SYMPOSIUM KK
Solid-Solid Interfaces from Observation to Modeling

November 28 - December 1, 2005

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* Invited paper
8:30 AM *KK1.1
Abstract Withdrawn

9:00 AM KK1.2
Liquid Metal Embrittlement of Grain Boundaries in Metallic Alloys: A systematic simulation investigation. Ho-Sook Nam1, Mikhail I. Mendelev2 and David J. Srolovitz1,1Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; 2Materials and Engineering Physics, Ames Laboratory, Ames, Iowa.

There are many examples in which a liquid metal in contact with a polycrystalline solid develops a deep liquid groove at the intersections of the grain boundaries and the solid-liquid interface. In some cases such as Al-Ga, Cu-Bi and Ni-Bi, the liquid film quickly penetrates deep into the solid along the grain boundary and leads to brittle intergranular fracture under the influence of even modest stresses. We have performed a series of molecular dynamical simulations using a set of binary embedded atom method potentials that were tuned to reproduce phase diagrams characteristic of systems exhibiting liquid metal embrittlement. We report on a series of molecular dynamics simulations of how liquid films propagate into grain boundaries at the atomic-scale level as a function of the thermodynamic properties of the liquid species such as solubility, diffusivity, and melting point. These results are compared with general trends gleaned from a series of experimental studies in the literature.

9:15 AM *KK1.3
Glass in Crystalline Ceramics. C. Barry Carter, Shelley R. Gilliss and Jessica Riesterer; Ch. E. & Materials Science, U of Minnesota, Minneapolis, Minnesota.

The behavior of glass in, and on, ceramic materials has been studied for many years, but more than 25 years since it was first shown that thin amorphous films are often present in ceramic materials at grain boundaries and at triple junctions. Experimental techniques are now becoming available which can provide new understanding of the structure, chemistry and bonding in these glassy layers. These techniques will be reviewed in this talk. The main emphasis of the paper will be the study of movement of material in the glass, how this glass changes in composition during processing and how this change affects processing. The talk will be illustrated by observations on individual glass droplets on the surface and moving grain boundaries in polycrystalline materials that have been studied by a combination of AFM, EBSD and FIB. In the past, research has been concentrated on the movement of the crystalline material, i.e., the grain boundaries. New observations of the Marangoni effect, and the possibility that Benard convection can be driven by concentration effects caused by changes in temperature, i.e., heating and cooling during processing, emphasizes that movement of matter within the glass must be understood for the basic science of LFG to be understood.

10:15 AM *KK1.4

The spreading of high temperature liquids (moltens metals and oxides) plays a key role in many modern technologies such as brazing, soldering or thin film fabrication. These technologies are crucial in fields as diverse as the synthesis of new structural materials, microelectronics, optoelectronics and many others. However, and despite the obvious parallel with the room temperature spreading of organic liquids, high-temperature spreading has defied many attempts of description or generalization. This is in part due to the fact that wetting at high temperatures is usually accompanied by interdiffusion and chemical reactions and the forces that drive reactive spreading and the mechanisms that control its kinetics are still very poorly understood. The challenge is to link macroscopic measurements such as the dynamic contact angle or the speed of the moving liquid front to phenomena occurring at the microscopic and even atomic level at the vicinity of the triple solid-liquid-vapor junction. In this work, high speed photography is used to analyze the spontaneous spreading on small drops and capillary rise around metallic fibers. In non-reactive systems, the results are consistent with spreading controlled by the friction of the triple junction rather than by viscous dissipation in the liquid. A molecular-kinetics approach is used to analyze the atomic dynamics at the triple line and the physical implications of the relevant parameters (wetting activation energies, atomic frequencies and distance between adsorption sites on the solid surface) are discussed. The analysis of reactive systems reveals many situations in which, opposite to what is usually believed, interfacial chemical reactions do not enhance spreading. The results are used to speculate on a theory that divides reactive spreading into its constitutive steps: fluid flow, adsorption, ridging and compound formation. The goal is to identify which steps drives reactive spreading and controls its kinetics. Finally, evidence for the formation of Marangoni driven films in high-temperature systems is also presented. The final objective is to provide results and analysis that will guide the formulation of a unifying theory of wetting dynamics. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC05-76SF00098.

10:45 AM KK1.5
Crystallization of Calcium Aluminate Phases: Bulk vs Interface. Arzu Altay1, Mehmet Ali Gulgun2 and C. Barry Carter1; 1Chemical Eng. & Mat. Sci., University of Minnesota, Minneapolis, Minnesota; 2Material Sci. and Eng., Sabanci University, Istanbul, Turkey.

Crystallization behavior of CaAl2O4 (calcium dihydroxide, CA2) and CaAl22O29 (calcium hexa-aluminate, CA6) were studied using two different experimental approaches. In the first route, polymeric precursors for the CA2 and CA6 powders were prepared by mixing stoichiometric proportions of the nitrate salts into a 5 wt% aqueous solution of poly(vinyl alcohol) (PVA). The precursor-to-ceramic-powder-conversion and phase transitions were studied by differential thermal and thermogravimetric analysis (DTA/TGA), powder X-ray diffractometry (XRD) and transmission electron microscopy (TEM). Simultaneous DT/TG analysis showed the amorphous powders with CA6 stoichiometry first crystallized into γ-Al2O3 at 930°C and then transformed into CA6 at 1175°C. For the second approach amorphous thin films of CA2 and CA6 were deposited on sapphire substrates by pulsed laser deposition (PLD) in an oxygen ambient atmosphere. All reaction couples were heat treated in air either at 1300°C or 1400°C for various times after deposition. Atomic force microscopy (AFM) was used to monitor the microstructural changes of the films during crystallization. Interfaces between the films and the substrates were examined by TEM on the cross-sectional samples prepared by focused ion-beam (FIB). After the heat treatments, while CA6 films wetted the substrate surface, CA2 films remained dewetted sapphire. No reaction layer was observed between the wetting CA6 films and the substrate. However an interfacial reaction layer was observed between the dewetted CA2 droplets and the substrate. This reaction layer at the interface was identified as γ-Al2O3 from the fast Fourier transform (FFT) of the high-resolution TEM images. Phase transition paths observed in two experimental approaches are discussed and compared in relation to the spatially-confined1 crystallization behavior of the various calcium aluminate phases and the equilibrium-phase diagram of the CaO-Al2O3 system.

11:00 AM KK1.6
Interfacial Adsorption of Rare Earth Elements in Silicon Nitride Ceramics. Paul Becher1, Gayle Painter1, Naoya Shibata2, Klaus van Bentheim1, Frank Averill3 and Stephen Pennycott1; 1Oak Ridge National Lab, Oak Ridge, Tennessee; 2University of Tokyo, Tokyo, Japan; 3University of Tennessee, Knoxville, Tennessee.

Rare earth (RE), as well as other elements, have a strong effect on anisotropic grain growth in silicon nitride ceramics, which contain amorphous intergranular films. Scanning transmission electron microscopy (STEM) observations have shown that the RE elements attach to the prismatic planes of silicon nitride grains in an ordered manner. Subnanometer details confirm first principles calculations that reveal differences in both the segregation and adsorption strengths of individual RE elements at the grain surfaces. Two-dimensional ordering of the RE adsorption on the prismatic plane is predicted and supported by STEM observations, which also reveal order extending into the multi-grain glass pocket. Preliminary results obtained by a new 3D imaging technique and electron energy-loss spectroscopy will be presented to support the analysis of the atomic and electronic structure of the amorphous/crystalline interfaces.

11:15 AM KK1.7
Atomic-scale mechanism of dopant-controlled nonlinear current-voltage characteristics in ZnO grain boundary. Yukiko Sato1, James P. Buban2,3,4, Ken-ya Yao4, Masayuki Matsumot1, Naoya Shibata1,5, Fumiyasu Oba3, Masatada Yodogawa1, Takahisa Yamamoto1 and Yuichi Ikshura1; 1Department of Advanced Materials Science, The University of Tokyo, Tokyo, Japan; 2Institute of Engineering Innovation, The University of Tokyo, Tokyo, Japan; 3Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 4Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan.

ZnO polycrystals are widely utilized as surge protecting devices
varicose) because of their highly nonlinear current-voltage (I-V) characteristics. It is recognized that the nonlinear I-V characteristics should be a consequence (DBS) forming boundary

1. Double Schottky barriers are expected to be formed when acceptor-like electronic levels are introduced at the boundaries. However, the formation mechanism of the acceptor-like electronic levels is not yet understood. We have performed a detailed investigation of ZnO single grain boundaries by combining experimental and theoretical techniques [3]. Undoped and Pr-doped ZnO bicrystals were fabricated to exhibit the same misorientation angle, corresponding to a misorientation angle of 7°. Characteristic and atomic structure of the boundaries were investigated by DC-four probe method and high-resolution electron microscopy, respectively. Atomic and electronic structures of the boundaries were also calculated by first-principles methods. The results obtained for the undoped ZnO case revealed that the boundary is composed of two types of structural units, where the first type has under-coordinated (threefold) sites and the second type has over-coordinated (fivefold) sites, in contrast to the fourfold coordinated ZnO. These results suggest that such local miscoordinated atomic sites should not exhibit deep unoccupied states in the band gap of ZnO, suggesting that the DSB is not formed in the undoped boundary. Correspondingly, the measured I-V characteristic of the boundary is linear, which is consistent with the above results. On the other hand, the Pr-doped boundary showed apparent non-linear I-V characteristics. The Pr-doped boundary was found to have a single type of structural unit containing over-coordinated sites, which is similar to the second type of units found in the undoped case. Z-contrast STEM (scanning transmission electron microscopy) imaging revealed that the Pr atoms specifically segregate to the over-coordinated Zn sites. EELS (electron energy loss spectroscopy) showed that the oxide state of Pr dopant is likely to be trivalent, suggesting that the Pr itself should not form acceptor-like levels at the grain boundary. However, the Pr dopant was found to introduce atomic vacancies around the grain-boundary core, which is considered to be the origin of acceptor-like electronic levels. Thus, the changes in vacancy formation energy may be a key factor for the formation of the DBSs in ZnO grain boundaries. [1] G. E. Pike et al., J. Appl. Phys. 50, 3414 (1979). [2] Y. Sato et al., Appl. Phys. Lett. 84, 5311 (2004). [3] Y. Sato et al., J. Mater. Sci. in press.

11:45 AM KK1.9 Direct Observation of Cooperative Doping Mechanisms in Grain Boundaries in Ca-doped YBa$_2$Cu$_3$O$_{7-\delta}$

Robert Friedrich Kilic, 1 James P. Buban, 1 Mario Varela, 2 Alberto Franceschetti, 2-3 Christian Joos, 4 Yimei Zhu, 5 Nigel Browning, 5 Sokrates Pantelides, 2 3 and Stephen Pennycook, 2 1 Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York; 2 Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 3 Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; 4 Institute of Engineering Innovation, The University of Tokyo, Tokyo, Japan; 5 Department of Chemical Engineering and Materials Science, University of California-Davis, Davis, California; 4 Institute fuer Materialphysik, University of Goettingen, Goettingen, Germany.

Atomic-column resolved electron energy-loss spectroscopy (EELS) was used to study the effects of Ca-doping on the local atomic and electronic structure of tilt grain boundaries in YBa$_2$Cu$_3$O$_{7-\delta}$. Grain boundary doping, in particular by Ca, has been shown to increase the grain boundary critical current density, and it has been previously suggested that Ca$^{2+}$ substitutes for Y$^{3+}$ in the grain boundary to provide additional holes. By using atomic resolution Z-contrast imaging in a scanning transmission electron microscope (STEM) in conjunction with EELS and first-principles calculations, we will show that in the highly strained regions of the grain boundary plane, Ca segregates to Cu and Ba sites depending on the sign of the strain. Thus, Ca doping at the grain boundary does not provide holes directly. However, due to the resulting strain relief, the oxygen deficiency in the vicinity of the grain boundary is reduced and thus the hole concentration increases. The results demonstrate that to improve grain boundary $J_c$, ionic size may be more important than the electronic nature of the impurity.

SESSION KK2: Grain Boundary Structure

Chairs: Doug Medlin and Donald Siegel
Monday Afternoon, November 28, 2005
Fairfax A (Sheraton)

1:30 PM *KK2.1 Direct and Common Features of Grain Boundaries in Iridium when Compared with Other FCC Metals. Marc J. Cawkell, 1 Hyoun Seop Kim, 1,2 and Vaclav Vitek, 1 1 Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; 2 Department of Metallurgical Engineering, Chungnam National University, Yuseong, Daejeon, 305-764, South Korea.

