SYMPOSIUM KK

KK: Atomic Scale Materials Design-Modeling and Simulation

December 1 - 4, 2003

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* Invited paper

SESSION KK1: Mechanical Properties
Chair: Samuel B. Trickey
Monday Morning, December 1, 2003
Constitution A (Sheraton)

8:30 AM *KK1.1
Chemical Realism In Chemo-Mechanical Processes For Multi-Scale Simulations. Rodney J. Bartlett, Carlos Taylor, Keith Runge, Marshall Cory and Piotr Rozyczko; Quantum Theory Project, University of Florida, Gainesville, Florida.

Simulations can only be as accurate as are the forces provided to the MD. Yet for many problems, including all bond breaking processes and optical properties, we require a fully quantum mechanical treatment of the forces. *Abinitio* correlated, electronic structure theory like coupled-cluster theory is *predictive* to within small error bars for most properties of molecules of 10-20 atoms. DFT can extend this predictability to maybe 100's of atoms in some cases. But neither can provide forces quickly enough for large scale MD simulations. Using aspects of coupled-cluster theory, we show that there is a quantity we call the transfer Hamiltonian that can account for the quantum mechanical treatment of forces; and these can be obtained with sufficient efficiency that they can be tied to MD in direct dynamics modes. The transfer Hamiltonian is chosen to be of the NDDO form common to semi-empirical quantum chemistry, but its atomic parameters are obtained via a genetic algorithm to ensure that the forces are the same as those of *abinitio* methods for representative clusters. Since the form of Hamiltonian is short-range, the atomic parameters saturate with the cluster size leaving a size-independent, converged form of Hamiltonian. All calculations are done fully self-consistently and are quantum state specific in that they account for different dissociation paths like radicals versus ions. We illustrate the application of the transfer Hamiltonian to chemo-mechanical processes by considering the fracture of silica in the presence of water and other examples. This work is supported by the NSF under grant DMR-0325553.

9:00 AM KK1.2
Evaluation of mechanical response of smectite interlayers during hydration using steered molecular dynamics. Dinesh R Katti, Steven Schmidt, Pijush Ghosh and Kalpana Katti; Civil Engineering, North Dakota State University, Fargo, North Dakota.

Smectite clays are materials of importance to geotechnical and geoenvironmental engineering and in the field of clay-polymer nanocomposites. These minerals exhibit large swelling and exert swelling pressure in interaction with fluids. Understanding the interaction between clay and water or other fluids is important for the proper use of these materials. In this work the mineral structure of a model system, pyrophyllite is used to construct a model of the mineral montmorillonite through appropriate isomorphous substitutions. The response of the interlayer is evaluated using molecular dynamics simulations. Steered molecular dynamics simulations are conducted. Forces are applied to the surface (basal oxygen) to evaluate the displacement versus applied pressure in the interlayer and hence the swelling pressure between two clay layers at atomic scale. Swelling response is measured for single and double layers of water. The simulations indicate that under applied compressive stresses of 0-16.5 GPa, the nanoscale stress deformation response of the interlayer is almost linear. The predominant deformation of the clay model results from deformation of interlayer spacing. Deformation of the clay layers observed in this stress range, although not insignificant, is small. Further, at low stresses (0-2 GPa), as the clay layers approach each other, the non-bonded interlayer forces are dominant over the mechanical applied forces. However, as the stresses are increased the mechanical forces overcome this effect and the interlayer spacing decreases linearly. In addition, compressive response of individual components, the clay layer and interlayer at are found. This work gives insight into the molecular interfacial interaction between clay and solvent molecules under externally applied loads. The paper describes the construction of the model, the simulation procedure, and results of steered molecular dynamics simulations obtained.

9:15 AM KK1.3
Simulation Studies of Size Effects in Plastic Deformation. Robin Selinger, Brian B. Smith and Scott Weingarten; Physics, Catholic Univ., Washington, District of Columbia.

In order to study size effects in plastic deformation, we perform atomistic simulation studies of deformation of a polycrystal in a strain-gradient geometry. The polycrystal's initial grain structure is generated via a Potts model technique. The sample is confined between parallel walls whose radii of curvature gradually decrease with time, producing an applied bending strain. Mechanical response is measured via a generalized bending moment as a function of strain. We examine yield mechanisms as a function of temperature and look for evidence of size effects in plastic response. These results are compared with mesoscale simulations of size effects in plastic deformation. Using an idealized simulation of screw dislocations in two dimensions, we model anti-plane plastic deformation in a strain gradient geometry and characterize the resulting size effects. Mechanical response of the interior of the sample is consistent with the Bingham plastic law, while the boundary region has an anomalously hard plastic response. We explain why the Bingham plastic law breaks down near the boundary where dislocation image interactions strongly reduce the local dislocation density, and examine factors determining the thickness of the anomalously hard boundary layer. We discuss implications for understanding size effects in plastic deformation.

9:30 AM KK1.4
Mechanisms of Void Growth in Shocked Metals. Jaime Marian, Jaroslaw Knap and Michael Ortiz; Graduate Aeronautical Laboratories, California Institute of Technology, Pasadena, California.

Void growth and coalescence are known to be important ductile fracture mechanisms in metals. Under shock conditions, such as those encountered in explosively loaded materials, the attendant high deformation rates may induce the formation of spall layers characterized by a large concentration of nano and microvoids arranged in spatial patterns. The diffusion, growth and coalescence of these voids can lead to material failure under these extreme conditions. Therefore, a detailed understanding of the main mechanisms by which these voids grow and interact is required in order to construct reliable multiscale models of spallation in metals. Recently, molecular dynamics (MD) simulations have revealed the nucleation of large dislocation loops in Cu and Al. However, the size constraints inherent to MD make it difficult to obtain a complete picture of the relevant mechanisms. In this paper, we employ the quasicontinuum method (QC) in order to study voids and samples of realistic size under meaningful deformation conditions. In QC the continuum and atomistic scales are seamlessly bridged, thereby providing information at the atomic scale where required, yet allowing a coarse-grained description of the material where the magnitude of the deformation is small. Results showing the nucleation and transport of dislocation loops are presented for fcc metals such as Al and Cu.

9:45 AM KK1.5
Dislocation Glide in Model Ni(Al) Solid Solutions by Molecular Dynamics. georges p. martin[1], Erwan Rodary[1], David Rodney[2] and Yves Brechet[2]; [1]CEA, Chatenay Malabry, France; [2]INP, Grenoble.

The glide of an edge dislocation in an EAM random solid solution: Ni (1 to 8at% Al), is simulated by molecular dynamics. The EAM potential has been optimized to reproduce correctly the relevant properties of the face centered cubic solid solution and of the L12 Ni3Al phase. Glide is studied at fixed temperature and applied stress. Three parameters, Ss , B and Sd , are found necessary to describe the rate of shear for a given applied shear stress. Ss is the static threshold stress, below which the glide distance of the dislocation is not sufficient to insure sustained shearing. Sd is the dynamical threshold stress, which reflects the friction of the pinning potential on the moving dislocation. B, is the friction coefficient which relates the effective stress (S- Sd) to the glide velocity. Ss, Sd and B increase linearly with the solute content. In the viscous regime, the glide of the dislocation segment is described by a simple "stop and go" model. A random population of obstacles with a distribution of waiting times is assumed to oppose the glide of the dislocation segment. Detailed analysis of the trajectory of the latter yields the mean obstacle density and the distribution of waiting times, as a function of stress and composition. The values found for the mean waiting time per obstacle suggest that the unlocking of glide proceeds by the collective motion of few (3 to 5) atoms. The obstacles are argued to be made of configurations of the large Al atoms which are brought in positions of strong mutual repulsion in course of the glide process. The solute-solute short range repulsion, rather than the direct dislocation-solute interaction, is thus argued to be the mechanism mainly responsible for chemical hardening. A simple way for taking advantage of the above results in the frame of multiscale modeling is exemplified.

10:30 AM KK1.6
Multiscale Modelling of Fracture: Combined Cohesive Models and First Principles Calculations. Santiago Serebrinsky[1], Emily A Carter[2] and Michael Ortiz[1]; [1]Graduate Aeronautical Laboratories, California Institute of Technology, Pasadena, California; [2]Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California.

Cohesive theories of fracture have been a recourse to obtain fracture properties of materials under several conditions. Application of the method to analyze the effect of different constraints usually required

calibration to fit experimental data for specific samples. In this way, a successful description of some fracture features has been achieved. In this work, we point to obtain a more fundamentally based construction to determine fracture properties. We propose a method to coarse grain ab initio calculations of material properties that allows for the computation of fracture properties at the macroscopic level by means of cohesive surfaces, thrusting the application of multiscale calculations to fracture. The method involves several steps linked in succession, viz., a) calculation of atomic-level cohesive laws by first principles (e.g. density-functional theory), b) renormalization of the cohesive laws to account for many planes taking part in the fracture process, c) elastic correction to avoid double counting of elastic properties, d) embedding of the renormalized law into a finite element calculation with cohesive elements. A detailed description of each step is presented. Actual and prospective applications of the method, including hydrogen embrittlement and stress corrosion cracking, are discussed in terms of macroscopic as well as microscopic variables. The results obtained so far are highly promising.

10:45 AM KK1.7
Hybrid Quantum-Classical Dynamics Simulation of Water Enhanced Fracture of Strained Silicon. Rachid Belkada[1], Shuji Ogata[2] and Takahiro Igarashi[3]; [1]Japan Science and Technology Corporation, Kawaguchi, Saitama, Japan; [2]Nagoya Institute of Technology, Nagoya, Aichi, Japan; [3]Japan Science and Technology Corporation, Kawaguchi, Saitama, Japan.

Silicon based devises are becoming miniature and widely used in various fields. Bulk Si is not normally associated with fatigue. However, a combined effect of high stresses and harsh environment can produce static fatigue also referred to stress corrosion cracking. Recently, this phenomenon was reported in microelectromechanical systems [1], which are fabricated using sub-micron-size Si-components. Existence of stress corrosion cracking in Si is still unclear, though stress corrosion cracking in silicon oxide is well known. Understanding combined effects of strain and environmental molecule in nono-sized Si system requires a dynamic simulation of realistic system with chemical reaction. In this paper, we investigate the stress corrosion cracking in bulk Si by H_2O using a hybrid quantum-mechanical/molecular-dynamics code [2]. The chemically reacting atomic regions are treated by the density functional theory. These regions are coupled in a seamless manner to the rest of the classical atomic system, which are described by molecular dynamics and interacting via an empirical inter-atomic potential. We perform the simulation for a Si model under tension with several H_2O molecules around the crack front. Dangling bonds on the crack surfaces are saturated by H atoms. Our preliminary simulation results demonstrate the possibility of H_2O to react with Si-Si bonds in contrast to a previous theoretical study based on the molecular orbital theory [3]. In the present simulation, we examine crack plane orientation dependencies on the fracture initiation in Si. This work is supported by ACT-JST. [1] C. Muhlstein et al., Sensors and Actuators, A94, 177 (2001). [2] S. Ogata et al., Comp. Phys. Comm., 138, 143 (2001). [3] W. Wong-Ng et al., Comp. Mater. Sci., 6, 63 (1996).

11:00 AM KK1.8
Hybrid scheme between large-scale electronic structure methods and its application to fracture simulation. Takeo Hoshi[1], Ryu Takayama[2,1] and Takeo Fujiwara[1]; [1]Department of Applied Physics, University of Tokyo, Hongo, Bunkyou-Ku, Tokyo, Japan; [2]ACT-JST, Japan Science and Technology Corporation, Tokyo, Japan.

A hybrid scheme between large-scale electronic structure methods is developed and applied to fracture simulation of silicon with up to more than 100,000 atoms using a standard single-CPU work station. We have developed several order-N methods as large-scale electronic structure methods. The order-N method is the name of electronic structure calculations in which the computational cost is proportional to the system size. We have developed the (i) variational and (ii) perturbative order-N methods with generalized Wannier states (J. Phys. Soc. Jpn, vol. 69, No.12, pp.3773-3776 (2000)). We also use (iii) the recursion method and (iv) the exact diagonalization method. Practical calculations were done using transferable tight-binding Hamiltonians. Now we construct a hybrid scheme between the above methods. The hybrid scheme is advantageous to large-scale, fully quantum mechanical calculations, because the above methods are different in the accuracy, computational cost, and/or applicability. The hybrid scheme is formulated by dividing the occupied Hilbert space; The one-body density matrix is decomposed into two partial matrices or 'subsystems' that are constructed from several occupied wave functions. Such subsystems are orthogonal with each other. Each subsystem is obtained with a mapped Hamiltonian under the orthogonal constraint to the other subsystem. Since the mapped Hamiltonian is well defined in quantum mechanics, each subsystem can be solved by any quantum mechanical method, such as the diagonalization and order-N methods. In result, different subsystems are solved by different methods, which is the present hybrid scheme. Test calculations are done by the combinations between (1) the diagonalization and perturbative methods, (2) the variational and perturbative methods, (3) the recursion and perturbative methods. Several test calculations are also done with parallel computers. The hybrid scheme is applied to molecular dynamics simulation in the fracture of nanocrystalline silicon with upto more than 100,000 atoms (cond-mat / 0210366 v3). Dynamical fracture processes are simulated under external loads in the [001] direction. The hybrid scheme is done by the combination of the perturbative and variational order-N methods based on the localized Wannier states. Wannier states are solved by the perturbative method in the bulk region, in which the Wannier states keep the character of sp3 bonding states during the simulation. On the other hand, Wannier states are solved by the variational method near the fractured region, where some of the Wannier states change their character drastically from the sp3 bonding state into surface ones. We observe the formation of cleaved surfaces with surface reconstruction processes. The elementary process is analyzed from a quantum mechanical viewpoint. Step formations are also observed in larger samples. Several related calculations are also done.

11:15 AM KK1.9
Hybrid Electronic-Density-Functional/Molecular-Dynamics Scheme for Multi-scale Simulation of Ceramics and Semiconductors. Shuji Ogata[1], Rachid Belkada[2] and Takahiro Igarashi[2]; [1]Nagoya Institute of Technology, Nagoya, Aichi, Japan; [2]Japan Science and Technology Co., Kawaguchi, Saitama, Japan.

In recent years, there has been much development in the hybrid quantum-mechanical/molecular-dynamics (QM/MD) schemes for multi-scale simulation of materials. In our hybrid schemes, a QM region composed of a small number (less than a few hundreds) of atoms and treated with the density-functional theory, is embedded in a large-scale MD system. In the former scheme [1], we used the link-atom method to couple between the QM and MD regions. Degrees of coupling between the QM and MD regions were, however, fairly sensitive to the shape and size of the QM region. In this paper, to overcome the difficulty, we propose a novel hybridization scheme, which requires no link-atoms and is applicable to a wider range of ceramics and semiconductor materials at various settings including surfaces and cleavages. We perform detailed investigations on mechanical coupling between the QM and MD regions and effects of hybridization on electronic structures of the QM region. We apply the present scheme to the stress corrosion cracking of both Si and alumina systems by environmental water and hydroxyl molecules, to understand its microscopic mechanisms. In the case of Si [2], the hybrid simulation results show that the reaction of water molecules at a silicon crack tip is sensitive to the stress intensity factor K. For a relatively small value of K, a water molecule either decomposes and adheres to dangling-bond sites on the crack surface or oxidizes Si, resulting in the formation of a Si-O-Si structure. For a higher value of K, a water molecule either oxidizes or breaks a Si-Si bond. [1] S. Ogata et al., Comp. Phys. Comm. 138 (2001) 143; S. Ogata et al., Comp. Phys. Comm. 149 (2002) 30. [2] S. Ogata et al., J. Appl. Phys., submitted.

11:30 AM KK1.10
Atomistic simulation of the interaction between a microcrack and hard inclusions in β-SiC. Alessandro Mattoni[1], Luciano Colombo[1] and Fabrizio Cleri[2]; [1]INFM and Department of Physics, University of Cagliari, Monserrato (CA), Italy; [2]Unita' Materiali e Nuove Tecnologie, ENEA, Roma.

Silicon carbide is a relevant structural material employed for the fabrication of composites. In these compounds the SiC matrix is reinforced by hard fibers, usually made of carbon or carbon-coated SiC. Microcracks in such a composite can propagate within the matrix and should be arrested or deflected by the hard inclusions. The overall effect of the hard fibers is to increase the dissipation of external fracture work with respect to the bare matrix. We study the perturbation induced by hard inclusions on the stress and strain field of an elliptical microcrack in crystalline b-SiC by means of atomistic large-scale molecular dynamics simulations. The interaction between Si and C atoms is described by a Tersoff empirical model potential. Constant traction border conditions are employed to represent the external load in plane strain approximation. The three-dimensional microcrack geometry is represented as a thin shell with periodic borders in the two directions perpendicular to that of the applied load. Hard inclusions, which are meant to describe the effect of reinforcing fibers, are represented by cylindrical sections of graphitic- and diamond-like carbon surrounding the microcrack with different densities and geometrical arrangement. The size of the inclusions is always comparable to that of the microcrack. The configurations containing inclusions are annealed at low temperature and relaxed at T=0 K. The resulting interface between matrix and inclusions can be

either perfectly coherent and under tensile stress, or disordered, thereby reducing the interfacial stress. The static perturbation induced on the microcrack is characterized by mapping the stress and strain fields of the microcrack with and without the inclusions. Effects due to the non-additivity of the perturbations from the individual inclusion are elucidated by plotting differences between the respective stress and strain fields. The influence on the stability of the microcrack in presence of hard inclusions is characterized by studying the variation in the Griffith critical load as a function of density and geometry of the hard inclusions.

11:45 AM KK1.11
Lattice Trapping Barriers To Brittle Fracture In Silicon.
Noam Bernstein and D. W. Hess; Center for Computational Materials Science, Naval Research Laboratory, Washington, District of Columbia.

Simulations of fracture in silicon, a prototype brittle material, have the potential to give insight into fundamental properties that control the behavior of the material at the crack tip. We show that in many empirical potentials there is a large energy barrier to brittle fracture caused by the discrete nature of the atomic lattice. In some cases the barrier is large enough to completely suppress brittle fracture, explaining the ductile behavior seen in many simulations. In contrast, a multiscale simulation method that dynamically couples a quantum-mechanical tight-binding description of bonding at the crack tip to a larger empirical-potential simulation shows brittle fracture with only minimal lattice trapping, in agreement with experiment. A simple model for the interplay between the energy to break the crack tip bond and elastic energy relaxation correctly predicts the barrier for both the empirical-potential and coupled simulations. The success of the model indicates that the bond breaking process is highly local, and that deviations from linear elasticity at the crack tip are essential for determining the extent of lattice trapping. Two length scales emerge from the model: one for bond breaking, and another for elastic relaxation. Finally, we present ongoing work on dynamically coupled simulations for the fracture process in silicon at high temperatures, and fracture in other materials.

SESSION KK2: Electronic Materials and Properties
Chair: Noam Bernstein
Monday Afternoon, December 1, 2003
Constitution A (Sheraton)

1:30 PM *KK2.1
Atomic Scale Studies of High-κ Gate Dielectrics.
Kyeongjae Cho[1], Gyuchang Jun[2], Jeong-hee Ha[2], Shriram Ramanathan[2], David Chi[2], Susanne Stemmer[3] and Paul C. McIntyre[2]; [1]Department of Mechanical Engineering, Stanford University, Stanford, California; [2]Department of Materials Science & Engineering, Stanford University, Stanford, California; [3]Department of Materials, University of California-Santa Barbara, Santa Barbara, California.

Future gate dielectrics in CMOS devices will scale to sub-0.5 nm equivalent oxide thickness (EOT). At these dimensions, alternative oxides with higher dielectric constants (κ) than SiO_2 will be required. To date, fundamental structure-property relationships of these ultra thin layers are not understood. High-κ oxides are often comprised of complex, $a-priori$ unknown multiple layers resulting from interfacial reactions, interdiffusion, nonstoichiometry, phase separation and crystallization. Such complex structures make a fundamental understanding of defects and interfaces and their relationship to MOSFET properties difficult. In this talk, we will discuss our current atomic scale studies of high-κ gate dielectric materials with emphasis on interface structure and composition using state-of-the-art experimental and theoretical characterization methods. First principles density functional theory (DFT) calculation is used to study the atomic and electronic structures of diverse phases of silica and hafnia to identify the structure-property relationship as well as their thermodynamic stability. The DFT results are compared with experimental data from x-ray absorption near-edge fine-structure analysis of oxygen K-edges and high-resolution transmission electron microscopy for phase separation in Hf-silicate thin films subjected to high-temperature anneals. The oxygen K-edge fine-structures can be interpreted as an overlap of features from amorphous silica and crystalline hafnia phases in the phase separated microstructures. We also describe the use of deposited HfO_2/SiO_2 nano-laminates to probe the kinetics of phase separation in this binary system. The comparative analysis between theory and experiment elucidates the atomic scale structures and kinetic behaviors leading a quantitative understanding of Hf-silicate materials properties. Acknowledgement: This research is support by SRC contract 1015.001. We also acknowledge many helpful discussions with TI high-k research group (Luigi Colombo and Shaoping Tang).

