SYMPOSIUM KK

Solid-Solid Interfaces from Observation to Modeling

November 28 - December 1, 2005

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* Invited paper

SESSION KK1: Grain Boundaries - Ceramics and Liquids
Chair: Eugen Rabkin
Monday Morning, November 28, 2005
Fairfax A (Sheraton)

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Abstract Withdrawn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-Seok Nam[1], Mikhail I. Mendelev[2] and David J. Srolovitz[1]; [1]Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; [2]Materials 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 dynamics 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-level scale as a function of 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. It is now 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 briefly reviewed in this paper. The main emphasis of the paper will be the study the 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 boundary migration. 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 LPS to be understood.

10:15 AM *KK1.4
Kinetics of High Temperature Liquid Spreading.
Antoni P. Tomsia and Eduardo Saiz; Materials Sciences Div., Lawrence Berkeley Lab, Berkeley, California.

The spreading of high temperature liquids (molten 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 or 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 delineate 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-AC03-76SF00098

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

Crystallization behavior of $CaAl_4O_7$ (calcium dialuminate, CA_2) and $CaAl_{12}O_{19}$ (calcium hexa-aluminate, CA_6) were studied using two different experimental approaches. In the first route, polymeric precursors for the CA_2 and CA_6 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 that amorphous powders with CA_6 stoichiometry first crystallized into γ-Al_2O_3 at 930°C and then transformed into CA_6 at 1175°C. For the second approach amorphous thin films of CA_2 and CA_6 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 CA_6 films wetted the substrate surface, CA_2 films dewetted sapphire. No reaction layer was observed between the wetting CA_6 films and the substrate. However an interfacial reaction layer was observed between the dewetted CA_2 droplets and the substrate. This reaction layer at the interface was identified as γ-Al_2O_3 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-confined″ crystallization behavior of the various calcium aluminate phases and the equilibrium-phase diagram of the CaO-Al_2O_3 system.

11:00 AM KK1.6
Interfacial Adsorption of Rare Earth Elements in Silicon Nitride Ceramics. Paul Becher[1], Gayle Painter[1], Naoya Shibata[2], Klaus van Benthem[1], Frank Averill[3] and Stephen Pennycook[1]; [1]Oak Ridge National Lab, Oak Ridge, Tennessee; [2]University of Tokyo, Tokyo, Japan; [3]University 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 atomistic 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.
Yukio Sato[1], James P. Buban[2], Teruyasu Mizoguchi[2], Naoya Shibata[2], Fumiyasu Oba[3], Masatada Yodogawa[1], Takahisa Yamamoto[1] and Yuichi Ikuhara[2]; [1]Dapartment of Advanced Materials Science, The University of Tokyo, Tokyo, Japan; [2]Institute of Engineering Innovation, The University of Tokyo., Tokyo, Japan; [3]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan.

ZnO polycrystals are widely utilized as surge protecting devices

(varistors) because of their highly nonlinear current-voltage (I-V) characteristics. It is recognized that the nonlinear I-V characteristics should be ascribed to double Schottky barriers (DSB) formed at grain boundaries [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 has not been fully understood yet. Here, we have performed a detailed investigation of ZnO single grain boundaries by combining experimental and theoretical techniques [2,3]. Undoped and Pr-doped ZnO bicrystals were fabricated to exhibit the same misorientation angle, corresponding to a sigma value of 7. I-V 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 fourfold coordination in bulk ZnO. Theoretical calculations predicted 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 nonlinear I-V characteristics. The Pr-doped boundary was found to have a single type of structural unit containing over-coordinated sites, which is similar at 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) revealed that the charge 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 enhance the formation of Zn 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 must be a key factor for the formation of the DSBs 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.

11:30 AM KK1.8
Investigating the Atomic Origins of Mechanical Strengthening of Alumina Grain Boundaries via Y-doping.
James Paul Buban[1], Katsuyuki Matsunaga[1], Naoya Shibata[1], Takahisa Yamamoto[2] and Yuichi Ikuhara[1]; [1]Institute of Engineering Innovation, University of Tokyo, Tokyo, Japan; [2]Advance Materials, University of Tokyo, Chiba, Japan.

It is well known that the addition of small amounts of rare earth elements strongly increases the mechanical strength of fine-grained polycrystalline alumina (Al_2O_3). In particular high-temperature deformations of polycrystalline alumina can be drastically reduced. Recent work has shown that Y strongly segregates to the grain boundary plane [1], but the segregation mechanism as well as the grain boundary strengthening mechanism is poorly understood. Here, we will show an atomic scale model of grain boundary doping in alumina, based upon both atomic-scale resolution Z-contrast imaging in the scanning transmission electron microscope (STEM) and a combination of theoretical techniques – static lattice calculations as well as first principles calculations. Microscopy was performed on a pair of bicrystals of the same misorientation angle (18° corresponding to a $\Sigma 31$) with the only difference being the grain boundary of one bicrystal was doped with Y. The STEM results show that atomic structures of both the undoped and Y-doped grain boundaries are nearly identical apart from the presence of Y in the doped specimen. In particular structure units composed of rings of 7 aluminum ions, exhibiting large tensile strain, are periodic along grain boundary plane. We observed that with the Y ions are found to segregate periodically to specific sites at the center of the 7-membered rings along the grain boundary. Using static lattice calculations (based on Buckingham type potentials), we found that the lowest energy grain boundary structure matched well with the structure found in the image of the undoped grain boundary. Furthermore, investigation of the energetics of Y-segregation to various sites along and near the grain boundary plane revealed that the center of the 7-membered ring is indeed the most energetically favorable site for the segregation of Y. Finally, first principle calculations indicate that the bonding strength is increased when Y segregates to the grain boundary plane. Our overall findings show that Y, having a large ionic radius, selectively segregates to very specific grain boundary sites by a strain relaxation mechanism at the expanded regions, and furthermore, strengthens the boundary's weakest areas by altering the local atomic bonds. [1] Matsunaga, K., Nishimura, H., Muto, H., Yamamoto, T., & Ikuhara, Y., *Appl.Phys.Lett.*, 82, 1179-1181 (2003). [2] Chen, J., Xu, Y.N., Rulis, P., Ouyang, L.Z., Ching, W.Y., *Acta.Mater.* 53, 403-410 (2005)

11:45 AM KK1.9
Direct Observation of Cooperative Doping Mechanisms at Grain Boundaries in Ca-doped $YBa_2Cu_3O_{7-\delta}$.
Robert Friedrich Klie[1], James P Buban[4], Maria Varela[2], Alberto Franceschetti[2,3], Christian Jooss[6], Yimei Zhu[1], Nigel Browning[5], Sokrates Pantelides[3,2] 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; [6]Institut 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 $YBa_2Cu_3O_{7-\delta}$. 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 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 increased. 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
Distinct and Common Features of Grain Boundaries in Iridium when Compared with Other FCC Metals. Marc J. Cawkwell[1], Hyoung 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 mediated, as in any other FCC metal, by 1/2<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 many-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 us to identify those grain boundary 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, related to directional bonding, are responsible for its propensity to intergranular fracture. This research was supported by the DOE BES grant. No. DE-PG02-98ER45702 (MJC, VV).

2:00 PM KK2.2
Scanning force microscopy study of grain boundary grooving in molybdenum bicrystals. Eugen Rabkin[1], Angelina Gabelev[1], Leonid Klinger[1], Valery N. Semenov[2] and Sergei I. Bozhko[2];

[1]Department of Materials Engineering, Technion, Haifa, Israel; [2]Institute of Solid State Physics, Chernogolovka, Russian Federation.