While iridium is an excellent material for use in aggressive environments due to its resistance to corrosion, it can fail by both intergranular fracture and transgranular cleavage at temperatures up to 500 degrees C. Moreover, this brittle fracture is usually preceded by extensive plastic deformation. Another major factor is that the FCC metal, by $\{110\}$ dislocations gliding on $\{111\}$ planes. Such brittle fracture does not occur in any other FCC metal and it is likely hidden in the atomic structures and properties of dislocations and grain boundaries. In order to investigate atomic structures of such extended defects we have developed Bond-Order Potential for iridium that represents correctly angularly dependent bonding arising from the unfilled d band. In this paper we concentrate on grain boundaries, in particular their atomic structures, propensity to fracture and sliding. The atomistic calculations of boundary structures and properties are carried out using the Bond-Order Potential for iridium and, in parallel, the same boundaries are studied using the central-force model-body Finnis-Sinclair type potential for copper. The latter calculations represent a generic study of grain boundaries in FCC materials without any directional bonding. Comparison of the results obtained using the Bond-Order Potential with those attained using central-force potentials allows to identify physical features that are common to all FCC metals and those that are specific to the FCC metal with directional bonding, specifically iridium. In a separate study we carried out atomistic studies of dislocations in iridium and established on the basis of these results reasons for transgranular cleavage in highly deformed iridium. The goal of this study is to ascertain whether it is the same dislocation mechanism that is responsible for intergranular fracture or whether some special features of grain boundaries in iridium, such as directional bonding, are responsible for its propensity to intergranular fracture. This research was supported by the DOE BES grant. No. DE-P002-98ER45702 (MJC, VV).

2:00 PM KK2.2 Scanning force microscopy study of grain boundary grooving in molybdenum bicrystals. Eggen Rabkin, 1 Angelina Gabelev, 1 Leonid Klinger, 1 Valery N. Semenov 2 and Sergei I. Bozhko;
High temperature annealing of Mo bicrystals resulted in the grain boundary grooves with the blunted roots, whereas the electron backscattering diffraction measurements indicated that the grain boundary is still in the vicinity of the groove root. This apparent contradiction was resolved by noting that the minor grain boundary migration during annealing can lead to the blunting of initially sharp groove root, while the high surface anisotropy prevents the nucleation of a new sharp root at the flat facet in the vicinity of final grain boundary position. As a result, an apparently blunt grain boundary groove is formed. At the locations where the system managed to overcome the nucleation barrier a characteristic channel-like groove morphology was observed, with the blunted roots being adjacent to each other. The quantitative model of simultaneous grain boundary grooving and migration was developed. The results of calculations were in excellent agreement with experimental data on topography, indicating that it was demonstrated that disregarding of surface anisotropy results in severe underestimation of the grain boundary energies.

2:15 PM **KK2.3**

**Length-Scale of Correlations in Grain Boundary Networks.** Megan Frary and Christopher A. Schuh; Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Statistical descriptions of grain boundary networks tend to focus upon the connectivity among “special” grain boundary types, such as low-angle or coincidence boundaries. Recent results from experiments, computer simulations, and analytical models have shown that the distribution of such special boundaries is nonrandom at the nearest-neighbor level, but the discussion has not yet extended to the study of longer-range correlations. In the present work, we explore the connectivity among special grain boundaries at the next order of magnitude, and demonstrate that the boundary network is characterized by a network of nanometer-sized voids.

**3:30 PM **KK2.4**

**Finite size effects on grain boundary structures and interactions with dislocations.** Emmanuelle A Marguir, Douglas L. Medlin and Francois Leonart; Materials Physics, Sandia National Laboratory, Livermore, California.

The emergence of nanocrystalline materials has raised the issue of the size effects on grain boundary structures, which by deviating from their ideal structures in infinitely long bicrystals may impact the deformation mechanisms operating in nano-materials. Here, we demonstrate that both the shape of the γ-surface (i.e., the variation in b-terminal translation of a grain boundary), and the spatial distribution of grain boundary junctions play an important role in the relaxation of grain boundaries of nanometer length scale. Specifically, HREM observations on Au thin films have allowed the systematic study of size effects on the deformation of grain boundary junctions. Our results indicate that the detailed understanding of the [112] grain boundary now allows for the study of grain boundary interactions with dislocations, an essential aspect of material deformation. Particularly, we focus on the structural relaxation of the <111> dislocation at symmetric [111] and [112] boundaries, and find extended stacking faults bridging two [111]/[112] grain boundary junctions. We address the forces and interactions that drive the emission of extended defect structures from grain boundaries. Indeed, this issue has become increasingly important in nanostructured materials for which the distances between interfaces are sufficiently small that individual interfaces cannot be isolated in isolation. Of broader significance, many simulations and experiments in the literature have indicated that the emission of extended defects plays a role in the deformation of nanocrystalline materials. The detailed connection of such emission processes to the Σ3 and Σ6 dislocation structures is still a matter of debate.

**The specific mode by which strain is accommodated at a grain boundary depends ultimately on the defects that are amenable at the interface and structure and topology of those defects is, therefore, vital to connecting atomic and mesoscale descriptions of grain boundary behavior. In this presentation we discuss the structure and function of interfacial disconnections (i.e. line defects possessing both Burgers and dislocation character) at a 90 degree twist boundary in gold. This grain misorientation is interesting because while it aligms several pairs of low index planes and directions, the ratios of periodic lengths in all the parallel directions (with the exception of the shared 90 deg) are irrational.** We have combined high resolution transmission electron microscopy (HRTEM) observations with atomistic simulations to analyze defects separating short (4-6 nm) [111]/[112] terraces along the boundary. By measuring the dislocation content of the disconnections, we show how the defects accommodate the 5.7 % misfit in the directions parallel to the interface and thereby enable coherence across the [111]/[112] terraces. This structural relaxation is markedly different from that at [111]/[110] grain boundaries in this same material. Our previous observations have found an incoherent structure with no grain localization. The comparison between these two cases points to the very important coupling between grain boundary inclination and the particular mode by which incompatibilities between adjacent grains are accommodated.

4:15 PM **KK2.6**

**Atomatic structure of asymmetrical grain boundaries in FCC metals.** Juan Anthony Brown¹, Yuri Mishin² and Douglas L. Medlin³; ¹School of Computational Sciences, George Mason University, Fairfax, Virginia; ²Materials Physics Dept., Sandia National Lab, Livermore, California.

Most of the previous atomistic studies of grain boundaries (GBs) have been focused on symmetrical geometries due to their relative simplicity. However, real polycrystals are dominated by asymmetrical crystallographic orientations. We present results of systematic atomistic simulation studies of asymmetrical <110> tilt GBs in copper with the Sigma11 misorientation between the grains over the entire range of inclination angles. The methodology includes molecular statics, molecular dynamics and the embedded-atom method. The energetics and structural trends of the GBs have been studied in great detail and compared with experimental observations. Highly asymmetrical GBs are observed to develop regular arrays of intrinsic stacking faults (ISFs) extending into one of the grains. Such boundaries can be considered as disassociated into a low-angle GB formed by the Shockley partials and a new high angle grain boundary which is no longer Sigma11. The material between the two boundaries represents an FCC-based long-period structure which is more general than the 9R structure found at FCC GBs in previous experimental and simulation studies. GBs with relatively small inclinations with respect to a symmetric one develop facetted structures, at least one of the facets being the symmetrical boundary. This faceting behavior has been interpreted in terms of thermodynamic theories of faceting transitions with the atomicistic input for the Σ6 angles. The effect of precipitate stresses on the GB structures has also been examined. Preliminary results of similar atomistic simulations for several asymmetric <110> 90 deg tilt GBs in Au will also be presented, along with the effect of precipitate stresses on the GB structure. Both Cu and Au simulation results are compared with HRTEM observations of the Sigma11 and 90 deg <110> boundaries in thin films. This combination of modeling and experiment leads to a better understanding of the structure of asymmetrical GBs and mechanisms of their impact on mechanical behavior of metals.

4:30 PM **KK2.7**

**Evolution of Faceted Grain-boundary Grooves by Surface Diffusion.** Ashwin Ramasubramaniam¹ and Vivek B. Shenoy²; ¹California Institute of Technology, Pasadena, California; ²Division of Engineering, Brown University, Providence, Rhode Island.

Thermal grooving at a grain boundary is well-understood when the surface of the groove is entirely rough (finite surface stiffness) at its root. In this situation, the grain-boundary energy is uniquely related to the surface energy of the groove at its root via the dihedral angle that is obtained by enforcing equilibrium (balance of capillary forces) at the triple-junction. However, when a groove-root is faceted, the non-analyticity of the surface energy at the facet orientation leads to anisotropy in both the enforcement of equilibrium at the groove-root and the relation between the facet energy and the grain-boundary energy. In this work, we show that equilibrium at the groove-root requires careful consideration of the torque, which can adjust itself to maintain the fixed facet orientation thereby achieving a net balance of capillary forces. This is in stark contrast to the case of a rough root where the grain-boundary energy is in one-to-one correspondence with the observed dihedral angle. Using this insight, we show via a simple graphical method that
the grain-boundary energy and surface energy function are entirely adequate to determine if a groove-root is faceted or rough thereby obviating the need for any ad hoc specification of the dihedral angle as a boundary condition. The evolution of thermal grooves is studied using a variational approach that can handle infinite surface stiffnesses and naturally allow for facet formation. The mobility of the triple-junction, which is known to lead to deviations from Mullins’ 1/4 scaling law, is also explicitly included in the model. A key observation is that low junction-mobilities can lead to the formation of kinetic groove-shapes – in particular, groove-roots that are anticipated to be rough facets. Such considerations alone are seen instead to attain nearby facet orientations at low junction mobilities. Such kinetically limited facets at groove-roots can never be obtained if the equilibrium angle is prescribed as a boundary condition for the evolution equation as is often done.

4:45 PM KK2.8
Combining Coarse-grained and Geometrical Approaches to Study Grain Faceting. Denis Boyer and David Ronen; Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Mexico City, D.F., Mexico.

We implement coarse-grained nonlinear models, introduced in an other context for describing pattern formation, to investigate grain boundary faceting in solids. Solutions of time dependent partial differential equations for a local order parameter show that tilt grain boundaries feel an intrinsic periodic pinning potential and tend to align along minimal lines. The approach is found to be consistent with the results of a higher dimensional crystallography theory inspired from the framework of quasicrystals. The geometrical theory predicts similar grain boundaries and the pinning sites correspond to Bollmann’s O-lattice points. We find that symmetric high-angle planar tilt grain boundaries can destabilize to form zig-zag facets. A similar facet formation process is observed for asymmetric interfaces. At least two different facets can emerge: facets can either remain finite length on the nanometer scale, or grow as a power law of time (or possibly slower at very large times). Our predictions agree well with experimental HREM observations of grain boundaries in various metals and ceramics.

SESSION K3: Grain Boundary Migration and Diffusion
Chair: Emmanuelmeine Marquis
Tuesday Morning, November 29, 2005
Fairfax A (Sheraton)
8:30 AM *KK3.1

Except in a very few special cases, the atomistic mechanisms by which grain boundaries migrate remain unknown. In this work, the atomistic migration mechanism for grain boundaries in nickel has been studied using molecular dynamics simulation. An atomic jump path has been identified in our simulation. Three different types of displacements are classified. Analysis suggests that the most important of these corresponds to a cooperative translation of a row of atoms parallel to the tilt axis. This event triggers the motion of the boundary perpendicular to the boundary plane. The excess volume in the grain boundary plays an important role in the different types of motions. The transfer of excess volume starts the cooperative motion and the excess volume in grain boundary determines the motion perpendicular to the boundary. Additional simulations show that changes to the system that interfere with the cooperative motion significantly slow grain boundary migration.

9:00 AM KK3.2
Growth and Stability of Grain Boundary Triple Junctions in Copper, Shashank Shekhar and Alex King; School of Materials Engineering, Purdue University, West Lafayette, Indiana.

Grain boundaries and triple junctions are important structural elements of a polycrystal. In order to facilitate experimental studies on triple junctions, it is necessary to grow reproducible and consistent tricrystals with stable triple junctions. Herring’s equation has been applied to find a set of tricrystals that will give rise to stable triple junctions, and the conditions for such stable triple junctions was determined to be stable for grains oriented with a junction lying in the common [100] direction. Two tricrystals with misorientations close to this were obtained using directional solidification in Bridgman furnace. The orientations of the crystals and the misorientations between the grains were determined using Laue diffraction and confirmed by Electron Back Scattered Diffraction Pattern (EBSP) analysis. Small deviations from the target geometry were measured in one of the tricrystals, and slightly larger deviations in the other. Marked differences were observed in the structures of the triple junctions, and these are described and discussed in this presentation.

Acknowledgment: This work is supported by the US Department of Energy, under contract number DE-FG01-01ER45940.

9:15 AM KK3.3
Impact of Microstructure on Grain Boundary Diffusion in Polycrystals. Kwamina Bedu-Amisah1, Jeffrey M. Rickman2, Helen M. Chau3 and Martin F. Harmer4; 1Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania; 2Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania.

The impact of a complex microstructure on polycrystalline diffusion is investigated using both numerical and analytical techniques. A methodology is first validated for Fisher’s idealized model of diffusion in a prototypical, isolated grain boundary system and then applied to a Voronoi model of a microstructure resulting from homogeneous nucleation and growth. Diffusivity behavior is quantified by fitting uptake curves as a function of time for different ratios of grain boundary to lattice diffusivities. Such curves can be used to estimate an unknown grain boundary diffusivity given certain microstructural assumptions. In addition, approximate analytical equations describing diffusant uptake in polycrystalline microstructural models are developed and found to agree well with the numerical results. Finally, a connection between our results and those obtained via experiment is established.