2:00 PM KK2.2
Electronic structure calculations of Nitrogen and Hydrogen in diamond twist grain boundaries.
Michael Sternberg[1], Peter Zapol[1,2] and Larry A Curtiss[1,2]; [1]Materials Science Div., Argonne National Laboratory, Argonne, Illinois; [2]Chemistry Div., Argonne National Laboratory, Argonne, Illinois.

Diamond films with grain sizes of 3 to 10 nm grown in methane/argon plasmas show an increase of several orders of magnitude in n-type conductivity upon nitrogen addition to the plasma [Bhattacharyya *etal.*, Appl. Phys. Lett. **79**, 1441 (2001)]. Our previous computational studies have shown that nitrogen impurities are more stable in the grain boundaries than in the bulk. Using a density-functional-based tight-binding method, we have investigated the atomic and electronic structure of $\Sigma 13$ and $\Sigma 29$-(100) diamond twist grain boundaries containing hydrogen and nitrogen at the same time. We have studied the formation of $N-H$ complexes and associated changes in the electronic structure of the films for different hydrogen to nitrogen concentration ratios. We have also calculated participation ratios in order to find mobility edges in these systems and investigate the formation of defect sub-bands in the forbidden gap of diamond. These studies are being used to understand the experimentally observed changes in the electronic properties of the films associated with changes in the plasma composition during the growth process.

2:15 PM KK2.3
Stability of High-Energy Grain Boundaries in Nanocrystalline Si and SiC: Parallel MD, Tight-Binding MD, and Hybrid Tight-Binding/Classical MD Studies.
Kenji Tsuruta[1], Chieko Totsuji[1], Hiroo Totsuji[1] and Shuji Ogata[2]; [1]Electrical & Electronic Engineering, Okayama University, Okayama, Japan; [2]Systems Engineering, Nagoya Institute of Technology, Nagoya, Japan.

Classical and tight-binding (TB) molecular-dynamics (MD) simulations are performed to study thermal stability of some typical high-energy grain boundaries in nanocrystalline silicon and silicon carbide. We find that the thickness of amorphous-like grain boundaries in Si is independent of interatomic potentials, sigma values, and initial setup of the simulations. Thermal stability of SiC grain boundaries is, on the other hand, quite sensitive to local bonding characters, i.e. presence/absence of Si-Si and C-C bonds at each grain boundaries. We also employ a hybrid TBMD/classical MD method to investigate triple junctions of nanocrystalline Si and SiC. The behavior of impurities such as hydrogen atoms at these grain boundaries are analyzed by the method. (Work supported by ACT-JST and Grant-in-Aid for Young Scientists (B) No. 14750554 by MEXT.)

2:30 PM KK2.4
A critical re-addressing of silicon self-diffusion based on temperature-accelerated tight-binding molecular dynamics.
M. Cogoni[1], Luciano Colombo[1], F. Montalenti[2], B. Uberuaga[3] and A. Voter[3]; [1]INFM and Department of Physics, University of Cagliari, Monserrato (CA), Italy; [2]INFM and Department of Materials Science, University of Milano-Bicocca, Milano, Italy; [3]Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Many fundamental materials properties (e.g. microstructure evolution under processing, mass transport, bulk thermodynamics) are ruled by the diffusion of native point defects (self-diffusion). Recently, a thorough quantum mechanical picture - based on tight-binding molecular dynamics (TBMD) simulations - of silicon self-diffusion has been presented, that is both consistent with state-of-the-art experimental data and able to predict separately the vacancy and self-interstitial (dumbbell) contributions [Jaaskelainen et al., Phys. Rev. B vol.64, p.233203 (2001)]. We have extended the above investigation by developing for the first time a quantum (tight-binding) simulation scheme in the framework of the novel temperature-accelerated dynamics (TAD) method [Voter et al., Annu. Rev. Mater. Res. vol.32, p.321 (2002)]. TAD-TBMD simulations have provided a more comprehensive picture on self-diffusion, especially in the case of self-interstitials. In particular, new pathways for dumbbell migration have been pointed out, suggesting that a rich hierarchy of diffusivity mechanisms (differing in migration energies and prefactors) should be indeed admitted. In this work we discuss either the technical implementation of the present TAD-TBMD scheme and we critically re-address the self-diffusion phenomena in crystalline silicon.

2:45 PM KK2.5
Diffusion of oxygen in Si: quantum-chemical simulations.
Vasilii E Gusakov and Leonid I Murin; Inst. of Solid State and Semiconductor Physics, Minsk, Belarus.

In the present work the results of quantum-chemical simulation of diffusion of interstitial oxygen atom (O_i) in silicon and influence of uniform pressure upon the value of a diffusion barrier are presented. It is shown, that in the elementary diffusion act three nearest Si atoms

are involved and the value of a diffusion barrier is determined by an optimum configuration of these silicon atoms. For the first time both the prefactor and diffusion barrier have been calculated and are in excellent agreement with experimental results: ΔE_{calc}=2.59 eV; D_{calc}= 0.3 cm^2 c^{-1} and $\Delta E_{exp.}$ =2.53 - 2.56 eV; D_{exp}=0.13 - 0.26 cm^2 c^{-1} respectively. Uniform pressure results in reduction of the diffusion barrier value and as a function of pressure ΔE_{diff} is well described by the following expression $\Delta E_{diff}(P)/\Delta E_{diff}(P=0)$ = 1 - 1.69 10^{-3} P (kbar). We have found, that the calculated pressure dependence of the diffusion barrier value well describes an encrease in the oxygen thermal donors formation rate observed experimentally in Si heat-treated under homogeneous pressure.

3:30 PM KK2.6
Rapid Crystallization of Si-B and Si-Ge Alloys. Erik J Albenze and Paulette Clancy; School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York.

Technological solutions are being sought to reduce unwanted boron diffusion in ultra-shallow source/drain regions in advanced electronic devices. One approach involves the use of pulsed lasers (in the nanosecond or microsecond regimes) to anneal post-implantation materials in order to induce crystallization and repair implantation damage. One such approach involves employing explosive crystallization to anneal damage in boron-doped silicon or SiGe alloys. In this paper, the explosive crystallization of $Si_{1-x}B_x$ and $Si_{1-x}Ge_x$ alloys has been studied using a non-equilibrium Molecular Dynamics simulation method and a Stillinger-Weber potential model. We have shown recently that this computational approach is capable of emulating explosive crystallization, giving rise to a high speed process by which amorphous material is converted to crystal, facilitated by a mediating liquid layer. The driving force behind this reaction is the enthalpy of fusion and the difference in melting temperatures between the two solid phases (crystalline and amorphous). We have investigated the effect of boron doping level and Ge concentration on the speed of the ensuing explosive crystallization process and on the structure of the resultant material. In the case of $Si_{1-x}Ge_x$ alloys, the results show that the growth front velocity does not scale linearly with composition, in agreement with experimental results, despite the apparent conformality of the alloy's constituents. For the case of boron-doped silicon, we focus on the ability of explosive crystallization to prevent transient enhanced diffusion.

3:45 PM KK2.7
Defect Structures in Tin-doped and Tin-Zinc Co-doped Indium Oxide Transparent Conductors. Donald E Ellis, Oliver Warschkow, Miljacic Ljubomir and Jason A Sese; Physics and Astronomy, Northwestern University, Evanston, Illinois.

Tin-doped and tin-zinc co-doped indium oxide (ITO and ZITO) are transparent conducting oxides with many applications in areas such as display technology, solar panels, opto-electronic devices etc. The electrical properties of these materials are critically dependent on Sn and Zn doping levels and the applied oxygen partial pressure during preparation. However, the details of the underlying defect chemistry at an atomistic scale remain poorly understood. We report results using an empirical atomistic model and focus in particular on the binding energy of interstitial and structural oxygen in the In_2O_3 lattice. This binding energy is modulated through the presence of nearby Sn and Zn cation defects. We propose that the ability of ITO and ZITO to form n-type carriers upon reduction is directly related to the amount of loosely bound, and thus reducible oxygen in the lattice. In ITO, n-type carriers are produced through reduction of interstitial oxygen which charge balance Sn-dopants. The reducibility of interstitial oxygen however is strongly influenced by the number of nearby Sn dopants leading to increased binding at high Sn-doping levels. This explains the experimentally observed decay in carrier concentration at medium to high tin-doping level. In ZITO, our calculations indicate that structural oxygen atoms in the vicinity of Zn dopants become less strongly bound which increases their reducibility, leading to increased conductivity compared to non-doped In_2O_3.

4:00 PM KK2.8
First-principles investigations of N-V-O complexes in Si. Hiroyuki Kageshima[1], Akihito Taguchi[1] and Kazumi Wada[2]; [1]NTT Basic Research Labs., NTT Corp., Atsugi, Kanagawa, Japan; [2]Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nitrogen (N) doping in Si has received keen attention because it significantly reduces the concentrations of both defects and dislocation loops. To obtain high quality Czochralski-grown silicon, control of vacancy (V) aggregation and oxygen (O) precipitation are the two key factors. It is experimentally obvious that the N doping suppresses V aggregation and affects the formation of O precipitates. Although the N doping effect on V aggregation has been theoretically investigated, the effect on O aggregation has not theoretically been investigated. In this paper, we report the formation of coupled complexes of N, V, and O investigated by using the first-principles calculations. Since our previous investigations of the N-doping effect showed that N forms very stable complexes of {N2-V2}, we have considered the reaction, {N2-V2} + O -> {N2V2-O}. As widely accepted, an O atom is assumed to occupy the bond center (BC) site when isolated. We considered various possible sites of O around {N2-V2}, and then compared the total energies under lattice relaxation to estimate the stability. Our calculations found that {N2-V2} and O forms several stable complexes. In the most stable complex, an O atom locates the second nearest neighbour site of an N atom. The O atom moves to the empty space made by the {N2-V2} complex, perhaps reducing the strain. The energy benefit in the formation of this complex is as large as 0.95 eV. Therefore, the {N2-V2} complex effectively captures an O atom during the growth. Our prediction together with enhanced oxygen precipitation observed experimentally is strongly suggestive that the complexes would act as the oxide nucleation sites. Thermodynamical properties of the complexes will be also discussed to make clear the O aggregation processes.

4:15 PM KK2.9
First principles investigation of point defects in cubic silicon carbide. Fabio Bernardini, Alessandro Mattoni and Luciano Colombo; INFM and Dept. of Physics, University of Cagliari, Monserrato, Italy.

Silicon carbide is a very promising material for semiconductors devices applications which have to work under extreme conditions. Yet, the applications of SiC in real devices have been hampered because of the difficulties to grow high quality material. Both extended and point defects as antisites, interstitials and vacancies are present in sizeable concentration in silicon carbide. Native defects in SiC have been occasionally studied theoretically both by first principles and semi-empirical methods. A throughout overview on the structure, electronic properties and formation energies of point defects in SiC based on large cell calculations is still missing. Such an investigation is important per se and as a preliminary work to allow a reliable parameterization of semi-empirical methods like the tight-binding approach. In this work we performed a systematic investigation of point defects in SiC using present state-of-the-art first principles computational methods. We find that the carbon vacancy is the dominant defect in p-type SiC. That Si and C antisites are the most common defects in the n-type material. Interstitial defects are less favorite from the energetic point of view with respect to vacancies and antisites. Likewise pure silicon, the dumbbell structure is the lowest-energy configuration for the self-interstitial defects.

4:30 PM KK2.10
Multi-Scale Investigation of Molecular Oxygen Decomposition and Incorporation into Si(100)-(2x1) Surface. Alain Esteve[1], Nicolas Richard[2], Anissa Alimessaoud[1] and Mehdi Djafari Rouhani[1,3]; [1]LAAS-CNRS, Toulouse, France; [2]DCRE, CEA-DAM, Bruyeres le Chatel, France; [3]Laboratoire de Physique des Solides, Toulouse, France.

The silicon/silicon dioxide interface displays the most remarkable properties of all semiconductor/oxide interfaces of the microelectronic industry. Despite a considerable research effort in both experimental and theoretical domains to push the technology towards nanometer scales, little is known about its growth mechanism: oxygen decomposition, incorporation into silicon and subsequent structuring of the interface is poorly understood and still subject to controversy. Nevertheless, this knowledge becomes crucial to any process modelling tool for ultimate SiO2 technologies including emerging high-k materials where intermediate SiO2 is invariably formed at the Silicon/High-k interface. Recently, STM and Infrared advanced characterization techniques [1,2] have demonstrated new insight into the atomic scale understanding of the early stage of silicon oxidation. In particular, precise atomistic configuration are derived from the experimental data that enlighten the dissociation phenomena and underline the presence of a specific transition state to account for oxygen migration. We present first principle calculations of molecular oxygen interaction with silicon Si(100)-(2x1) surface aimed at reproducing the experimental picture and at completing the theoretical one [3]. Non dissociative and dissociative chemisorption are discussed as a function of the surface morphology and chemistry. Further oxygen incorporation into Si-Si bonds, migrations, agglomeration and associated energy barriers are investigated in detail. We finally show how these results are extrapolated to build a Kinetic Monte Carlo procedure enabling direct oxidation process simulation. This multiscale approach provides a unique opportunity to link the discussed experiments with the ab initio level thus enhancing the advantages of both methods taken separately. Preliminary results are presented in that direction. [1] Y.J. Chabal, K. Raghavachari, X. Zhang, E. Garfunkel, Phys. Rev. B 66, 161315(R) (2002) [2] G. Dujardin, private communication. [3] K. Kato, T. Uda, K. Terakura, Phys. Rev. Lett. 80, 2000 (1998) ; Y. Widjaja, C.B. Musgrave, J. Chem. Phys. 116, 5774 (2002).

4:45 PM KK2.11
Simulation Tool for Metal-Organic Vapor Phase Epitaxy of III-V Compound Semiconductors. Roman Talalaev[1], Yuri Shpolyanskiy[2], Alex Galyukov[1] and Yuri Makarov[1]; [1]STR, Inc., Richmond, Virginia; [2]Soft-Impact, Ltd., St.Petersburg, Russian Federation.

Introduction of simulation and modeling into development of MOVPE technology becomes more and more intensive in the last years [1,2]. Modeling may be used for both process and reactor optimization purposes. Besides the description of transport phenomena (flow, heat, species), an adequate chemistry model is necessary to predict deposition rates and uniformities and layer compositions. In this paper we present an integrated approach to simulation of III-V materials growth by MOVPE. The low temperature kinetic effects are described using a general mechanism - the blocking of group III species adsorption sites by methyl radicals.. Deposition at intermediate temperatures that occurs under mass-transport limited growth conditions necessitates detailed modeling of transport processes accounting for reactor geometry features. These conditions are characteristic for MOVPE of group III arsenides and phosphides and the modeling results for this material will be presented. Another advantage of the formulated model is its ability to predict the growth rate and composition of the epitaxial layers at high deposition temperatures where the desorption of species from the surface is the rate limiting process. High temperature conditions are usually applied in MOVPE of group III nitrides and examples of the predictive modeling of the deposition of these materials will be given. The developed models have formed a basis for the development of an advanced simulation tool for MOVPE processes - STR CVD-Module. Materials systems considered in the tool are as follows: 1) epilayers in the Al-Ga-In-As-P system used for growing heterostructures for light emitting diodes, solar cells, laser diodes, high-electron mobility transistors, hetero-bipolar transistors and vertical cavity surface emitting lasers. 2) epilayers in the Al-Ga-In-N system used for growing heterostructures for high-electron mobility transistors, light emitting diodes and laser diodes. The developed software is largely oriented to MOVPE engineers and researchers working both in industries and academia and is aimed to make modeling the routine and necessary step in new equipment and material design. [1] S.W. Bland, J. Mater. Sci.: Mater. El. 13, 679 (2002) [2] S.Yu. Karpov, J. Crystal Growth 248, 1 (2003)

SESSION KK3: Poster Session I
Monday Evening, December 1, 2003
8:00 PM
Exhibition Hall D (Hynes)

KK3.1
Investigation of the Detailed Structure of Atomically Sharp Ge/SiO2 Interfaces. Tao Lian[1], Wolfgang Windl[1], Sergei Lopatin[2,3] and Gerd Duscher[2,3]; [1]Materials Science and Engineering, The Ohio State University, COLUMBUS, Ohio; [2]Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina; [3]CMS Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Although the literature provides a multitude of (theoretical) structural models for Si/SiO2 interfaces, no method for experimental detection of the exact interfacial structure exists to date. In this paper, we suggest such a method, where we use impurities - in the present case, Ge atoms - as a probe to determine the interface structure by a combination of theory and experiment, which we call AIDA-TEM (Ab-Initio Dopant Analysis by Transmission Electron Microscopy). The experimental part of AIDA-TEM consists of two TEM-based methods, Z-contrast imaging to study the segregation of heavy atoms and EELS for light elements, both with single-atom resolution. Z-contrast can detect the segregation sites of impurities with single-atom accuracy relative to the interface in amorphous as well as crystalline materials. EELS can detect the conduction band density of states (DOS) of the different atoms, which depends on the species as well as on the neighboring atoms. The same dopants are tested in theoretical calculations for their preferred segregation sites and conduction band DOS. The identification of key features of the winning structural models (whose dopant segregation and conduction band DOS patterns match the TEM findings) enables us then to propose realistic models of interface structures. In this paper, we will apply AIDA-TEM to study the segregation behavior of Ge in oxidized Ge-implanted Si. Our results are commensurate with an atomically sharp interface.

KK3.2
New bond-order potentials for compound systems. Karsten Albe[1], Paul Erhart[1], Janne Nord[2] and Kai Nordlund[2]; [1]Institute of Materials Science, Materials Modeling Division, TU Darmstadt, Darmstadt, Germany; [2]Accelerator Laboratory, University of Helsinki, Helsinki.

Atomistic modeling of materials properties and processes on realistic time and length scales is mostly only possible if analytical potentials are used that are able to describe a variety of different bonding configurations. As it comes to technologically important systems realistic potentials are very often not available. Here we will report on bond-order potentials of the Brenner-Tersoff type that were recently developed for metal carbides, GaN, GaAs and SiC. We show that this angular dependent many-body potential type is not only capable to describe covalently bonded systems, but also d-transition metals including bcc-structures if second neighbor interaction is included. The basic methodology and fitting scheme is presented and virtues as well as shortcomings will be discussed by comparing with alternative schemes.

KK3.3
DFT Atomic-Scale Modeling of Mixed Co-Rh Transition-Metal Clusters. Samuel Dennler[1], Joseph Morillo[1] and Gustavo M. Pastor[2]; [1]CEMES, CNRS, TOULOUSE, France; [2]LPQ-IRSAMC, CNRS, TOULOUSE, France.

In the last decades, theoretical and experimental studies have demonstrated that size and dimensionality reduction of materials give rise to a large range of original physical and chemical behaviors [1]. This has opened the possibility of generating specifically designed nanomaterials with tailored properties. In particular, small transition-metal clusters are today the subject of considerable interest due to their possible applications in magnetic recording technologies. Alloying *3d* and *4d* elements is an effective way to combine a large magnetic moment with a high anisotropy due to the *4d* strong spin-orbit coupling and the *3d* high magnetic moments. Indeed, a strong enhancement of the saturation magnetization in CoRh nanoparticles [2] compared to the bulk alloy value [3] was recently demonstrated. This motivates a systematic understanding of their microscopic properties, for which atomic-scale calculations are very fruitful. To this purpose small free $Co_N Rh_M$ clusters ($N+M \leq 13$) have been studied [4] within the density-functional theory. In all cases the cluster geometry has been fully optimized from different initial configurations and for several relevant magnetic moments in order to locate the ground-state among the multiple close-lying isomers. The correlation between structural, chemical order and magnetic properties is analyzed. Comparison of magnetic and non-magnetic calculations reveals the significant role of magnetism on stability and cohesion. It appears that in most cases the average magnetic moment per atom is more than twice larger than in macroscopic alloys and increases with increasing Co concentration. The presence of Co induces a remarkable exaltation of the Rh local magnetic moments, in qualitative agreement with the experiment, while Co seems to retain its magnetic properties even in a highly mixed environment. For the larger icosahedral nanoparticles, in all cases there is a tendency to Rh surface segregation, associated to chemical disorder around the equiatomic composition. [1] P. Villaseñor-González et al, Phys. Rev. B 55, 15084 (1997); A.J. Cox et al, Phys. Rev. Lett. 70, 3323 (1993). [2] M.C. Fromen et al, J. Magn. Mag. Mat. 242-246, 610 (2002); D. Zitoun et al, Phys. Rev. Lett. 89, 37203 (2002). [3] G. Moraitis et al, Phys. Rev. B 54, 10 (1996); S. Dennler et al, to be published. [4] S. Dennler, J. Morillo and G.M. Pastor, Surf. Sci. 532-535, 334 (2003); Eur. J. Phys. D (in press, 2003).

