OF OXIDE LAYERS OF BULK Si₀.₉₋ₓGeₓ
W. Suzuki, T. Nenoto, T. Inui, Y. Takanashi, S. Sakuragi, Science University of Tokai, Dept. of Materials Science and Technology, Chiba, JAPAN

Silicon germanium (Si₀.₉₋ₓGeₓ) alloys are important as a material not only for microelectronic devices but also for thermoelectric devices to be used in energy conversion. Recently, Si₀.₉₋ₓGeₓ alloy has also attracted much interest as a solar cell material with the high conversion efficiency (AM5) 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 Si₀.₉₋ₓGeₓ, 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 Si₀.₉₋ₓGeₓ by using such conventional methods like metal oxidation; 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 becomes predominant. Dry and wet oxidations were performed at 800-850°C for 1-10 h, and oxidized layer 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 GeOₓ near the surface, but it changed from GeOₓ to SiOₓ with increasing the depth. On the contrary, for the wet-oxidized sample, a mixture of GeOₓ and SiO₂ was observed over the whole oxide layer. The mobile-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 lowering formation free energy of SiO₂ than GeOₓ and higher diffusion velocity of Ge in the oxide.

AA3.48
CARRIER CONTROL OF DOPED SrTiO₃ SINGLE CRYSTAL FILMS GROWN UNDER LAYER-BY-LAYER GROWTH MODE
Akira Ono, 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 optoelectronics. In particular, SrTiO₃ is an important substrate material for artifical nanostructures. 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, SrTiO₃ is important because of its electrical properties (semiconducting, superconducting, and dielectric), and an important substrate material. However, controllable doping of epitaxial SrTiO₃ thin films has not yet been fully established. We have studied the growth and electrical properties of In-doped and Ga-doped SrTiO₃ films, and report the range of doped-grown doped carrier.

AA3.49
ORDERING AND CONDUCTIVITY IN YTiRA STABILIZED ZIRCONIA FROM FIRST PRINCIPLES
Alexander Bogicevic, Christopher Wolveton, Gary Cokus, Ford Research Laboratory, Dearborn, MI; Anton van der Ven, Gerhardo Ceder, MIT, Cambridge, MA; David Reuter, David Renn, UC Davis, CA; E. H. Siedel, Ford Research Laboratory, Dearborn, MI.

Atomic 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 ageing characteristics. Here we report a finite-temperature first-principles study of the stability of ionic conductivity in y-rich yttria stabilized zirconia. The ordering problem on the cubic crystal (zc) and monoclinic (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 inequivalent cation sites find pyrochlores highly unstable, and produce a highly competitive ordered structure in the Zc-rich end of the phase diagram, in addition to the known Zc-Y₂O₃ 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 Hosssn
Tuesday Morning, November 28, 2000

8:30 AM **AA4.1
INFLUENCE OF MISFIT AND INTERFACIAL BINDING ENERGY ON THE SHAPE OF OXIDE PRECIPITATES IN METALS, B.J. Rood and J. Th. M. De Hosssn, Department of Applied Physics, Materials Science Centre and Netherlands Institute for Metals Research, University of Groningen, Groningen, NETHERLANDS.

Transmission electron microscopy revealed Mn₃O₄ precipitates with two types of dominant shapes in Pd₃Mn₃. %Mn that was internally oxidized in air at 1000°C. One type is octahedrally shaped and bounded by {111} planes of the Mn₃O₄. These observations were compared with earlier observations in the Ag/Mn₃O₄ system and the octahedrons show a relatively larger transection by {100} in Pd than in Ag. Further, a second type of precipitate shape, comprising about 1/3 of the precipitates in Pd, was not observed in Ag. It corresponds to a plate-like structure, showing an orientation relationship where the tetragonal axes of Mn₃O₄ are parallel to the cube axes of Pd, as in plate plane normal the axis of Mn₃O₄. The conclusions of the present analysis based on HREM 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 precipitation shape as bounded by semi-coherent interfaces is important only if the misfit strain is large and 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 AI/METAL OXIDE INTERFACES Donald J. Scalapino, University of Illinois at Urbana-Champaing, 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 oxides on adhesion at three related Al(111)/metal-oxide(001) interfaces. We have looked at the interface structural and electronic properties of the oxide and Fe₂O₃ as they appear 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 adhesion sites. The influence of the oxide oxides has been determined by comparing the results of adhesion energy, interfacial structure, and bonding type across the three different systems.