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 and sharp 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 of the grooves. It was demonstrated that disregarding of surface anisotropy results in serious 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 been extended to the study of longer-range correlations. In the present work, we explore the correlations among special and general (i.e., non-special) boundaries at longer length scales by calculating the configurational entropy of grain boundary structures. We find that correlations among grain boundary types exist to at least the third nearest-neighbor level even when there is no spatial correlation in the crystallographic texture of the material. Furthermore, we show that the percolation threshold for special boundary connectivity is strongly affected by these higher-order crystallographic constraints.

3:30 PM *KK2.4
Finite size effects on grain boundary structures and interactions with dislocations. Emmanuelle A Marquis, Douglas L. Medlin and Francois Leonard; Materials Physics, Sandia National Laboratory, Livermore, California.

The emergence of nanocrystalline materials has raised the issue of finite 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 boundary energy with translation) and local elastic strain at 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 structure of $\Sigma 3$ {112} grain boundaries. 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 $\frac{1}{3}$<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 considered 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 properties and structure of the emitting interfaces, however, remains far from clear. Our work points out the relative importance of interfacial and elastic energies in controlling the equilibrium structures of such configurations.

4:00 PM KK2.5
Accommodation of Grain Boundary Coherency Strain by Interfacial Disconnections. Douglas L. Medlin[1], D. Cohen[1], R. C. Pond[2], J. A. Brown[3] and Y. Mishin[3]; [1]Materials Physics Dept., Sandia National Laboratories, Livermore, California; [2]Department of Engineering (Materials), University of Liverpool, Liverpool, United Kingdom; [3]School of Computational Sciences, George Mason University, Fairfax, Virginia.

The specific mode by which strain is accommodated at a grain boundary depends ultimately on the defects that are admissible at the interface. Understanding the structure and topology of such defects is, therefore, vital to connecting atomistic 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 step and dislocation character) at a 90 degree <110> tilt boundary in gold. This grain misorientation is interesting because while it aligns several pairs of low index planes and directions, the ratios of periodic lengths in all the parallel directions (with the exception of the shared <110> axis) 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 coherency across the {111}/{112} terraces. This structural relaxation is markedly different from that at {100}/{110} grain boundary facets in this same system, for which previous observations have found an incoherent structure with no strain 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
Atomistic structure of asymmetrical grain boundaries in FCC metals. Juan Anthony Brown[1], Yuri Mishin[1] and Douglas L. Medlin[2]; [1]School of Computational Sciences, George Mason University, Fairfax, Virginia; [2]Materials 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 GBs in polycrystalline materials 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 dissociated 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 symmetrical one develop faceted 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 atomistic input for the GB energies. The effect of applied shear stresses of 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 applied shear stresses on their 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 sturcture 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 Ramasubramaniam[1] and Vivek B. Shenoy[2]; [1]California Institute of Technology, Pasadena, California; [2]Division 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 ambiguities 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 for a range of grain-boundary energies 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 know to lead to deviations from Mullins' $t^{1/4}$ 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 from energetic 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 Boundary Faceting. Denis Boyer and David Romeu; 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 boundary structures, 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 cases seem to emerge: facets can either remain of finite length on the nanometer scale, or grow as a power law of time (or possibly slower at very large times). Our predictions compare well with experimental HREM observations of grain boundaries in various metals and ceramics.

SESSION KK3: Grain Boundary Migration and Diffusion
Chair: Emmanuelle Marquis
Tuesday Morning, November 29, 2005
Fairfax A (Sheraton)

8:30 AM *KK3.1
Atomistic Mechanism for Grain Boundary Migration: Analysis of MD Simulations of a Σ5 Boundary.
David J. Srolovitz and Hao Zhang; Mechanical & Aerospace Eng., Princeton University, Princeton, New Jersey.

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 a series of Σ5 tilt 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 the 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 slows 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 a tricrystal with Σ5, Σ5, and Σ25 grain boundaries 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-Amissah[1], Jeffrey M. Rickman[2], Helen M. Chan[2] and Martin P. Harmer[2]; [1]Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania; [2]Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania.

The impact of a complex microstructure on polycrystalline diffusion is investigated using both numerical and analytical methods. The 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. Diffusive behavior is quantified by obtaining 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. W. Cahn[2], Y. Mishin[1], A. Suzuki[1] and J. E. Taylor[3]; [1]School of Computational Sciences, George Mason University, Fairfax, Virginia; [2]Materials Science and Engineering Lab., National Institute of Standards and Technology, Gaithersburg, Maryland; [3]Courant 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, superplasticily, 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. Cahn[1], Y. Mishin[2] and A. Suzuki[2]; [1]Materials Science and Engineering Lab., National Institute of Standards and Technology, Gaithersburg, Maryland; [2]School 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.

At the tip, a groove forms to reduce the combined free surface and grain-boundary energy. The groove is small and adjusts quickly. Thus, in both methods, it can be treated as migrating at constant speed. We have studied this migrating groove profile assuming that the surface evolves by surface diffusion and that the surface energy is isotropic [Min & Wong, Acta Mater. 50, 5155 (2002)]. We found that the grain-boundary tip is tilted in the migration direction with an inclination angle q that depends only on the dihedral angle. This work extends the analysis to strongly anisotropic surface energy. We find that when the surface energy is anisotropic the inclination angle q depends also on the crystallographic orientations of the bicrystal. If the exposed groove surface is far from the facet orientations, then the groove is smooth and has the same shape as an isotropic groove except that the size is reduced by a factor that depends on the degree of anisotropic. We will present a systematic analysis of the effect of surface energy anisotropy on migrating grain-boundary grooves.

11:15 AM KK3.7
Phase Field Model of Solid-State Sintering. Yu U. Wang, Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia.

Sintering is a well-known complicated material process involving multiple diffusion mechanisms (along surface and grain boundary, through lattice and vapor), grain boundary migration, particle rigid-body translation and rotation. The high-diffusivity paths along the solid-solid interfaces, i.e. grain boundaries, play a key role in the densification of sintered powder compact. The diffusion of atoms from grain boundaries to nearby high-curvature growing neck surfaces leads to approaching of centers of particles through rigid-body motions. This work develops a phase field model of solid-state sintering, which treats the rigid-body motions of particles and surface diffusion, grain boundary diffusion, volume diffusion, vapor transport, as well as grain boundary migration. Consideration of rigid-body motions results in modifications to both Cahn-Hilliard nonlinear diffusion equation and Ginzburg-Landau (Allen-Cahn) structural relaxation equation. Computer simulations are presented.

11:30 AM KK3.8
Microstructure Evolution in Nanocrystalline Ni at High Temperature. Diana Farkas, Materials Science, Virginia Tech, Blacksburg, Virginia.

Microstructure evolution in digital samples of nanocrystalline Ni was investigated at high temperatures using fully atomistic 3D molecular dynamics simulations. The digital samples initially contain 15 grains of random orientations and 5 nm average grain size. The simulations utilize embedded atom empirical potentials to study the motion of the various grain boundaries present upon heat treatments at temperatures from 800 to 1300 K for times up to 6 ns. Significant grain boundary mobility is observed and some grains are seen to significantly grow at the expense of others. The process is also followed from an energetic point of view, with a total energy evolution of the sample decreasing as a function of time with a square root dependence. The relationship of grain boundary mobility and grain boundary structure in these samples is discussed.