KK3.4
Abstract Withdrawn

KK3.5
Adsorption of H, NH_x, BH_x and BBr_x on A (110) Surface of c-BN: A Quantum-Mechanical DFT Study. Igor Arvidsson and Karin M E Larsson; Materials Chemistry, Uppsala University, Uppsala, Sweden.

Cubic boron nitride has a wide field of applications due to of its extraordinary physical and chemical properties. When using vapour deposition techniques such as ALD, the grown films usually become a mixture of various phases like c-BN, hexagonal BN and amorphous BN. To be able to optimise the growth of c-BN using thin film layer techniques, it is of highest importance to achieve a better understanding of the different reaction mechanisms that are occurring at the surface during the deposition. Therefore, various adsorption processes involving a (110)-crystal surface of cubic BN has been investigated theoretically using a DFT approach. A three-dimensional slab mode was used to simulate the surface. The various modeling parameters that were used in the calculations of the adsorption energies have been chosen by performing a series of extensive test calculations, in which the effect of the parameters on adsorption energies has been carefully estimated. In order to prevent a collapse of the upper surface atoms (from a cubic to a hexagonal structure)

surface-terminating species have to be induced in the model. This work focuses on H as a most promising saturating species. Its adsorption energy and geometrical structure has been calculated to both a surface boron and nitrogen atom. Furthermore, adsorption processes of several plausible gaseous boron- and nitrogen-containing growth species have also been studied. The results show that NH and NH_2 are the species that will have the strongest tendency to become bonded to B, without any mixing of boron species. To nitrogen sites it is the boron species BH, BH_2 and BBr that are most suitable for growth at a (110) surface.

KK3.6
A model for nanocrystalline diamond growth. Peter Zapol and Michael Sternberg; Materials Science Div., Argonne National Laboratory, Argonne, Illinois.

Diamond growth in hydrogen-poor argon plasmas results in a polycrystalline film with grain sizes in the range of 3 to 10 nm. Growth mechanisms of this material have to be very different from conventional CVD growth. Unlike use of methyl radical and acetylene precursors in conventional diamond growth mechanisms, ultrananocrystalline diamond growth process involves the C_2 dimer as predominant growth species. On the basis of calculated reaction mechanisms of C_2 with diamond surfaces, we are proposing a model that can account for very high renucleation rates necessary to produce diamond with grain sizes in the nanometer scale. This nonempirical model invokes transition state theory to calculate reaction rates from the energies and barriers calculated using electronic structure methods. Resulting renucleation rates and grain sizes provide a mechanism for nanocrystalline diamond growth in the absence of hydrogen. The temperature dependence of renucleation rate as a function of the C_2 density in the plasma was obtained from the model. It shows that a grain size reaches its maximal value at the temperatures of about 800°C. A comparison of the computed results with available experimental data is provided and further predictions are discussed.

KK3.7
Structural and Electronic Properties of Metallic Alloys: An Ab-Initio Virtual Crystal Approximation Study. Omar de la Pena, Jazidy Alvarez, Gabriel Murrieta and Romeo de Coss; Department of Applied Physics, Cinvestav-Merida, Merida, Yucatan, Mexico.

The Virtual Crystal Approximation has been used to study the structural and electronic properties of $Nb_{1-x}Mo_x$, $Mg_{1-x}Al_xB_2$, and $MgB_{2-x}C_x$. We show that the $ab-initio$ VCA is useful in the study of metallic systems where the alloying elements are adjacent in the periodic table. The results were obtained by means of total-energy calculations using the full-potential Linearized Augmented Plane Wave method and the Generalized Gradient Approximation for the exchange-correlation potential. We present results for the structural parameters, elastic constants, and electronic structure. We find that the behavior of the calculated alloy lattice parameters show deviations from the Vegard's rule, in agreement with the experimental data. We show that the observed anomaly in the elastic constants of $Nb_{1-x}Mo_x$ around x=0.4 is an electronic topological transition effect. In addition, the evolution of the lattice parameters (a and c) as a function of x in $Mg_{1-x}Al_xB_2$ and $MgB_{2-x}C_x$, is analyzed. We show that the experimental data of a(x) and c(x) for these alloys are reproduced by the calculations and the behavior is explained in terms of changes in the chemical bond. This research was supported by Consejo Nacional de Ciencia y Tecnologia (CONACYT, Mexico).

KK3.8
Crossover from tunneling to the bulk scaling limit in correlated nanostructures. Jim Freericks, Physics, Georgetown University, Washington, District of Columbia.

We employ an inhomogeneous form of the dynamical mean field theory to examine transport in a device constructed of two ballistic metal leads and a barrier region. The barrier can be tuned through a metal insulator transition, and its thickness can be varied from a single plane to hundreds of planes. We study the junction resistance as functions of the barrier thickness, the strength of the correlations, and the temperature. We see a crossover from an exponential dependence of the resistance on the barrier thickness to a linear dependence (indicating the bulk scaling limit has been reached). We extract appropriate energy and length scales that describe how this crossover occurs as a function of temperature. This analysis is useful to determine the parameter regimes where devices are dominated by quantum tunneling effects.

KK3.9
Molecular modelling of W, Ti and Ta ALD precursors to determine penetration threshold in porous low k dielectrics. Thomas Abell[1], Ken Somers[2], Marc Hendrickx[2], Luc Vanquickenborne[2], Arnout Ceulemans[2] and Karen Maex[3]; [1]Intel, Leuven, Belgium; [2]Dept. of Chemistry, K.U. Leuven, Leuven, Belgium; [3]IMEC, Leuven, Belgium.

Atomic layer deposition (ALD) is an attractive method to deposit Cu diffusion barrier films for semiconductor interconnect applications due to the high conformality of deposition. However, integration of ALD with porous low k dielectric materials is problematic due to the ability of gaseous ALD precursors to penetrate and deposit inside the porous structure of dielectrics that degrade their electrical properties. This work attempted to estimate the penetration threshold of various precursor and probe molecules using Gaussian 98 modeling and a simple surface penetration schema. The size and shape of precursor molecules for the deposition of W, Ti and Ta-based diffusion barrier materials (WNC, TiN, TaN, etc.) were modeled and fit to various geometric envelopes to determine the smallest pore diameter that these molecules would enter in their minimum conformations or configurations. For the WNC process WF_6 was estimated to enter pores with circular cross-sections larger than 6.2 Å. This implies that WF_6 will enter any material that will also allow penetration of the 6.8 Å diameter molecule toluene, the probe molecule for ellipsometric porosimetry. Deposition of W inside blanket films of microporous (<2 μm diam.) dielectrics was confirmed by XRR measurement and is documented for mesoporous (>2 μm diam.) dielectrics. Triethylborane (TEB), one of the reactants in the WNC process, was estimated only to penetrate into circular cross-sections of 7.8 Å or elliptical cross-sections of 5.8 x 8.0 Å. This indicates the possibility of WF_6 penetration beyond TEB, a F getter, but not beyond the 3.8 Å NH_3 reactant. F etching at the interface of the deposition has been observed. Modeling of other molecules for the deposition of Cu barrier films was performed. Precursors TDMAT and TDEAT were modeled for ALD TiN deposition indicating minimum elliptical cross-sections of 9.1 x 9.9 Å and 10.7 x 12.2 Å ,respectively, for penetration. Calculations for precursors PDMAT and PDEAT used in the ALD deposition of TaN films indicated elliptical cross-sections of 9.1 x 9.9 Å and 11.4 x 11.6 Å ,respectively, are required for penetration. The Ti and Ta precursors are larger in cross-section which implies that they are less likely to penetrate into microporous dielectric films. It is also expected that the increased geometrical complexity of the molecules will hinder their movement inside the pore structure of a porous dielectric.

KK3.10
Correlation of Atomic-scale Simulation to Experimental Results of the Formation and Growth of Oxide Nanostructures on Copper Thin Films. Richard John McAfee, Xuetian Han, Judith Yang and Guangwen Zhou; Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Parallel and personal computing systems can inexpensively perform simulations containing thousands of atoms, whereas experimental methodologies are approaching the same spatial and temporal scale as simulations under highly controlled conditions. The work presented here introduces current and future work relating kinetic Monte Carlo (kMC) and Molecular Dynamic (MD) computer simulation of island nucleation and growth of Cu_2O islands to directly correlate with in situ Ultra High Vacuum - Transmission Electron Micorscope (UHV-TEM) experimental results of copper thin films oxidized at various temperatures and pressures of oxygen. Copper passivation is critical to understand at the nanoscale since a recent advance in microprocessor design allowing for increased speed and reduced operating temperatures has been the replacement of aluminum with copper as the interconnect material. The effect of oxidation on the properties and performance of the interconnect material becomes more significant as the dimensions decrease. Additionally, the spatial distribution of oxide islands on a metal substrate may form in a self-organizing manner, important in nanotechnology applications. In-situ oxidation experiments of Cu(100) at low pressures of oxygen at 600°C show similar island morphology to Ge grown on a Si substrate. Therefore, the theory and body of work available for semiconductor simulation provides a starting point and the algorithms. Initial simulation results show reasonable agreement with experiment. The effects of various simulation parameters on results may lead to a better understanding of the materials science of nanoscale oxidation and new or improved manufacturing techniques to prevent problems resulting from oxidation, to add new functionality, and/or to reduce cost. Methods developed for this system will be applicable to systems other than metal-oxides.

KK3.11
Ab initio based modeling of transition metal monoxides having defect lattices. D. A. Andersson[1], P. A. Korzhavyi[1] and B. Johansson[1,2]; [1]Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden; [2]Physics, Uppsala University, Uppsala, Sweden.

The presence of defects (vacancies, interstitials, etc.) in materials

based on transition metal oxides influence their chemical and physical properties, such as stability, catalytic activity, diffusivity, hardness and electrical conductivity. Experimental measurements of atomic defects and interpretation of the results are often difficult due to the complexity of these materials. Theoretical calculations based on quantum mechanics can nowadays be a complementary way of obtaining information about defects and their behavior in oxide materials. In the present paper this will be exemplified by results for titanium and vanadium monoxides. Transition metals in groups IV and V in the periodic table tend to form oxides based on the cubic NaCl structure near equiatomic composition. Titanium and vanadium monoxides can have large fractions of vacancies on both the metal and non-metal sublattices. Depending on the temperature and pressure these vacancies can either be ordered or disordered. We have treated the ordered structures with a pseudo-potential method using a plane wave basis set, while the calculations for the structures with disordered vacancies were performed within the framework of the muffin-tin orbital Green's function technique. For TiO our calculations confirm that a monoclinic vacancy-containing phase is stable at low temperature and pressure. At high pressure a transition to the vacancy free NaCl structure is predicted. The transition from a structure with disordered vacancies to the NaCl structure has experimentally been shown to occur at much lower pressures and it is discussed how this relates to the present theoretical results for defect containing and defect free TiO. The stability, conductivity as well as the structural and mechanical properties of TiO and VO are discussed in terms of the electronic structure. The authors gratefully acknowledge support from the Swedish Foundation for Strategic Research through the Center for Computational Thermodynamics (CCT).

KK3.12
Abstract Withdrawn

KK3.13
Formulation of a Heterovalent Virtual Crystal Approximation. Nicholas J Ramer, Chemistry, Long Island University - C. W. Post, Brookville, New York.

In recent years, new formulations of the virtual crystal approximation (VCA) have been devised. These implementations have improved upon previous versions of the VCA, which provided in some cases only qualititative agreement with experimental and large-scale solid-state calculations. One new method focused on constructing a VCA potential that possess correctly averaged electronic atomic properties [Phys. Rev. B 62, R743 (2000)]. This method, however, was formulated for averaging homovalent atoms into the virtual atom. In the case of heterovalent atoms, this method can be reformulated using non-trivial averaging methods for the atomic potentials and atomic orbital energies. This heterovalent VCA formulation has been utilized to study Mg1/3Nb2/3. Electronic properties for the VCA atom are compared to all-electron results for the component atoms.

KK3.14
The Constant Traction Method For Molecular Dynamics Simulations of Systems Under Mechanical Loading. Fabrizio Cleri[1] and Luciano Colombo[2]; [1]Unita' Materiali e Nuove Tecnologie, ENEA, Roma, Italy; [2]INFM and Dipartimento di Fisica, Universita, Cagliari, Italy.

We describe the constant-traction molecular dynamics method to perform simulations of a generic atomistic system under an applied external load at finite temperature. The main objective of the method is to ensure consistency between the atomistic model and the macroscopic continuum-mechanics description (the Cauchy-Euler principle). Examples of simulations for different kinds of extended defects under an external load, such as a grain boundary, an elliptical microcrack and a screw dislocation in an fcc crystal are presented, and compared with the results of the corresponding continuum mechanics description. Recent developments concerning the extension of the method to semi-empirical and ab-initio molecular dynamics will be discussed.

KK3.15
Ab initio study of divacancy clusters in silicon. Dmitry Makhov and Laurent J. Lewis; Department of Physics, University of Montreal, Montreal, Quebec, Canada.

At room temperature, vacancies resulting from irradiation of silicon are mobile and quickly form divacancies. The presence of divacancies can be detected using, in particular, infrared or positron annihilation spectroscopy. However, for divacancy annealing at T=250 C, there is a contradiction between the results given by these two methods: whereas infrared absorption decreases quickly with time, the positron lifetime remains unchanged [1]. In order to understand this phenomenon, we have calculated the formation energy, geometry, and positron lifetime for divacancy clusters in various configurations. The calculations were performed within the pseudopotential DFT method. Positron lifetimes were computed using unperturbed electron densities taken from the DFT calculations, while the correlation potential and annihilation enhancement factors were determined within the semiconductor model [2]. It is found that there exists configurations consisting of nearby (but not directly bounded) divacancies that have quite low formation energies. It is proposed that the interaction between the divacancies may change the optical properties of the system, while leaving the positron lifetimes unchanged. [1] R. Poirier et al, Nucl. Instr. Meth. in Phys. Res. B, 206 (2003) 85. [2] M.J. Puska et al, Phys. Rev. B, 39 (1989) 7666.

KK3.16
Theoretical Study of Point Defects in ZrO2-Silicon Interfaces. Masashi Nakatomi and Koichi Yamashita; University of Tokyo, Tokyo, Japan.

We present a numerical study of point defects in ZrO2-silicon interfaces. The structure of ZrO2-silicon interface has been determined by molecular dynamics calculations. We used a slab model that consists of nine atomic layers of silicon and nine atomic layers of ZrO2. Three atomic layers of the slab that containing seventeen oxygen atoms, eight silicon atoms and nine Zr atoms correspond to a ZrO2-silicon interface. We then have performed density functional theory calculations to investigate the band structure of the inteface using the plane wave basis VASP code. The results demonstrate that lengthen Zr-O bonds and interstitial oxygen atoms give defect levels in the band gap. In particular, the defect levels due to intestitial oxygen atoms are locate closely on the top of the valence band, and may therefore affect the efficiency of gate dielectrics.

KK3.17
Molecular Dynamics Simulation on the Morphological Transformation of Dislocation Loops in FCC Metals. Hideo Kaburaki[1], Tomoko Kadoyoshi[1], Futoshi Shimizu[1], Hajime Kimizuka[2], Shiro Jitsukawa[3] and Ju Li[4]; [1]Center for Promotion of Computational Science and Engineering, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan; [2]Energy and Environment Technology Department, The Japan Research Institute, Tokyo, Japan; [3]Department of Materials Science, Japan Atomic Energy Research Institute, Tokai, Japan; [4]Department of Materials Science, The Ohio State University, Columbus, Ohio.

Irradiation of fcc metals by charged or neutron particles induce atomic collision cascades, where vacancies and interstitials aggregate to form varieties of clusters ranging from nano- to micrometer size. Typical clusters in FCC metals, which are observed in the transmission electron microscope and influence significantly the mechanical properties of irradiated materials, are hexagonal interstitial and vacancy dislocation loops with stacking fault inside. Also, stacking fault tetrahedra and unfaulting of dislocation loops are frequently observed, however their formation process and transformation mechanism have not been known in detail. We performed large-scale molecular dynamics simulation using the EAM potential of Cu and Al combined with the visualization techniques for defects to study the dissociation process of dislocation loops, and, in particular, successfully observed that fully dissociated dislocation loops of various sizes transform to other structures under some conditions. From these results, we have found the critical condition for the self-organized formation of a stacking fault tetrahedron from the dissociation of modified hexagonal vacancy dislocation loop. With the application of the shear stress to the dislocation loop, we also found atomistically the unfaulting process of a dislocation loop where Shockley partials are emitted to sweep the stacking fault leading to a perfect dislocation loop. We also present the atomistic result on the interaction of an edge dislocation with the above clusters and the relation to the mechanical properties of materials.

KK3.18
Dislocations and Grain Boundaries in Polycrystalline Tungsten Wires. Matous Mrovec[2,1], Christian Elsaesser[1], Peter Gumbsch[1,2] and Vaclav Vitek[3]; [1]Fraunhofer IWM, Freiburg, Germany; [2]IZBS, University of Karlsruhe, Karlsruhe, Germany; [3]University of Pennsylvania, Philadelphia, Pennsylvania.

The mechanical properties of polycrystalline tungsten wires are controlled by the motion of screw dislocations and their interaction with grain boundaries. In our study we have investigated the structure and energetics of these extended defects using bond-order potentials that are based on tight-binding theory. The validity and transferability of the potentials have been verified by comparison to the results of first principles calculations for several simple structures including the {211} twin boundary and its shear resistance. Large scale calculations of several other grain boundaries and of the interaction of a dislocation with these boundaries are than performed using the bond-order potentials.

KK3.19
Surface Segregation Energies of BCC Binaries from Ab Initio and Quantum Approximate Calculations. Brian S. Good, NASA Glenn Research Center, Cleveland, Ohio.

We compare dilute-limit segregation energies for selected BCC transition metal binaries computed using ab initio and quantum approximate energy methods. Ab initio calculations are carried out using the CASTEP plane-wave pseudopotential computer code, while quantum approximate results are computed using the Bozzolo-Ferrante-Smith (BFS) method with the most recent parameterization. Quantum approximate segregation energies are computed with and without atomistic relaxation. The ab initio calculations are performed without relaxation for the most part, but predicted relaxations from quantum approximate calculations are used in selected cases to compute approximate relaxed ab initio segregation energies. Results are discussed within the context of segregation models driven by strain and bond-breaking effects. We compare our results with other quantum approximate and ab initio theoretical work, and available experimental results.

KK3.20
Direct Experimental and Simulation Comparisons of the Nanoscale Oxidation Behavior of Cu(100). Xuetian Han, Rich McAfee and Judith C Yang; Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Surface oxidation process plays critical roles in environment stability, high temperature corrosion, electrochemistry, catalysis and some thin film growth. Because of its importance, much work has been done to investigate this process using many different techniques, yet fundamental understanding of the initial oxidation kinetics, from the oxide nucleation to coalescence, is still surprisingly not well understood. We have extensive experimental results of the nano-oxidation process of Cu(100) thin films via in situ UHV-TEM at various temperatures and oxidation pressures. The initial oxdiation kinetics bear a striking resemblance to heteroepitaxy, where oxygen surface diffusion is the primary mechanism of Cu_2O island nucleation and growth. Yet, theoretical analysis is necessary for deeper understanding of these nano-scale processes. In this paper, a simulation program based on the kinetic Monte Carlo method, to directly correlate with the experimental observations, will be introduced. By using this program, the two dimensional Cu(100) oxidation behavior can be simulated with various initial and final conditions. Some correlations, like deposition rate vs. nucleation rate, temperature vs. saturated island density and temperature vs. sticking probability., are being established. A reasonable match of the simulated data and the experimental data has been found. This simulation effort effectively evaluates the in situ experimental results and is essential for the fundamental understanding of the nanoscale metal-gas reactions.