10:00 AM *KK3.4
Coupling grain boundary motion to shear and grain rotation. J. F. Cahn1,2, K. L. Johnson1, A. Suzuki1, and J. E. Taylor1; 1School of Computational Sciences, George Mason University, Fairfax, Virginia; 2Materials Science and Engineering Lab., National Institute of Standards and Technology, Gaithersburg, Maryland; 3Courant Institute of Mathematical Sciences, New York University, New York, New York.

By molecular dynamics (MD) simulations over a wide temperature range, we have confirmed that a shear stress applied to high-angle planar tilt grain boundaries (GBs) causes them to move. Conversely, motion of such GBs results in a shear deformation in the region they traverse. We have identified the atomic mechanisms of this coupling of GB motion and shear, which leads to a set of two geometric relations, which differ in sign, between the shear and the tilt angle for <001> tilt GBs in fcc crystals. For each relation we have determined the shear stress needed to move the GB at low temperatures. The MD results confirm that these geometric relations holds accurately up to temperatures where GB sliding becomes a competing mechanism. The stress needed to move the GB at low temperature is an accurate predictor of which relationship holds, and of the tilt angle for which we find an abrupt change from one relation to the other with a change in the sign of the shear. These results suggest a re-interpretation of the role of GBs in various disparate materials phenomena, such as plastic deformation, superplasticity, recrystallization, grain growth and grain rotation.

10:30 AM *KK3.5
The transition from grain boundary sliding to grain boundary motion coupled to shear. J. W. Cahn3, Y. Mishin4 and A. Suzuki5; 3Materials Science and Engineering Lab., National Institute of Standards and Technology, Gaithersburg, Maryland; 4School of Computational Sciences, George Mason University, Fairfax, Virginia.

Grain boundary (GB) sliding is a well-documented phenomenon, which we found by molecular dynamics (MD) simulations to occur when shear stresses were applied to high-angle planar tilt GBs at high temperatures. We define GB sliding as relative tangential motion of the two grains which does not couple into the GB motion which we find at low temperature. There is a crossover temperature range in which we see in these simulations that sliding and coupling occur as individual stick-slip events. With decreasing temperature the peak stresses needed for these events increase at different rates. Individual coupled motion events become more frequent until there are no more sliding events. These simulations suggest mechanisms for both types of events and the reason for the transition.

11:00 AM KK3.6
The Effect of Strong Surface Energy Anisotropy on Migrating Grain-boundary Grooves. Donghong Min and Harris Wong; Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana.

Grain-boundary migration controls grain growth and is important in materials processing and synthesis. Two commonly used methods for measuring grain-boundary mobility are the “quarter-loop” and Sun-Bauer methods. In these methods, a grain boundary migrates and its tip position along a free surface is recorded to infer the mobility.
Properties in a Model Ni-Based Superalloy.
Chantal K. Sudbrak1, Kevin E. Eoon1, Ronald D. Nobe2 and David N. Seidman2; Materials Science and Engineering, Northwestern University, Evanston, Illinois; 2NASA Glenn Research Center, Euclid, Ohio.

The γ/γ′ interface in Ni-based superalloys is a solid/solid interface of both technological and fundamental importance. Atom-probe tomography, with its atomic-scale spatial resolution, is employed to characterize in detail this complex interface with sub-nanometer compositional profiles and analyze during γ′ nucleation, growth, and coarsening for an 873 K isothermally decomposing Ni-Al-Cr superalloy. Observed chemical transients in the matrix adjacent to the interface are consistent with theoretical predictions for diffusion-limited growth. Evaluation with a multicomponent coarsening model, utilizing CALPHAD descriptions of nondilute thermodynamics, allows the interfacial energy to be measured, as well as establishing that an observed Al enhancement in the γ′ precipitates, which decays, results from capillarity. Measured equilibrium interfacial widths, which are component dependent, are discussed in light of recent lattice kinetic Monte Carlo simulations. This research is supported by the National Science Foundation, grant DMR-0241928.

2:00 PM **KK4.2**
Impact of Vacancy Diffusion on the Early Decomposition Stages of Alloys and the Role of Heterophase Interfaces on Coarsening. Zugang Mao1, Chantal K. Sudbrak1, Kevin E. Yoon1, Georges Martin2,3 and David N. Seidman1; 1Materials Science and Engineering, Northwestern University, Evanston, Illinois; 2CEA, Cabinet du Haut Commissaire, Paris, France.

The kinetic pathway for nucleation and growth is commonly thought to be dictated by the initial supersaturation of solutes in the solid solution undergoing phase separation. We demonstrate that the details of the diffusion mechanism, in the solid solution affect deeply the early stage morphologies of precipitates. Our argument is based on a combined use of atomic-scale observations, with atom-probe tomography (APT) and lattice kinetic Monte Carlo simulation of a Ni(Al,Cr) alloy. By an optimized choice of thermodynamic and kinetic parameters we first reproduce the experimental APT observations. We then modify only the long-range vacancy-solute binding energy, without altering the thermodynamic driving force for phase separation, thereby demonstrating that the microstructural evolution changes from a coagulation to an evaporation-condensation coalescence mechanism. The changes can only be accounted for with nonzero values for the vacancy chemical potential and off-diagonal terms of the Onsager matrix, at variance with classical models. This research is supported by the National Science Foundation Division of Materials Research.

2:15 PM **KK4.3**
Multi-scale Mechanics and Physics of Thermal Sprayed Interfaces. Andrew Gomilstone and Sanjay Sampath; Materials Science and Engineering, Stony Brook University, Stony Brook, New York.

Thermal sprayed (TS) materials deposited by the molten impact and rapid quenching of particles exhibit a lamellar microstructure, characterized by a multitude of interfaces. Microscopically, such interfaces are discontinuities in material structure, or extremely thin regions of imperfect bonding. At the nano-scale, they reveal structural complexities strongly dependent on the material, TS process type (kinetic and thermal state) and conditions (parameters, environment). The details of bonding, non-planarity, separations (nano-meso) and/or interphases, have enormous implications for mechanical, thermal and electrical properties. In addition, these attributes exhibit strong anisotropy and size-dependence. In the TS literature, 'interfaces' are widely recognized as a critical and perhaps limiting aspect in design, but little effort has been made to explore beyond this initial description. From an application perspective, a quantitative understanding of TS 'inter-structure' and properties has thus become the next critical step in the development of coating models for design, performance prediction and the realization of prime reliance in performance of, e.g., thermal barrier coatings, compliant thermo-mechanical multilayers, and biomedical implants. From a scientific perspective, an opportunity exists for a systematic study of 'nano-lamellium' interfaces and their implication for thermal barrier realization. There is a rich literature on interfaces between similar and dissimilar materials addressing adhesion and transport phenomena in the context of surface chemistry and interfacial separation. At the NSF-MSEC Center for Thermal Spray Research (CTSR), we are employing this fundamental background and expanding it to the nontrivial complexities associated with TS interfaces, including local disorder, non-planarity and separations. In this talk, we will discuss expectations as well as the importance of interfaces to TS properties, characterization efforts aimed at identifying key topological and
chemical attributes, and experiments and modeling to extract interfacial properties from complex mesoscale geometries. In addition, we will describe our novel methods to design and fabricate; a key enabler will be the TS process itself which is now emerging as a flexible and predictable tool. Acknowledgement: Supported through NSF MRSEC award DMR 0080021.

3:30 PM KK4.4 First-Principles Study of Native Defects and Impurities in Rutile TiO₂. Jan He1, Michael M. Finnis2 and Susan B. Simon1; 1Department of Materials Science and Engineering, University of Florida, Gainesville, Florida; 2Atomic Simulation Centre, School of Mathematics and Physics, Queen’s University of Belfast, Belfast, United Kingdom.

We report density-functional theory calculations of the formation energy, electronic structure and structural relaxation of native defects and a variety of impurities in rutile TiO₂ in their neutral and charged states. The results are coupled with thermodynamic calculations to extend them to a variety of gas conditions and temperatures. The results show that the preferred native defects depend on the Fermi level, temperature, oxygen partial pressure and defect charge state. In particular, oxygen and titanium vacancies are found to be more stable when they are fully charged at room temperature, while the situation for interstitials is more complex. At room temperature oxygen vacancies are more stable than titanium interstitials over almost all the Fermi levels considered in the reduced state, but at temperatures greater than 1400 K the reverse is true. In the case of impurities, specific attention is focused on impurity configurations, and the strength of chemical bonding between the impurity and its neighbors. In addition, details of the electronic states of native defects and impurities are compared. This study is helpful for understanding impurity segregation at grain boundaries and interfaces of transition metal oxide materials. This study is supported by NSF under grant #DMR-0082794.

4:00 PM KK4.6 Growth and coarsening of precipitates and their dependence on interfacial and strain energy. Alexander Heinrich, Christian Klahe, Talaat Al-Kassab and Reiner Kirschheim; Institute for Material Physics, University of Goettingen, Goettingen, Germany.

The nucleation and growth of new phases has been studied in supersaturated metals and alloys by means of the tomographic atom probe (TAP). Besides the well known spherically shaped nuclei or cylindrically shaped particles have been found at certain temperatures and annealing times. The long axis of these non-spherical particles is directing in the soft (100) directions of the Cu-matrix. These findings are compared with published small angle neutron scattering (SANS) data. In addition, the nucleation, growth and coarsening of oxide particles is studied in internally oxidized Ag-Mg and Ag-Al alloys by using TEM and SANS. It will be shown that both growth and coarsening are strongly affected by the composition of the oxide/Ag-interface which could be revealed by SANS as well as by TAP. All these experimental findings are discussed qualitatively and quantitatively.

4:15 PM KK4.7 Atomistic Simulations on the Interface Bonding Between the Aluminum Oxide and the Underlying Metal. N. Leventhal, B. Vesselin Stoilov and Ahmed Alpas; Mechanical, Automotive and Materials Engineering, University of Windsor, Windsor, Ontario, Canada.

Although it is commonly accepted that the intrinsic near-surface deformation behavior of Al-Si alloys is intricately related to the properties of the interface between the polycrystalline matrix (Al) and second phase inclusions (Si), little is known about the specific deformation and debonding mechanisms. Here we develop molecular-dynamics (MD) simulations to elucidate the interactions between the atoms at the Al-Si interfaces during room-temperature plastic deformation of these materials. The MD embedded atom method (EAM) potential and the Verlet integration scheme have been used. The interface has been modeled as a two-dimensional structure, and MD simulations were carried out using about 100000 atoms. The evolution of the subsurface microstructure of Al-Si systems has been studied to develop constitutive relationship (stress-strain, traction-displacement) for the incoherent aluminum-silicon interfaces. Furthermore, the debonding, fracture of the Si inclusions, the influence of the local temperature and the deformation rate on the interfacial strength. Point defect vacancy defects near the surface have been found to decrease the maximum shear stress at which the failure propagates in the bulk. It has been further demonstrated that the crack nucleation strongly depends on the local temperature distribution as well as on the relative orientation of the Al and Si crystals.

4:45 PM KK4.9 Interfacial Structures for Martensitic Phases in Metastable β′-TiAl-Based Alloys. Mark Aindow1, S. P. Alpay2 and Ming Wu2; 1University of Connecticut, Storrs, CT, Connecticut; 2Mernery Corporation, Bethel, Connecticut.

Alloys based on Ti-Mo have attracted considerable attention for biomedical applications, in part because they do not have the sensitization issues that can be associated with alloys containing Ni. One of the most attractive properties of these alloys is a pronounced pseudelastic response, although this is known to depend critically upon the composition and thermal history of the alloy in question. In our studies we have performed detailed investigations of microstructure/property relationships in these alloys using in-situ XRD and TEM. Two different stress-induced orthorhombic martensites have been identified. The first is the well-known a double prime phase: this was irreversible, nucleated heterogeneously at pre-existing sub-grain boundaries, adopted the habit plane one would expect on the basis of the PTMC prediction, and exhibited a fully coherent step-terrace interface structure with the β′ matrix. The second is a previously unreported reversible form which we denote a triple prime. The in-situ XRD data indicate that a triple prime adopts an intermediate crystal structure closely related to those of β′ and a double prime. This is only retained in TEM specimens from samples strained beyond the pseudelastic limit wherein 32 twin form within the a triple prime laths. In these cases the β′/a triple prime interface appears unusually diffuse. The influence of the interface structures for these two stress-induced martensites upon the reversibility of the deformation will be discussed.
KK5.1

Formation of Voids in Diffusion Bonding of Copper Alloys to Nickel Metals. Hideyuki Ikebata, Hiroshige Miura, Katsuhisa Ishii, and Yoshitaka Shimozaki. 

In copper-nickel system, it is well known that the excess vacancies due to the differences in the intrinsic diffusivities of the binary couple play an important role in void formation. We have studied an effect of solute elements in copper alloys on void formation at interface in diffusion bonding of these alloys to nickel metal. Addition of silver or aluminum element to copper metal prevents generation of voids. We found that the formation of vacancy clusters leading to the voids was restricted by the formation of a solute-atom-vacancy complex. Calculation of ordering energy between a solute atom and a vacancy was performed by “Quasidynamical method” with the many-body inter-atomic potential. Then, we obtained a negative value of ordering energy which favors to generate the solute atom-vacancy complex.