11:45 AM KK3.9
Observation of Enhanced Diffusion at Triple Junctions in Copper. Raghavan Narayanan, Mysore A Dayananda and Alex King; School of Materials Engineering, Purdue University, West Lafayette, Indiana.

It has been hypothesized that, at low temperatures, diffusion through triple junctions can be faster than either grain boundary diffusion or bulk diffusion. We have conducted diffusion experiments in the copper-nickel system by coupling tri-crystals of copper, grown using the vertical Bridgman technique, with well-prepared polycrystalline nickel specimens. The diffusion couples were annealed for various times at 973K. Elemental concentration maps of the grain boundaries and triple junctions were obtained using an electron microprobe, and we found the depth of nickel penetration along the triple junctions to be 3-4 times greater than that along the grain boundaries. Our experiments have been designed with a view to allowing for comparison with results from atomistic models, and the prospects for this are explained and discussed. Acknowledgment: This work is supported by the US Department of Energy, under contract number DE-FG01-01ER45940.

SESSION KK4: Alloys and Inclusions
Chair: David Seidman
Tuesday Afternoon, November 29, 2005
Fairfax A (Sheraton)

1:30 PM *KK4.1
Atom-Probe Tomography Studies of the γ/γ' Interfacial Properties in a Model Ni-Based Superalloy.
Chantal K. Sudbrack[1], Kevin E. Yoon[1], Ronald D. Noebe[2] and David N. Seidman[1]; [1]Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]NASA Glenn Research Center, Cleveland, 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-naonometer compositional profiles as they evolve 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 sponsored 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 Mao[1], Chantal K. Sudbrack[1], Kevin E. Yoon[1], Georges Martin[1,2] and David N. Seidman[1]; [1]Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]CEA, 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 Gouldstone 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 efforts have 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 'non-equilibrium' interfaces and their implications for novel material 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-MRSEC 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 examples illustrating 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 strategies to design and control interfacial character; 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 TiO_2. Jun He[1], Michael M. Finnis[2] and Susan B. Sinnott[1]; [1]Dept. of Materials Science and Engineering, University of Florida, Gainesville, Florida; [2]Atomistic 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 TiO_2 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, defect levels for 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-0303279.

3:45 PM KK4.5
A High-Resolution Electron Microscope Study of Phase Transformation and Recrystallization in Two-Phase Titanium Aluminide Alloys. Fritz Appel, Institute for Materials Research, GKSS Research Centre Geesthacht, Geesthacht, Germany.

Titanium aluminide alloys based on the intermetallic phases gamma-TiAl and alpha-2-Ti3Al suffer from insufficient creep resistance and structural stability. Long-term creep leads to a conversion of the lamellar morphology into a fine speroidized microstructure due to phase transformation and recrystallization. The paper presents a high-resolution electron microscope study of the relevant microprocesses. The results imply that the structural changes are closely related to mismatch structures and coherency stresses present at the interfacial boundaries. Coarsening probably arises from the reduction of surface energy attained by the elimination of microstructural features with small principal radii of curvature. Further, phase transformation and recrystallization processes are driven by non-equilibrium phase composition and significant chemical disorder, which in Ti-rich two-phase alloys can easily be retained after high temperature heat treatments followed by fast cooling. The alpha-2/gamma phase transformation leads to a heterogeneous precipitation of interstitial elements that had been solved in the prior alpha-2 phase. The experimental findings will be used to model the creep behaviour of the material.

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

The nucleation and growth of new phase has been studied in supersaturated Cu-Ti and Cu-Co alloys using the tomographic atom probe (TAP). Besides the well known spherically shaped nuclei cigar 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-Mn alloys by using both TAP and SANS. It could 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 and Silicon Surfaces. Levent Inci, 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 large-scale molecular-dynamics (MD) simulations are utilized to elucidate the interactions between the atoms at the Al-Si interfaces during room-temperature plastic deformation of these materials. The Modified embedded atom method (MEAM) potential and the Verlet integration algorithm 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 system has been studied to develop a 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 for these systems have been studied. Point 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.

4:30 PM KK4.8
The Displacive-Diffusional Transformation of $R_5(Si,Ge)_3$ in $R_5(Si_x,Ge_{1-x})_4$ Complex Alloys, where R is Gd, Tb, Dy and Er. Ozan Ugurlu[1], Leonard Scott Chumbley[1], Thomas A. Lograsso[2] and Deborah L. Schlagel[2]; [1]Materials Science and Engineering, Iowa State University / Ames Lab., Ames, Iowa; [2]Ames Laboratory, Ames, Iowa.

$R_5(Si_x,Ge_{1-x})_4$ alloys are prime candidates for use in magnetic refrigeration due to their giant magneto caloric effect. The matrix phase typically consists of a complex monoclinic and/or orthorhombic crystal structure, depending upon temperature, composition and applied magnetic field. Recently, an hexagonal second phase with a composition of $R_5(Si_x,Ge_{1-x})_3$ has been observed in these alloys using electron microscopy. This second phase has a shape of thin-plates and grows in 2 irrational directions with an 80ø angle between them. Electron diffraction using transmission electron microscopy (TEM) was used to determine the orientation relationship as [10-10](1-211)p//[010](10-2)m. The solid-solid interface between the second phase and matrix has been determined as having a step-like structure using high resolution electron microscopy (HREM). Images coupled with diffraction patterns showed that (0001)p and (100)m planes are edge-to-edge along the interface. Invariant line theory and Dg approach can be used to explain the orientation of the interface boundary, and the transformation mechanism proposed is best described as being both displacive and diffusional in nature.

4:45 PM KK4.9
Interfacial Structures for Martensitic Phases in Metastable β Ti-Mo-based Alloys. Lichun Zhang[1], Mark Aindow[1], S. P. Alpay[1] and Ming Wu[2]; [1]University of Connecticut, Storrs, CT, Connecticut; [2]Memry 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 pseudoelastic 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 α 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 α triple prime. The in-situ XRD data indicate that α triple prime adopts an intermediate crystal structure closely related to those of β and α double prime. This is only retained in TEM specimens from samples strained beyond the pseudoelastic limit wherein {332} twins form within the α triple prime laths. In these cases the β/α 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.

SESSION KK5: Poster Session: Solid/Solid Interfaces
Chairs: John C. Hamilton, Eugen Rabkin, David Seidman and Donald Siegel

KK5.1
Formation of Voids in Diffusion Bonding of Copper Alloys to Nickel Metals. Hideyuki Ikeda[1], Hirohisa Masumoto[2], Kazumasa Nishio[3] and Toshitada Shimozaki[4]; [1]Mechanical Engineering, Kagoshima National College of Technology, Aira-gun, Kagoshima, Japan; [2]Environmental Symbiosis Engineering, Kurume Institute of Technology, Kurume, Fukuoka, Japan; [3]Biological Functions and Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka, Japan; [4]Center for Instrumental Analysis, Kyushu Institute of Technology, Kitakyushu, Fukuoka, Japan.