KK3.21
A Nonorthogobal Tight Binding Hamiltonian for the Study of Nanocrystalline Materials. Anna Maria Mazzone, Istituto IMM, CNR, Bologna, Italy.

Many current researches in solid state physics and in material science focuse on nanocrystalline materials. These materials are formed by the assemblage of crystalline grains with nanometer dimensions and their features may noticeably deviate from the ones of the parent solid. In spite of the intensive experimental efforts concentrated in this field, the understanding of these effects is generally qualitative and is jeopardized by the large structure of the grains which is beyond the present capabilities of *abinitio* methods. With the aim of a computationally efficient and physically accurate method in this study we present a nonorthogonal tight-binding Hamiltonian based on the extended Hueckel approximation. A versatile parametrization, which elaborates on current models, has been developed to describe large structures of compound composition and with a complex shape. The Hamiltonian has been extensively tested on a wide range of structures, i.e. bulk materials, surfaces and small clusters of either metallic and covalent composition. In the field of nanocrystals the method has been applied to tin dioxide crystalline grains, a material of both theoretical and practical relevance due to its use for solar cells, heat reflecting filters and as a gas sensor.

KK3.22
Molecular Dynamics Simulation of Stress and Cappilarity Induced Grain Boundary Migration in Nickel. Hao Zhang[2], Mikhail I Mendelev[2] and David J Srolovitz[2]; [1]Princeton Materials Institute, Princeton, New Jersey; [2]Department of Mechanical and Aerospace Engineering, Princeton Materials Institute, Princeton, New Jersey.

Control of crystallographic texture during materials processing is key to achieving a wide range of desirable physical properties. All processes that modify texture are based upon microstructural evolution occurring though the motion of grain boundaries. Quantitative simulation of such types of microstructural evolution must be based upon grain boundary mobilities, which are functions of the five crystallographic parameters that describe each grain boundary. We will present the results of a series of studies of 3-d molecular dynamics simulations of grain boundary migration as a function of grain misorientation and grain boundary inclination. These studies were performed with embedded atom method type potentials fitted to represent nickel. In the first study, stored elastic energy was used to drive the migration of nominally flat <001> tilt grain boundaries. The grain boundary velocity was found to be linear function of driving force for all grain boundary misorientations and inclinations. Simulations performed at different temperatures were used to extract the activation energy for boundary migration. In the second study, we simulated steady-state curvature driven boundary migration in a half-loop geometry for the same boundary misorientations used in the first study. These simulations provide a means of determining reduced boundary mobilities (i.e., the product of the grain boundary mobility and stiffness). Together, these two data sets allow us to answer the outstanding question "does grain boundary mobility depend on the nature of the driving force?"

KK3.23
Abstract Withdrawn

SESSION KK4: Nano-systems, Surfaces, and Interfaces
Chair: Anatoli Korkin
Tuesday Morning, December 2, 2003
Constitution A (Sheraton)

8:30 AM *KK4.1
Carbon Nanotube Structures and MD Simulations at the Realistic Limit. Kimmo Kaski, Maria Huhtala and Antti Kuronen; Research Centre for Computational Science and Engineering, Helsinki University of Technology, ESPOO, Finland.

Carbon nanotubes as all-carbon molecules of tubular form exemplify modern nanometer scale material structures, where the number of atoms ranges from less than a million up to few tens of millions. Such systems are quite ideal for computational studies like Molecular Dynamics (MD) simulations because they can be done at the realistic limit, rendering them in a way predictive. However, the goodness of their predictivity is dependent on the model potential, for which the empirical potentials developed by Brenner have turned out to be quite successful, e.g. in describing structural properties of single walled tubes (SWT's). Nevertheless, in cases like the SWT under strong bending where structural deformation can be large and defects form, more accurate dynamical tight-binding method needs to be used in conjuction. Since the TB method is limited for studying systems of the order of thousand atoms we have focused it only to areas of large deformations in the tube. In this report we demonstrate that the joint use of MD and dynamical TB simulations can yield insight to carbon nanotube structures and their deformations.

9:00 AM KK4.2
Ballistic Conductance of Functionalized Carbon Nanotubes: First-principles Simulation. Young-Su Lee[1], Marco Buongiorno Nardelli[2] and Nicola Marzari[1]; [1]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Department of Physics, North Carolina State University, Raleigh, North Carolina.

Functionalization of carbon nanotubes has drawn much attention due to their potential applications e.g. as bio/chemical sensors or in molecular electronic devices. In the interest of controlling electronic properties, sidewall functionalization represents a very promising avenue since the delocalized pi bonding is vulnerable to covalently attached functional groups. High degree of sidewall functionalization has been reported ; however, it's still unclear how the charge distribution is distorted by functional groups and whether it preserves other unique and versatile properties of the clean carbon nanotubes. In this work, we calculate the ballistic conductance of functionalized nanotubes using first-principles simulations. A combination of Car-Parrinello molecular dynamics with the maximally-localized Wannier-functions method allows us to deal with relatively big systems and to investigate the bonding in the chemically-modified region. We focus here on the variations of the ballistic conductance obtained by attaching electron-donating and electron-accepting functional groups.

9:15 AM KK4.3
Development, validation, and application of mesoscopic theory and simulation for quantum dot formation. Abhijit Chatterjee[1], Dionisios G. Vlachos[1] and Katsoulakis A. Markos[2]; [1]Department of Chemical Engineering and Center for

Catalytic Science and Technology (CCST), University of Delaware, Newark, Delaware; [2]Department of Mathematics and Statistics, University of Massachusetts, Amherst, Massachusetts.

Formation of periodic domains of nanoparticles on growing films, such as semiconductor quantum dots, metallic nanoparticles and nanowires, via self-organization routes occurs through cooperative phenomena where intermolecular forces and strain-induced interactions are critical. Molecular simulation tools, such as kinetic Monte Carlo (KMC) algorithms use a molecular level description of the intermolecular interactions, and therefore, are ideal tools for studying pattern formation of nanoparticles on surfaces. However, KMC simulations are limited to short length and time scales, whereas experimental data often invoke scales beyond the realm of these atomistic simulation tools. This is particularly the case for long-range strain-induced interactions. In this talk, we introduce novel coarse-grained Monte Carlo (CGMC) simulations that can be used to link the microscopic scales with self-organization phenomena in the scale of microns or more. It is shown that in the case of fast diffusion, coarse-graining in space leads also to significant coarse-graining in time, and as a result, it partially alleviates the hydrodynamic slowdown. As a result, CGMC is ideally suited to handle realistic diffusion rates that are beyond microscopic KMC simulations. Comparison to microscopic KMC and rigorous asymptotics clearly demonstrate that these new CGMC tools satisfy detailed balance, capture the correct noise, and exhibit tremendous CPU savings. CGMC simulation is applied to the formation of quantum dots over large length and time scales and the roles of strain field and thermal fluctuations in their nucleation and periodic self-organization are elucidated. We will also present the corresponding continuum partial differential equations, which are amenable to nonlinear analysis, for identifying conditions where nanoparticle self-organization occurs.

9:30 AM KK4.4
Laser-Focused Atom Deposition on Anisotropic Substrates. 2D Monte Carlo Simulation. Florin Nita[1,2] and Alberto Pimpinelli[1]; [1]LASMEA, Blaise Pascal University, Clermont-Ferrand, France; [2]Institute of Physical Chemistry, Romanian Academy, Bucharest, Romania.

Last years a lot of efforts were made, in the beginning to obtain, and after that to increase the quality and the density of the nanostructure arrays. One of the techniques used to obtain such arrays is the laser-focused atom deposition. A standing wave region is created in the proximity of a crystal surface, if a laser beam is directed parallel to this surface and then retroflected. The wavelength of the standing wave is l/2 where l is the optical wavelength, and this region acts like an array of cylindrical lenses for an incoming neutral atoms beam. The role of the surface diffusion anisotropy in the fabrication of nanostructures by laser-focused ("cold") atom lithography, and on the stability of these nanostructures is studied using 2D kinetic Monte Carlo simulations. Two different wave profiles were used in the simulations. The simulations were performed using one- and two-dimensional standing wave fields and two different diffusion models (limited and total diffusion model) on anisotropic surfaces, such as (110) surfaces of FCC crystals, or reconstructed surfaces such as Si(100). The simulations were made with and without Schwoebel barriers. Our diffusion-deposition models reproduce both qualitative and quantitative experimental results. They show that the time evolution of height, FWHM and background for the profiles obtained using the same standing wave are different for different orientations of the standing wave field to the easy diffusion direction of the adatoms on the surface: parallel ($\parallel$) and perpendicular ($\perp$), respectively. Our results suggest that it is possible to reduce the feature width in nanostructures, such as quantum dots or quantum wires, using laser-focused atom deposition techniques on an anisotropic substrate. This work was supported by EC Contract No. IST-2001-32264 (NANOCOLD).

10:15 AM *KK4.5
Variable Stoichiometry, Defects and Reconstructions at Oxide Surfaces. Nicholas Harrison, Chemistry, Imperial College London, London, London, United Kingdom.

Under the operating conditions of many devices oxide surfaces are highly defective, often reconstructed and may have a stoichiometry distinct from that of the bulk crystal. The electronic and magnetic structure of the surface may be very different from that of the bulk or idealised surfaces. In many applications, particularly those which depend on nano-structured materials, materials design depends on the control of this complex surface environment. Recent developments in first principles simulation have significantly increased the reliability of the computed ground state energy surfaces in strongly interacting oxides. It is now not unrealistic to attempt to predict the stoichiometry, structure, electronic and magnetic properties for rather complex systems under realistic operating conditions. These developments will be reviewed and their application to the surface electronic structure and magnetism in a number of transition metal oxides will be discussed.

10:45 AM KK4.6
Ab-initio Simulations of Homoepitaxial Growth of SiC(111). Maria Clelia Righi[1,2], Carlo Antonio Pignedoli[1,2], Alessandra Catellani[3], Rosa Di Felice[1,2] and Carlo Maria Bertoni[1,2]; [1]INFM-National Research Center on nanoStructures and bioSystems at Surfaces (S3), Modena, Italy; [2]Dipartimento di Fisica, Universita' di Modena e Reggio Emilia, Modena, Italy; [3]CNR-IMEM, Parco Area delle Scienze, Parma, Italy.

Silicon Carbide (SiC) is one of the most promising wide-bandgap semiconductors for harsh environment applications. The development of a SiC-based technology was so far delayed because of difficulties in the materials production. Experiments of solid-source molecular beam epitaxy have shown that an accurate SiC layer-by-layer growth on SiC(111) surface is possible under Si-stabilized conditions [1], suggesting that the surface reconstruction plays a relevant role in determining the growth mode and the film quality. We investigated this point by simulating the initial stages of β-SiC growth on the SiC(111)-$sqrt3$ x $sqrt3$ surface. We found that the surface reconstruction influences the kinetics of adatom incorporation in such a way that a layer-by-layer growth may be favored: the local environment of the $sqrt3$ x $sqrt3$ reconstruction shapes a multilevel potential energy surface for the deposited C adatoms that induces their channeling towards the correct crystalline sites. Moreover, the anisotropic subsurface C diffusion, along with the observed C-C interactions, favors the nucleation around the each Si adatom of the original reconstruction. The formation of several small nuclei, instead of few large islands is conducive to a layer-by-layer growth. In addition to this, our quasistatic quantum mechanical simulations reveal that the gain in surface energy obtained by capping the growing surface with the right dose of Si atoms that are necessary to recover the $sqrt3$ x $sqrt3$ reconstruction, is sufficient to activate the spontaneous transition of the system from a metastable defective configuration to the SiC crystal structure, thus revealing a surface-driven mechanism able to stabilize defect-free layer deposition on Si-rich surfaces. [1] A. Fissel et al., Appl. Phys. Lett. 66, 3182 (1995); Appl. Phys. Lett. 68, 1204 (1996).

11:00 AM KK4.7
Elastic Interaction of Oxygen atoms on a Graphite Basal Plane. Philippe Peyla, Andrei Incze and alain pasturel; LPM2C, Universite Joseph Fourier, Grenoble, France.

We calculate the elastic interaction energy between two oxygen atoms deposited on a graphite basal plane. Simulations are performed with atomic ab initio calculations (VASP) and continuum theory of elasticity. The comparison between the results obtained with the two different methods, despite their usual length scale domain of application, is very good; attractive and repulsive behaviors are found. We speculate that this type of interaction could play an important role in the rearrangement of oxygen atoms experimentally observed after a weak oxidation of a graphite surface. First results about elastic interaction of oxygen atoms on a graphite surface have been published in Phys. Rev. B66, (Brief Report), 172101 (2002).

11:15 AM KK4.8
Atomic and electronic structure modelling of nanoamorphous films in silicon nitride ceramics (+). Duc Nguyen-Manh[1], David J.H. Cockayne[1], Markus Doeblinger[1], Adrian Sutton[1] and Adri van Duin[2]; [1]Department of Materials, University of Oxford, Oxford, United Kingdom; [2]Beckman Institute, Carlifornia Insitute of Technology, Pasadena, California.

The presence of the thin intergranular films (IGF) between crystals can significantly influence mechanical, thermodynamic and chemical properties of bulk ceramic materials. Because of this, there is increased interest in understanding the local bonding structures of the IGF and a variety of modelling and experimental studies are being used to investigate the crystalline-amorphous interfaces and the chemical compositions of IGFs. In order to gain insight on the interfacial structures, electronic properties and chemistry of these thin films, we have developed the transferable and reliable reactive force field (RFF) scheme not only for molecular dynamic simulations but also for bond-order characterization. The parameters for this RFF, which take into account many-body environmentally dependent contributions from over/under coordination effect, were obtained from fitting with density functional theory (DFT) calculations on the structure energy barriers and bonding properties for a number of silicon oxide and nitride clusters and on the equation of state for condensed phases of SiO2, Si3N4 and Si2N20. Molecular dynamic (MD) simulations have been performed to generate atomic structure of nanoamorphous IGFs formed between various basal and prism planes of silicon nitride crystals. We found that although bonding formation of Si-N and Si-O bonds are dominant in stabilizing silicon oxynitride

film, a formation of nitrogen triple-bond dimers is observed during the MD runs at 2000K. We have studied the dependence of ratio N/(N+O), which plays a crucial role in thermodynamic properties of Si-O-N amorphous films, on different temperature regimes and IGFs thickness. Our MD simulations show that the N2 formation is substantially reduced when the ratio N/(N+O) 1/3 which is in a good agreement with electron energy loss spectroscopy (EELS) quantitative studies of composition and chemical profiles in interfacial regions. The calculated radial distribution function is decomposed into different contributions and compared with those experimentally measured using nanometer scale electron diffraction techniques. Finally, the bond-order behaviour across the IGFs is analyzed in details from simulated interfacial atomic structures within both RFF framework and DFT electronic structure calculations from an efficient ab-intio tight-binding PLATO code. (+) This work is supported by EC/US collaborative grand (GRD2-200-30351) on "Nanometer scale induced structure between amorphous layers and crystalline materials".

11:30 AM KK4.9
Hybrid Atomistic/Continuum Model for Multi-Scale Simulation of Surface Evolution. Paul Spencer, Simon Gill and Alan Cocks; Department of Engineering, University of Leicester, Leicester, United Kingdom.

A combined atomic/continuum scale method to simulate the evolution of a surface via diffusion is presented. The atomic scale description uses the Kinetic Monte Carlo (KMC) method to simulate diffusion as discrete random hopping events. The continuum description represents diffusion as a deterministic flux. The Hybrid scheme links the two descriptions using a Blending Region. Both atomistic and continuum characteristics are simultaneously represented in this region allowing material to move across the KMC/continuum interface in a consistent manner. This method naturally allows for the co-existence of multiple length and time scales within a single simulation. The effectiveness of the scheme is demonstrated using a Solid-on-Solid potential for simple surface profiles.

11:45 AM KK4.10
Accurate Determination Of Voltage-Current Characteristics For Single Molecules. P. Delaney and Jim C. Greer; NMRC, University College, Cork, Ireland.

The development of molecular scale electronic devices has been hampered by the experimental difficulties associated with contacting and measuring the electrical properties of individual molecules. It must be equally acknowledged that theoretical treatments of charge transport across molecular devices are hampering molecular electronic design efforts due to problems such as the large discrepancies found between calculated and experimental current-voltage characteristics, and as well disagreement between differing theoretical treatments. Typically, theoretical treatments predict currents two to three orders of magnitude higher than experiment. It is desirable to be able to apply the highly developed methods of quantum chemistry and electronic structure theory to the problem of designing atomic scale electronic devices and components. However, it remains a difficult problem to extend the machinery of electronic structure theory, largely developed to study closed or periodic systems, to incorporate open system boundary conditions needed to describe electronic transport. If open boundary conditions are introduced into density functional theory (DFT) calculations, several problems arise. For example, the exchange-correlation functional is current dependent, a fact not explored to date within molecular electronic studies. Recently, it has been highlighted that the currents theoretically predicted with DFT methods can vary by over an order of magnitude simply due to the choice of exchange-correlation functional. A further problem is that application of a single particle distribution function to the Kohn-Sham eigenvalues is an ambiguous procedure. In our approach to the electronic transport problem, we side step these issues by miminizing the energy of a molecule in contact with metallic contacts within a many-body basis and with open system boundary conditions formulated in a manner appropriate to the case of correlated many-body wave functions. Application of the method leads calculation of current-voltage characteristics for prototypical molecular systems within the same order of magnitude as experimental observations.

SESSION KK5: Methods I
Chair: Jim Greer
Tuesday Afternoon, December 2, 2003
Constitution A (Sheraton)

1:30 PM *KK5.1
Real-space Multiscale Simulations for Metals: Implementation of Density-functional with Embedded Atom Coupling. Efthimios Kaxiras[1,2], Nick Choly[2], Gang Lu[2] and E. Weinan[3]; [1]Physics, Harvard University, Cambridge, Massachusetts; [2]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; [3]Applied Mathematics, Princeton University, Princeton, New Jersey.

The use of multiscale simulations for materials is evolving into a major theme in the treatment of realistic systems. Applications to covalently bonded systems have already been successfuly performed, incorporating all the relevant length scales from the quantum mechanical to the continuum. What has made such seamlessly coupled schemes feasible is the possibility of terminating the quantum region at the boundary with the classical region, using fictitious atoms specifically designed to saturate dangling covalent bonds [1]. The case of metallic materials provides a much greater challenge to the seamless inclusion of the quantum region, whose non-localized electronic states cannot be easily terminated at the boundary with the classical region. We report on our recent progress in achieving such a coupling scheme for metals. We have developed a methodology which relies on kinetic energy functionals, in the context of density functional theory, to represent the quantum mechanical region and embedded-atom type potentials for the classical region. The use of a quantum method that relies exclusively on the electronic density is advantageous in the sense that terminating boundary conditions for all the electronic wavefunctions are not required. The use of the embedded-atom approach is also ideally suited, since it derives from arguments which invoke the electronic density to describe the energetics in the classical region. A major new development is the use of a real-space formulation, which allows the imposition of arbitraty boundary conditions to the quantum region. This makes it feasible to treat structures with arbitrary types of extended defects (such as dislocations, grain boundaries, interfaces). We will describe tests and initial applications of the method to selected examples, such as hydrogen-induced embrittlement of aluminum. [1] F.F. Abraham, J.Q. Broughton, N. Bernstein and E. Kaxiras, Computers in Physics 12, 538 (1998); Europhysics Letters 44, 783 (1998); Phys. Rev. B 60, 2392 (1999).

2:00 PM KK5.2
Multiscale Modeling of Small Molecules in Zeolite-4A. N. A. Modine, M Chandross and E Jaramillo; Sandia National Labs, Albuquerque, New Mexico.

Confinement within the nanoscale pores of a zeolite strongly modifies the physical and chemical behavior of small molecules such as water, ammonia, and carbon dioxide. Realistic modeling of such phenomena requires simultaneously capturing the detailed behavior of chemical bonds and the possibility of collective dynamics occurring in a complex unit cell (672 atoms in the case of Zeolite-4A). Classical simulations alone cannot reliably model the breaking and formation of chemical bonds, while quantum methods alone are incapable of treating the extended length and time scales characteristic of complex dynamics. Therefore, we have taken a mixed quantum/classical approach. We report our progress in developing an efficient algorithm for embedding a small region treated with density functional theory within a larger system represented by classical potentials. We compare Green's function and energy minimization approaches to finding a localized representation of the electronic structure, and we discuss results for the behavior of water, ammonia, and the ammonium ion in Zeolite-4A. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE- AC04-94AL85000.