KK5.2

First-principles calculations of 6H-SiC (000-1)-to-2x2 surfaces and interfaces. T. Tanaka, N. Honda, H. Ishikawa, Y. Hasegawa, T. Tamura, M. Ikeshita, and H. Ichikawa. 

Silicon carbide (SiC) is one of the best candidate for high-performance electronic devices. In order to build the high-quality devices, it is essential to control SiC surfaces and oxide/SiC, metal/SiC and metal/oxyde/SiC (MOS) interfaces. In this paper, we have performed the atomic and electronic structures of 6H-SiC (000-1)-to-2x2 surfaces and interfaces using the first-principles norm-conserved pseudopotential (NCP) method and the projector augmented wave (PAW) method. First we developed an appropriate supercell of the (000-1)-to-2x2 surface and obtained stable atomic configurations through relaxation processes by Hellmann-Feynman forces, which converged within 0.01 eV/atom. Obtained surface structures are consistent with the recent experiment [1]. This surface structure involves the three Si adlayer atoms and a Si adatom. The Si adlayer consists of two types of trimers, the smaller one bonded each other and the larger one bonded to once Si adatom. It is interesting that the triangular bonding of Si occurs stably at the smaller trimer with enough bond charge. The present structure minimizes the number of dangling bonds and also minimizes the total energy. Moreover, we have shown two kinds of the top C-Si bilayer of SiC and the Si adatom, corresponding to the observed non-dispersive two surface states of the valence-band spectra. In order to clarify the surface structure stability, we have performed the free energy analysis by the chemical potential evaporation. The result shows in SiC system the dangling bond of C is energetically unstable rather than that of Si. The oxide/SiC, metal/SiC and metal/oxyde/SiC interfaces have been treated. In the oxide interface, we treated the several models of SiO2 and Si2O5 silicate adlayers and compared with the sqrt(3)xsqrt(3) model [2]. In the metal/SiC interfaces, we have dealt with the several types of metals as Al, Ti, Ni, Cu, Pt and Au, and calculated the Schottky barrier height (SBH) which is important property [3]. In combination with the oxide and metal interface, we have calculated the metal/oxyde/SiC interfaces. The results show an obvious effect of metal species. This work was performed as a part of National Research Grid Initiative (NAREG) by Ministry of Education, Culture, Sports, Science and Technos. (MEXT), Japan. [1] Y. Hoshino, R. Fukuyama, Y. Matsubara, T. Nishimura, S. Tanaka, M. Kohyama, and Y. Kido, Phys. Rev. B 73, 195331 (2006). [2] W. Lu, P. Pollmann, and J. Hoekstra, Phys. Rev. B 61, 1347 (2000). [3] S. Tanaka and M. Kohyama, Phys. Rev. B 64, 235308 (2001); Mat. Res. Soc. Symp. 640, H5. 18 (2001); Appl. Surf. Sci. 216, 471 (2003); J. Hoekstra and M. Kohyama, Phys. Rev. B 57, 2334 (1998); M. Kohyama and J. Hoekstra, Phys. Rev. B 61, 2072 (2000).

KK5.3


We have studied the chemical state of the atoms at the interface of (Al2O3-Ta2O5) bi-layer systems using angle-resolved X-ray photoelectron spectroscopy (AR-XPS). XPS studies of interfaces are usually performed with ion-beam etching, however, the etching bombardments damage the chemical bonding. In contrast, AR-XPS measurements are performed only by changing the take-off angle of the signals and do not use ion-beam etching, so they are effective for the study of the chemical bonding within a few nm from the film surface. Al2O3 (3nm thick)/Ta2O5 (10nm thick) and Ta2O5 (3nm thick)/Al2O3 (10nm thick) films were deposited on silicon wafers by reactive sputtering in Ar/O2 mixture gas and electron-beam gun evaporation. Then, the XPS spectra were measured in the sputtering deposition, while oxide targets were used in the evaporation. The Ta4f and Al2p photoelectron spectra were measured by a Quantum 2000 system, where the photoelectrons were excited by AlKα monochromatic X-rays. The 6H/Al2O3-Ta2O5 film deposited by sputtering was deconvoluted into four peaks; two of them were the Ta-O bond originating from Ta2O5, while the other two peaks were the Ta-X bond originating from another target compound. As for the deposited Ta4f, the XPS spectrum of the Al2O3-Ta2O5 film deposited by sputtering was deconvoluted into four peaks; two of them were the Ta-O bond originating from Ta2O5, while the other two peaks were the Ta-X bond originating from another target compound.

KK5.4

Study on the Transport Behavior and Mechanism of Ag/TCNO bi-layer Thin Films. Ping Liu, Yiming Jiang, WeiWei Wu, Cheng Zhong and Jin Li. Materials Science, Fudan University, Shanghai, China.

Functional organic thin films have attracted much attention in recent years because of the diversity of their molecular structure and their special properties in electricity, optics and magnetism. Many studies involved in this aspect concerned with metal-organic complex thin films. Because the transport behavior between metal and organic is a basic problem, study of transport in this thin film will have great scientific and practical significance to the preparation of special thin films, the realization of controllable nano-structure, the stability and failure analysis of thin film. Silver tetracyanoquinodimethane (AgTCNQ), a typical metal-organic complex, has been widely studied because of their particular electrical and optic bistable properties. However, research on transport process in metal and organic interface is lack both in qualitative research on transport law and quantitative research on transport parameter. Ag and TCNQ bi-layer films of different thicknesses with stoichiometric composition were prepared on glass substrate by successively deposition of Ag and TCNQ under a vacuum of 1x10-3Pa. The thickness of Ag and TCNQ was monitored and controlled by quartz crystal oscillator. Metal-organic complex AgTCNQ was formed through Ag+ transport in the organic film after annealing at room temperature and in ambient environment. The transport behavior in the film was studied by using transmission spectrum. After the sample was prepared, its transmission spectrum was continuously recorded by spectroscopy during annealing. The shape change of the spectrum shows the transport process of Ag/TCNQ bi-layer film. When the shape of the spectrum curve is no change, it was considered that the transport process was completed and the transport time was confirmed. By examining the evolution of the transport time of films with different thickness, a abnormal accelerated transport phenomenon was observed with the decrease of the thickness of the film. We find that the transport time (>32.5nm), transport precocls accords well with parabolic law between transport distance and transport time. When film was ultra thin (<25nm), the transport process matches with inverse logarithm law approximately. When the thickness of the film was set between the two cases, transport went into a transitional stage. Tunneling model and non-tunneling model were established respectively based on whether the tunneling condition was satisfied or not to explain the difference of transport behavior. So, it can be seen that the theoretical models are well consistent with the experimental data.

KK5.5

Influence of Humidity on Chemical Transport Behavior in Cu/TCNQ Metal-organic Thin Films. WeiWei Wu, Yiming Jiang, Ping Liu, Cheng Zhong and Jin Li. Materials Science, Fudan University, Shanghai, China.

A Cu/TCNQ metal-organic bi-layer thin film with total thickness of 130nm was prepared by successive vacuum evaporation of Cu and TCNQ. 7.7,8-tetracyanoquinodimethane (TCNQ) on glass substrate under the pressure of 1710-3 Pa. The thickness of Cu and TCNQ was monitored and controlled using a quartz crystal oscillator to obtain the molar proportion of Cu and TCNQ as 1:1. The Cu/TCNQ coulombic potential was formed by Cu+1 chemical diffusion during annealing in both dry and wet environments. The influence of humidity on chemical transport behavior in the film was studied. The results
showed that the wet environment can obviously accelerate the forming rate of Cu-TCNQ complex. The transport time needed to form the complexes in 80%, 90%, 95%, 97% and 99% humidity has been measured, which was 120, 90, 30, 20, 18, and 17 minutes respectively. The evolution of the transport time with environmental humidity has been shown and a linear relationship was found between the transport time and the relative humidity reciprocal. A electrochemical reaction model was proposed to demonstrate the accelerating effect. The theoretical explanation for the linear relationship was given. The transport mechanism in the film in dry and wet air was discussed. The Cu-TCNQ complex formed respectively through both physical transport in dry environment, and electrochemical reaction in aqueous solution in wet environment. As a conclusion the adsorption of H2O molecules on the film is found to be the control step of the transport under the wet condition.

**KK5.6** Structure and Failure of fcc/bcc Heterophase Boundaries in Metals. Adham Hashibom1,2, Peter Gambech1,2, Christian Elkeasser1 and Yuri Mishin1,4. Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany; 2Institut fuer Zueinassenlehre von Bauteilen und Systemen ZIBS, University of Karlsruhe, Karlsruhe, Germany; 3George Mason University, Fairfax, Virginia.

Heterophase interfaces between fcc and bcc metals exist in many microelectronic devices and composite materials. The Copper-Tantalum system is one such technologically important fcc/bcc interface system, where Ta is used as diffusion barrier to keep the Cu from interacting with the Si of the chip. Compared to other interphase boundaries, for example metal/ceramic interfaces, the failure processes at the heterophase boundary are poorly understood. In this study, the structure, diffusion, and mechanical properties of the interfaces are investigated via atomistic simulations employing a newly developed Cu-Ta interatomic potential which is based on a generalization of the embedded atom method. The addition of angular-dependent interactions to the interatomic potential is derived by fitting to a large set of experimental data including defect and surface energies, and to a set of theoretical data from first-principles calculations. The results for the elastic properties, interface energies, vacancy formation energy profiles, and additional defects at the interface will be presented.

**KK5.7** Thermodynamic Control of SiO2/Si Interface Structures at Extremely Low Oxygen Activity. Ming Yang1, Ana Ramos2, Sung-Yoon Chung3, Martine Gautier-Soyer3, Rowland M. Cannon4, and Yet-Ming Chiang1. 1Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; 2DSM/DRECAM/SPCSI, CEA Saclay, Gif sur Yvette, Cedex, France; 3Materials Science and Engineering, Inha University, Incheon, South Korea; 4Lawrence Berkeley Laboratory, Berkeley, California.

We studied the equilibrium structures of silica grown on [001] silicon at extremely low oxygen partial pressures that are close to bulk Si/SiO2 equilibrium. [001] Si was equilibrated with metal/metal-oxide buffers, e.g., Zr/ZrO2, in closed systems at temperatures of 700-1100°C, in order to systematically control the ambient oxygen activity at extremely low levels. Angle-resolved XPS, APX, and NEXAFS measurements were then performed to determine the average coverage, stoichiometry and structure of the oxides. At a wafer temperature of 700°C, we found that the saturation oxygen activity corresponding to bulk Si/SiO2 equilibrium does not result in the growth of a reducing oxide film of unconstrained thickness. Instead, nanoscale, substoichiometric silicon oxide islands were observed to form on silicon surface. For some range of oxygen activity above the saturation value, the amount of oxidized silicon remains relatively constant, but the oxide morphology evolves towards plateaus, and the composition towards stoichiometric SiO2. Finally, at sufficiently high oxygen activity, kinetically-limited growth of thicker films, typical of thermal oxidation of silicon is observed.

**KK5.8** Thermogravimetric Study of Mass Transport at Ag/Nb2O5 Interfaces. Lawrence P. Cook, Winnipeg Ng and Zhi Yang, NIST, Gaithersburg, Maryland.

Metallic silver is frequently used as the metallization in ceramic packaging applications, where the embedded passive devices may encompass a large variety of chemistry of chemicals. Nb2O5 is a common constituent of dielectric passives, and reaction between Ag and Nb2O5 is known to occur, usually with a deleterious effect on device performance. Consequently it is important to understand the kinetics of this reaction. Since the reaction involves the uptake of oxygen at the interface, it is possible to study the process thermogravimetrically, which allows a direct determination of the rate. Microscopic observations show that Ag is highly mobile relative to Nb, and that transport of Ag controls the rate of reaction under oxidizing conditions. Kinetic studies point to multiple diffusion processes influencing the transport of Ag. Surface diffusion is the dominant mechanism.

**KK5.9** Structure and Interfaces of Precipitates in AlMgSi Alloys. Remko Visser1,2, Cédric L. Marionna1,3, Maudine A. van Huis1, Sigmund J. Andersen1,2, Jökk Jansen1,3, Anders G. Froseth1,3 and Randi Holmestad1,2. 1Institutfor Fysikk, NTNU, Trondheim, Norway; 2Dept. of Synthesis and Properties, SINTEF, Trondheim, Norway; 3Kavli Institute of Nanoscience, TUDelft, Delft, Netherlands; 4Paul Scherrer Institute, Villigen, Switzerland.

The attractive physical and chemical properties of ceramics (in terms of corrosion, formability, weldability, etc) of Al-Mg-Si (6xxx) alloys have made them become widely used in industry. Their most striking feature is the large increase in strength during precipitation hardening. This process involves the formation of Mg-Si and Al-Mg-Si metastable phases during heat treatments at moderate temperatures (100 to 200 °C). Although formerly believed to be a rather simple alloy system, a combination of experimental techniques - High Resolution Electron Microscopy (HREM) image analysis, Material Science Methods (MSML) structure refinement and Density Function Theory (DFT) modelling - has revealed the existence of a wide range of precipitate structures: Super Saturated Solid Solution → clusters with varying Mg and Si contents → GP zones → β’→ β’ + B1’ + U1’ + V2’ → -betastar- (stable) Most of the precipitates form as crystals of only nm scale dimensions and different phases are present at any given stage in the precipitation sequence. Electron nanodiffraction allows for diffraction data to be recorded from individual crystals and (together with the high sensitivity of electron energy loss spectroscopy) sufficient diffraction information for quantitative analysis. Careful analysis of the experimental results together with DFT modelling shows close similarities in the relation between matrix and precipitate structure for most of the phases. We present results of a structure determination of several recently discovered precipitate phases, and show how their alloy strengthening potential in part can be explained by the matrix-precipitate interface structure.