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 copper alloy 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)-2x2 surfaces and interfaces. Shingo Tanaka[1], Yasushi Hoshino[2,3], Tomoyuki Tamura[4], Shoji Ishibashi[4], Yoshiaki Kido[2] and Masanori Kohyama[1]; [1]MATSCI-UBIQEN, AIST, Ikeda, Osaka, Japan; [2]Dept. of Physics, Ritsumeikan Univ., Kusatsu, Shiga, Japan; [3]Dept. of Electronic Science and Engineering, Kyoto Univ., Kyoto, Kyoto, Japan; [4]RICS, AIST, Tsukuba, Ibaraki, Japan.

Silicon carbide (SiC) is expected as 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/oxide/SiC (MOS) interfaces. In this paper, we have performed the atomic and electronic structures of 6H-SiC(000-1)-2x2 surfaces and interfaces using the first-principles norm-conserved pseudopotential (NCPP) method and the projector augmented wave (PAW) method. First we developed an appropriate supercell of the (000-1)-2x2 surface and obtained stable atomic configurations through relaxation processes by Hellmann-Feynman forces, which converged within 0.01 eV/nm per each 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 charges. The present structure minimizes the number of dangling bonds and also minimizes the total energy. However, there remain two kinds of dangling bonds at 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 as the chemical potential of Si. The result shows that in SiC system the dangling bond of C is energetically unstable rather than that of Si. The oxide/SiC, metal/SiC and metal/oxide/SiC interfaces have been treated. In the oxide interface, we treated the several models of Si2O3 and Si2O5 silicate adlayers and compared with the $sqrt3$x$sqrt3$ 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/oxide/SiC interfaces. The results show an obvious effect of metal species. This work was performed as a part of National Research Grid Initiative (NAREGI) by Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.
[1] Y. Hoshino, R. Fukuyama, Y. Matsubara, T. Nishimura, S. Tanaka, M. Kohyama, and Y. Kido, Phys. Rev. B 73, 195331 (2005). [2] W. Lu, P. Krueger, and J. Pollmann, Phys. Rev. B 61, 13737 (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, 2672 (2000).

KK5.3
AR-XPS study of the chemical bonding state at the interface of bi-layer systems. Yasuyuki Nakagawa and Hiroshi Kurokawa; Advanced Technology R&D Center, Mitsubishi Electric Corporation, Amagasaki, Japan.

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 ion 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 on the distribution of the chemical bonding state within a few nm from the film surface. Al2O3 (3nm thick)/Ta2O5 (100nm thick) and Ta2O5 (3nm thick)/Al2O3 (100nm thick) films were deposited on silicon wafers by reactive sputtering in Ar/O2 mixture gas and electron-beam gun evaporation. Metal targets were used 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 Al-Ka monochromatic X-rays. The Ta4f spectrum of the Al2O3/Ta2O5 film deposited by sputtering was decomposed 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 tantalum compound. As for the Al2O3/Ta2O5 film deposited by evaporation, only the Ta-O doublet peaks were observed in the Ta4f spectra. On the other hand, we could not see any Ta-X or Al-X peak in the spectra of Ta2O5/Al2O3 films, either by sputtering or evaporation. These results show that the chemical state of the atoms at the interface of (Al2O3-Ta2O5) bi-layer systems is sensitive not only to the deposition method but also to the order of the materials.

KK5.4
Study on the Transport Behavior and Mechanism of Ag/TCNQ 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 structures 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 films 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 tetracyanoquinodiimethane (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 transprot 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 1 x 10-3Pa. 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 ambinet environment. The transport behavior in the film was studied by using transmission spectrum. After the sample was prepared, its transmission spectra was continuously recorded by spectroscopy during annealing. The shape change of the spectrum curves showed the transport process of Ag/TCNQ bi-layer film. When the shape of the spectrum curve stoped to change, it was considered that the transport was completed and the transport time was confirmed. By examining the evolution of the transport time of films with different thinckness, a abnormal accelectrated transport phenomenon was observed with the decrease of the thickness of the film. When film was relatively thick (>32.5nm), transport precoss 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, thansport 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 behaviour. It was found 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; 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 (7,7,8,8-tetracyanoquinodimethane) on glass substrate under the pressure of 1?10-3 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 complex can be formed by Cu+ 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 complex in 80%, 81%, 86%, 90%, 92% and 93% humidity has been measured, which was 120, 90, 30, 20, 18, and 17minutes 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 environmental 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 is formed respectively through solid chemical 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 Hashibon[1,2], Peter Gumbsch[1,2], Christian Elsaesser[1] and Yuri Mishin[3]; [1]Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany; [2]Institut fuer Zuverlaessigkeit von Bauteilen und Systemen IZBS, University of Karlsruhe, Karlsruhe, Germany; [3]George 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 fcc/bcc heterophase boundaries 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 by the addition of angular-dependent interactions. 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 Tang[1], Ana Ramos[2,1], Sung-Yoon Chung[3], Martine Gautier-Soyer[2], Rowland M. Cannon[4] and Yet-Ming M. Chiang[1]; [1]Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; [2]DSM/DRECAM/SPCSI, CEA Saclay, Gif sur Yvette, Cedex, France; [3]Materials Science and Engineering, Inha University, Inchon, South Korea; [4]Lawrence Berkeley Laboratory, Berkeley, California.

We studied the equilibrium structures of surficial oxide 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 700-1100C, in order to systematically *control* the ambient oxygen activity at extremely low levels. Angle-resolved XPS, AFM, and TEM measurements were then performed to determine the average coverage, stoichiometry and structure of the oxides. At a wafer temperature of 700C, it was found that the saturation oxygen activity corresponding to bulk Si/SiO2 equilibrium does not result in the growth of a *wetting* 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, Winnie Wong-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 chemistries. 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. Rene Vissers[1], Calin D. Marioara[2], Marijn A. van Huis[3], Sigmund J. Andersen[2], Jouk Jansen[3], Anders G. Froseth[4,1] and Randi Holmestad[1]; [1]Institutt for Fysikk, NTNU, Trondheim, Norway; [2]Dept. of Synthesis and Properties, SINTEF, Trondheim, Norway; [3]Kavli Institute of Nanoscience, TU Delft, Delft, Netherlands; [4]Paul Scherrer Institute, Villigen, Switzerland.

The attractive physical and chemical properties (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, Multi Slice Least Squares (MSLS) structure refinement and Density Function Theory (DFT) modelling - has revealed the existence of a whole new range of precipitate structures: Super Saturated Solid Solution → clusters with varying Mg and Si contents → GP zones → β" → β' + B' + U1 + U2 → —*betaup*— (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 (owing to the high scattering probability of electrons) still obtain 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 these phases. We present results of the 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. Liverios Lymperakis and Joerg Neugebauer; Max-Planck-Institut fuer Eisenforschung GmbH, Duesseldorf, 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 $ab-initio$ accuracy and has been applied to an isolated dislocation. In the present 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 aluminum. In a first step the strain field arising from an infinite 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 describe 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 macroscopically relevant single isolated grain boundary, while the asymptotic limit of very small but still finite tilt angles corresponds to the macroscopically relevant single isolated dislocation. Based on this phase diagram we address the issue of grain boundary stability and we discuss recent experimental results. [1] L. Lymperakis, J. Neugebauer, M. Albrecht, T. Remmele, and H.P. Strunk, Strain induced metallization and deep electronic states around threading dislocations in GaN, Phys. Rev. Lett. **93**, 196401 (2004) .

KK5.11
Innovations in atom-probe tomography: observations of solid-solid interfaces. David J. Larson, Keith Thompson and Thomas F. Kelly; Imago Scientific Instruments, Madison, Wisconsin.