2:15 PM KK5.3
From DFT to TB: The Mo-C system. Matous Mrovec[2,1], Rebecca Janisch[3] and Christian Elsaesser[1]; [1]Fraunhofer IWM, Freiburg, Germany; [2]IZBS, University of Karlsruhe, Karlsruhe, Germany; [3]Max-Planck Institute of Metals Research, Stuttgart, Germany.

In the course of developing a multi-scale model for the description of chemical vapor deposition of diamond-like films on metal substrates we have investigated the Mo-C system as a substrate-film case study. In order to describe the system at various length and time scales, different methods are needed. As the initial step, the system has been investigated by means of the density functional theory with the mixed-basis pseudopotential approach. The results of these ab-initio calculations provide us with extensive information about global and local electronic properties of various phases in the system and serve also as a benchmark for less rigorous schemes. The database of first-principles results is used for the construction of two semi-empirical schemes - the environment-dependent tight-binding model (EDTB) of Haas et al. and the bond-order potentials (BOP) of Pettifor et al. These two models are based on the tight-binding theory but they differ in underlying mathematical formalism and physical applicability. While EDTB is a traditional k-space method, BOPs are cast in the real space. Here we present first results assessing the performance and reliability of both models for application in large scale simulations.

2:30 PM KK5.4
Development of New Tight-Binding Quantum Chemical Molecular Dynamics Method and Its Application to Electronics Materials. Momoji Kubo[1], Naoyuki Isoda[1], Takahiro Oyama[1], Katsumi Sasata[1], Akira Endou[1], Akira Imamura[2] and Akira Miyamoto[3,1]; [1]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Sendai, Miyagi, Japan; [2]Department of Mathematics, Faculty of Engineering, Hiroshima Kokusai Gakuin University, Hiroshima, Hiroshima, Japan; [3]New Industry Creation Hatchery Center, Tohoku University, Sendai, Miyagi, Japan.

Recently, we succeeded in the development of new tight-binding quantum chemical molecular dynamics method, which realizes more than 5,000 times acceleration compared with the regular first-principles molecular dynamics method. It indicates that 10 years calculation by the first-principles molecular dynamics can be finished within only one day by our accelerated quantum chemical molecular dynamics program. This methodology enables us to perform the large-scale simulations and to clarify the chemical reaction and electron transfer dynamics in the electronics materials. We successfully applied the above program to the etching process, chemical mechanical polishing process, crystal growth process, and various processes related to the electronics materials fabrication [1-3]. The chemical reaction dynamics and electron transfer dynamics during the above processes were clearly elucidated by using our new program. Especially, we successfully designed new materials for plasma display and the validity of our designed materials is experimentally investigated. Finally, we confirmed that our accelerated quantum chemical molecular dynamics program is a very powerful tool to clarify the electronic-level dynamics and to design new electronics materials. [1] T. Yokosuka, H. Kurokawa, S. Takami, M. Kubo, A. Miyamoto, and A. Imamura, Jpn. J. Appl. Phys., 41 (2002) 2410. [2] K. Sasata, T. Yokosuka, H. Kurokawa, S. Takami, M. Kubo, A. Imamura, T. Shinmura, M. Kanoh, P. Selvam, and A. Miyamoto, Jpn. J. Appl. Phys., 42 (2003) 1859. [3] T. Yokosuka, K. Sasata, H. Kurokawa, S. Takami, M. Kubo, A. Imamura, and A. Miyamoto, Jpn. J. Appl. Phys., 42 (2003) 1897.

3:15 PM *KK5.5
Transformation of Harrison's Tight-Binding Theory from a Qualitative Approach to a Quantitative Tool. Lei Shi[1] and Dimitris A Papaconstantopoulos[2]; [1]George Mason University, Fairfax, Virginia; [2]Center for Computational Materials Science, Naval Research Laboratory, Washington, District of Columbia.

Harrison's tight-binding theory (TB) [1] provides an excellent qualitative description of the electronic structure of the elements across the periodic table. However, Harrison's universal TB parameters produce energy bands and densities of states that are in serious disagreement with the results one gets from standard density functional theory codes such as those based on the APW, LMTO or pseudopotential methods. In this work we have developed a procedure that maintains the simplicity of Harrison's approach but gives an impressive improvement that puts the theory on a quantitative basis. To accomplish this we proceeded as follows: 1. We introduced the p-onsite energy as the only additional parameter to the s and d onsite energies used by Harrison, and increased the size of the secular equation to 9x9 for the transition metals. 2. We fitted simultaneously the APW energy bands of bcc Nb and fcc Pd using as adjustable parameters the above three onsite energies, Harrison's parameter Rd and the ten prefactors of the two-center integrals, keeping Harrison's functional form. 3. We kept the ten prefactors determined above as frozen, and then we fitted the all the 3d, 4d, and 5d elements using the onsite energies and Rd as adjustable parameters. We did the above fitting at the experimental value of the lattice constants and we reproduced the APW results remarkably well. With the inclusion of one additional parameter we also have been able to describe the lattice constant dependence of the energy bands. We believe that our scheme will work equally well for sp elements, will also describe total energies and has possibilities for extensions in binary materials. [1] W.A Harrison, "Electronic Structure and the Properties of Solids", Dover Publications, Inc., New York 1989. W.A.Harrison "Elementary Electronic Structure",World Scientific 1999

3:45 PM KK5.6
Full-potential Locally Self-consistent Multiple Scattering (FP-LSMS) Method. Malcolm Stock[2], Aurelian Rusanu[3], Yang Wang[1], Don Nicholson[2] and J.S. Faulkner[3]; [1]Pittsburgh Supercomputing Center, Carnegie Mellon University, Pittsburgh, Pennsylvania; [2]Oak Ridge National Laboratory, Oak Ridge, Tennessee; [3]Department of Physics, Florida Atlantic University, Boca Raton, Florida.

In this presentation, we introduce the Full-potential Locally self-consistent multiple scattering (FP-LSMS) method that we recently developed. The FP-LSMS method is an order-N approach to the ab initio electronic structure calculations for solids. It is based on full-potential multiple scattering theory, and allows to eliminate the muffin-tin approximation for both potential and charge density. In the parallel implementation of the method, we allow multiple atoms to be distributed on each processor. We also implemented the screened structure constants with sparse matrix algorithm which speeds up the multiple scattering matrix calculation significantly. We will demonstrate the order-N scaling of the method, and we will also show a preliminary application of the method.

4:00 PM KK5.7
First Principles Molecular Dynamics in a Uniform Magnetic Field. Wei Cai and Giulia Galli; Chemistry and Materials Science, Lawrence Livermore National Lab, Livermore, California.

While ab initio, plane-wave methods in the absence of external fields are widely used because of their computational efficiency, ab initio electronic structure calculations and first principles molecular dynamics simulations in a finite, uniform magnetic field have not yet been attempted. To treat a uniform magnetic field non-perturbatively, the Hamiltonian needs to depend on a vector potential that destroys translational invariance, thus making the use of plane-wave basis impractical. A new method is presented which allows one to perform ab initio calculations in a finite magnetic field by retaining the computational efficiency of plane-wave like basis and fast Fourier transform techniques. This method has been successfully applied to systems such as an interacting electron gas in quantum wells and dense hydrogen fluids under uniform magnetic fields. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

4:15 PM KK5.8
Improved Electrostatics for Large-Scale Biomolecular Simulations. Celeste Sagui[1], Pawel Pomorski[1], Thomas Darden[2] and Christopher Martin Roland[1]; [1]Physics, NC State University, Raleigh, North Carolina; [2]National Institute for Environmental and Health Sciences, Research Triangle Park, North Carolina.

Reliable biomolecular simulations are extremely difficult, because they involve complex systems such as macromolecules bathed in a solvent environment, long-range electrostatic interactions, correlation effects and a high sensitivity to both temperature and dynamical effects. In particular, an accurate and numerically efficient treatment of the classical electrostatics force fields is absolutely essential for a meaningful biomolecular simulation. Why is this? Classical codes such as AMBER and CHARMM assign "partial charges" to virtually every atom in a simulation in order to model the interatomic potentials. There are two main problems associated with the current treatment of classical electrostatics: (i) how does one eliminate the artifacts associated with the point charges, and thereby improve the electrostatic potentials in a physically meaningful way? (ii) how does one efficiently simulate the very costly long-range interactions? Here, we present results on a recently developed distributed multipole method. Based on the Particle-Mesh Ewald summation (PME) method, this formalism can treat electrostatic multipoles up to hexadecapoles without prohibitive additional computational costs. The required multipoles may be effectively computed via the maximally localized Wannier functions. Outlook and future of this method for large-scale biomolecular simulations will be discussed.

4:30 PM KK5.9
Atomistic Simulations of Dislocation Core Structures in Iridium Using Bond-Order Potentials with Lattice Greens Function Boundary Conditions. Marc Cawkwell[1], Vaclav Vitek[1], Duc Nguyen-Manh[2] and David G. Pettifor[2]; [1]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; [2]Department of Materials, University of Oxford, Oxford, United Kingdom.

We have recently developed a bond-order potential (BOP) for iridium which was found to provide not only an excellent description of cohesion in f.c.c. Ir but also shows good transferability to more open structures as well as structures with reduced symmetry. This BOP reproduces the elastic constants and negative Cauchy pressure of f.c.c. Ir through the introduction of a many-body repulsive term in the total energy and also yields excellent predictions for the energy of the intrinsic stacking fault and other simple crystal defects. We have applied this BOP in the atomistic simulation of dislocation core structures in f.c.c. Ir in order to better understand plastic deformation and ultimately the origin of the brittle cleavage under tensile loading in this material. The lattice Greens function boundary conditions advanced by Woodward, Rao and others have been implemented in our simulations during relaxation, thus enabling us to self-consistently treat the long-range strain fields induced by dislocations. The relaxed core structures of the screw, 30°, 60° and edge dislocations have been computed and using image simulation, we

have compared the structures of the screw and 60° dislocations to HRTEM images. This research was supported the U.S. Department of Energy, BES Grant. no. DE-FG02-98ER45702.

SESSION KK6: Poster Session II
Tuesday Evening, December 2, 2003
8:00 PM
Exhibition Hall D (Hynes)

KK6.1
Carbon Nanotubes As Mechanical Gigahertz Oscillators.
Douglas Soares Galvao[1], Sergio Legoas[1], Vitor Rafael Coluci[1], Scheila Furtado Braga[1], Pablo Zimmerman Coura[2] and Socrates Oliveira Dantas[2]; [1]Applied Physics, State University of Campinas, Campinas, Sao Paulo, Brazil; [2]Departamento de Fisica, UFJF, Juiz de Fora, Minas Gerais, Brazil.

The technological advances have led to the need of creating functional devices at nanometer scale. There have been continuing efforts for fabricating nanomechanical systems operating in high frequencies, but gigahertz range is beyond our present micromachining capabilities. A breakthrough in this area has been obtained by Cumings and Zettl [1]. They demonstrated the controlled and reversible telescopic extension of multiwalled carbon nanotubes (MWNT), thus realizing ultralow-friction nanoscale linear bearings. These results indicate that the fabrication of nanomechanical systems operating in high frequencies is now a possible realization. Similarly to graphite, the intershell interaction in MWNT is predominantly van der Waals [1], and since the interlayer corrugation is small it is expected that individual cylinders of MWNTs might easily slide or rotate with respect to one another. Depending on the distance separation between two adjacent nanotubes, it is possible to have an almost perfect sliding surface. The van der Waals interactions between the nanotubes create a restoring force that cause the inner tube to retract and can be the physical basis (and within our present technological capabilities) to build nanodevices [1]. Using static models on a slightly modified Cumings and Zettl set up, Zheng et Jiang [2] have showed that multishelled nanotubes could lead to gigahertz nanooscillators. We have carried out molecular dynamics studies for these systems, in the framework of classical mechanics with standard molecular force fields [3], in order to analyze the reliability of such nanodevices and to determine the importance of temperature and time fluctuations, The calculations were carried out considering structures containing up to 6,000 carbon atoms. Different nanotubes types (single and multiwalled armchair, zigzag, chiral, and combinations) were analyzed. Our results show that sustained oscillatory behavior is possible (for all kind of tube combinations) only when a perfect coupling (when the radii differences between inner and outer tubes are of $\sim$ 3.4 Angstroms) occurs. For other couplings, although the telescopic and retractive movements are possible, dissipative forces and momentum exchange among the nanotubes compromise the sustained oscillatory regime. Our results showed that multishell nanotubes can be used to make functional nano-oscillators in gigahertz range. [1] J. Cuming and A. Zettl, Science 289, 602 (2000). [2] Q. Zheng and Q. Jiang, Phys. Rev. Lett. 88, 045503 (2002). [3] S. B. Legoas, V. R. Coluci, S. F. Braga, P. Z. Coura, S. O. Dantas, and D. S. Galvao, Phys. Rev. Lett. 90, 055504 (2003).

KK6.2
Abstract Withdrawn

KK6.3
First-Principles Calculations of Site Preference for 3d Ternary Elements in the NbCr2 Laves Intermetallic Compounds.
Jian Sun[1], Bing Jiang[2] and David J. Smith[1,2]; [1]CSSS, Arizona state university, Tempe, Arizona; [2]Department of Physics and Astronomy, Arizona State University, Tempe, Arizona.

Laves intermetallic compounds are expected to be used as magnetic and magnetic-optical materials and hydrogen storage materials, and, recently, are also considered to be potential high temperature structural materials. Alloy designing is the most important method to be used to modify or improve the desired physical and mechanical properties of the Laves intermetallic compounds. Basically, alloying alters locally the electronic structure and bonding nature, which, in turn, influences the physical and mechanical properties of materials. In order to clarify the origin of these phenomena, it is very important to determine the crystalline sites of ternary elements in the Laves compounds. Recently, first-principles calculations have become a powerful tool for these purposes. In this paper, the full-potential linearized augmented plane wave method with the generalized gradient approximation (LAPW_GGA) has been used to calculate the electronic structure and the total energy of the NbCr2 Laves compounds. Structural stability of the NbCr2 Laves compounds with the 3d ternary elements of Ti, Mo, W and V, and the site preference energies of these ternary elements in these compounds have been studied systematically. The relations between the electronic structure and site preference of ternary elements will also be discussed. Finally, the calculated results will be compared with the experimental results of the site preference of ternary elements in the NbCr2 Laves compounds, which obtained by atom location by electron channeling enhanced microanalysis (ALCHEMI).

KK6.4
Kinetic Monte Carlo Simulation of Star-Shaped Diamond Crystals Grown from the Vapor Phase.
Radhika Chandrasekhar Mani and Mahendra Kumar Sunkara; Chemical Engineering, University of Louisville, Louisville, Kentucky.

Star-shaped crystal is one of the common five-fold twin observed in Diamond, as well as other crystal systems like Gallium Nitride and Gibbsite. The ratio of growth velocities in different crystallographic directions (α-factor) has been traditionally used to explain faceting of diamond crystals. The α-factor could not explain the reason for the formation of star-decahedral crystal versus a decahedral crystal, both of which are stable morphologies of CVD diamond bounded by {111} facets. We have performed Kinetic Monte Carlo (KMC) simulations to determine rules that govern the kinetic faceting of star-shaped multiply twinned crystals. In our simulations, we start with a seed cluster (20 atoms) and apply rules that define the site-selective growth chemistry for KMC scheme and grow the crystal to a certain size (10000 atoms). At this size, the shape of the cluster is compared with that observed in experimentally grown crystals. The simulations starting with a seed cluster containing two stacking faults, using growth rules that include simple adsorption and desorption of single methyl radicals, simulate a perfect decahedron. Inclusion of an additional step of etching atoms bonded twice to the surface allowed the growth of a star-decahedral cluster [1]. Though these simulations yielded the growth of star-shaped crystals, the reasons for the formation of kinetically stable concave {111} facets across twin boundaries are not clear. In this regard, we are currently performing simulations using detailed site selective surface chemistry to further understand the reasons for formation of star morphology versus perfect decahedral morphology. The results on diamond multiply twinned crystals could be extended to understand the growth of other related material systems, i.e., Gallium Nitride from molten gallium and boron nitride from gas phase. The dearth of the fundamental understanding of growth chemistry limits our ability to grow large single crystals. [1] R. C. Mani, M. K. Sunkara, Diam. Relat. Mater., 12(3-7), 324, 2003.

KK6.5
Highly Optimised Empirical Potential for Carbon.
Fei Gao[1], Thomas J Lenosky[2], Eric J Bylaska[1], Anter A El-Azab[1] and William J Weber[1]; [1]MS K8-93, Pacific Northwest National Laboratory, Richland, Washington; [2]MS k8-93, Pacific Northwest National Laboratory, Richland, Washington.

A highly optimized empirical potential for carbon is developed in the framework of modified embedded atom method (MEAM) using five cubic splines to describe pairwise and three-body terms, a form which has been successfully applied to silicon and several metallic systems. The potential parameters are fitted to a large ab initio database and experimental data using the force-matching method. The potential model provides a good description of energetics for all atomic coordinations, and realistically describes interlayer forces in graphite, with the c/a ratio being very close to the experimental value. Phonon properties and elastic constants agree well with experiments and ab initio calculations, and amorphous networks created by liquid quench have similar properties to the theoretical results calculated previously. The potential model is employed to study the structures and formation energies of point defects and small defect clusters in diamond and graphite. The predictive power of the potential is demonstrated in application to graphitic carbon nanotubes and fullerenes.

KK6.6
Ab Initio Study of MoP, a New Hydrodenitrogenation Catalyst.
Victor Milman[1], Bjoern Winkler[2] and Roberto Gomperts[3]; [1]Accelrys, Cambridge, United Kingdom; [2]Institut fur Mineralogie Abt. Kristallographie, Johann Wolfgang Goethe-Universitat, Frankfurt a. M., Germany; [3]SGI, Hudson, Massachusetts.

The structure and properties of the new catalyst, MoP, is investigated using planewave pseudopotential DFT technique as implemented in CASTEP program. The adsorption and hydrodenitrogenation (HDN) process of *o*-propylaniline on MoP(100) is chosen as an example. We analyze adsorption geometry and energetics for the *o*-PA molecule on the Mo-terminated MoP(100) surface. The energy barrier for one of the HDN reactions (*o*-PA$\rightarrow$propylbenzene) is determined using the LST/QST transition state search method.

KK6.7
A Generalized Charge Transfer Embedded Atom Method Potential for Metal/Metal Oxide Heterostructures.
Xiaowang Zhou and Haydn N. G. Wadley; Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

Atomistic simulations of metal/metal oxide heterostructures are attractive as these materials are continously found to possess unique properties for many advancing technologies. Unlike the embedded atom method (EAM) potentials that have been successfully used in metal systems, the potentials needed for atomistic simulations of metal/metal oxide heterostructures have yet to be developed. The traditional fixed charge ionic potentials are problematic in describing the ionic interactions in metal oxides. For instance, they do not allow different oxidation states, cannot ensure charge neutrality without constraining chemical composition, significantly overestimate the cohesive energy, and do not allow the ionic component of the interaction to vary as the environment changes from metal to oxide through a metal/oxide interface. A charge transfer ionic potential (CTIP) model proposed by Streitz and Mintmire has attempted to overcome these deficiencies. However, we found that this CTIP model is unstable and can only be applied to single metal-oxygen binary systems. By incorporation of the physical principle of elemental valency, we have resolved both problems of the original CTIP model. The improved CTIP potential has been combined with an existing EAM potential to dynamically address both ionic and metallic components of the interatomic interactions in O-Al-Zr and O-Al-Co-Ni-Fe systems.

KK6.8
GaAs Interatomic Potential Development for Simulated Molecular Beam Epitaxial Growth.
Dewey A Murdick[1], Xiaowang Zhou[1], Daivd G Pettifor[2], Duc Nguyen-Man[2] and Haydn N G Wadley[1]; [1]University of Virginia, Charlottesville, Virginia; [2]University of Oxford, Oxford, United Kingdom.