9:15 AM AA4.3
CLASSICAL INTERACTION POTENTIAL FOR Nb₂AI₂MNA INTERFACES K. Albe, R.S. Averbeck, University of Illinois at Urbana-Champaign, Urbana, IL; R. Benedek, D.N. Siddman, 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 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 tailored to the actual chemical bonding of the constituents (A. Levy et al., Acta mater. 47 (1999) 4145). A more realistic alternative is to adopt the modified embedded atom method (MEAM) potential, which has previously
microscopy techniques. For experiments requiring chemical analysis at very high spatial resolution, energy dispersive spectroscopy (EDS) and particle electron energy loss spectroscopy (PEELS) were performed on a VG HB5000 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 can be characterized by dissolution of the substrate at the liquid-solid-vapor interface, and by epilayer 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 site of the contact angle in Young’s equation. High spatial resolution EDS analysis showed the presence of a relative large quantity of Al in Ni in contradiction with the Ni-Al oxide equilibrium phase diagram. Use of the spatial difference technique indicated the existence of an Al excess (segmented) 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$_2$(100) BOUNDARIES: ABINITIO CALCULATIONS. Yong Ma, Susan B. Sinnot, 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 and photonic systems. We report on the interfacial and adhesion energies of Ni(111)-ZrO$_2$(100) interfaces that have been calculated using density functional theory within the generalized gradient approximation, thus providing one of the first calculations for an important, polar metal-oxide interface. Geometric optimization of both oxygen-terminated and titanium-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


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 intercalating lines were obtained for sp-metal and transitional d-metal oxides, with the noticeable exception of NiO laying on the sp-metal oxide intercalating line. The fitting equations for the two cases were: $E_g (eV) = 1.35 \times (X_M + X_O)^2 - 1.49$ for d-metal oxides and $E_g (eV) = 2.17 \times (X_M + X_O)^2 - 2.71$ 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$_2$B$_x$O$_{y+z}$ containing only d-metal and sp-metal cations, substituting to the metal electronegativity, $X_M$, the arithmetic mean for the cationic group, $\bar{X}$. 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 $\bar{X}_{OH}$ = 2.85. It will be shown that the proposed correlations seem to hold both for mixed d,sp-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-metal mixed oxides.

References:
1130 AM AA4.9
A SUB NANOSTUDY OF SEGREGATION AT CIO/AgAu HETEROINTERFACE. Jason T. Sebastian, Olof C. Hellman, David N. Sidman, Northwestern University, 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 heterogeneous interfaces. We present recent results of a 3DAP study of solute segregation at C-M/M heterophase interfaces prepared by internal oxidation. In particular, results on the CIO/AgAu (where Au is the segregating species) system are presented. In the 3DAP atomic reconstructions, the interfaces of the nano-meter-size CIO 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 (prograph) method. The Gibson excess of solute at the C-M/M interfaces is calculated, where possible, from the experimental data. Trends in the measured value of the Gibson excess as a function of segregation amendment treatment are discussed.

Research supported by the U.S. Department of Energy. J.T.S. was supported by a Department of 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. Krauz, J.M. McNaney, R.M. Cannon and H.O. Ritchie, Materials Science Division, Lawrence Berkeley National Laboratory, and Department of Materials Science and Engineering, University of California, Berkeley, CA.

The structural integrity of oxide/oxide 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/oxide interfaces by conductive strength and fracture toughness tests, very few investigations have looked at time dependent failure of interfaces under cyclic or static loading. Tests have been conducted on sandwich specimens consisting of 1-100 μm thick aluminum layers bonded between both polycrystalline and single crystal aluminum oxide to determine cyclic fatigue 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 aluminum. Static loading in a moist environment also caused interfacial cracks to deviate into the aluminum or arrest. Due to the poor crack growth resistance of the aluminum, cracks leaving the interface propagated at faster rates than those at the interface. Trends in crack growth rates 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
Chair: Tom Wood and I-Wei Chen
Tuesday, Afternoon, November 28, 2010

Commonwealth (Sherrington)

1:30 PM *AA5.1
UNDERSTANDING METAL OXIDE SURFACES AT THE ATOMIC SCALE. Ulrike Dehmel, 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 TiO2 AND SiO2. Kim F. Bennett, Lai-Qiong Wang, Pacific Northwest National Laboratory, Materials Resources, Richland, WA.