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 analyze metal specimens formed in 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 atomic-scale compositional analysis of a variety of materials. The materials can be prepared in either the traditional needle-shaped geometry or in the form of microtips residing on planar surfaces. The local electrode technology also enables faster data collection rates and a larger field of view than conventional atom probes. Typical images acquired using this technique have a cross-section of up to ∼100 nm and require only hours (as opposed to days) of data collection time. Site specific sample preparation allows one to isolate a small, localized feature such as a grain boundary or a semiconductor transistor region and create a wide field-of-view atom 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 crosses a multitude of disciplines including metallurgical, thin film, semiconductor, and organic.

KK5.12
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.[1] Rare earth metals, 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 delocalised surface electronic structure. We present here an STM study of the behaviour of holmium on 6H-silicon carbide(0001) and how it compares with that on Si(111). $\frac{1}{2}$ 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.I. Johansson, Phys. Stat. Sol. (b) 202, 501 (1997)

KK5.13
Abstract Withdrawn

KK5.14
HRTEM and ab-initio calculation analysis of metallic ion implanted silicon grain boundaries. Norihito Sakaguchi, Kentaro Yonezuka, Rei Kokado and Hideki Ichinose; CAREM, Hokkaido University, Sapporo, Japan.

Unique atomic structure of a coincidence grain boundary has a potential for the development of quantum devices, namely, quantum dot, quantum wire, etc 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 (accelerate voltage; 300 keV and 400 keV) installed at CAREM, Hokkaido University was employed. Resolution of the MB-HVEM is shown to be 0.118 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 substitution site of implanted metallic ions in a periodic coincidence boundary, collaborating with ab-initio calculation.

KK5.15
Si Ridges in Laser Processing for TFT Fabrications: Formation and Planarization. Jaehyun Moon[1], Choong-Yong Sohn[2], Choong-Heui Chung[1], Yong-Hae Kim[1] and Jin Ho Lee[1]; [1]Basic Research Lab., Electronics and Telecommunications Research Institute, Daejeon, South Korea; [2]LCD R&D Center, LG-Philips, Anyang, South Korea.

The majority of thin film transistor (TFT)s have a structure of a Si active layer supported by a SiO2 buffer layer. In the TFT processing route, active layer forming Si layer is firstly deposited in 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 supporting phase, the layer stacking is inherently meta-stable. 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 Si ridges formed after laser crystallization of a-Si films have been studied means of atomic force and secondary electron microscopies. 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 crystallizing 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 point, re-emering 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.

KK5.16
Structural Investigations of the interface between Cu (100) and Cu2O oxide island. Xuetian Han and Judith C Yang; Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Surface oxidation processes play critical roles in environmental stability, high temperature corrosion, electrochemistry and catalysis. Thin oxide films, formed by direct reaction between metal surfaces and gaseous O2, and are also widely used as sensors, dielectrics, and corrosion inhibitors. We have extensive 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 heteroepitaxy, 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.

KK5.17
B2-Structures: A Statistical-Thermodynamic Model for Ordering Phenomena. Olga Semenova[1], Regina Krachler[2] and Herbert Ipser[1]; [1]Department of Inorganic Chemistry - Materials Chemistry, University of Vienna, Vienna, Austria; [2]Department 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 predict 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.

KK5.18
Ceria Zirconia Interfaces Examined by Modeling and Microscopy. Ram Devanathan, Fei Gao, Chongmin Wang, Suntharampillai Thevuthasan, William J Weber and Subhash C Singhal; Pacific Northwest National Laboratory, Richland, Washington.

We have used atomistic simulation and high-resolution transmission

electron microscopy (HRTEM) to examine the structure of the interface between yttria-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 from a cubic CeO_2 film grown epitaxially on YSZ that show misfit dislocations occurring with a uniform spacing of about 3.3±0.5 nm.

KK5.19
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. Hideki Ichinose[1], Norifumi Sakaguchi[1], Naoki Takayanagi[1], Hideyo Ohkushi[2] and Hideyuki Watanabe[2]; [1]Center for Advanced Reserach of Energy Conversion Materials, Hokkaido University, Sapporo, Japan; [2]The Diamond Research Center, AIST Tsukuba, Tsukuba, Japan.

Since any extreme semiconductor devises 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 newly designed ECR-CVD system. A large scale 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 impunity 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. Atomic resolution HVTEM 0.1nm in resolution at 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. Detailed investigation by EELS, however, showed that there present quite small amount of oxygen in the interface. An atomic structure image which represent 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 V-I 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 Spinodal Decomposition. Yongwoo Kwon[1], Katsuyo Thornton[2] and Peter W. Voorhees[1]; [1]Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]Materials Science and Engineering, University of Michigan at Ann Arbor, Ann Arbor, Michigan.

Spinodal decomposition is observed in a variety of materials ranging from polymers to metals. This process frequently produces a complicated and highly interconnected 3D interfacial 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, FR2797, 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 calculations. 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-TM (TM = 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-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-2001-00584. 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 Tolkiehn and Dmitri V. Novikov; HASYLAB, DESY, Hamburg, Germany.

We propose a novel method for the investigation of dopant and adsorbate atom positions in single crystal materials with high mosaicity. 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 mosaic copper gold alloy sample and demonstrate the determination of the La and Mn atom positions in a mosaic lanthan strontium manganate crystal. The new kinematical X-ray standing waves (KXSW) method can be applied to natural minerals, metallic and organic single crystals, and for the study of interface and surface processes. [1] J. Zegenhagen, Surf. Sci. Rep. 18, 202 (1993) [2] M. Tolkiehn, 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 determined the structure of several surface oxides on Ru, Pd, Rh and AlNi 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 ORhO 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

almost two decades [2-3] as a model for technologically important oxide supported catalysts. Despite large effort, its structure has yet remained unresolved. Again, combining STM with DFT finally resolved the structural puzzle [4]. The stoichiometry of the film is determined to be ...$(NiAl)_4$-$Al_4O_6Al_6O_7$, deviating from the usually assumed formal Al_2O_3 stoichiometry. The topmost oxygen atoms are pyramidally and tetrahedrally coordinated, as suggested by room temperature STM images. The present model also reproduces measured core level shifts [2] and the high-resolution electron-energy-loss spectra (HREELS)[3]. The solution of the structure was the starting point to determine the structure of the domain boundaries and the nucleation centers of Pd clusters (which predominantly sit at domain boundaries) as well as of Pt clusters (which also nucleate in undisturbed unit cells). [1] J.Gustafson, A.Mikkelsen, M.Borg, E.Lundgren, L.Köhler, G.Kresse, M.Schmid, P.Varga, Y.Yuhara, X.Torrelles, C.Quiros, J,N,Andersen, Phys.Rev.Lett. 92(2004)126102 [2] R.M. Jaeger, H. Kuhlenbeck, H.-J. Freund, M. Wuttig, W. Hoffmann, R. Franchy, H. Ibach, Surf. Sci. 259, 235-252 (1991). [3] M. Frank, K. Wolter, N. Magg, M. Heemeier, R. Kuehnemuth, M. Bäumer, H.-J. Freund, Surf. Sci. 492, 270-284 (2001). [4] G. Kresse, M. Schmid, E. Napetschnig, L. Köhler, M. Shishkin, P. Varga, Science 308(2005)1440.—