Molecular dynamic (MD) atomic simulations allow assembly phenomena encountered during molecular beam epitaxy growth to be analyzed in detail and allow the optimization of process conditions for desired structures and compounds. However, such simulations are limited by the quality of the potential energy functions that describe atomic interactions. To date, no published interatomic potential for GaAs can accurately describe bulk and surface properties, while simulating crystalline vapor deposition. A proposed resolution to these limitations is a bond-order potential (BOP) that is derived from tight binding theory. BOP classically approximates the electronic density of states and captures important physical phenomena that previous empirical potentials such as Stillinger-Weber and Tersoff do not address. Examples include a better handling of heterogeneous bonding, a more complete treatment of σ-bonding, and incorporation of π-bond interactions through dihedral angle effects. Present GaAs parameterizations of BOP predict a moderately transferable potential capable of crystalline vapor deposition in MD simulations. It is anticipated that BOP captures sufficient physics for simulation of (Ga,Mn)As ternary systems which may be used in spin-dependent devices.

KK6.9
Ab-initio Transport Properties of Carbon-Based Nanostructures.
Arrigo Calzolari[1,2], Nicola Marzari[3] and Marco Buongiorno Nardelli[4,5]; [1]S3-National Research Center, INFM, Modena, Italy; [2]Department of Physics, University of Modena and Reggio Emilia, Modena, Italy; [3]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [4]Department of Physics, North Carolina State University, Raleigh, North Carolina; [5]CCS-CMS, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Understanding the electronic and conduction properties of nanostructures is a fundamental step towards further miniaturization of electronic devices. In particular, atomic-sized carbon systems have recently attracted great attention because of their peculiar characteristics. In fact, due to their low-dimensionality such systems may exhibit electrical properties very different from the corresponding bulk material. We present a comprehensive study of the electronic and conduction properties of two carbon-based nanostructures: i.e. an allotropic linear carbon chain (known as Carbyne), and a small carbon nanotube in presence of substitutional defects. The study is based on a novel approach to calculate both the electronic and the coherent transport properties of extended nanostructures from first principles [1]. Our multi-step method is based on: (a) ab-initio, DFT, pseudopotential, plane wave calculations of the electronic structure of the system under investigation; (b) calculation of maximally localized Wannier functions (WF's) and the of real space Hamiltonian matrix in the WF basis set; (c) calculation of quantum conductance from the Landauer formula in the lattice Green's functions scheme. The description of the system in terms of its Wannier functions allow us to directly link the electronic transport properties to the intrinsic nature of the chemical bond, giving new insights onto the essential mechanisms that govern the electron flow at the nanoscale. [1] A. Calzolari, N. Marzari, I. Souza, and M. Buongiorno Nardelli, submitted (2003).

KK6.10
Ideal Tensile Strength of B2 Structure 3d Transition Metal Aluminides.
Tianshu Li[1,2], J. W. Morris[1,2] and D. C. Chrzan[1,2]; [1]Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California; [2]Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, California.

The ideal tensile strength of the B2-type (CsCl) transition-metal aluminides FeAl, CoAl, and NiAl have been investigated using an *abinitio* electronic structure total energy technique employing the local density approximation and ultrasoft pseudopotentials. The ideal tensile strength is computed along the [100], [110], and [111] directions. Even though these materials have nearly identical lattice parameters and similar electronic structures in their unstressed states, they exhibit dissimilar mechanical behavior under the simulated ideal tensile tests. The ideal strength (18GPa) and corresponding critical strain (14%) of FeAl under [100] tension are both much lower than those of CoAl and NiA. FeAl is consequently weakest in tension along [100] rather than either [110] or [111]. This behavior is in contrast to the predictions for NiAl and CoAl. Furthermore, these predictions are consistent with the experimentally observed fracture behavior for these materials. This work is supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Science under contract DE-AC03-76SF00098.

KK6.11
Simulation of STM Images of Au/TiO_2(110).
Kazuyuki Okazaki[1], Yasushi Maeda[2], Yoshitada Morikawa[3], Shingo Tanaka[1,3], Koji Tanaka[1] and Masanori Kohyama[1,3]; [1]Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology, Ikeda, Japan; [2]Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; [3]Research Institute of Computational Science (RICS), National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

The gold is not expected to be a good catalyst for oxidation or hydrogenation since reactive molecules such as O_2 and H_2 do not adsorb on gold surfaces. However, dispersed nano-size gold particle on metal oxides such as TiO_2 can act as a catalyst for the room-temperature oxidation of CO and the epoxidation of propylene in a gas containing oxygen and hydrogen. To understand the mechanism of the unique activity of Au/TiO_2 system, we have theoretically investigated the stable adsorption site and the electronic structures of Au/TiO_2(110) based on the density functional theory. We have examined the adsorption of one Au adatom per (2×2) surface unit cell on three types of TiO_2(110) surface condition; the perfect stoichiometric surface, the surface with the defect of the bridging-oxygen, and the reconstructed 1×2 surface with Ti_2O_3 rows. We used the *abinitio* pseudopotential method. For the stoichiometric surface, the most stable adsorption site is the on-top site above the bridging-oxygen atom and electrons transfer from Au atoms to O atoms. For the surface with the defect of the bridging-oxygen atom, the most stable site is the bridging site between the four-fold Ti atoms along the [001] direction, that is the bridging-oxygen vacant site, and electrons transfer from Ti atoms to Au atoms. For the reconstructed 1×2 with the Ti_2O_3 rows, the most stable site is the neighborhood site of the Ti atoms in the Ti_2O_3 rows and electrons transfer from Ti atoms to Au atoms. We have also simulated the scanning tunnel microscopy (STM) image for the three types of surfaces. We discussed the dependence of the STM images on the surface condition of TiO_2(110) and the adsorption site due to be compared with the experimental results.

KK6.12
A Monte Carlo Study of Kinetics of Precipitation in Aluminum Alloys: from Ab-Initio Calculations to Classical Nucleation Theory.
Emmanuel Clouet[1,2], Maylise Nastar[2] and Christophe Sigli[1]; [1]Pechiney Centre de Recherches de Voreppe, Voreppe, France; [2]Service de Recherches de Metallurgie Physique, CEA / Saclay, Gif-sur-Yvette, France.

Zr and Sc precipitates in aluminum alloys to form the compounds Al_3Zr, Al_3Sc, and $Al_3Zr_{(1-x)}Sc_x$ which for low super-saturations of the solid solution have the $L1_2$ structure. The aim of the present study is to model at an atomic scale this kinetics of precipitation and to build a mesoscopic model based on classical nucleation theory so as to extend the field of super-saturations and annealing times that can be simulated. In this purpose, we use some ab-initio calculations [1,2] and experimental data to fit an Ising model describing thermodynamics of the Al-Zr-Sc system. Kinetic behavior of this

system is described by means of an atom-vacancy exchange mechanism. This allows us to simulate with a kinetic Monte Carlo algorithm kinetics of precipitation of Al_3Zr and Al_3Sc. These kinetics are then used to test the classical nucleation theory. In this purpose, we deduce from our atomic model an isotropic interface free energy wich is consistent with the one deduced from experimental kinetics and a nucleation free energy. We test different mean-field approximations (Bragg-Williams approximation as well as Cluster Variation Method) for these parameters. The classical nucleation theory is coherent with the kinetic Monte Carlo simulations when CVM is used: it manages to reproduce the cluster size distribution in the metastable solid solution and its evolution as well as the steady-state nucleation rate. We find too that the capillary approximation used in the classical nucleation theory works surprisingly well when compared to a direct calculation of the free energy of formation for small $L1_2$ clusters. **Acknowledgments** : This work was funded by the joint research program "Precipitation" between Pechiney, Usinor, CNRS, and CEA. **References** [1] M. Asta and V. Ozolins, Phys. Rev. B **64**, 094104 (2001). [2] E. Clouet, J. M. Sanchez, and C. Sigli, Phys. Rev. B **65**, 094105 (2002).

KK6.13
Ab-initio Study of π-stacking in Thiophene Oligomers.
Damian Ariel Scherlis and Nicola Marzari; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Thiophene oligomers display very promising electronic and structural properties, that make them extremely attractive as building blocks for organic conducting polymers and for electroactuators. While a significant amount of basic research has been carried out in the past years, there are still several issues that, while central to molecular design and engineering, remain elusive. The mechanisms of charge transport, the interaction between stacked oligomers, and the role of the solvent are all aspects that require a thorough understanding. We use here an extensive combination of quantum chemistry approaches and ab-initio molecular dynamics simulations to elucidate the stacking energetics, and to correlate it with the order of the oligomers and their different oxidation states. Moreover, we show that the presence of the solvent drastically changes the thermodynamical stability of the different dimers. Our results help rationalize the use and efficiency of novel thiophene-based materials proposed for nanotechnology applications.

KK6.14
Abstract Withdrawn

KK6.15
Simulating Pb Vacancies in Pb-based Perovskites.
Eric Cockayne and Benjamin P Burton; Ceramics Division, NIST, Gaithersburg, Maryland.

Relaxor ferroelectrics (RFE) with optimal properties for electromechanical applications are typically Pb-based perovskites. Experiments show that creating one to five percent Pb vacancies in the RFE $PbSc_{1/2}Nb_{1/2}O_3$ (PSN) and $PbSc_{1/2}Ta_{1/2}O_3$ (PST) significantly affects their dielectric properties. Atomic scale modeling and simulation of RFE should account for the influence of Pb vacancies on their properties. We studied Pb-O divacancies in $PbTiO_3$ using first-principles (FP) density functional theory methods. We use the modern theory of polarization to calculate the dipole moment of a nearest-neighbor Pb-O divacancy. The dipole moment of the divacancy is greater than the dipole moment per unit cell in defect-free Pb-based perovskite ferroelectrics, which indicates that Pb-O divacancies can be an important source of local "random" fields in RFE. Finally, we use the FP results to implement a random array of Pb-O divacancies into an effective Hamiltonian for PSN and simulate the temperature-dependent dielectric constant as a funtion of vacancy concentration.

SESSION KK7: Methods II
Chair: Diana Farkas
Wednesday Morning, December 3, 2003
Constitution A (Sheraton)

8:30 AM *KK7.1
Learn-On-The-Fly: An Adaptive Classical/Quantum Hybrid Molecular Dynamics Scheme. Gabor Csanyi, Tristan Albaret, Mike C. Payne and Alessandro de Vita; Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

An embedded molecular dynamics scheme is presented which spans the lengthscale gap between feasible classical and quantum mechanical computer simulations. It is ideal for problems in which only a small fraction of the atoms need to be treated accurately, yet a large number of atoms is explicitly required to correctly represent the geometry and the elastic properties. The method facilitates automatic selection of quantum regions and uses force matching to continously and locally modify the classical potential to reproduce the quantum trajectories. The correctness of macroscopic observables is demonstrated using native defects of silicon. A simulation of brittle fracture in silicon reproduces the main experimental features using several hundred thousand classical atoms and a few thousand atoms in the tight binding approximation near the crack tip.

9:00 AM KK7.2
Feature Activated Molecular Dynamics for Accessing Large Length Scales. Manish Prasad and Talid Sinno; Department of Chemical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

An increasingly important goal in materials process modeling is the incorporation of atomistic information to create physically realistic models at coarser scales. Efforts to couple disparate length and time scales have relied either on concurrent or sequential approaches, based on the physics of the problem. In the former, where length scales cannot be completely decoupled, the challenge is to seamlessly connect multiple representations together into a single simulation. These frameworks can greatly leverage the scope of an atomistic simulation, without necessitating that complex atomistic phenomena, such as defect aggregation in solids, be coarse-grained. A new hybrid scheme based on molecular dynamics (MD) suitable for modeling the evolution of atomic defects and their aggregates in solid-state materials is described here. Such species are typically present in very dilute quantities in crystalline solids, and their effects on the surrounding lattice are usually short-ranged, thereby making MD simulation computationally expensive for large numbers of defects. In this approach, only regions around defects and impurities are simulated with MD ("active" regions), while regions further away ("static" regions) are assumed to be perfect and act as boundary conditions for the active regions. This assumption is justified as long as the active regions are large enough to contain all the defects and their associated lattice distortion. A unique feature of this technique is that the interfaces between the active and static regions are not fixed and can evolve dynamically by the systematic "turning-on" and "turning-off" of atomic thermal excitation (activity). This approach provides for "seamless" activation and deactivation of lattice atoms in the presence of defect diffusion, aggregation and fragmentation. This is achieved by placing a thermal envelope around the individual defects. The envelope function determines the size of active region and the activity of atoms in the system. The hybrid MD approach is tested and validated by comparison to regular MD predictions of transport and formation properties of vacancies and small clusters in crystalline silicon. Next, the predictions of a large-scale hybrid system are compared with previous MD results for the vacancy aggregation problem involving a lattice of 215,000 Si atoms and 1,000 vacancies is evolved in the NVT ensemble at 1600 K. These comparisons establish that the hybrid MD scheme with multiple dynamical regions is equivalent to a regular MD simulation. The computational performance of the scheme is demonstrated for different system sizes and defect concentrations. It is shown that the computational time per MD step is essentially independent, for a given number of defects, from the actual size of simulation system, making it suitable for modeling of very dilute systems. The overhead involved in doing additional identification/separation of active and static regions is also negligible.

9:15 AM KK7.3
Adaptive Importance Sampling of Rare Transition Events.
Maurice de Koning[2,1], Wei Cai[1], Babak Sadigh[1], Malvin H Kalos[1] and Vasily V Bulatov[1]; [1]Lawrence Livermore National Laboratory, Livermore, California; [2]Instituto de Fisica, DFMT, Universidade de Sao Paulo, Sao Paulo, SP, Brazil.

We present a new approach to the simulation of rare transition events using the Importance Sampling Monte Carlo framework. The method approaches the problem by enhancing the probability of sampling sequences of states, or paths, that constitute successful transition events between two meta-stable states. This is accomplished by means of an Importance Function, which modifies the transition probabilities of the original unbiased Monte Carlo dynamics. In addition to preserving the relative sampling probability of different successful transition paths, the approach enhances the probability of sampling a successful transition event by a known amount, facilitating the evaluation of transition rates. In this manner, the rare-event problem is transformed into an optimization problem, that of finding the best-possible Importance Function for the transition at hand. We developed an adaptive algorithm that iteratively adjusts the Importance Function until satisfactory efficiency is achieved. The method is demonstrated on low-dimensional model problems, as well as on a realistic atomistic system of dislocation motion in silicon. Comparison with other existing methods will be discussed. This work was performed under the auspices of the U. S. Department of Energy

by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. MK acknowledges support from the Brazilian agency FAPESP.

9:30 AM KK7.4
A novel, fast and reliable accelerated molecular dynamics method: theory and applications. Francesco Montalenti[1], Blas P. Uberuaga[2], Graeme Henkelman[2] and Arthur F. Voter[2]; [1]Materials Science Department, University of Milano, Bicocca, Milano, Italy; [2]Theoretical division, Los Alamos National Laboratory, Los Alamos, New Mexico.

In fundamental surface phenomena such as crystal growth and island diffusion, experimentally relevant time scales are of the orders of seconds or longer, i.e., several orders of magnitude longer than the typical time scale achievable by standard molecular dynamics simulations. Accelerated molecular dynamics techniques [1] provide a useful tool to close this gap substantially. In this work we show that two methods based on very different philosophies can be combined to obtain a fast and reliable accelerated molecular dynamics technique, dimer-TAD. In dimer-TAD, the dynamics out of a state is described using the temperature-accelerated dynamics (TAD) method [2,3], enhanced by the knowledge of the minimum barrier out of the state coming from a set of dimer-method [4] saddle searches. As an application of the method, we simulate diffusion of islands of various sizes on (100) fcc metal surfaces, reaching time scales of seconds at T=300 K. A complex diffusion scenario is revealed, where multiple-atom mechanisms play a key role in determining island shape and mobility.

10:15 AM KK7.5
A Nose-Poincare Quasicontinuum Model. Laurent Michel Dupuy and Rob Phillips; Mechanical Engineering, California Institute of Technology, Pasadena, California.

In this paper, we extend the quasicontinuum method to study the dynamical properties of defects in metals at finite temperature. The Nose-Poincare method is a technique to perform deterministic and Hamiltonian molecular dynamics at constant temperature. Here we present a derivation of this method to perform simulations in a mixed atomistic and continuum setting through the use of coarse-grained potentials. In this way, the number of degrees of freedom is significantly reduced, allowing to simulate large systems on relatively small computers. Although the behavior of all the atoms is not considered, it is shown that the equilibrium properties of a full atomistic system in the canonical ensemble are recovered. The validity of the proposed method is demonstrated by computing thermal properties of a defect-free single crystal.

10:30 AM *KK7.6
Prediction of Nanostructural Evolution Based on First Principles*. Zhenyu Zhang, [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Department of Physics, Univ. of Tennessee, Knoxville, Tennessee.

Recent advances in atomic-scale characterization and control in fabricating low-dimensional structures at surfaces have offered unprecedented opportunities for precise and quantitative understanding of the underlying mechanisms involved in the fabrication processes. Such modeling efforts, in turn, can lead to the dicovery of new growth pathways for innovative materials design. In this talk, I will attempt to illustrate the power of this synergy between experiment and theory using a few recent examples in which some new concepts in growth science have been established. Particular emphases will be made on the role of atomic processes at island corners in controlling the shapes and orientations of monatomic-layer-high islands [1,2], and on the role of true upward adatom diffusion processes in nanocrystal formation via faceting [3,4]. * Work done in collaboration with the co-authors listed in Refs. 2-4, and supported in part by US Department of Energy, US National Science Foundation, and National Natural Science Foundation of China. [1] T. Michely, M. Hohage, M. Bott, G. Comsa, Phys. Rev. Lett. 70, 3943 (1993). [2] J. Wu, et al., Phys. Rev. Lett. 89, 146103 (2002). [3] F. Buatier de Mongeot, et al., Phys. Rev. Lett. 91, 016102 (2003). [4] W. G. Zhu, F. Buatier de Mongeot, U. Valbusa, E. G. Wang, and Z. Y. Zhang, submitted to Phys. Rev. Lett.

11:00 AM KK7.7
An improved KLMC method for simulating atomic layer deposition of metals. Michael Mueller and Karsten Albe; Institute of Materials Science, TU Darmstadt, Darmstadt, Germany.

We present an improved kinetic lattice Monte-Carlo scheme for modeling layer deposition of fcc metals that not only describes single atom jumps, but also cluster diffusion on surfaces. Regular lattice sites as well as stacking fault positions are included and a new EAM-bond counting scheme is used for calculating activation barriers during the simulation run. The method is applied to simulate sub-monolayer growth of Ir on Ir(111), where we achieve very good aggreement of calculated islands distributions and islands shapes with results from STM-measurements.

11:15 AM KK7.8
Atomistic Model of Polycrystalline Thin Film Evolution under Stress. Hanchen Huang[1], L. G. Zhou[1], George Gilmer[2] and Timothy Cale[3]; [1]Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; [2]Materials Science and Technology, Lawrence Livermore National Laboratory, Livermore, California; [3]Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Texture is pivotal to the performance of thin films, and its nucleation and evolution are a direct result of atomistic processes. Complementing characterization experiments, atomistic modeling and simulations are helpful or essential in achieving the optimal texture. Our atomistic model ADEPT has been implemented to simulate nucleation and evolution of two textures at the atomic level and under realistic deposition rates. In this work, we present the implementation of multiple-texture model. The spatial positions of atoms are represented accurately within one atomic diameter, naturally enforcing an accurate representation of atomic density averaged over one unit cell. The model is tested on a model system: copper. Atomic energetics of copper are used in the ADEPT simulations, and the results serve the purpose of both model validation and interpretation of our experiments on copper texture evolution.

11:30 AM KK7.9
Application of the NRL Tight-Binding Model to FCC Metal Surfaces. Michael I Haftel, Noam Bernstein, Michael J Mehl and Dimitris A Papaconstantopoulos; Center for Computational Materials Science, Naval Research Laboratory, Washington, District of Columbia.

We employ the NRL tight binding (TB) model to predict the interlayer surface relaxations and surface energies for the low-index faces of fcc Ni, Pd, Rh, Pt, Au, and Ir. We compare the TB calculations, utilizing self-consistent charge transfer, with experimental measurements, density functional theory (DFT) calculations, and semiempirical methods. We find that for these metals the TB model largely reproduces the DFT and experimental trends with respect to the exposed face and layer depth. We find that the inclusion of self-consistency in the TB surface calculations is essential in obtaining this agreement, as the TB calculations without it predict large first interlayer expansions for many of these surfaces, whereas the full self-consistent calculations either predict small expansions or contractions. We also examine the energetics and relaxations of the (011) missing row reconstruction for these metals. The NRL-TB model predicts that Au and Pt undergo this reconstruction, while Ir, Ni, Pd, and Rh do not, whereas experimentally this reconstruction is observed for Pt, Au and Ir. The interatomic relaxations of the (011) missing row structure for Pt, Au and Ir are in good agreement with DFT calculations and experiment.