**KK5.10** Ab-initio based multiscale calculations of low-angle grain boundaries in Aluminium. Lévrier Lympérakis and Joerg Neugebauer, Max-Plank-Institut fuer Eisenforschung GmbH, Düsseldorf, Germany.

A major challenge in describing extended defects such as low-angle grain boundaries is the large range of different length scales: The boundary consists of an array of dislocations where the core structure of each dislocation is rather localized, while the strain field is long range. In a previous study we have developed an ab-initio based multiscale approach that combines elements of density functional theory (DFT), empirical potentials, and continuum elasticity theory[1]. This approach allowed to treat systems consisting of a few 105 atoms with a -100 accuracy and has been applied to an isolated dislocation. In this study we have extended the formalism to an infinite array of ordered dislocations as realized in a low angle grain boundary. Based on this formalism we have studied the structure and the energetics of various low angle grain boundaries in Aluminium. In a first step strain field arising from the array of parallel dislocations has been used to create supercells containing a pair of boundaries having various tilt angles and boundary separation distances. In a second step DFT calculations have been used to described the highly strained material close the boundary region. The long range strain field has been described by modified embedded atom method (MEAM) calculations. The smaller scale ab-initio and the larger scale MEAM calculations are coupled by utilizing implicit boundary conditions. Based on this approach we have derived a diagram which predicts the energetically most stable boundary as function of the misorientation angle and the boundary-boundary separation distance. The asymptotic limit of large separation distances corresponds to the single isolated grain boundary, while the asymptotic limit of very small but still finite tilt angles corresponds to the macroscopically relaxed single isolated dislocation. Based on this phase diagram we address the issue of grain boundary stability and we discuss recent experimental results. [1] L. Lympérakis, J. Neugebauer, M. Albrecht, T. Remmele, and H.F. Strunk, Strain induced metallization and deep electrical states around threading dislocations in GaN, Phys. Rev. Lett. 93, 196401 (2004).


Atom probe tomography can provide 3-D atomic-scale structural and compositional materials analysis that is difficult to duplicate using
other high-resolution techniques. In spite of its unique analytical capabilities, the atom probe historically has been used only by a small number of experts to prepare metal specimens for the shape of a very sharp needle. Recent developments in local electrode atom probe (LEAP) technology and associated specimen preparation methods have enabled the three-dimensional atomically resolved imaging of a variety of materials. The materials can be prepared in either the traditional needle-shaped geometry or in the form of microtubs residing on planar surfaces. The local electrode technology also enables faster data collection rates and a larger field of view on the atom probe. They are using this technique have a cross-section of up to ~100 nm and require only one hour (as opposed to days) of data collection time. Site specific sample preparation allows one to isolate a small, localized feature such as grain boundary or a semiconductor transistor region and create a wide field-of-view atom map of the region of interest. Recently a variety of material types have been analyzed using the LEAP technology. The significance of these developments cross a multitude of interesting metallurgical, thin film, semiconductor, and organic.

**K5.12**

Holmium Growth on SiC-6H(0001) Studied by Scanning Tunnelling Microscopy, Steven Tear and Ed Perkins; Dept of Physics, University of York, York, United Kingdom.

Silicon carbide is a substrate that has attracted considerable interest in recent years. It is a large band-gap semiconductor, and is stable to very high temperatures, raising the prospect of electronics that could operate in such hostile conditions. In recent years, such as holmium, are known to form novel structures on Si(111) and Si(100), feature low Schottky barriers with n-type silicon, and a deconvoluted surface electronic structure. We present here an STM study of the behavior of holmium on 6H-silicon carbide(0001) and how it compares with that on Si(111). 4 to six monolayers of holmium was deposited onto the silicon-rich SiC-6H(0001)-3×3 reconstruction at room temperature, followed by an anneal at ~600°C. This gave rise to a complex LEED pattern, and a large number of reconstructions were observed on the surface. Most notable is the growth of a rectangular overlayer on the hexagonal substrate, which exhibits a long-range ripple distortion, possibly due to strain or stacking. Other ordered reconstructions are observed, in addition to large waffle-like structures formed on the surface after a series of holmium depositions and annealing. These structures are strikingly different to what is seen on Si(111). [1] P. Martensson, F. Owman, L.J. Johansson, Phys. Stat. Sol. (b) 202, 601 (1997)

**K5.13**

Abstract Withdrawn

**K5.14**

HRTEM and ab-initio calculation analysis of metallic ion implanted silicon grain boundaries. Noriko Sugakuchi, Kentaro Yonezu, Rei Kakado and Hideki Ichinose; CAREM, Hokkaido University, Sapporo, Japan.

Unique atomic structure of a coincidence grain boundary has a potential impact of quantum devices, namely, quantum dot, quantum wire, and their application as well. When the atomic and electronic structure and their correlation is shown in a coincidence boundary we will get a new guideline for the design of the quantum materials. In the present study, we report the result of HREM observation of structural change of the silicon grain boundaries by metallic ion implantation such as gold and tungsten, aiming development of a new quantum device based on grain boundary control. High atomic number and chemical stability of the both implanted elements were supposed helpful to observe them by atomic structure imaging of a HRTEM. The multi-beam high-voltage electron microscope (MB-HVEM) equipped with two sets of ion accelerators (20 kV, 300 kV and 20 kV, 300 kV) at CAREM, Hokkaido University was employed. Resolution of the MB-HVEM is shown to be 0.18 nm in point to point resolution. We can directly observe the atomic structure and its change due to heating during metallic ion implantation. It was shown that the implanted metallic elements were preferentially substituted at grain boundaries by subsequent heating. The atomic structure of the grain boundaries was slightly modified by the segregation. We will discuss about the substitutional site of implanted metallic ion in a periodic coincidence boundary, collaborating with ab-initio calculation.

**K5.15**

Si Ridges in Laser Processing for TFT Fabrications:Formation and Planarization. Jieyun Moon1, Choong-Yong Sohn2, Choong-Heui Chung1, Yong-Hae Kim1 and Jin Ho Lee1; 1Basic Research Lab., Electronics and Telecommunications Research Institute, Daejeon, South Korea; 2LCD R&D Center, LG-Philips, Anyang, South Korea.

The majority of thin film transistor (TFT) s have a structure of a Si active layer on a buffer layer. In the TPT processing route, active layer forming Si layer is firstly deposited on an amorphous Si (a-Si) form on the buffer layer, and later laser irradiated to form crystalline Si films. As a-Si films have higher surface energy than its phase, the layer forming and annealing step is an inherently metastable. Since the a-Si film is completely melted during the laser crystallization process, it is very important to suppress liquid film dewetting. Otherwise liquid Si would and recede to form droplets and expose the underlying SiO2 layer. However, as liquid Si film solidifies very rapidly, instead of droplets, ridges are observed frequently. In this study, the characteristics of ridges formed after laser crystallization of a-Si films has been studied using atomic force microscopy. We report on the ridge height dependency on parameters such as laser energy density and initial a-Si film thickness, and on a simple scheme to lessen ridge height which leads to improved TFT performance. The heights of ridges which are formed after crystallization amorphous Si films, vary linearly with the commencing film thickness. To reduce the height of the ridges, we have exercised single shot post-laser treatments at various laser energy densities. Upon increasing the energy density distinct regions come forth, namely leveling, planarization phase, re-emerging regime, and eventually dewetting. To elucidate the observed phenomenon, relevant parameters influencing the planarization process are discussed from energy perspective. We conclude that the optimum laser energy for planarization corresponds to the energy at which ridge peak curvature blunting is maximum. Post laser treatments on ridges have an effect of leveling the heights of ridges and lead to improved TFT characteristics.

**K5.16**

Structural Investigations of the interface between Cu(100) and Cu2O oxide island. Xuexiu Han and Judith C Yang; Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Surface oxidation processes play critical role in environmental stability, high temperature corrosion, electrochemistry and catalysis. Thin oxide films, formed by direct reaction between metal surfaces and gaseous O2, are also widely used as sensors, dielectrics, and corrosion inhibitors. We have explored the experimental results of the nano-oxidation process of Cu(100) thin films via in situ ultra-high vacuum transmission electron microscopy (UHV-TEM) at various temperatures and oxidation pressures. The initial oxidation kinetics bear a striking resemblance to heterogeneous, where oxygen surface diffusion is the primary mechanism of Cu2O island nucleation and growth. The morphology of a Cu2O island oxidizing on a Cu surface is strongly temperature-dependent. Yet fundamental understanding of the interface structure between Cu and the various oxide islands, is still surprisingly not well understood. High resolution transmission electron microscopy (HRTEM) and electron energy loss spectrum (EELS) investigations provided valuable information about the structural properties of the oxide scales and Cu/Cu2O interfaces.

**K5.17**

B2-Structures: A Statistical-Thermodynamic Model for Ordering Phenomena, Olga Semenova1, Regina Krachler2 and Herbert Iger1; 1Department of Inorganic Chemistry - Materials Chemistry, University of Vienna, Vienna, Austria; 2Department of Inorganic Chemistry - Bioinorganic, Environmental and Radiochemistry, University of Vienna, Vienna, Austria.

A new and unified statistical-thermodynamic model for non-stoichiometric binary B2-phases with triple defects and a hybrid type of defects (a mixture of anti-structure and triple defects) was developed on the basis of the Ising approach which is a very powerful tool for studying LRO, SRO, as well as order-disorder phase transitions in intermetallic phases. A Bragg-Williams mean-field approximation is employed for description of the atomic arrangement in the structure. Based on a general formalism and the mean-field theory the model equations to calculate point defect equilibria and thermodynamic activities as function of composition and temperature. On the other hand, this new approach allows to create parameters for the pair interaction energies in B2-intermetallics based on experimental data for thermodynamic activities. These new revised pair interaction energy sets were calculated for the B2-compounds NiAl, FeAl, CoGa, NiGa, PdAl and CoAl.

**K5.18**


We have used atomistic simulation and high-resolution transmission
electroscopy (HRTEM) to examine the structure of the interface between yttrium-stabilized zirconia (YSZ) and gadolinium doped ceria (GDC). Molecular dynamics simulations show coherent regions separated by misfit dislocations with a spacing of about 3 to 5 nm. Monte Carlo simulations were used to examine segregation of Gd, Y and oxygen vacancies at the interface. The simulation results are in good agreement with HRTEM results fromubic CO2 film grown epitaxially on YSZ that show misfit dislocations occurring with a uniform spacing of about 3.3±0.5 nm.

KK5.10
Transferred to KK1.5

KK5.20
Atomic and Electronic Structure Analysis of Oxygen Terminated Diamond and Metal Interfaces by Atomic Resolution HRTEM, EDS and EELS. Hidetoshi Ishigame1, Norifumi Sakaguchi1, Naoki Takayanagi1, Hideyo Okuhira2 and Hideyuki Watanabe1.

Since any extreme semiconductor devides have to be connected to outer circuit to work as a devise, the property control of the junction to the bonding wire is key term even in diamond devise which is supposed as a second generation semiconductor. In this study, atomic and electronic structure of a diamond / Ti, Al junction was investigated in correlation with V-I properties to obtain basic information which is available for the design of a diamond semiconductor devise. Silicon grade diamond was produced employing a new design with a 4 doped system. A single plate-like single-crystal diamond several ten micro meter in thickness was grown on either (200) or (220) surface of a heated silicon substrate at 860K. Top surface of the platelet crystal was very flat and was parallel to each of the substrate crystal plane, being (200) or (200). Half peak width of the Raman scattering spectra was 2.6cm-1 showing low impurity content of the platelet crystal less than 1ppm for N and B. The diamond plate was terminated by oxygen and then was evaporated by Ti or Al. The Atomic HRTEM image in resolution 0.1nm most was employed for the atomic structure investigation. The diamond/Ti interface originally showed non linear Schottky type I-V profile. The EDS investigation of the interface did not show any sign of segregated oxygen in it. A similar investigation by EELS, however, showed that there present quite small amount of oxygen in the interface. An atomic structure image which represents projected atomic potential of each atomic column showed slight difference of the image contrast of the uppermost layer of the diamond suggesting that diamond is connected to Ti via oxygen. The Schottky type I-V profile changed to linear Ohmic type one by heating. In the heated interface no sign of the present oxygen was shown.

KK5.21
Abstract Withdrawn

KK5.22
Three-Dimensional Simulation and Characterization of Coarsening in Complex Microstructures Following Solidification. Katsuya Kwon1, and Peter W. Voorhees3.