9:00 AM *KK6.2
Structure and Bonding at Abrupt Copper/Alumina Interfaces - An Ab-Initio Density-Functional-Theory Study. Adham Hashibon[1,2], Christian Elsaesser[1] and Manfred Ruehle[2]; [1]Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany; [2]Max-Planck 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 atomistic 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 α-Al_2O_3 (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 α-Al_2O_3, and in the second one the Cu is rotated with respect to the Alumina by 90° around 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 α-Al_2O_3 (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 *KK6.3
Structure and Bonding at Pd/(0001)ZnO Interface. Manfred Ruehle[1], Mitsuhiro Saito[1] and Thomas Wagner[2]; [1]MPI f. Metallforschung, Stuttgart, Baden-Wuerttemberg, Germany; [2]MPI 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 nature of the 2 different surfaces of ZnO. Pd was deposited on both different polar surfaces and the atomistic structures of the different Pd/ZnO interfaces were determined by quantitative high-resolution transmission electron microscopy (QHRTEM) 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 atomistic structure of the coherent regions between the misfit dislocations could be determined by QHRTEM. 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 lengths. Unlike the extensive studies of growth front 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(100) as a model system, 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 $t^{\beta loc}$ of the local slope, where t is the oxidation time. The interface width $w(l,t)$ scales as $t^{\beta loc}l^H$ when the oxidation time is large or the size l of the region over which w is measured is small, and as $t^{\beta+\beta loc}$ when l is large or t is small (here, H is the Hurst exponent, and β is the dynamic scaling exponent). 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 Cu^{2+} cations across the oxide layer under the action of the chemical potential gradient between the gas-oxide interface and oxide-metal interface.

10:45 AM KK6.5
Characterization of Oxides and Oxide-Metal Interfaces in Zr-Based Alloys Using Synchrotron Radiation and Transmission Electron Microscopy. Aylin Yilmazbayhan[1], Arthur Motta[1], Marcelo Silva[1], Else Breval[4], Robert Comstock[2], Barry Lai[3], Zhonghou Cai[3], Yong Chu[3] and Jan Ilavsky[3]; [1]Department of Mechanical and Nuclear Engineering, Penn State, University Park, Pennsylvania; [2]Science and Technology Center, Westinghouse Electric Company, Pittsburgh, Pennsylvania; [3]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; [4]Materials Research Institute, Penn State University, University Oark, 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 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 layers 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 examines a bulk sample, 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 1010 hcp Zr phase. These results are qualitatively confirmed by TEM diffraction analysis in 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. Florin Nita[1,2] and Riccardo Ferrando[1]; [1]INFM and Genova University - Physics Department, Genova, Italy; [2]Institute 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 coefficient of small Pd_n adatom clusters ($n = 1 \div 10$) 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 a potential fitted to ab initio calculations for Pd-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 the effective diffusion barriers corresponding to each Pd_n cluster have been extracted. 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 Monte Carlo simulations and a good agreement 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. C. Ying, I. Vattulainen, J. Merikoski, T. Hjelt, T. Ala-Nissila, Phys. Rev. B 58, 2170 (1998) [3] G. Haas, A. Menck, H. Brune, J.V. Barth, J.A. Venables, K. Kern, Phys. Rev. B 61, 11105 (2000) [4] P. Jensen, Rev. Mod. Phys. 71, 1695 (1999).

11:15 AM KK6.7
Development Of Adhesion Layer Dynamics For Metal Ceramic Interfaces. Marian S. Kennedy[1], Richard P. Vance[1], Neville R. Moody[2] and David F. Bahr[1]; [1]Mechanical and Materials Engineering, Washington State University, Pullman, Washington; [2]Sandia National Laboratories, Livermore, California.

Metal ceramic solid-solid interfaces make up a majority of the interfaces currently utilized in both the semiconductor industry and the emerging micro-electro-mechanical industry, particularly in regards to metallization on oxides and nitrides. The mechanical reliability of these interfaces can be greatly improved by choosing an appropriate adhesion layer. These improvements in adhesion are often ascribed to the improvement in chemical bonding between layers, texture, strain transfer, and plasticity. This current study examines the improvement of the Pt/SiO2 interface by the addition of a Ti interlayer. The thickness of the Ti interlayer was varied from 2 to 17 nm of nominal thickness, with the 2 nm layer not providing complete film coverage but an island morphology. All films in this study were deposited by DC magnetron sputtering. Measurements of the practical work of adhesion were carried out with three test techniques; four point bending, indentation induced blistering and spontaneous buckles with the addition of a stressed overlayer. Initial testing has shown that the interface strength rises by a factor of two with the addition of an adhesion layer. With no titanium adhesion layer, the toughness of the platinum-silicon dioxide interface in mode I ranges from 0.4 to 0.7 N/m. Annealing processes to increase adhesion were carried out and show the formation of a titanium oxide layer between the metal and silicon oxide. This paper will describe a mechanics based model for the adhesion energy as a function of interlayer thickness. The authors gratefully acknowledge the support of Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:30 AM KK6.8
Mechanical Properties of Alumina/Metal Interfaces: First-Principles Calculations and the Development of Interatomic Potentials. Masanori Kohyama[1], Shingo Tanaka[1], Siqi Shi[1], Rui Yang[2], Sergey V. Dmitriev[3], Nobuhiro Yoshikawa[3] and Yoshihiko Hangai[4]; [1]Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; [2]Department of Computer Science, Australian National University, Canberra, Australian Capital Territory, Australia; [3]Institute of Industrial Science, The University of Tokyo, Meguro-ku, Tokyo, Japan; [4]Department of Mechanical System Engineering, Gunma University, Kiryuu, Gunma, Japan.

Metal/oxide interfaces are used in various applications such as coatings, composites, electronic devices, catalysts, fuel cells and so on. Alumina/metal interfaces are especially important in thermal-barrier coatings or electronic devices. Thus the studies of mechanical properties of alumina/metal systems are of great importance. However, we cannot easily estimate the adhesive and mechanical propeties of such interface systems because of unique bonding characters between quite different insulating and metallic materials. In addition, recent studies have clarified that the interface stoichiometry greatly affects the adhesion and properties of alumina/metal interfaces. Namely, the interfaces between metals and O-terminated (O-rich) and Al-terminated (stoichiometric) alumina surfaces should have quite different characters. In this paper, first, we have applied ab intio calculations based on the density-functional theory to alumina(0001)/Cu(111) and alumina(0001)/Ni(111) interfaces in order to clarify the adhesive and mechanical properties. We have examined the effects of interface stoichiometry and metallic species [1]. We have observed strong Cu-O and Ni-O interactions with both ionic and covalent characters at the O-terminated interfaces, in contrast to electrostatic and Al-metal covalent interactions at the Al-terminated ones, which are compared with recent electron microscopy observations [2] and XPS experiments in details. Second, we have performed theoretical tensile tests [3], which can clarify intrinsic tensile strength and the process of failure dominated by the behavior of atoms and electrons. Third, we discuss how to combine ab intio results with more realistic and large-scale simulations of deformation and fracture of alumina/metal systems. For molecular-dynamics and quasi-continuum simulations, we have constructed interfacial effective interatomic potentials [4] including the effects of interface stoichiometry from the ab initio interlayer potential curves. We discuss the development of database of ab initio results for mesoscopic simulations. The present study was supported by NEDO as Nano-Coating Project. [1] R. Yang et al., Phil. Mag. Lett. 84 (2004) 425; S. Tanaka et al., Mater. Trans. 45 (2004) 1973; R. Yang et al., Phil. Mag. (2005) in press. [2] T. Sasaki et al., Appl. Surf. Sci. 241 (2005) 87, [3] M. Kohyama, Phys. Rev. B 65 (2002) 184107, [4] S.V. Dmitriev et al., Acta Mater. 52 (2004) 1959, Comp. Mater. Sci. (2005), in press.