11:45 AM KK7.10
Atomic Simulations of Hydrocarbon Decomposition on Metal Surfaces Induced by a Sliding Diamond Tip.
Stacie LeSure Gregory, Kai Wang and Donald W. Brenner; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Nanoscale devices containing moving components have been envisioned for applications that include energy storage, chemical sensing, and molecular heating/cooling. While the operation of idealized molecular gears and pumps has been demonstrated using molecular simulations, real-world devices of this type are far from insured, with issues of mechanical stability, defect tolerance, and lubrication yet to be resolved. To gain insight into these and related tribological issues, we have initiated a joint experimental and modeling effort aimed at understanding tribochemical reactions at the nanoscale under ultra-fast sliding conditions, specifically the competing roles of enhanced equilibrium rates via surface heating versus non-equilibrium mechano-chemistry. The experimental effort, which is being carried out in Krim's laboratory at NC State, takes advantage of the unique capabilities of an instrument that combines scanning-tunneling microscopy with the Quartz Crystal Microbalance (STM-QCM). Molecular dynamics simulations were used to model hydrocarbon decomposition on nickel due to a sliding tip. Initial simulations predict that chemisorbed acetylene is more robust than methyl under ultra-fast sliding conditions on a nickel (111) surface. Surface chemistry in this system is initiated by loss of hydrogen, which has a higher tendency to occur for methyl than acetylene, consistent with the formation of unsaturated lubricous films typically seen at sliding surfaces. Detailed reaction mechanisms, including the role of thermal versus mechanical driving forces for chemical

reactivity, will be presented for a variety of chemisorbed molecular species, and the resulting reaction products will be compared to results of the STM-QCM experiments. This work was funded by the Department of Energy from grant DE-FG02-01ER45936.

SESSION KK8: Alloys; Soft and Disordered Matter
Chair: Judith Yang
Wednesday Afternoon, December 3, 2003
Constitution A (Sheraton)

1:30 PM *KK8.1
Predictions of Stable Crystal Structures and Alloy Morphologies From 105 Atom First-principles Theory of Binary Metal Alloys.** Alex Zunger, NREL, Golden, Colorado.

Conventional DFT-based theory is currently able to address only ∼1000 atom /cell structures,whereas real microstructures consist of many more atoms. Similarly, DFT-based theory is not able to search the space of all possible structural configurations of even simple binary ordered AB crystal structures.These limitations can be overcome by mapping the DFT onto a GENERALIZED,MULTI-BODY Ising like expansions. We have previously developed such an efficient expansion,called the "Mixed Basis Cluster Expansion" (MBCE). In this talk I will discribe some recent applications of this approach : (1) Prediction of unsuspected "infinitly Adaptive Ordered Crystal Structures" in CuAu and NiPt systems.These structures form a series of fully ordered unit cells with large number of atoms per cell,yet all of these are real "ground States" at T=0. These structures are identified by searching ∼ 3 *10**6 possible structures(In collaboration with M. Sanati and L. Wang). (2) Prediction of complex crystal structures in "simple" binary BCC systems of, e.g, Mo-Ta, showing how complexity emerges from simplicity(in collaboration with V. Blum) (3) Prediction of microstructure shapes in Cu-Au and Al-Zn precipitates, showing how 10**5 atom large microstructures can be predicted with DFT-like accuracy (in collaboration with M. Sanati and S. Muller). (4) Prediction of ordering of vacancies in simple binary solids such as ScS (in collaboration with G. Hart)

2:00 PM KK8.2
How Well Do Diffuse Scattering Measurements of Alloys Determine the Many-Body Correlations? Gene E Ice[1], Cullie J Sparks[1], Rozaliya I Barabash[1], Don Nicholson[1], Lee Robertson[1] and Christopher Wolverton[2]; [1]Metals and Ceramics Div., Oak Ridge National Laboratory, Oak Ridge TN, Tennessee; [2]Ford Motor Co., Dearborn, Michigan.

Diffusely scattered x-rays (neutrons) are sensitive to the correlations among atom positions. Only pair correlations can be recovered from diffuse scattering measurements as a measure of the average chemical neighborhood and average spacing between the different atom species. Though it has never been shown that these average pair correlation functions can uniquely determine the actual atomic arrangements, it has been shown that pair correlations do restrict the value of higher order correlations1 . Recently, numerical simulations have shown the uniqueness of reconstructing multiphase morphologies from pair correlations2. Here we present numerical analyses of the reconstruction of substitutional crystalline alloys from pair correlations derived from both pair and many-body interactions. With regular, forward Monte Carlo, pair and many body interactions were used to calculate snapshot images of short-range ordered 64,000-atom Monte Carlo cells. We refer to these 64000-atom configurations as "input". The averaged Warren-Cowley pair correlations were obtained from each of the input configurations, and these pair correlations were then used in a reverse Monte Carlo simulation to reconstruct "output" 64,000-atom configurations. We compare in detail the pair and many-body (containing up to six atoms) probabilities between the input and output configurations. We also contrast input vs. output configurations for those configurations initially derived from pair-only and pair+multibody interactions. Pair correlations are shown to strongly constrain the many-body correlations. In the case of the configuration derived from pair-only interactions, the many body correlations of the output configuration were in good agreement with the input correlations. The pair+multibody interactions yielded an input configuration that was well simulated by the pair correlations except for the distribution in the first shell. The input vs. output for many body correlations extending beyond first nearest neighbors agree well, even for lattices derived from multibody interactions. For this typical case, pair correlations are shown to define the morphology of the locally ordered or clustered domains. 1.J. Gragg, J. Bardham and J. Cohen, in: Critical phenomena in Alloys, magnets and superconductors, R. Mills, E. Ascher and R. Jaffee, eds., McGraw-Hill NY (1977), pp. 309-337 2.M.G.Rozman and Marcel Utz, Phys.Rev.Lett. 89, 135501, (2002).

2:15 PM KK8.3
The Mobility and Kinetics of Solutes in a Ni-Al-Cr Superalloy: A Kinetic Monte Carlo Simulation Study. Zugang Mao[1], Georges Martin[2,1] and David N Seidman[1]; [1]Materials Science & Engineering, Northwesern University, Evanston, New York; [2]Service de Recherches en Metallurgie Physique, Centre des Etudes Atomique, Saclay, France.

The diffusivities in Ni, of Al or Cr solute atoms and clusters of these solute atoms, dimers through sexamers, are studied utilizing three-dimensional kinetic Monte Carlo (KMC) simulations; the parameters employed are compatible with existing thermodynamic and diffusion data for this ternary alloy. We demonstrate that, at 873 K, the diffusivities of Al or Cr clusters (dimers, trimers, quadrimers, and pentamers) or mixed Al-Cr clusters are greater than the diffusivity of a single Al or Cr atom in Ni, where diffusion occurs via a monovacancy mechanism. The monovacancy-cluster attractions are the origin of this fast diffusion of clusters, which is a consequence of long-range solute-solvent interactions. They are suppressed by introducing ghost vacancy/solute interactions that alter neither the thermodynamics nor the macroscopic diffusion coefficients of the alloy. Furthermore the temporal evolution of the nanostructure of a Ni-5.2 Al-14.2 Cr at.% model superalloy is studied both with and without vacancy-solute interactions. With vacancy-solute interactions about 40% of the gamma prime precipitates are interconnected by necks after an aging time of about four hours, whereas without solute-vacancy interactions the necks are completely absent. These results are compared to recent three-dimensional atom-probe (3DAP) microscopy experiments being performed at Northwestern University on the same alloy (Sudbrack, Yoon, Isheim, Mao, Noebe, Seidman, 2003), and it is shown that the detailed experimental observations of gamma prime precipitates in the gamma matrix, as a function of aging time, are in semi-quantitative agreement with the KMC results. This implies that the coarsening mechanism of the gamma prime precipitates in this alloy most likely occurs by a cluster-diffusion-coagulation mechanism and not by the classical mechanism, which involves the evaporation of a single atom (monomer) from a shrinking precipitate and its condensation on a growing precipitate. Research supported by the National Science Foundation (K. L. Murty, grant officer).

2:30 PM KK8.4
Pipe diffusion of Mg in a binary Al-Mg alloy. Catalin Picu and Dawei Zhang; Rensselaer Polytechnic Institute, Troy, New York.

Solute diffusion in an Al rich binary Al-Mg alloy is studied by means of atomistic simulations. The activation energy for diffusion of Mg in the bulk is evaluated in the dilute solution limit for the nearest neighbor and the ring mechanisms. Further, diffusion of Mg along the core of edge, 60o and screw dislocations is studied. It is observed that, similar to the bulk, Mg diffusion in absence of vacancies is energetically prohibitive at room temperature. The paths of minimum activation energy are identified for vacancy-assisted diffusion, for all three types of dislocations. Most diffusion paths have activation energies larger than 75% of the equivalent bulk quantity. This analysis is relevant for the discussion on the mechanism of dynamic strain aging in these alloys. The data presented here show that pipe diffusion, which is currently considered as the leading mechanism responsible for dynamic strain aging and the Portevin-LeChatelier effect, is too slow to account for the observed mechanical behavior under most experimental conditions.

2:45 PM KK8.5
First Principles Calculation of Diffusion in Binary Alloys. Anton Van der Ven and Gerbrand Ceder; Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Diffusion in multicomponent solids plays an important role in battery and fuel cell applications as well as during the synthesis of a material as this is often accompanied by phase transformations involving atomic redistribution. We have extended the tools of alloy theory (theory of first principles phase-diagram calculations) for the study of diffusion in solids with configurational disorder. We have applied this formalism to study diffusion in Al-Li alloys as a function of alloy composition and temperature from first principles. We predict that the vacancy concentration in this alloy has a strong dependence on the short-range order among lithium and aluminum atoms with the vacancy prefering aluminum over lithium in its first nearest neighbor shell. Furthermore, the vacancy concentration is predicted to depend strongly on alloy composition within the ordered Al3Li L12 phase. While the vacancy prefers aluminum rich environments, first principles calculations of activation barriers predict that Li has a lower activation barrier than Al for exchange with a neighboring vacant site. With the cluster expansion formalism combined with kinetic Monte Carlo simulations, we have calculated the alloy diffusion coefficient using Green-Kubo relations. Together with first principles free energy curves, the calculated diffusion coefficient can be used in phase-field models to predict the kinetics of precipitation transformations in this alloy.

3:30 PM *KK8.6
Langevin Molecular Dynamics Simulations of Self-Assembly of Tethered Nano Building Blocks. Sharon C Glotzer[1,2], Elaine R Chan[1], Mark A Horsch[1], Monica H Lamm[1], Charles (Xi) Zhang[2] and Zhenli Zhang[1]; [1]Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan; [2]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

The application of nanotechnology to areas such as photonics and electronics, chemical and biological sensors, energy storage and catalysis requires the assembly of nanoscale objects such as nanoparticles and nanostructured molecules into functional materials and devices. Currently, few demonstrated assembly approaches offer a comprehensive, predictable, and generally applicable scheme for the rational assembly of nanoparticles into one-, two-, and three-dimensional ordered structures. Inspired by recent advances in synthesis and functionalization, we seek to develop an intuitive framework for predicting the assembly of nanoparticles functionalized with organic tethers. Simulation offers a unique opportunity in this regard, provided appropriate models can be devised and the length and time scales relevant to the assembly process can be efficiently accessed. In this talk, we present new results of Brownian dynamics (Langevin MD) simulations of tethered nanocrystals and polyhedral oligomeric silsesquioxanes and their self-assembly into complex ordered structures. We show how tuning thermodynamic parameters and architectural features of model nano building blocks can control aspects of local and global ordering of the nanoparticles. We further demonstrate that for certain categories of tethered nano building blocks the morphologies obtained may be predicted using concepts from block copolymer microphase separation and liquid crystal phase ordering, while for other categories the unique packing constraints introduced by nanoparticle geometry and by nanoparticle-polymer tether topology lead to structures far richer than those found in conventional block copolymer, surfactant, and liquid crystal systems, including nanowires, nano-shells, and nano-cylinders. This work is supported by grants from the National Science Foundation (DMR-0103399 and CTS-0210551) and the U.S. Department of Energy (DE-FG02-02ER46000).

4:00 PM KK8.7
Design and testing of dendrimer templates using structural and functional analysis by new cross-linking methods. Hiroshi Taiko, Tahir Cagin and William A Goddard; Material and Process Simulation Center, Beckman Institute(139-74), Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California.

A new computational scheme was developed to create cross-linked structures of polymers from reactive molecules. This scheme uses a combination of Monte-Carlo (MC) and Molecular Dynamics (MD). Each cross-linking step has a separate MC and MD components. The MC part provides several structures with one new cross-link. The MD part evaluates the potential energy for these structures, and adopts the lowest energy structure as the continuous growing direction. These MC/MD calculations are repeated to find the final multiply cross-linked molecular structure. This scheme was applied to predict the structure of the cross-linked Dendrimer, proposed by Prof. Zimmerman and Suslick of the University of Illinois (ref1). Their dendrimer used a heme-core and resulted in multiple allyl-functions, one at the end group of each dendron. These allyl-functions were cross-linked using a Grubbs Ru-based ring-closing metathesis catalyst. This dendrimer contained 64 allyl-functions, so that the maximum number of cross-links was 32. The experiment detected 29 cross-links. We developed 30 independent cross-linked structures, leading to 24 to 31 cross-links with an average of 28 cross-links, in good agreement with experiments. We find that 60% of the cross-links are inter-dendron. After creating the cross-links the experiments eliminate the porphyrin core by hydrolysis, and found that the cored dendrimer was selective for binding specific heme molecules. We have carried out the same calculations with the computational cored Dendrimers and find results similar to the experiment. This indicates that such simulations might be useful in designing new dendrimer template systems. ref1: Steven C. Zimmerman, et al NATURE Vol.418 (319), 25 July 2002

4:15 PM KK8.8
A Computational Procedure for Modeling Molecular Devices: Application to a [2] Catenane and a Quaterthiophene-substituted Azobenzene. Xiange Zheng and Karl Sohlberg; Department of Chemistry, Drexel University, Philadelphia, Pennsylvania.

Here we demonstrate a procedure for modeling the co-conformational bistability of switchable molecular devices. In this procedure, full-torsional-space conformational searching based on empirical molecular modeling is first carried out to generate a large ensemble of chemically reasonable conformations. Next, lower-level electronic structure calculations are performed for all conformations to identify physically significant structures. Higher-level electronic structure calculations are then carried out for a subset of conformations. This is followed by statistical analysis of the results to correlate structural features to energy. We have applied this procedure to two prototype molecular device systems in order to investigate their switching mechanisms and multiple stability: (I) an electrochemically-switchable [2]catenane and (II) a photo-switchable quaterthiophene-substituted azobenzene. For system (I), the procedure yields structural preferences that are in excellent agreement with experiments for both the singlet and doublet states. For system (II), again the computations recover the experimentally observed structure/energy profile, showing that the structures with a trans-azobenzene configuration are more extended and have lower energy than those with the cis-azobenzene configuration. We propose that the procedure has promise for use as a molecular device design tool.

4:30 PM KK8.9
Pore Structure and Physical Properties of Simulated Silica Gels. Sudin Bhattacharya, Liping Huang and John Kieffer; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Molecular dynamics simulations based on a recently developed charge-transfer three-body potential were used to generate nano-porous silica gel structures. In these simulations care was taken to reproduce the sol-gel condensation reaction that lead to the gel backbone formation as realistically as possible and to thereby produce credible gel structures. By varying the reaction conditions different gel structures were created. These gels obtained by simulated assembly were then examined to reveal the relationships between their structure and properties. Structural analysis was carried out in terms of geometric and dimensional correlations. Thermal and mechanical properties were derived from the vibrational density of states obtained through normal mode analysis. In this presentation we will report our findings and discuss how the non-Euclidean dimensionality of the gel structure affects its vibrational behavior and any derivative properties.

4:45 PM KK8.10
Understanding medium-range order of amorphous systems under high pressure through molecular dynamics simulations. Lilian P Davila[1,2], Maria-Jose Caturla[3,2], Alison Kubota[2], Babak Sadigh[2], Tomas Diaz de la Rubia[2], James F. Shackelford[1], Subhash H. Risbud[1] and Stephen H. Garofalini[4]; [1]Dept. of Chemical Engineering & Materials Science, UC Davis, Davis, California; [2]Lawrence Livermore National Laboratory, Livermore, California; [3]Dept. Applied Physics, University of Alicante, Alicante, E-03690, Spain; [4]Dept. of Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Structural transformations of the medium-range order and the dynamic behavior of silica glass at high pressures is still not well understood despite years of research. Recent papers have shown how this medium-range order can be manipulated experimentally resulting in materials of scientific and technological interest. We have used MD simulations to study the behavior of fused silica under pressure using empirical interatomic potentials developed by Feuston and Garofalini. In this article we present two different simulation schemes for studying the structural transformations in fused silica under high pressures, and show their equivalence. Both methods reproduce the equation of state (EOS) obtained from flyer plate experiments. We have centered our studies in the structural changes occurring in the material with increasing pressure and the correlation between the medium-range order, through the structure factor, and the characteristic ring distribution of these amorphous glasses. An analysis of the ring distribution and structure factor reveals the microscopic changes occurring in this material and allows for an interpretation of the equation of state. The transition from elastic and plastic behavior is directly related to structural variations exhibited in the ring size distribution of this glass. During elastic compression, the ring distribution stays practically unchanged. However, this distribution varies continuously after the transition to the plastic regime takes place. This study can help understand the nature of fused silica, influencing applications that depend on its structure under these conditions with implications in geophysics, glass technology and optics. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

SESSION KK9: Poster Session III
Wednesday Evening, December 3, 2003
8:00 PM
Exhibition Hall D (Hynes)

KK9.1
Investigation on Filling of (10,10) Single-Walled Carbon

Nanotubes with Epoxy Resin/Curing Agent Molecules and Interfacial Bonding of the Resulting Nanocomposite. Tiehu Jiang[1], Olivier Marietta-Tondin[1], Zhiyong Liang[1], Chuck Zhang[1], Ben Wang[1] and Leslie Kramer[2]; [1]Industrial Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida; [2]Lockheed Martin Missiles and Fire Control - Orlando, Orlando, Florida.

One of the many technical challenges associated with developing single-walled nanotube (SWNT) reinforced composites involves improving interfacial bonding between the SWNTs and the polymer matrix. This study investigated a promising method for improving interfacial bonding. The method consists of first inserting resin and curing agent molecules into chopped SWNTs with open ends. During the curing phase, chemical bonding occurs between the inserted molecules and the resin structure outside the tube, which should result in the formation of mechanical bonding bridges and locks between SWNTs and resin matrix. Such phenomenon could potentially increase the interfacial bonding strength and the load transfer capability between the SWNTs and the resin. The possibilities of filling open-ended (10,10) SWNTs with epoxy and curing agent molecules were examined theoretically with molecular dynamics (MD) simulation. Two popular resin systems were studied: Epon 862 resin/EPI-CURE W curing agent and diglycidyl ether of bisphenol A (DGEBA) resin/diethylenetriamine (DETA) curing agent. Even though the selected epoxy resin molecules have relatively long and complex molecular chains, the MD simulation results revealed that all four of these molecules could be inserted into (10,10) SWNTs. The simulation also showed that SWNTs exhibited a dynamic and flexible behavior during the molecular chain filling. The influences of initial molecular position, orientation and non-bond interaction cutoff distance on the molecular filling were also investigated. The potential energy of the molecular interactions during filling was calculated. The MD simulation of a single SWNT pullout with and without resin molecule filling was conducted using a simplified molecular model to illustrate the differences of the interfacial shear stress in the composites. The experimental validation of the MD results is ongoing based on the nanostructure observations and mechanical characterizations of Epon 862 matrix/chopped SWNT composites.

KK9.2

Adatom Diffusion Mediated by Surface Crowdions. Wei Xiao, P Alex Greaney and D C Chrzan; Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, California.

The embedded atom method and nudged elastic band technique are used to explore diffusion of Cu adatoms on Cu (001) for various strain states. Specifically, diffusion via adatom hopping and adatom exchange are considered. Under extreme shear strains, the exchange diffusion mechanism is altered. Instead of merely displacing a neighboring atom, the exchange mechanism leads to the formation of a surface crowdion. The crowdion is metastable and extremely mobile and may lead to rapid, extremely anisotropic diffusion on these strained surfaces. The relationship between the identified crowdions and the reconstructions of some noble metal surfaces is discussed. This work is supported by the National Science Foundation, under grant EEC-0085569.