Spinodal decomposition is observed in a variety of materials ranging from polymers to metals. This process frequently produces a complicated and highly interconnected 3D interface morphology possessing both positive and negative curvatures. Such a microstructure cannot be fully described by information obtained from its two-dimensional cross-sections. Characterizing the morphology of these structures in three-dimensions has proven challenging. We employ analyses of the three-dimensional curvature and the genus in two-phase microstructures obtained by large-scale phase-field simulations using the Cahn-Hilliard equation. We investigate the evolution of microstructures following the critical and off-critical quenches using quantifiable measures such as the interfacial shape distribution (the probability of finding a patch of interface with a given pair of principal curvatures) and topological quantities like the genus of the microstructures. We will discuss quantitatively the microstructural evolution and the presence of scaling using these measures.

KK5.23
Surface Energy of Complex Metallic Alloys. Jean-Marie Dubois, FR2979, CNRS, Nancy, France.

Based on comparative tribological pin-on-disk experiments performed in vacuum, we have found a simple way to estimate with good accuracy the surface energy of complex, and simple, Al-containing metallic specimens. The comparison is made to pure metals and reference samples the surface energy of which is known either from experiment or from calculation. The method we propose is especially relevant in so far that computation of the surface energy is not feasible for complex compounds the unit cell of which may contain hundreds to thousands atoms. As long as wear is negligible, it turns out that the friction coefficient measured in vacuum is dominated by the adhesion between the surface of interest and the steel pin used in the present study. Within restrictive conditions that will be discussed in the paper, the friction coefficient is shown to be proportional to the surface energy and inversely proportional to the hardness of the sample material. This approximation allows us in turn to estimate the surface energy of unknown specimens. We have applied rather extensively this economical method to series of binary and ternary Al-M (Ti = 3d, 4d & 5d transition metals) compounds with the aim to gain better insight in the friction and cold-welding behavior of metallic alloys placed in vacuum. We have found that the surface energy of such compounds decreases first with the filling of the sp- and d-bands and second with the structural complexity of the crystal whereas as a matter of fact mechanical deformation of the sample exerts a very restricted influence on friction. As a result, quasicrystals show a surface energy that falls in the range 0.5-0.8 J/m2 whereas it increases to 2 J/m2 in metallic compounds like the omega or lambda compounds. Furthermore, varying the nature of the counterpart, we observed a clear correlation between solid-solid adhesion and number of electronic states necessary to form a rigid electron band when joining sample and pin. Therefore, these results shed new light on non-lubricated friction between naked metallic bodies.

Acknowledgements: The present work was supported in part by the European Commission under contract G5RD-CT-2001-00704. The friction tests were performed at Austrian Research Centres-Seibersdorf (Austria) and benefited from help of J. Brenner and A. Merstallinger.

KK5.24
Direct Determination of Atom Positions in Non-perfect Crystals with Kinematical X-ray Standing Waves. Martin Tölfkien and Dmitri V. Novikov; HASYLAB, DESY, Hamburg, Germany.

We propose a novel method for the investigation of dopant and adorbate atom positions in single crystal materials with high sensitivity. The method is related to the well-established X-ray standing waves (XSW) approach [1], however it is based upon the kinematical diffraction theory. Thus it can be applied to non perfect single crystals without the necessity of special conditions as e.g. micro beams or backscattering geometry. We show a theoretical derivation of the XSW formation in the frame of a modified kinematical theory taking into account absorption effects. The developed method is verified by experiments on perfect and non-perfect crystals with known structure, where a good agreement of theory and experiment is observed [2]. We present kinematical XSW measurements on a mосасor gold alloy sample and demonstrate the determination of the La and Mn atom positions in a mосасor lanthanum strontium manganate crystal. The new kinematical X-ray standing waves method can be applied to natural minerals, metallic and organic single crystals, and for the study of surface and interface processes [1] J. Zegenhagen, Surf. Sci. Rep. 18, 292 (1993) [2] M. Tölfkien, D.V. Novikov, S.S. Fanchenko, Phys. Rev. B 71, 165404 (2005)

SESSION KK6: Oxide/Metal Interfaces
Chair: Donald Siegel
Wednesday Morning, November 30, 2005
Fairfax A (Sheraton)

8:30 AM **KK6.1**
Structure analysis of two-dimensional surface oxides by STM and DFT. Peter Varga, Institut f. Allgemeine Physik, Vienna University of Technology, Vienna, Austria.

The most frequently studied model systems in heterogenous catalysis are ultra-thin oxide layers used as supports for depositing transition metal clusters. The thin oxide layers (which are conductive) are of importance to allow the usage of conventional surface science techniques. In the last few years, we have investigated the structure of several surface oxides on Ru, Pd, Rh and AI1 surfaces by combining results from STM (scanning tunneling microscopy) images with atomic resolution and DFT based simulation calculations with VASP (Vienna ab-initio simulation package). In this talk two examples will be given. The first example concerns the structure and stability of the surface oxide grown on Rh(111) at high oxygen exposure. For Rh(111) it could be shown that the surface oxide consists of an ORH4 trilayer which is thermodynamic unstable but kinetically stabilized [1]. The reduction by H2 adsorption at room temperature could be observed directly in situ by STM. The second example concerns the alumina film grown on NiAl(110) which has fascinated researches for

9:00 AM *KK6.2 Structure and Bonding at Abrupt Copper/Alumina Interfaces - An Ab-Initio Density-Function Theory Study, Adnan Hashibon1,2, Christian Ehrenzeller2 and Manfred Ruehle3,1 Praunhofer Institute for Mechanics of Materials IIMF, Freiburg, Germany; 2Max-Plank Institute for Metals Research, Stuttgart, Germany.

The design and optimization of metal-ceramic composites for successful technological performance profits from a fundamental understanding of the local atomic structure and chemical bonding at the interface. The Copper/Alumina system as a model case for metal-ceramic composites has been subject to extensive experimental studies of electronic, mechanical and thermal properties. First-principles electronic-structure calculations were carried out to analyze the interfaces between Cu (111) and Al₂O₃ (0001) surfaces. Two experimentally observed orientation relationships were considered. In the first case the [1-10] direction of Cu is parallel to the [10-10] direction of Al₂O₃, and in the second one the Cu is rotated with respect to the interface normal direction [0001]. Numerous candidate models were treated for each case, covering all high-symmetry interface configurations, and with either Al or O termination of the Al₂O₃ (0001) surfaces. Full structural optimizations by relaxations of the positions of all atoms were performed. For the most stable configurations, site-projected densities of unoccupied electronic states were analyzed in detail. The theoretical results and connections to experimental observations by high-resolution transmission electron microscopy and electron energy loss spectroscopy will be discussed.

10:00 AM *KK6.8 Structure and Bonding at Pd/ZnO Interface, Manfred Ruehle1, Mitsuhito Suito1 and Thomas Wagner1,1 MPI f. Metallforschung, Stuttgart, Baden-Wuerttemberg, Germany; 2MPI f. Festkoerperforschung, Stuttgart, Germany.

The interface between the polar (0001) surfaces of ZnO and Pd were investigated. First the ZnO surfaces were annealed under well-defined Oxygen atmospheres and in UHV. Detailed surface XRD studies revealed the Pd/ZnO interface. The Pd was deposited on both different polar surfaces and the atomic structures of the different Pd/ZnO interfaces were determined by quantitative high-resolution transmission electron microscopy (HRTEM) studies. Both interfaces were atomically abrupt and - as expected - free of reaction products. The interface was atomically flat. Misfit dislocations could be identified adjacent to the interface in Pd. The atomic structure of the coherent regions between the misfit dislocation cores was determined by HRTEM. The Pd/ZnO interface is Zn terminated and the Zn atoms are positioned on Pd lattice sites. In contrast, the Pd/ZnO interface was O terminated. The experimental results are compared to results from theoretical simulations (different levels of modelling). The observations will be critically discussed.

10:30 AM KK6.4 Anomalous scaling of Cu surfaces During Oxidation, Guangwen Zhou, Dillion D. Fong, Pete M Baldo, John E Pearson, Loren J Thompson and Jeffery A Eastman; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Thin film surfaces evolve during growth into a rough morphology that is very often found to be statistically self-affine, exhibiting both spatial and temporal scaling behaviors over a large variation of dynamic length scales. In the extreme case, the growth is roughening in thin film deposition, little has been reported on the roughening behavior of the oxide/gas interface during metal oxidation despite the ubiquity and practical importance of oxidation. Choosing Cu as a model system in this study, we are investigating the surface roughness evolution of oxide films formed by direct reaction between metal surfaces and gaseous O₂, with the goal of establishing a correlation between the surface evolution and the oxidation mechanism. Atomic force microscopy is employed to measure the surface roughness of the oxidized Cu surfaces as functions of oxidation time and temperatures. We show that the kinetic roughening of a Cu surface undergoing oxidation obeys an anomalous scaling behavior characterized by a power-law dependence of the height fluctuations of the local slope, where t is the oxidation time. The interface width w(t) scales as t^(1/3+H) when the oxidation time is large or the size l of the region over which w is measured is small, and as t^(1-β) when l is large or t is small (here, H is the Hurst exponent and β is the dynamic scaling). It is also found that the Hurst exponent increases monotonically as the oxidation temperature increases from 250°C to 450°C. These results are interpreted in terms of a model based on the outward diffusion of Cu₂⁺ cations across the oxide layer and the action of the chemical potential gradient between the gas-oxide interface and oxide-metal interface.

11:45 AM KK6.5 Characterization of Oxides and Oxide-Metal Interfaces in Zr-Based Alloys Using Synchrotron Radiation and Transmission Electron Microscopy, Aylin Yilmazbayhan1, Arthur Motta1, Marcelo Silva1, Else Brevet1, Robert Comstock2, Barry Lai3, Zhonghou Cai4, Yong Chu5 and Jan Ilavsky3.

1Department of Mechanical and Nuclear Engineering, Penn State, University Park, Pennsylvania; 2Science and Technology Center, Winghamouse Electric Company, Pittsburgh, Pennsylvania; 3Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; 4Materials Research Institute, Penn State University, University Park, Pennsylvania.

Zirconium alloys are extensively used in the nuclear industry as nuclear fuel cladding and structural fuel assembly components. Improvements in the economics of reactor operator have resulted in extended cycle lengths, higher coolant temperature, and increased fuel duty. As a result, corrosion has again become a limiting factor on the useful lifetime of these alloys due to the continued growth of the oxide corrosion layer. Small changes in alloy chemistry and microstructure result in reproducible and significant differences in the growth rate and composition of the oxide. It is thought that the structure of the oxide-metal interface and the protective oxide layer is a major contributor to the observed differences between alloys. In order to develop a mechanistic understanding of the different oxidation rates in zirconium alloys, various alloys were fabricated and corrosion tested in high temperature water and steam. The structure of the protective oxide layer formed on model Zr-based alloys was investigated using both synchrotron radiation at the Advanced Photon Source at Argonne National Laboratory and transmission electron microscopy (TEM). Using a 0.2 micron size x-ray beam, oxide cross-sections were examined to determine phase content, oxide texture, and grain size as a function of distance from the oxide/metal interface. The technique can be used in situ, and thus avoids the artifacts of thin foil preparation for TEM, while maintaining high spatial resolution. The oxide is a mixture of monoclinic and tetragonal ZrO₂. A marked periodicity in phase content, grain size and texture was observed in the oxide structure, indicating a periodic corrosion process. This technique provided detailed information on the structure of oxide/metal interface. It was found that the oxide exhibits a distinct crystallographic texture, with the 200M pole aligned close to the oxide growth direction. At the interface, the new oxide forms with a tetragonal structure, in what constitutes a precursor tetragonal phase, which is only present at the interface and which transforms into a monoclinic phase about 0.2-0.3 microns into the oxide. The 002T pole in the precursor tetragonal oxide is found to be parallel to the 020M monoclinic pole, and to the 1010hcp Zr phase. These results are qualitatively confirmed by transmission electron diffraction analysis carried out on cross sectional samples. It is thought that the tetragonal phase is stabilized at the interface by small grain size and as the grains grow they transform to monoclinic structure. This orientation relationship is significantly more pronounced for oxides with lower growth rates. These results are discussed in terms of the current models of the corrosion process in Zr alloys and of the advancement of the oxide layer in different alloys.

11:00 AM KK6.6 Small Pd Cluster Diffusion on MgO Surface. Molecular Dynamics and Monte Carlo Simulations, Florian Nita1,2 and Riccardo Ferdinando1.

1INFN and Genova University - Physics Department, Genova, Italy; 2Institute of Physical Chemistry "IG Murgulescu" of the Romanian Academy, Bucharest, Romania.