11:45 AM KK6.9
Growth of a Reaction Layer between a Thin Film and a Substrate. Ramanathan Krishnamurthy and David Srolovitz; Department of Mechanical Engineering, Princeton University, Princeton, New Jersey.

Reaction layer growth at the interface between two solids is commonly accompanied by the development of non-planar morphologies and large stresses. We initially examine the diffusive morphological stability of such an interface in a misfitting thin film / substrate system under different interface coherency conditions. We demonstrate that an initially flat interface is unstable to rumpling regardless of the elastic mismatch between the film and the substrate, and the magnitude of the interface energy. We also examine the effect of the interface instability on the morphological stability of the film free surface. Next, we examine the growth and morphological evolution of reaction layers in a polycrystalline thin film / substrate system through a combined kinetics/thermodynamics/mechanics model. We predict the evolution of stresses within the film as well as the size and shape of the reaction product that grows preferentially along the grain boundaries of the film (pegs). These pegs grow preferentially when the stress-free strain associated with the reaction is large, the interface energy is small and when the grain size of the polycrystalline film is large compared to its thickness. The resultant predictions are consistent with a range of experimental observations for alloy oxidation and growth of intermetallic layers.

SESSION KK7: Interfaces with Silicon
Chair: Juan de la Figuera
Wednesday Afternoon, November 30, 2005
Fairfax A (Sheraton)

1:30 PM *KK7.1
Insights on the formation of epitaxial high-K oxides on silicon from first-principles. Peter E. Bloechl[1], Clemens Foerst[1,2], Christopher Ashman[1] and Karlheinz Schwarz[2]; [1]Institute for Theoretical Physics, Clausthal University of Technology, Clausthal-Zellerfeld, Germany; [2]Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria.

The ongoing miniaturization of semiconductor devices requires the replacement of the conventional SiO2-based gate oxides by so-called high-k oxides. High-K oxides allow to avoid quantum mechanical leakage currents through an otherwise ultra-thin gate oxide. We discuss the route towards formation of epitaxial high-K oxides with silicon using state-of-the-art electronic structure calculations and ab-initio molecular dynamics simulations. The interesting interplay of metal atoms with the silicon dimers of the Si(001) surface will be discussed, which lead to the sequence of different adsorption phases as function of coverage. Then the interface structures between SrTiO3 and LaAlO3 on silicon will be discussed. Special attention will be given to the interface chemistry and the requirements for obtaining an electronically inactive interface. We show that the band-offsets can be engineered for some of the interfaces by controlling the oxygen content at the interface. This is particularly important for the SrTiO3/Si(001) interface, which otherwise suffers from unacceptably low electron-injection barriers. If time permits, I will also touch upon the epitaxial growth of semiconductors on oxides.

2:00 PM KK7.2
Morphology Evolution of Metal Silicide and Metal Germanide Thin Films on Silicon. Mathieu Bouville[1], Dongzhi Chi[1] and David J. Srolovitz[2]; [1]Institute of Materials Research and Engineering, Singapore, Singapore; [2]Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey.

The formation and evolution of thin polycrystalline films formed from the reaction of metals on silicon (metal silicides) or germanium (germanides) is key to the performance in semiconductor devices. NiSi is a candidate material system for replacing $CoSi_2$ 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 failure mechanism is the agglomeration of NiSi to form isolated 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 carrier mobility in germanium. We use phase field 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. Experimental observations suggest that alloying Ni with Pt or implanting BF_2 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 modifies the grain boundary and/or interface energies, 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 $Ni(Pt)Si_xGe_{1-x}$ 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.
Rebecca L. Peterson[1], Karl D. Hobart[2], Fritz J. Kub[2] and James C. Sturm[1]; [1]Princeton Institute for the Science and Technology of Materials and Department of Electrical Engineering, Princeton University, Princeton, New Jersey; [2]Naval 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) 30nm $Si_{0.7}Ge_{0.3}$ layer is grown on bulk silicon and transferred by wafer bonding and Smart-Cut^{TM} onto a silicon handle wafer with a compliant layer of 1μm boro-phosphoro-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 <100> 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 where relaxation is quick and is supplemented 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, not by 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 66nm. To find analytical solutions 2-D buckling is solved in 1-D with a constant compressive strain in the 2^{nd} (perpendicular) dimension, equal to the initial film strain [2, 3]. Strain in the 2^{nd} dimension affects buckling by changing film membrane force and shear stress. To model 1-D buckling we instead use a constant *tensile* strain in the 2^{nd} dimension, and find good agreement with experiments. The models predict and we measure: a longer buckling time constant of 7.9min (we observe 9.0min); a longer buckling wavelength; and a smaller buckling amplitude. Further experiments on thinner 235nm 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 (2002) and APL in press (2005). 2) Huang and Suo, Int'l J. of Sol. and Str. 39, 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 Tedenac; 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 compared with those of 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 barrier thickness needed to be reduced and temperature efficiency needed to be improved for the ULSI devices application, tantalum nitride has become a potential material as a diffusion barrier. The aim of this project was to study the role of TaN and Ta/TaN barriers in the diffusion mechanisms of copper into silicon substrates, considering the 600 to 900°C temperature range. Thin TaN/Cu and Ta/TaN/Cu multilayers were deposited on silicon substrates using the physical vapor deposition (PVD) process. The optimisation of the PVD experimental parameters was first 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 Ta/TaN layers were then determined due to the correlation between the microstructural observations and Secondary Ion Mass Spectrometry analyses. The comparison between the TaN and Ta/TaN barriers evidenced the role of the Ta 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 Asaoka[1], Tatsuya Yamazaki[1,2] and Shin-ichi Shamoto[1]; [1]Neutron Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan; [2]Eiko Engineering Co., Ltd., Hitachinaka, Ibaraki, Japan.

Heteroepitaxial 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 $SrTiO_3$ and $BaTiO_3$ which are highly desirable oxides for future generation transistor gate dielectric and ferroelectric memory applications. In many cases, however, adsorption of deposited atoms causes a chemical reaction with active dangling bonds 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 heteroepitaxial growth. In fact, $SrSi_2$ and SiO_2 layers are formed between SrO films and Si substrates when SrO has been grown on Si(100) 2x1 and (111) 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 unreconstructed 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 situ characterization of 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 the thickness of the strained layer are highly reduced by using 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 Si/SiO2 Interfaces.
Lirong Pei[1], Wolfgang Windl[2], Steen Christian[3], Peter Pichler[3], Steve Pennycook[4] and Gerd Duscher[1,4]; [1]Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; [2]Materials Science and Engeering, Ohio State University, Columbus, Ohio; [3]LEB, University Erlangen-Nuremberg, Erlangen, Germany; [4]Condensed Matter Sciences Division, Oak Ridge Nation Lab, Oak Rdige, 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 of segregation. A combined theoretical and 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 calculation provides appropriate structure model by energy calculation of different preferred segregation sites. After implanting As (10^{16} cm^{-3}) 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 10nm 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 EELS, and compared with those measured by TXRF.The amount of segregation is in accordance with the theoretically determined value. Due to the overlap of Sb, Si and O edges, TXRF does not work for Sb doped samples. However, Z-contrast imaging shows a segregation of Sb to the interface for Sb ($3*10^{15}$ cm^{-3}) 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 Nordberg[1], Byoung-Nam Park[2], Pengpeng Zhang[2], Emma Tevaarwerk[1], George Celler[4], Paul Evans[2], Irena Knezevic[3], Max Lagally[2] and Mark Eriksson[1]; [1]Physics, University of Wisconsin, Madison, Wisconsin; [2]Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin; [3]Electrical and Computer Engineering, University of Wisconsin, Madison, Wisconsin; [4]Soitec 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, the sheet density of charge carriers decreases as the silicon thickness decreases. The sheet density of interface traps, however, does not typically scale with silicon layer thickness. Thus, although trap densities can be extremely low at the silicon/silicon-dioxide interface, it should, in principle, be possible to scale silicon-on-insulator so that the bulk silicon top layer 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. We show that the scaling just described is indeed observed in ultra-thin silicon-on-insulator. The resistance of the silicon layer and the resistivity itself increase sharply with decreasing film thickness, reaching a value of $1.1\times10^5 \pm 0.3\times10^5$ Ω-cm at a thickness of 16.5 nm and a doping concentration (p-type) of roughly 10^{15} cm^{-3}.