Interactions of water and HCOOH with stoichiometric and defective TiO2 [100], TiO2 [111], and SiO2 [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 TiO2-terminated SiO2 [100] surfaces results in different adsorption and desorption properties for H2O on SiO2 compared to the TiO2 [100] and [110] surfaces. Preliminary results for formate interaction with SiO2 [100] indicate strong adsorption consistent with experimental results, but in a distinctly different geometric arrangement due to absence of bridging oxygen atoms present for the TiO2 surfaces. Stepped SiO2 [100] surfaces have accessible oxygen sites for adsorbates, and are predicted to have increased reactivity for H2O, CH3OH, 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, Materials Sciences Division, under contract DE-AC05-76RL18330.

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. Cotomin, Dept. of Physics, University of Osnabrueck, Osnabrueck, GERMANY and Institute of Solid State Physics, Riga, LATVIA.

We present and discuss results of the calculations of the surface relaxation for NbO, BaTiO3, and NbOnOx perovskite crystals. By means of semi-empirical shell model, the positions of atoms in 11 near-surface layers placed atop a slab of rigid ions are optimized. This provides a determination of the surface relaxation and pseudopotential 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 plans calculation for the [110] surfaces. Future work includes performing calculations for [100] surfaces with a reduced number of layers. The [110] NbO3 and SrTiO3 surfaces O-termination is predicted to be lowest in energy whereas the KNO3 [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

We report in situ measurements of the atomic-scale structure of Pt/TiO2 (001) in the metal-organic chemical vapor deposition (MOCVD) environment using synchrotron x-ray scattering with a newly constructed Advanced Photon Source. Coherently-stained epitaxial films of Pt/TiO2 were grown in situ on SrTiO3 (001) substrates by MOCVD using methyl lead (TIL), trimethylsilyllead, and Pb2+ precursors. Annealing the films at ~750°C in O2 with or without TEL present produced surfaces having different reconstructions ([PtO-Rch] or [PtO-2Rch], respectively). The PtO-Rch surface is well ordered with a [2×2] symmetry. A surface structure consistent with that of a bilayer of PtO is consistent with the X-ray data. The TiO2-Rch surface is poorly ordered with [n×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-DM, under contract W-31-109-ENG-38, and by the State of Illinois, under HECA.

2:45 PM AA5.5

Experimental evidence in annealed lead-based B-site relaxor perovskites, e.g. PMN, indicates the 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
4:00 PM AA5.7
TIME EVOLUTION OF THE METASTABLE SURFACE STRUCTURE OF KTaO\textsubscript{3} \((001)\) STUDIED WITH HELIUM ATOM SCATTERING

E.A. Adams, J.A. Li, T.W. Tedlock, J. G. Skabara, S.A. Safronick, D.H. Van Winkle, Florida State University, Tallahassee, FL; F. Fishery, Valdosta State University, Valdosta, GA; L.A. Bonner, 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 \(\text{K TaO}_3\), produced by cleaving in situ in a UHV scattering chamber. Measurements taken immediately after cleaving indicate metastable satellite peaks with intensities greater than those 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 nearly zero while the specular peak increases, growing what appears to be normal specular representation from a \((1 \times 1)\) surface. A model of the initially cleaved surface, consisting of \(\text{K}\) and \(\text{TaO}_2\) islands and terraces of equal areas, respectively, separated by steps of one-half the bulk unit cell lattice spacing \((2.64\AA)\) is presented which agrees with the initial observations.

4:15 PM AA5.8
EXUDATING SILICATE LIQUID FROM POLYCRYSTALLINE ALUMINA N. H. Elashkar and C. Barry Carter, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Alumina-based liquids 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 glass 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 has brought out this geometry from a practical point of view. It is important to study the feasibility of eliminating the liquid from a polycrystalline compact. The present study is aimed at understanding the exudation behavior of morphite liquid from polycrystalline alumina. To minimize the effect of dopants and impurities, lanacol has been chosen. Lanacol is infiltrated with liquid morphite 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 SPHEROSIOXANE CLUSTER BINDING TO Si(001) BY SCANNING TUNNELING MICROSCOPY

K.S. Schneider, M.M. Buzas, H. Zabel, Chemistry Department, University of Michigan, Ann Arbor, Z. Zhang, Z. Zhou, Physics Department, University of Michigan, Ann Arbor, M. U.C. Pernik, 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 \(\text{H}_2\text{O}\) clusters bound to a \(\text{Si}(100)-2\times1\) surface. Atomically resolved STM images of these clusters bound to the \(\text{Si}(100)-2\times1\) surface have been obtained. We are able to identify the binding mechanism as activation of a single Si-H bond and monovacancy binding to the Si substrate. Filled and empty states images show good agreement with calculations for the HO\textsubscript{1} and LUMO states of the cluster. These results will be discussed in the light of recent numerical calculations and XPS studies.