We present a molecular dynamics study of temperature and size dependence of the diffusion of small Pd clusters (n = 1-10) deposited on the MgO(001)surface. The equilibrium
atomic structures of Pd clusters as function of their size have been determined on the basis of a semi empirical potential for the Pd-Pd interaction, and fitted to first-principles MD-MgO interaction \(^1\). The value of the diffusion coefficient was determined using memory expansion method \(^2\) and the size dependence of the time required to reach the hydrodynamical regime was established. From Arrhenius analysis of effective diffusion and molecular dynamics simulations were carried out to study the mechanism of 3D cluster diffusion and its dependence on cluster size. Using MD results we performed Molecular simulations and parameterization between our results and experimental data \(^3,4\) was obtained. Bibliography: 1 W. Vervisch, C. Mottet and J. Goniakowski, Phys. Rev. B 65, 245411 (2002); 2 S. Y. Ying, I. Vattulainen, J. Merikoski, T. Hjelt, T. Als-Nielsen, Phys. Rev. B 58, 2170 (1998); 3 G. Hau, A. Mecke, H. Brune, J.V. Barth, J.A. Venables, K. Kern, Phys. Rev. B 61, 11105 (2000); 4 P. Jensen, Rev. Mod. Phys. 71, 1665 (1999)."
The formation and evolution of thin polycrystalline films formed from the reaction of metals on silicon (metal silicides) or germanium (germanium silicides) depend on the growth conditions. NiSi is a candidate material system for replacing CoSi2 thanks to its lower resistivity even for linewidths lower than 100 nm and its lower Si consumption. However, it is less stable at elevated temperatures. An important limitation is the degradation of the alloyed islands — bit via eit — grain boundary grooving. As the film agglomerates into islands it may lose connectivity. The replacement of (part of) the silicon with germanium is attractive due to the higher melting point and grain boundary energy in germanium. Monte Carlo simulations to predict the evolution of the morphology of the polycrystalline metal germano-silicide film on a silicon substrate. Diffusion and interfacial energies play important roles in the evolution. Experiments and observations on NiSi with Pt or implanting BF2 increases the resistance of NiSi and NiGe to agglomeration. The mechanism by which these species modify the agglomeration is not known. We test two possible mechanisms: (i) platinum makes the NiGe boundaries softer, which changes the wetting angles and hence the driving force for boundary grooving or (ii) platinum slows the kinetics of agglomeration by slowing diffusion. In the case of NiPt(111)/Ge, we also explore the role of germanium segregation on the morphology evolution.Phase field simulations will aid in metal silicide optimization by determining the controlling mechanisms and key physical parameters.

2:15 PM KK7.3
One-dimensional vs. Two-dimensional Buckling of Compressively-Strained Films on a Compliant Substrate. Elyachet1, Pabase1, Karl D. Hobart1, Fritz J. Kub1 and James C. Sturm1. 1Princeton Institute for the Science and Technology of Materials and Department of Electrical Engineering, Princeton University, Princeton, New Jersey; 2Naval Research Lab, Washington, District of Columbia.

Compliant substrates are of great utility for strain engineering of thin films. However, the compliant layer may allow undesired roughening (buckling) of a strained film. A thorough understanding of buckling and methods to prevent it is needed. In this work we quantitatively describe, for the first time, one-dimensional buckling, and compare experimental and model results for 1-D and 2-D buckling. A compressively strained (001) 600 nm Si0.7Ge0.3 layer is grown on bulk silicon and transferred to a wafer bonded to a SiGe=Si=Ge wave onto a silicon handle wafer with a compliant layer of 1μm boro-phospho-silicate glass (BPSG). After transfer, SiGe is dry etched into islands. Upon high temperature anneal, BPSG flows and the strained SiGe film can relax either by lateral expansion or by undesired buckling. Both processes relieve initial compressive strain and thus are energetically preferred. For moderate anneals, large square islands maintain initial strain and 2-D buckling occurs as a mesh of ridges along <100> directions. Models [2] predict faster buckling along <110> than <110>, thus the crystal alignment. For rectangular islands, annealing results in compressive strain in the long island direction where relaxation is slow, and tensile strain in the short island direction that relaxes quickly and is suppressed by the Poisson effect [1]. So the short direction has no driving force for buckling and 1-D buckling is observed for islands aligned along <100> and <110>. Note buckling direction is now determined by island geometry or crystal direction. We measure buckling by Atomic Force Microscopy. Initially, buckling amplitude grows exponentially with time. Models predict a 2-D buckling time constant of 5.5min; we measure 5.1min. Eventually, buckling grows to relieve > 80% of initial strain, so buckling slows and reaches a minimum energy state with characteristic buckling wavelength and amplitude. For our observed 2-D wavelength of 2.1μm, energy modeling adapted from [3] correctly predicts a buckling amplitude of 60nm. To find analytical solutions, 2-D buckling is solved in 1-D with a good agreement with experiments. The models predict and we measure: a longer buckling time constant of 7.5min (we observe 9.0min); a longer buckling wavelength; and a smaller buckling amplitude. Further experiments on thinner 25nm BPSG show a more dramatic difference in 1-D and 2-D buckling time constants and have demonstrated the potential of thin BPSG to significantly slow buckling and reduce buckling amplitude. 1) Yin, et. al., JAP 91, 9716 (2006). 2) J. of Sol. and Str. 139, 1791 (2002). 3) Huang and Suo, JAP 91, 1135 (2002).

3:30 PM KK7.4
Diffusion Mechanisms in Si/TaN/Cu Multilayers. Florent Bernard, Nicole Frety, Joel Sarradin and Jean Claude Tedecoa; LPMC, Universite de Montpellier II, Montpellier Cx 5, France.

The progress of the ultra large scale integration (ULSI) device technology is strongly dependent on the development of new wiring materials exhibiting a lower electrical resistivity and a higher resistance to electromigration than the copper. In the last years, Ni and Cu have been chosen as the candidates to replace aluminium-based alloys. Copper has then become the most attractive material. However the copper diffusion into the silicon-based insulating layers during annealing, required for the device fabrication, leads to a degradation of the reliability of the ULSI devices. Therefore a barrier diffusion layer is needed to prevent the copper diffusion. Various barrier layers have been developed such as tungsten and titanium metals and nitrides, the thickness of which being of about 100 nm. The diffusion of copper in silicon substrates, considering the 600 to 900°C temperature range. Thin TaN/Cu and TaN/Cu multilayers were deposited on silicon substrates using the physical vapor deposition (PVD) process. The optimization of the PVD deposition parameters were performed correlating the microstructural observations and electrical properties, using the X-ray diffraction, Scanning Electron Microscopy, Energy Dispersive Spectrometry and Atomic Force Microscopy techniques. The diffusion mechanisms of copper into silicon though TaN and TaN/Cu layers were then determined due to the correlation between the microstructural observations and Secondary Ion Mass Spectrometry analyses. The comparison between the TaN and TaN/Cu barriers evidenced the role of the TaN layer in the diffusion mechanisms of copper into the silicon substrate.

3:45 PM KK7.5
Initial Growth Processes of Sr and SrO Films on H-terminated Si with Large Mismatch. Hidehito Asakura1, Tatsuya Yamazaki2 and Shin-ichi Shamoto1; 1Neutron Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan; 2Eiko Engineering Co., Ltd., Hitachinaka, Ibaraki, Japan.

Heteropitaxial growth of oxide films on Si substrates is of great interest in relation to a new function for conventional Si LSI circuits. Among the oxides, SrO is a well-known buffer layer on Si for SrTiO3 and BaTiO3 which are highly desirable oxides for future generation transistor gate dielectric and ferroelectric memory applications. In many cases of deposited atomic structure causes a chemical reaction with active dangle bonding on Si substrates resulting in the formation of silica or silicate at the interface. In the existence of surface dangling bonds, large mismatch also prevents the heteropitaxial growth. In fact, SrSiO3 and SrO layers are formed between SrO films and Si substrates when SrO has been grown on Si(100) 2x1 and (11I) 7x7 surfaces. We propose an interfacial buffer layer of hydrogen between the growing film and the Si substrate. It may make the surface stable, at the same time, the chemical bond to the growing film will become weak. A hydrogen atom with only single bond order is expected to provide a stable unconstructed 1x1 surface and weak chemical bond to the growing film appropriate for this purpose. According to this idea, Sr (which has large lattice mismatch with Si: 12%) and SrO epitaxial thin films have been prepared by introducing an interfacial monoatomic layer of hydrogen. In order to characterize the initial growth process has been carried out by using reflection high-energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS) and substrate curvature measurement for the film stress. At the beginning of Sr deposition, the intensity of the streaks from the Si becomes weak. Instead, new streaks with different line intervals appear clearly. These parallel diffraction streaks coexist in the thickness at two atomic Sr layer deposition. The measurement also indicates that a smooth and uniform Sr film grows, and the lattice constant changes from that of substrate to that of the film with an abrupt interface as sharp as one atomic layer. The orientation relationship between epitaxial Sr and Si is found to be Sr(111)/Si(111) and Sr[11-2]/Si[11-2]. The film stress and average thickness of the strain layer are highly reduced in H-terminated Si substrates. Our results suggest that weak quasi Van der Waals force on H-terminated Si surfaces enables the epitaxial growth for large mismatch films.

4:00 PM KK7.6
Dopant Segregation and Distribution at the Si/SiO2 Interfaces. Loring Pei1, Wolfgang Windl2, Stein Christian2, Peter Pilcher2, Steve Fennycook2 and Gerd Duches2; 1Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; 2Materials Science and Engineering, Ohio State University, Columbus, Ohio; 3LEB, University Erlangen-Nuremberg, Erlangen, Germany; 4Condensed Matter Sciences Division, Oak Ridge National Lab, Oak Ridge, Tennessee.

With the fast development of silicon-on-insulator (SOI) technology, interfaces of silicon to dielectric layers become increasingly important. However, a physical understanding of dopant segregation to such
interfaces at atomic resolution remains elusive in spite of intensive study. In this project, As and Sb are selected as dopants to achieve high concentration for high-resolution imaging. A novel experimental concept is served as a key to this study. Experimentally, high resolution Z-contrast imaging and EELS allows accurate determination of position and concentration of dopants. Ab-initio calculations provide structure model based on energy calculation of different preferred segregation sites. After implantation As (10^{16} cm^{-2}) at 32keV, the Si/SiO2 samples are annealed at 700°C, 900°C and 1000°C separately for 10 to 360min in N2, with a SiO2 thin film less than 5μm measured by ellipsometry. Combining the above three methods, as segregation to Si/SiO2 interface is observed for samples annealed at 900°C and 1000°C, but not for 700°C. Arsenic concentration profiles are analyzed close to the interface region for all samples by EELFs, and compared with those measured by TXRF. The amount of segregation is in accordance with the theoretically determined value. Due to the overlap of Si, Sb and O edges, TXRF does not work for Sb doped samples. However, Z-contrast imaging shows a segregation profile to the interface for Sb (3×10^{15} cm^{-2}) doped sample annealed at 900°C and 1000°C. Different from As doped samples, pentagon-shaped Sb clusters are detected within Si.

4:15 PM KK7.7
Towards Intrinsic Silicon in Ultra-Thin Silicon Crystals.
Eric Nordberg1, Byoung-Nam Park2, Pengpeng Zhang3, Emma Tevararwerk4, C.J. Fan5, Irena Knezevic6, Max Laggally2 and Mark Eriksson1; 1Physics, University of Wisconsin, Madison, Wisconsin, 2Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin; 3Electrical and Computer Engineering, University of Wisconsin, Madison, Wisconsin; 4Suntec USA, Peabody, Massachusetts.

Silicon-on-insulator (SOI) consists of a layer of single-crystal silicon supported on silicon-dioxide. SOI is now commonly available in thicknesses less than 100 nm. It is obvious that, at a fixed doping concentration of silicon, the density of charge carriers decreases as the thickness of silicon decreases. The sheet density of interface traps, however, does not typically scale with silicon layer thickness. Thus, although traps play an extremely important role in the trapping of charge carriers in the silicon/silicon-dioxide interface, it should, in principle, be possible to scale silicon-on-insulator so that the bulk silicon layer top is completely depleted, with a Fermi level pinned at mid-gap. In this limit, ultra-thin SOI should be an excellent approximation to intrinsic silicon. 

4:30 PM KK7.7
SiC/SiO2 Interfacial Compositions by EFTEM and Spectrum Imaging.
James Bentley1, K-C (Eric) Chang2, Yan Cao3 and Lisa M. Porter4; 1Metals and Ceramics Division, Oak Ridge National Lab, Oak Ridge, Tennessee; 2Dept. of Mat. Sci. and Eng., Carnegie Mellon University, Pittsburgh, Pennsylvania.

For a long time SiC has held promise as a material for advanced microelectronic devices, not least because among its attractive properties, just as for Si, SiC can be easily oxidized to form insulating SiO2 films. However, the electronic properties of the SiC/SiO2 interface are inferior. This is believed to be due in part to compositional inhomogeneities resulting from oxidation. We have performed extensive measurements by analytical electron microscopy of interfacial composition at the 1-nm scale on a large number of materials subjected to a wide range of processing conditions (variables such as 6H or 4H polytypes, C- or Si-terminated [0001] surfaces, wet or dry oxidation, oxidation temperature, reoxidation, and post-oxidation annealing in N2). Monolayer levels of inhomogeneously distributed excess carbon are present at the interface for certain processing conditions and SiC crystalllography. The carbon levels correlate with interface-state densities. Following post-oxidation annealing in N2, sub-monolayer levels of interfacial N (＜L=1.0 × 10^{15} cm^{-2}) have been measured. Special attention and processing was required to obtain the results. For EFTEM elemental mapping image alignment among the different core-loss series for a given area was critical for reliable measurements of interfacial composition. Shrinkage of the oxide due to electron beam damage during the inevitable prolonged exposures to obtain Si-L, C-K, O-K and low-loss series resulted in movement of Cr or poly-Si capping layer with respect to the SiC/SiO2 interface and compromised simple drift correction. In extracting N core-loss intensities from spectrum lines acquired in STEM mode, the most critical step by far was reliable background subtraction. Background shapes near the edges are significantly different for Si and N and SiO2 regions, mainly due to the presence/absence of the C-K edge.