4:30 PM KK7.8
SiC/SiO_2 Interfacial Compositions by EFTEM and Spectrum Imaging.
James Bentley[1], K-C. (Eric) Chang[2], Yan Cao[2] and Lisa M. Porter[2]; [1]Metals and Ceramics Division, Oak Ridge National Lab, Oak Ridge, Tennessee; [2]Dept. 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 SiO_2 films. However, the electronic properties of the SiC/SiO_2 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 NO). Monolayer levels of inhomogeneously distributed excess carbon are present at the interface for certain processing conditions and SiC crystallography. The carbon levels correlate with interface-state densities. Following post-oxidation annealing in NO, sub-monolayer levels of interfacial N ($<=1.0 \pm 0.1$ x 10^{15} cm^{-2}) have been measured. Special attention to data acquisition 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 layers with respect to the SiC/SiO_2 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 N edge are significantly different for SiC and SiO_2 regions, mainly due to the presence/absence of the C-K edge. Log-polynomial and modified variants of that scheme were among the procedures used for background fitting. Research at the ORNL SHaRE User Facility sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Financial support from DARPA via Contract No. N00014-02-1-0628 is gratefully acknowledged. The authors thank L.C. Feldman and S. Dahr (Vanderbilt Univ.), C.-Y. Lu and J. Cooper, Jr. (Purdue Univ.) and J.R. Williams (Auburn Univ.), for materials processing and continuing collaborations.

4:45 PM KK7.9
Abstract Withdrawn

SESSION KK8: Metal/Metal and Oxide/Oxide Interfaces
Chair: John C. Hamilton
Thursday Morning, 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 of 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 relieve the in-plane strain due to the misfit 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. Furthermore, 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. MAT2003-08627-C02-02. J.d.l.F gratefully acknowledges support through a "Ramon y Cajal" contract from the Education and Science Spanish Ministry.

9:00 AM *KK8.2
First-Principles modeling of Ni-Ni_3Al interfaces at finite temperature.
Axel van de Walle[1], Christopher Woodward[2] and Mark Asta[1]; [1]Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]AFRL/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 microscopic parameters. Two parameters that have proven especially difficult to obtain either via experimental or first-principles methods are the interface excess free energy and the interface width. Interface free energy is the main driving force for coarsening while interface width governs precipitate coalescence and sets the spatial resolution of the computation grid in phase-field methods. While first-principles methods are routinely used to obtain interface excess 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 (ATAT) is described and an application to Ni-Ni_3Al 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 bonding changes across a 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 some cases the sensitivity and resolution extends to 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[1]. In fact, the smallest feature 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[2]. However, electronic structure changes alter more than just electrical properties: electron energy loss spectroscopy (EELS) measurements of grain boundaries in Ni_3Al using an atomic-sized beam show that the measured loss of s-d hybridization can be quantitively related to the boundary cohesion, and the resulting transition from intergranular to transgranular fracture with boron doping[3]. 1 P. M. Voyles, D. A. Muller, J. L. Grazul, P. H. Citrin, and H.-J. Gossmann, *Nature*, **416** 826 (2002). 2 D. A. Muller et al, *Nature*, **399** 758 (1999) 3 D. A. Muller et al, *Phys.Rev.Lett* **75** 4744 (1995)

10:30 AM *KK8.4
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, facet 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 entirely on 2-D projections, neglecting variations in the third dimension. Here we show that the detailed 3-D shapes 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 with the free surface in materials with low stacking fault energy. 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 electron microscopy and the TEAM project. This work 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-ACO3-76SFOOO98.

11:00 AM KK8.5
Edge Energies: Atomistic 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 with a truncated octahedral shape. To the best of my knowledge, this work is the first atomistic 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-scale 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, three-dimensional structures on a surface, and inclusions in bulk materials) 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 or transition away from the Wulff shape. Although it is common to invoke edge energies in discussing the shapes 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 nano-scale. 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 straightforward to calculate 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, edge lengths and surface areas can be defined precisely as continuous variables. In an atomic model, edge lengths and surface areas are less well defined and can only take on discrete values. Because the definition of edge lengths and surface areas is not precise, it is not possible to divide the calculated total interface energy into separate edge and surface components. Here I propose a precise volumetric definition for edge lengths and surface areas of truncated octahedral fcc particles. This definition is precise over the whole range of particle sizes from atomistic to macroscopic. 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 KK8.6
Electronic Interface Properties of YBaCuO / LaCaMnO Superlattices. Hanns-Ulrich Habermeier[1], Jacques Chakhalian[1], Christian Bernhard[1] and Jochen Stahn[2]; [1]MPI-FKF, Stuttgart, Germany; [2]Paul 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 ground state of LaCuO4 converts into a superconductor upon hole doping; similarily, 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 techniques and characterized the films structurally (X-ray diffraction, TEM) and with respect to their electronic properties by transport, magnetization and spectroscopic ellipsometry measurements. Detaliied studies of the magnetic properties 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 kayer 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 KK8.7
Atomic scale studies of complex oxide interfaces. Maria Varela[1], Hans Christen[1], Claudia Cantoni[1], Klaus van Benthem[1], Andrew Lupini[1], Timothy Pennycook[1], Stephen Pennycook[1], Weidong Luo[2,1], Sokrates Pantelides[2,1], Vanessa Pena[3], Zouhair Sefrioui[3] and Jacobo Santamaria[3]; [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Dept. of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; [3]GFMC, 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 magnetoresistace (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 the 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 manganite based heterostructures, such as superconducting/ferromagnetic $YBa_2Cu_3O_{7-x}/La_{0.67}Ca_{0.33}MnO_3$ (YBCO/LCMO) superlattices or antiferromagnetic/insulating $LaMnO_3/SrTiO_3$ (LMO/STO) interfaces. High resolution 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

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11:45 AM KK8.8
Interfacial Structure and Defect Energy in Nanoscale CeO2/ZrO2 Films: A Molecular Dynamics Study.
Michael Dyer[1], Anter El-Azab[1], Fei Gao[2] and Ram Devanathan[2]; [1]Mechanical Engineering, Florida State University, Tallahassee, Florida; [2]Pacific 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.