SESSION AA6: OXIDE THIN FILM EPITAXY

Chairs: Harry L. Fuller and Darrell G. Schlom

Wednesday, November 29, 2000

Commonwealth (Sheraton)

8:30 AM AA6.1
ATOMIC SCALE CONTROL OF EPITAXIAL \(\text{SrRuO}_3\), \(\text{SrTiO}_3\), \(\text{SrRuO}_3\)/\(\text{SrTiO}_3\) HETEROSTRUCTURES USING IN-SITU HIGH PRESSURE RHEED FOR SPIN-POLARIZED PERPENDICULAR TRANSPORT

C.B. Eom, J.H. Cho, J.S. No, University of Wisconsin-Madison, Department of Materials Science and Engineering, Madison, WI; G.J. H. Rijnders, H. Regnault, D.H.A. Blank, University of Twente, Department of Applied Physics, Enschede, THE NETHERLANDS; W. Pan, University of Rochester, Department of Electrical Engineering, Ann Arbor, MJ. 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 \(\text{SrRuO}_3\), \(\text{SrTiO}_3\), \(\text{SrRuO}_3\)/\(\text{SrTiO}_3\) 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 \(\text{SrRuO}_3\), \(\text{SrTiO}_3\), \(\text{SrRuO}_3\)/\(\text{SrTiO}_3\) epitaxial heterostructures on perfect \(\text{TiO}_2\) terminated \(001\) \(\text{SrTiO}_3\) substrates using pulsed laser deposition including in-situ high pressure RHEED. \(\text{SrRuO}_3\) is an ideal system to study the heteropitaxial growth mechanism of various perovskite thin films and to fabricate high quality multilayered devices. \(\text{SrRuO}_3\) is a negatively spin polarized ferromagnetic oxide with a lattice parameter of 3.84\AA, i.e., a lattice mismatch with \(001\) \(\text{SrTiO}_3\) substrates of 0.64%. Our RHEED intensity data and AFM images suggest that the \(\text{SrRuO}_3\) films on \(\text{SrTiO}_3\) 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 \(\text{SrRuO}_3\). 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 to the film. In contrast, the \(\text{SrTiO}_3\) barrier layer on \(\text{SrRuO}_3\) bottom electrode grows in the two-dimensional layer-by-layer mode. Transmission electron microscopy images of a cross-sectional \(\text{SrTiO}_3\) 6 unit cell \(\text{SrRuO}_3\)/\(\text{SrTiO}_3\) heterostructure show that the trilayer is single domain with atomically sharp interfaces between \(\text{SrRuO}_3\) and \(\text{SrTiO}_3\). Such an atomic scale control of the interfaces and barrier layers in ferromagnetic oxide [FM-1FM] trilayer junctions allows for quantitative studies of spin-polarized transport across the ferromagnetic oxide [FM-1FM] trilayer junction interface, which will also be discussed.

9:00 AM AA6.2
KINETIC FLONTE CARLO STUDIES OF OXIDE MOCVD

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A simple model of metallic organic 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 (homoeopitaxial, 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 require accurate kinetic parameters. Several approaches for obtaining these parameters will be discussed.

**10:30 AM AA6.5**

**THE INTERRELATIONSHIP BETWEEN INTERFACES AND THE STRUCTURAL CUSTOMIZATION ON THE NANOSECOND SCALE OF OXIDE FILMS, SUPERLATTICES, AND NEW COMPOUNDS**


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 superstructures. Structural and chemical characterization of interfaces will be presented including high-resolution TEM, AFM, STM, TOF-SIMS, 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-mismatched intergrowths, and dislocations with a screw component. The latter result in a spiral growth mode and undesired surface roughness that the interface 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$_2$Ta$_2$O$_9$, Sr$_2$Nb$_2$O$_9$, Bi$_2$Ti$_3$O$_9$, and Bi$_4$(Pb, Sr)$_{10}$Ti$_{15}$O$_{39}$], Ruddlesden-Popper phases [Sr$_n$Ti$_{2n-1}$O$_{3n+1}$ and Sr$_4$Ru$_2$O$_{11}$], and metastable superstructures [PtO$_2$/SrTiO$_3$ and Bi$_2$O$_3$/SrTiO$_3$] grown by reactive molecular beam epitaxy (MBE) and pulsed laser deposition (PLD).