4:45 PM KK7.9
Abstract Withdrawn

SESSION KK8: Metal/Metal and Oxide/Oxide Interfaces
Chair: John C. Hamilton
Thursday, December 1, 2005
Fairfax A (Sheraton)

8:30 AM *KK8.1
From Isolated Dislocations to Grain Evolution in the Copper-Ruthenium Interface. Juan de la Figuera, Fisica de la Materia Condensada and Centro de Microanalisis de Materiales, Universidad Autonoma de Madrid, Madrid, Madrid, Spain.

Ultra-thin films represent a model of solid-on-solid interfaces where the interface itself is close enough to the film surface so that a variety of surface science techniques can be employed to study the interface. For example, through the distortions of the atom positions in the surface layer, dislocations can be located in-plane with atomic accuracy by means of scanning tunneling microscopy, even for dislocations buried several layers away from the film surface (although locating them in the out-of-plane direction requires additional knowledge of the system). The penetration depth of low energy electrons is also long enough for the dislocation structure in the film to be probed with electron microscopy and diffraction, opening the way to dynamic studies of the large scale evolution of the interface.

Copper on ruthenium is a well studied system, characterized in enough detail that we can supplement the experimental results with atomistic simulations of realistic situations. It is also remarkable because very different dislocation networks are observed as a function of copper thickness which change the in-plane atomic order and interconnectivity between copper and ruthenium, with abrupt changes in the dislocation ordering with each consecutive atomic layer in thickness. We will present observations and simulations of films of increasing thickness where dislocation climb and glide and dislocation interactions are directly observed. Further, a phase transition in the dislocation network present at the Cu/Ru interface has been observed by exposing the surface of the film to sulfur in films two and three atomic layers thick. This research was partly supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, and by the Spanish Ministry of Science and Technology through Project No. MAT2003-08027-C02-02. J.I.P gratefully acknowledges support through a "Ramón y Cajal" contract from the Education and Science Spanish Ministry.

9:00 AM *KK8.2
First-Principles modeling of Ni-Ni3Al interfaces at finite temperature. Axel van de Walle1, Christopher Woodward2 and Mark Asta1; 1Materials Science and Engineering, Northwestern University, Evanston, Illinois; 2AFRL/MLLM, Wright-Patterson AFB, Dayton, Ohio.

Modeling of precipitate nucleation and growth via mesoscopic approaches, such as phase-field methods, depends on the availability of a number of microstructural parameters that have proven especially difficult to obtain either via experimental or first-principles methods. This work is devoted to the interface free energy and the interface width. Interface free energy is the main driving force for coarsening while interface width governs precipitate coarseness and sets the spatial resolution of the computation grid in phase-field methods. While first-principles methods are routinely used to obtain interface free energy of perfect interfaces at absolute zero temperature, we describe a methodology that enable the calculation of interfacial properties at finite temperature. The method properly accounts for configurational disorder and lattice vibrations and is based on the concept of coarse-graining of the partition function in conjunction with the cluster expansion formalism. The implementation of the method with the help of the Alloy Theoretic Automated Toolkit (ATAK) is described and an application to Ni-Ni3Al interfaces is presented.

10:00 AM *KK8.3
Composition and Electronic Structure of Buried Interfaces and Point Defects Imaged at the Atomic Scale.
David A. Muller, Applied Physics, Cornell University, Ithaca, New York.

There is an intimate relationship between the electronic and physical properties of a material. Nowhere is this more pronounced than at interfaces, where the success or failure of a device, be it a turbine blade or a transistor, depends on the performance of the few monolayers. Atomic-resolution electron microscopy and spectroscopy is now capable of unraveling these bonding details at buried interfaces and clusters, providing both physical and electronic structure information. In this talk, the speaker will address imaging single dopant atoms or vacancies, allowing us to study the early stages of precipitate nucleation and growth, and identify the clusters responsible for electrical deactivation in integrated circuits. In fact, the same imaging technique in a modern transistor, the gate dielectric, is already little more than an interfacial layer just over 1 nm thick, and the fundamental physical limits to device scaling are set by the measured electronic structure. However, electronic structure characterization is complicated by the fact that the electronic properties of electron energy loss spectroscopy (EELS) measurements of grain boundaries in Ni_{2/3}Al using an atomic-sized beam show that the measured loss of s-d hybridization can be quantitatively related to the boundary cohesion, and the resulting transition from intergranular to transgranular fracture with boron doping. 1 P.M. Voyles, D. A. Muller, J. I. Grauz, P. H. Citrin, and H.-J. Gossmann, Nature, 416 826 (2002); 2 D. A. Muller et al, Nature, 390 758 (1997); 3 D. A. Muller et al, Phys. Rev. Lett. 75 4744 (1995).

10:30 AM #K8.4 TEM Characterization of Faceted Inclusions, Interfaces and Line Junctions. Ulrich Dahmen, NCEM, Lawrence Berkeley Laboratory, Berkeley, California.

With decreasing size of inclusions or precipitates, the effect of interfaces becomes more prominent. In the nanoscale regime inclusions are controlled by constraints that are negligible at larger sizes. Likewise, for strongly anisotropic interfaces, faceted junctions play a prominent role that increases with decreasing size. Direct observations by high resolution electron microscopy allow us to relate the size, shape and local interface structure to the behavior of nanoscale inclusions and interfaces. However, most electron microscopy studies of interfaces rely heavily on 2-D projections, neglecting variations in the third dimension. Here we show that the detailed 3-D shape of inclusions can have an important effect on their behavior such as melting or migration. This talk illustrates the atomic-scale structure of faceted interfaces and line junctions with examples from inclusions and grain boundaries. The three-dimensional distribution and shape of inclusions has been studied using tomographic reconstructions from high-angle tilt series. This structural information is related to dynamic observations on melting of Pb precipitates, Brownian motion of liquid metal inclusions in solid Al under kinetic limitation, and magic-size equilibrium shapes of solid precipitates in a solid matrix. We also present a new type of line dissociation at the intersection of grain boundaries and free surface, and provide evidence for local faulting effect. The importance of combining detailed atomic-scale characterization with observations of three-dimensional shape and dynamic behavior will be highlighted in a brief outlook on future directions in the field of nanoscale imaging and EELS. The talk is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

11:00 AM #K8.5 Edge Energies: Atomic Calculations of a Continuum Quantity. John C. Hamilton, Sandia National Laboratory, Livermore, California.

The present work was undertaken as part of an effort to understand the shape of Pb inclusions in an Al matrix. During that endeavor, a fundamental ambiguity in the definition of edge energies was discovered. In this talk, I will describe the ambiguity, propose a solution, and present a quantitative calculation of edge energies for free particles and for truncated octahedral shape. To the best of my knowledge, this defines the first atomic calculation of edge energies to be reported in the literature. The Wulff construction is a well-known graphical solution for the equilibrium shape of a crystal. The equilibrium shape minimizes the total surface energy, subject to the constraint of constant volume. For nano-objects, it is common to modify this equation by adding an edge energy term to the total interface energy. Theories for the equilibrium shape of nano-objects (including free particles, nano-dimensional structures on a surface, and other objects) often include edge energies. As the objects become smaller and smaller, edge energy becomes an increasing fraction of the total energy. This allows an evolution of the shape from free energy to the surface energy. Although it is common to invoke edge energies in discussing the shape of nano-objects, there do not appear to be any published quantitative calculations of edge energies. Such calculations are essential if we are to compare theories of equilibrium shapes with observations of shapes at the nanoscale. One might suppose that it would be straightforward to calculate edge energies using methods such as the embedded atom method (EAM) or density functional theory (DFT), since these methods are routinely used to calculate surface energies and interface energies. However, it turns out that it is not possible to formulate the calculation of edge energies atomistically, due to a fundamental ambiguity in the definition of edge energies. The problem arises because we are attempting to describe an atomic system using continuum concepts. In a continuum model, interface and surface energies are expressed as integrals over the interface and surface. When using this definition, I will describe an EAM calculation of the edge energy where a (100) facet meets a (111) facet, of the edge energy where a (111) facet meets a (111) facet, and of the vertex energies. In particular, I will give these values for a palladium particle.

11:15 AM #K8.6 Electronic Interface Properties of YBaCuO / LaCaMnO Superlattices. Hans-Ulrich Habermeier1, Jacques Chakhalian2, Christian Bernhard1 and Jochen Stahn3; IMPI-FKF, Stuttgart, Germany; 1Paul Scherrer Institute, Villigen, Switzerland.

Complex perovskite-type oxides exhibit a rich spectrum of functional responses including ferromagnetism, superconductivity, ferroelectricity etc. The groundstates of their electronic system is characterized by effects due to strong electron correlation and the energy scales for competing order are close together. An antiferromagnetic (=AFM) ground state of LaCuO4 converts into a superconductor upon hole doping; similarly, the antiferromagnetic ground state of LaMnO3 converts to a ferromagnet by introducing holes. We have fabricated YBaCuO/LaCaMnO superlattices and heterostructures by pulsed laser deposition and characterized the films structurally (X-ray diffraction, TEM) and with respect to their electronic properties by transport, magnetization and spectroscopic ellipsometry measurements. Detailed studies of the interfaces have been performed by neutron reflectivity and X-ray magnetic dichroism experiments. It could be shown that a magnetic moment in the cuprate layer is induced by the adjacent magnetic layer oriented antiferromagnetically to that of the manganite film. The implications of these findings for ferromagnetism in the cuprate and its role generating superconductivity will be discussed.

11:30 AM #K8.7 Atomic scale studies of complex oxide interfaces. Maria Varela1, Hans Christen1, Claudia Canton1, Klaus van Benthem1, Andrew J. Lupini1, Timothy Pennycook1, Stephen Pennycoke2, Weidong Luo3, Song Zhang1, Zhiqiang Duan1,2, Zsolt Szunerits1, Pablo Jonckheere1, Hannah Santamarina2, 1Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Dept. of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; 3GFMC Dept. Fisica Aplicada III, Universidad Complutense, Madrid, Spain.

Complex oxides with perovskite structure show a broad range of physical properties, from ferroelectricity to high Tc superconductivity, colossal magneto resistance (CMR), etc. When thin oxide films are combined into heterostructures, the physical properties of interest are often quite different from those of the bulk constituent materials. Understanding these properties relies on a comprehensive analysis at the atomic scale of the structure, chemistry and electronic properties of the interfaces. Scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS) are techniques ideally suited for this aim, since the success of aberration correction has pushed the achievable spatial resolution in STEM into the sub-Angstrom regime. This work will present several examples of atomic resolution studies of the relationship between structure, chemistry, and electronic properties of oxide interfaces in epitaxial thin film structures. In particular, we will focus on the study of interfaces in CMR manganese based heterostructures, such as superconducting/ferromagnetic YBa2Cu3O7-x/Lao.67CaO0.33MnO3 (YBCO/LCMO) superlattices or antiferromagnetic/insulating LaMnO3/SrTiO3 (LMO/STO) heterostructures. EELS images show that these are abrupt, coherent interfaces. Atomically resolved EELS becomes then a most valuable tool to ascertain the interface electronic properties. In YBCO/LCMO superlattices extensive charge transfer between the ferromagnet and the superconductor is found. In the LMO/STO case the Mn 3d band occupation also changes dramatically at the interface, suggesting the possibility of electronically doping induced interface magnetism. Acknowledgements: This research was sponsored by the Laboratory Directed Research and Development
Interfacial Structure and Defect Energy in Nanoscale 
CeO2/ZrO2 Films: A Molecular Dynamics Study.
Michael Dyer1, Anter El-Azab2, Fei Gao2 and Ram Devanathan2; 
1Mechanical Engineering, Florida State University, Tallahassee, Florida; 2Pacific Northwest National Laboratory, Richland, Washington.

Ceria and zirconia ceramics are well known for their ability to conduct oxygen ions, making them useful in constructing devices such as oxygen sensors and solid-oxide fuel cells. Increasing the ionic conductivity of these materials is a major point of interest, as this could result in an increase in efficiency and a decrease in operating temperature. Recent experimental results have shown that multi-layered alternating CeO2/ZrO2 thin films that are alloyed with Gd2O3 exhibit ionic conductivity that is superior to the individual monolithic materials. The enhanced ionic conductivity in these layered structures is attributed to the interfacial effects. Analytical modeling has shown that there are two possible mechanisms that lead to changes in the ionic conductivity: (a) the deviation of the equilibrium concentration of oxygen vacancies in the layered structure from the mean value due to thermodynamic equilibrium across the interfaces, and (b) the changes in the defect formation energies and kinetic barriers due to interaction with the epitaxial strain, the level of which is determined by the layer thickness and formation of interfacial dislocations. A molecular dynamics (MD) study is performed to determine the interfacial and defect structures in pure and Gd-doped layered CeO2/ZrO2 films, and the results are compared with the recent experimental observations.