**11:00 AM AA6.6**

**EPITAXIAL GROWTH OF ZnO AND MgZnO ON Si**

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$_3$ (STO), CeO$_2$, and MgO. The morphology and structural properties of ZnO/MgZnO films have been investigated in detail, including X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM) and Rutherford backscattering spectroscopy (RBS). Optical properties have been studied by photoluminescence (PL) at room temperature and ultraviolet (UV) and visible transmission microscopy. The growth conditions have 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 detail. By choosing appropriate buffer material and optimizing the PLD conditions, high quality ZnO/MgZnO epilayers have been obtained. Visible ZnO and MgZnO UV detectors with high gain and low cutoff wavelength have been successfully fabricated on Si.

**11:15 AM AA6.7**

**THE INTEGRATION OF TANTALUM OXIDE WITH TITANATE NITRIDE, TANTALUM NITRIDE, AND RUTHENIUM ELECTRODES FOR METAL-IN-SULFUR METAL CAPACITOR APPLICATIONS**


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 determine the extent of oxide oxidation at the tantalum oxide/titanium nitride and tantalum oxide/titanium nitride interfaces. Variations in the oxide/metal ratio for reactively sputtered tantalum nitride electrodes are correlated to the electrical performance of the capacitors and interpreted in terms of relative D-nucleation and growth stepflow growth within the first few unit layers. This transition depends on the miscut angle and termination of the substrate surface.

Additionally, this change in growth mode during the deposition of other perovskites will be discussed.
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 STRUCUTRE AT EPITAXIAL STO/S HETEROJUNCTIONS. S.A. Chambery, Y. Liang, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, WA; Z. Yu, R. Droopad, J. Ramdani, K. Elejabarri, Environmental Molecular 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 interface have not been determined experimentally, and the relationship between band offset and interface structure is completely unknown. We have used photocurrent 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 the interface structure. This structure is being modified by heating specimens consisting of thin (≈20nm) epitaxial STO films on Si(001) in an oxygen plasma within the MBE chamber, but after growth. Activated oxygen diffusion 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 CRYSTAL-LINE OXIDES EPITAXY ON SILICON. Shapmu Gan, Dan E. Mcready, Daniel J. Gaspar, Thevin Thevuthisaran, and Yong Liang, Pacific Northwest National Laboratory, Richland, WA.

Crystaline oxides such as SrTiO$_3$ (STO) are important alternative gate oxides to SiO$_2$ 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$_2$. The key to achieve this is produce an intrinsic interface layer that stabilizes in oxygen environment at high temperatures. Within the study 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 spectroscopy (LEED). It was found that the strained-layered covered surfaces exhibit a series of reconstructions such as (1x2), (3x2) and (1x1) structure, the surface termination 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 crystals, 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 transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and Rutherford backscattering spectroscopy (RBS) to characterize the interfacial chemistry and film structure. By combining these techniques, we correlated the interface structure with film properties, which allowed us to identify suitable interfacial templates for optimized growth.

SESSION AA7: STRUCTURE-PROPERTY RELATIONSHIPS

Chair: Kurt E. Nickolas and Gregory S. Rohrer
Wednesday, November 29, 2000
Commonwealth (Sheraton)

1:30 PM **AA7.1**
COMPUTER SIMULATION AND EXPERIMENTAL STUDY OF ADSORPTION ON SILICATE GLASS SURFACES. Carlo G. Pasquariello, Victor A. Bakken, Tamara Bokoven and William A. Steele, Department of Materials Science, The Pennsylvania State University, University Park, PA.

We have used the grand canonical Monte Carlo method to simulate isotherms of adsorption for Ar, CO$_2$, and H$_2$O on model surfaces of silicon 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 exerted a significant effect on the simulated adsorption isotherms for the dipolar molecules CO$_2$ and H$_2$O. It was found that coordination defects and distorted silica tetrahedral, defined by their dipole and quadrupole moments, give rise to hydrophobic adsorption sites on the surface. Upon annealing with an optimum cooling rate, these defects can be eliminated and a hydrophilic silica surface can be obtained. The experimentally determined isotherms were required on the basis of these simulations. The best fits 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 heterogeneity adsorption for silicate 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 presence of the polar adsorbates. This behavior is due to local variations in the surface electronic field. The strongest adsorption sites are associated with non-bridging oxygens and tetra-coordinated oxygens. These results are of interest for relating nanoscale characteristics of glass surfaces to microscopic 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 Menckhaus, Karl Heinz Hirsch, Ellen Ivens-Tulfa, Universität Kiel, Kiel [TH], Institut für Werkstoffe der Elektrotechnik, GERMANY; A. Cengiz Polat, Harry L. Tuller, MIT, Dept. of Materials Science and Engineering, Cambridge, MA.

The electrical and kinetic properties of ceramic and single crystal substrates of heavily donor-doped strontium titanate are studied in a function of oxygen partial pressure, temperature and donor content. Porous cerams, 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. Fe, Univ of Michigan, Dept of MSE, 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 metals were deposited on substrate 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 were controlled by the lattice mismatch across the substrate-film interface. The amount of the gas 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 mobility increased with increasing acceptor dopant ionic radius. A model correlating the microstructure to the electrical properties was developed.

2:30 PM **AA7.4**

Heterogeneous photocatalytic 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 photocatalytic reactions on titania, we have determined the relative photochemical reactivity and surface energy of strontium titanate and barium titanate as a function of orientation and surface. The films 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 determined from backscattered electron diffraction patterns recorded in a scanning electron microscope. To make a local measurement of the photocatalytic 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 the 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 the relative rate 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 structure on the relative rate of the photochemical reaction will be described.

3:30 PM AAT.5

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, WO3, is a very interesting semiconductor oxide in the field of gas-sensing applications. We have produced nanocrystalline WO3 films by advanced reactive gas deposition. Synthetic air was used instead of an inert gas for both the cooling and reaction purposes. Before introduction of synthetic air into the evaporation chamber, the chambers were evacuated to 3x10⁻⁶ Torr. The starting material, which was a tungsten pellet, was installed in the evaporation chamber where the heating and evaporation of the tungsten occurs. The tungsten oxides formed on the surface of the tungsten. 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 WO3 with a tetragonal crystal structure and an average grain size of around 6 nm. The gas-sensing properties of the films were studied. After an initial activation, the nanocrystalline WO3 films showed unique and excellent sensing properties at room temperature upon exposure to low concentrations of H2S in air. The optimum thickness of the WO3 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 WO3 films were insensitive to room temperature to many other tested gases, such as CO, NO, NO2, SO2 and H2.

3:45 PM AAT.7
NANOPOROUS CERIA FILMS PREPARED FROM COLLOIDAL SUSPENSION. Vladimir Petrovsky, Brian Gorman, Harlan U. Anderson, Tatiana Petrovsky, University Missouri-Rolla, FMARC, 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 made by spin coating a 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 range 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 of the sintering process. The film deposit thickness 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 growth 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 AAT.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 MSE, Ann Arbor, MI.

The sensitivity of semiconductor titanium oxide (SnO2) to reducing gases is determined by the electrical conductivity change in the material. This change in conductivity strongly depends on the layer of electronic 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 SnO2 thick films varying in thickness from 15 nm to 100 nm were deposited on sapphire substrates with different crystallographic orientations by pulsed laser deposition. Films grown on the (1012) sapphire (c-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 increased 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 AAT.8
DESIGN AND MODELING OF A SELECTIVE COMPOSITE GAS SENSOR. Brian Climer, Nancy Savage, Bruce Patton, Prabir Dutta, Center for Industrial Sensors and Measurements, The Ohio State University, Columbus, OH.

Mixtures of amine and halide TiO2 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 McLean's General Effective Medium (GEM) equation. We find that the sensor response (n-type or p-type) to 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/CH4 amine/halide 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 AAT.9
GRAIN BOUNDARY EFFECTS ON THERMAL CONDUCTIVITY IN YTTRIA-STABILIZED ZIRCONIA BY MOLECULAR DYNAMICS SIMULATION. PK 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-defined regions, we directly impose a temperature gradient in a manner similar to experiment. The energy added 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.


4:45 PM AAT.10

TiO2 thin films are attractive for numerous microelectronic applications such as metal-oxide-semiconductor devices, optical waveguides, electrochromic display devices, and surface acoustic wave (SAW) devices. TiO2 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 TiO2 thin films are required. TiO2 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 TiO2 thick films fabricated by atomic layer solution deposition (ALD) technique. The doped TiO2 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 \textit{MFM} and \textit{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$_2$O$_5$ thin films. Thin films with 0.9 Ta$_2$O$_5$:0.1 Al$_2$O$_3$ composition exhibited improved dielectric and insulating properties compared to Ta$_2$O$_5$ 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$_2$O$_5$ thin films as capacitor dielectric layer for DRAM and integrated electronic applications.