KK9.3

Ab initio calculation of the precipitates in Al-Cu alloys. Shaoqing Wang[1,2], Manfred Schneider[2], Hengqiang Ye[1] and Gunter Gottstein[2]; [1]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, LiaoNing, China; [2]Institute of Physical Metallurgy and Metal Physics, RWTH, Aachen, Germany.

Precipitation hardening is one of the most widely used mechanisms for structure strenthening of metal alloys. A large number of nano-structured precipitates, called Guinier-Preston (GP) zones, will form when the low Cu-content Al-Cu alloy cools down. These precipitates are crystallographically coherent with matrix and enhance the mechanical property of the alloy. In present study, various possible structure configurations of GP zones are investigated by first-principles ground-state calculations. The studies are based on the plane-wave pseudopotentials (PW-PP) method in the framework of density-functional theory and the local density approximation. From the analysis of formation enthalpy of these configurations, the most advisable atomic structures of GP zones are obtained. The formation mechanism of GP zones in Al-Cu alloys is reasonably elaborated on present theoretical results. The evolution of GP zones in Al-Cu alloy is considered as a process of condensation of layered Al-Cu structures.

KK9.4

The Atomic Structure and Transport Properties of the Large-Angle Grain Boundaries Σ5 (Misorientation Angles 36.87° and 53.13°) Containing Oxygen Vacancies in YBCO. V. S. Boyko, S. Bhaskaran and O. White; Department of Physical and Biological Sciences, The New York City College of Technology, CUNY, Brooklyn, New York.

Knowledge of the nature and properties of the grain boundaries (GBs) in YBCO is of primary importance for the development of high-Tc cables and tapes, as well as Josephson devices. Different mechanisms have been suggested to explain the influence of GBs on superconducting properties of YBCO. Chisholm and Pennycook [M.F. Chisholm and S.J. Pennycook, Nature, v. 351, p. 47, 1991] suggested that superconductivity at GBs suppressed by strain. For the large-angle GBs, the dislocation model of GBs becomes inapplicable and the strain field of GBs cannot be analytically calculated. The only reliable method of determining it is by direct modeling, using appropriate interatomic potential and simulation techniques. The goal of this paper is to evaluate the influence of the real structure of GBs (presence of point defects and charges) on the suppression of superconductivity at GBs. The atomic structure of large-angle symmetric tilt GBs Σ5 (misorientation angles 36.87° and 53.13°) with neutral and charged oxygen vacancies in YBCO is studied by computer simulation. As in [V.S. Boyko and A. M. Levine, Phys. Rev. B, v. 64, p. 224525, 2001], we apply to the obtained atomic structures the techniques of bond-valence-sum analysis [N.D. Browning et al., Physica C, v. 294, p. 183, 1998] and strain analysis [V.S. Boyko, J. Malinsky, N. Abdellatif, and V.V. Boyko, Phys. Lett. A, v. 244, p. 561, 1998] to determine the thickness of nonsuperconducting layers enveloping GBs and evaluate their transport properties. The two methods bring outcomes that are consistent with each other. Based on our results we can conclude that the presence of oxygen vacancies may improve (at least at some concentrations) transport properties of large-angle GBs in YBCO. Experiments [M.A. Navacerrada et al., Appl. Phys. Lett., v.76, p. 3289, 2000; Phys. Rev. B, v.61, p. 6422, 2000] demonstrated that the irradiation of GBs in YBCO results in the appearance of oxygen vacancies, as well as increasing Jc. Our computer simulation data might be considered as a possible explanation of these experimental observations.

KK9.5

Bridging atomic and continuum scales for modeling stress-defect interactions: the importance of supercell size. Mathieu Bouville[1], Michael L Falk[1] and Krishna Garikipati[2]; [1]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; [2]Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan.

Vacancies in silicon undergo an elastic relaxation that contributes to the formation energy of the defect. This elastic relaxation also couples the defect energy to an externally applied stress. Understanding this coupling is important for modeling the effects of stress on microstructure and predicting mass transport in the crystal. Formation volumes and energies are generally obtained using ab initio methods as only they can take into account the quantum mechanical effects that dominate close to the vacancy. However, ab initio simulations use relatively small supercells (a few hundreds of atoms), which can lead to strong vacancy-vacancy interactions with periodic images that bias the results. Empirical potentials on the other hand are not accurate close to the vacancy but they allow for larger simulations and are therefore useful for exploring the effects of the system size on simulation results. Using molecular dynamics (MD) in Stillinger-Weber silicon and continuum elasticity we show that periodic boundaries can interfere with the calculation of the formation volume. More precisely we study how the system size affects the relaxation both at the defect and close to the boundaries of the supercell. These empirical calculations can improve the accuracy of ab initio calculations by providing an accurate estimate of the error that results from the small supercell. The relative importance of elasticity and atomic-scale effects will be discussed.

KK9.6

Impurity Effects on the Fracture of Nanocrystalline Fe Using Atomistic Simulations. Brian Hyde, Antoine Latapie and Diana Farkas; Materials Science, Virginia Tech, Blacksburg, Virginia.

Crack propagation studies in nanocrystalline -iron samples with grain sizes ranging from 6 to 12 nm are reported at temperatures ranging from 100K to 600K using atomistic simulations an empirical many body potentials. The mechanisms of plastic deformation energy release are studied in detail. Intergranular fracture is shown to proceed by the coalescence of nano-voids formed at the grain boundaries ahead of the crack. The simulations also show that at an atomistic scale the fracture resistance and plastic deformation energy release mechanisms increase with increasing temperature. The influence of carbon impurities present on the grain boundaries is studied and our results show that the presence of C impurities increase fracture resistance.

KK9.7

Seeing the Atomic Orbital: First-Principles Study of the Effect of Tip Termination on Atomic Force Microscopy. MingHunag Huang[1], Martin Cuma[2] and Feng Liu[1]; [1]Materials

Science and Engineering, University of Utah, Salt Lake City, Utah; [2]Center for high performance computing, University of Utah, Salt Lake City, Utah.

We perform extensive first-principles calculations to simulate the topographical atomic-force-microscope image of an adatom on the Si(111)-(7x7) surface, demonstrating the feasibility of imaging not only the atoms but also the atomic orbitals. Our comparative study of tip terminations shows that two subatomic features can appear for a single adatom when it is imaged by a Si(001)-type tip having two dangling bonds on its apex, while only one feature would appear if it were imaged by a Si(111)-type tip having one dangling bond on the apex. The key condition for seeing the atomic orbitals is to bring the tip so close to the surface that the angular dependent force dominates the tip-surface interaction. This work is partially supported by DOE.

KK9.8
Simulating Surface Diffusion and Surface Growth in Ceramics. Duncan J. Harris[1], Mikhail Lavrentiev[2], John H. Harding[1], Neil L. Allan[2] and John A. Purton[3]; [1]Physics and Astronomy, University College London, London, United Kingdom; [2]Chemistry, University of Bristol, Bristol, United Kingdom; [3]Synchrotron Radiation, CCLRC Daresbury Laboratory, Warrington, Cheshire, United Kingdom.

Attempts to simulate surface diffusion and growth in ceramics often run into problems of timescales. It is not possible to run a molecular dynamics simulation for long enough to reach the timescales set by, for example, Molecular Beam Epitaxy. We demonstrate that a combination of the temperature-assisted hyperdynamics scheme of Voter and coworkers with kinetic Monte Carlo can reach the timescales required while retaining an unbiased selection of the diffusion processes. Our computer simulations show that exchange processes dominate ionic surface diffusion on terraces in ceramics. However, the process differs essentially from surface exchange diffusion in metals because the Coulombic bonding between ions ensures that the ions must diffuse in pairs. The ionic molecule therefore moves across the surface by alternate exchanges of the cation and anion with the corresponding ions in the surface while the counterion remains close by, held by Coulombic attraction. Diffusion along steps is also an exchange process; except now the ions of the molecule exchange with the ions at the edge of the upper terrace. We also present results for hetero-interfaces and ternary systems. Here the different lattice parameters of the ionic molecule and substrate and the different Madelung potentials in the substrate greatly complicate the diffusion behaviour. We also discuss the important issue of whether it is possible to grow atomically sharp interfaces in ceramic hetero-interfaces, or whether the exchange mechanism makes mixing unavoidable.

KK9.9
Ab Initio Study of the Structural Stability and Magnetic Properties in the Immiscible Co-Ag and Fe-Cu Systems. L.T. Kong, H.R. Gong and Baixin Liu; Dept. Mat. Sci.& Eng., Tsinghua University, Beijing, China.

The structural stabilities and the magnetic properties of some possible metastable alloys in the equilibrium immiscible Co-Ag and Fe-Cu systems were studied by ab initio calculations based on the projector augmented wave (PAW) pseudopotentials [1, 2]. Ab initio calculations first identify that the metastable fcc and bcc structured Co are both ferromagnetic and have a larger magnetic moment than the equilibrium hcp Co. For the Co-Ag system, calculations reveal that the ferromagnetic states of the $D0_{19}$, $D0_{19}$, and B2 structures are energetically favored for the $CoAg_3$, $CoAg_3$, and CoAg alloys, respectively. Experimentally, a $D0_{19}$ $CoAg_3$ alloy has ever been obtained, thus supporting the ab initio calculations. From the calculation results, it seems to suggest that the magnetic moments of Co tend to be enhanced by an expansion of its average atomic volume, yet reduced by the alloying of the non-magnetic element of Ag [3]. While in the Fe-Cu system, calculations reveal that both fcc structured $FeCu_3$ and FeCu alloys are ferromagnetic and the Cu alloying probably played a role in stabilizing the fcc Fe, which is frequently nonmagnetic or anti-ferromagnetic, in a ferromagnetic state. Interestingly, the above calculation results agreed well with the retrievable experimental observations [4]. Reference: 1. G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999). 2. J.B. Liu, Z.C. Li, B.X. Liu, G. Kresse and J. Hafner, Phys. Rev. B 63, 132204 (2001). 3. L. T. Kong, R.F.Zhang, Z.C.Li and B.X.Liu, Phys. Rev. B, (to be published) 4. S. Amirthapandian, B.K. Panigrahi, A.K. Srivastava, A. Gupta, K.G.M. Nair, R.V. Nandedkar and A. Narayanasamy, J. Phys.: Condens. Matter 14, L641 (2002).

KK9.10
Water Interaction with Polar Semiconductor Surfaces: The Case of SiC(001). Alessandra Catellani[1], Giancarlo Cicero[1,2] and Giulia Galli[3]; [1]CNR-IMEM, Parma, Italy; [2]INFM & Torino Polytechnic, Torino, Italy; [3]Lawrence Livermore National Laboratory, Livermore, California.

The study of water adsorption on surfaces is an essential prerequisite to understanding the initial stages of wet oxidation processes. Furthermore, the characterization of the interface between water and solid surfaces of appropriate Z number is key for the design of suitable devices operating in biological ambient. Here we present the investigation of a prototype water/bio-compatible surface: H2O on SiC. Using first principles simulations we have studied the adsorption of water molecules on SiC(001) surfaces at finite temperature. Our results indicate that these polar SiC surfaces closely resemble their respective covalent Si and C counterparts. Implications for surface functionalization are outlined.

KK9.11
Molecular Simulation of the Mechanical Properties of a Model POSS/Polymer Nanocomposite. Franco M Capaldi[1], Mary C Boyce[1] and Gregory C Rutledge[2]; [1]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Chemical Engineering, Massacusetts Institue of Technology, Cambridge, Massachusetts.

Polyhedral Oligomeric Silsesquioxanes (POSS) consist of a (roughly spherical) inorganic silicon-oxygen framework with pendant organic groups surrounding the core. These molecular cages may be either blended into a polymer or covalently tethered to the polymer chains to creat POSS/polymer nanocomposites. The pendant organic groups are chosen to promote compatibility of the particles with the polymer matrix. The resulting nanocomposites have been shown to exhibit increased thermal stability and improved mechanical properties. Significantly, some POSS nanocomposites exhibit reduced melt viscosity while exhibiting a higher Tg and an increased stiffness below Tg. Using parameters determined from molecular simulation, we find that simple continuum models fail to capture the significant increases in the modulus of these nanocomposites. In order to determine the reasons for the failure of continuum theory, the mechanical properties of a model elastomer/POSS nanocomposite with perfectly dispersed POSS particles are determined through molecular dynamics simulation.The influence of the type of organic pendant group and the length of tether connecting the POSS cage to the chain backbone on the polymer chain dynamics, modulus, and structure are also investigated.

KK9.12
Molecular Dynamics Simulations of Velocity Distribution and Local Temperature Changes During Rapid Cooling Processes in Excimer-Laser Annealed Silicon. Byoung Min Lee, S. Munetoh and T. Motooka; Dept. of Materials Science and Engineering, Kyushu University, Fukuoka, Kyushu, Japan.

Thin-film-transistors fabricated from Si films deposited on glass substrate can perform in a number of applications such as active-matrix liquid-crystal displays and CMOS devices. In order to improve the device performance, high-quality poly-Si films with large grain sizes are required. However, since it is experimentally difficult to observe directly the crystal growth behavior, the details of Si thin film growth is not well understood in atomic scale. In this work, we have performed molecular dynamics simulations in order to investigate local temperature changes of the system during rapid cooling processes in excimer-laser annealed Si. A MD cell with typical size of $48.87 \times 48.87 \times 97.75 \AA^3$ including 11664 Si atoms was used for simulations. The interatomic forces were calculated using the Tersoff potential and atomic movements were determined by solving Langevin and Newtonian equations by assuming that temperatures at the substrate and surface are 1500K and 300K, respectively. The velocity distributions in melted Si during rapid cooling processes were found to be the Maxwell-Boltzmann type and steady-state temperature distribution was obtained between the substrate and surface in 100ps. The dynamical behavior of Si during rapid cooling processes was also studied.

KK9.13
Combined Theoretical and Experimental Evidence for Carbon-Vacancy Binding in Austenitic Steels. Ronald Gibala[1] and Christopher Wolverton[2]; [1]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; [2]Scientific Research Laboratory, Ford Motor Company, Dearborn, Michigan.

We have performed first-principles gradient-corrected density functional calculations to determine the binding energy of nearest-neighbor carbon-vacancy pairs in face-centered cubic iron (austenite). A value of 36 kJ/mol is obtained. This result is compared to values obtained or implied from several sources of experimental data on austenitic alloys, and generally good agreement is found. Experimental data examined include: point-defect anelasticity, self diffusion, high-temperature steady-state creep, strain aging and

strain-age hardening, and radiation damage. Several other stability calculations, primarily for metastable carbides, in the Fe-C alloys have been made and will be reported.

KK9.14
Electronic Structure of Silicon Nanocrystals with Metallic Contacts. Anna Maria Mazzone, Istituto IMM, CNR, Bologna, Italy.

The intensive efforts conveyed in these years on transport properties of electronic devices with nanoscale dimensions have finally make clear that the contact influences critically the overall performance of the device and the theoretical progress in this field lags behind the technological advancement. Considered the many applications of nanocrystalline silicon for electronic, optical and photovoltaic devices the focus of this contribution is on the effects of metallic contacts on silicon nanostructures and the study is performed using quantum mechanical calculations at semi-empirical level, based on the MNDO approach, and LDA ,with pseudopotentials and LCAO wavefunctions. The size and shape of the nanocrystals realistically compares with the ones of standard nanocrsytalline technology. The results of an extensive investigation on the functional dependence of the electronic configuration of the system on the size and shape of the nanocrystals, on the composition (Al,Ti and Ni) and geometry of the contacts, as well as of the LDA functional, are presented. The study is complemented by an analysis of the results in the light of the Boltzmann transport equation.

KK9.15
Trends in native-defect- enhanced diffusion of acceptors in silicon. Giorgia M. Lopez[1], Claudio Melis[1], Paolo Schirra[1], Paola Alippi[2] and Vincenzo Fiorentini[1]; [1]Dept. of Physics, University of Cagliari, Monserrato, Italy; [2]IMM, CNR, Catania, Italy.

We study from first principles within density functional theory trends in the energetics and migration properties of the B, Al, Ga, and In acceptors and their complexes with Si self-interstitials and vacancies in c-Si. Native-defect-enhanced diffusion is found to be preferred in all cases over "stand-alone" diffusion. Non-trivial anomalies both in vacancy- and interstitial-assisted motion are identified, among which e.g. In having zero vacancy-exchange barrier, and unstable second-neighbor Si vacancy; the Ga-I complex being metastable against transformation into a Ga Td interstitial; the capture radius being 2nd, 3rd, and beyond 4th neighbors for Ga, In, and B respectively. Observable consequences for diffusion are discussed.

KK9.16
Virtual Fabrication of Electronic Nanomaterials of Prescribed Charge Transport Properties. Liudmila A Pozhar, MLBP, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

The focus of this presentation is on further advances in theoretical and computational methods to investigate prospects of effectively three-dimensional fabrication of sub-10nm nanostructured electronic materials [such as sub-nanoheterostructure (NHS) units] with pre-designed electronic properties. The discussed fundamental quantum-theoretical approach and its results permit development of sub-nanometer scale electronic materials in which functionality and hardware integration requirements are satisfied at the stage of the materials fabrication. The desired physical properties (in particular, conductivity) of such materials are achieved using predictions of the discussed fundamental quantum-theoretical approach in synergy with the equilibrium quantum statistical mechanical computations and simulations. The developed approach furnishes explicit expressions for the tensorial conductivity, dielectric and magnetic susceptibilities of spatially inhomogeneous systems (such as semiconductor quantum dots, artificial atoms, etc.) in terms of the equilibrium two-time temperature Green functions that reflect electronic structure of the systems. These Green functions can be approximated theoretically or recovered computationally. The latter case opens rich opportunities for virtual (i.e., theory-based, computational) fabrication of electronic nanomaterials, devices and systems by design.

KK9.17
Formation Pathways for Single Wall Carbon Nanotube Multiterminal Junctions. Inna Ponomareva[1], A. N. Andriotis[2] and M. Menon[3]; [1]Institute of Biochemical Physics, Moscow, Russian Federation; [2]Inst of Electronic Structure & Laser, Foundation for Research & Technology-Hellas, Heraklio, Crete, Greece; [3]Dept of Physics & Astronomy, Univ of Kentucky, Lexington, Kentucky.

The carbon nanotube junctions have recently emerged as excellent candidates for use as building blocks in the formation of nanoscale electronic devices. In particular, in a three-terminal junction, the third terminal could be used for controlling the switching mechanism, power gain, or other transisting applications that are needed in any molecular electronic circuit. Recent experimental works have demonstrated the feasibility of using controlled electron irradiation in tailoring the junction geometry to create desired multiterminal junctions of nanotubes[1]. Using tight-binding molecular dynamics simulations we illustrate the formation of single wall carbon nanotube T- Y- and X-junctions through an energetically efficient pathway in which all atoms maintain the sp2 arrangement throughout. Different combinations of nanotubes (metallic and semiconducting) are considered. We further report I-V characteristics of some of these junctions. This work was supported by NSF (ITR-0221916), INTAS 00-237 and Russian program "Topic directions in condensed matter physics". [1] M. Terrones et. al., Phys. Rev. Lett., Vol. 89, 07505 (2002).

KK9.18
Development of kinetic Monte Calro simulator for initial nucleation process of nanoparticles. Seiichi Takami, Mitsuo Umetsu and Tadafumi Adschiri; Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, Japan.

This study aims to develop a simulator that reveal the course of nucleation as well as the size- and shape-distribution of obtained nanoparticles. We developed a simulator that reveals the initial nucleation course of nanoparticles under given environmental conditions including pressure, temperature, and the concentration of source. This simulator is based on kinetic Monte Carlo method that facilitates connection between macroscopic parameters with atomic growth processes. In our simulator, the growth process of nanoparticles comprises three elementary processes, that is, sticking, diffusion, and desorption. The frequency of each process is calculated based on the environmental conditions. In one simulation step, the simulator performs the following procedures. 1) Count all possible elementary processes and calculate their frequency 2) Determine an elementary process to occur 3) Change the shape of nano-particle To confirm the validity of our simulator, we studied the nucleation and growth process of nanoparticles. Within the elapsed simulation time, the most seed particles stayed as 'vapor'. However, once they grew larger than several Å, the size of nanoparticles continued to grow. This behavior agrees with classical nucleation theory. In this presentation, we will describe the results of simulation and comparison with classical nucleation theory.

SESSION KK10: Other Systems
Chair: Nicola Marzari
Thursday Morning, December 4, 2003
Constitution A (Sheraton)

8:30 AM KK10.1
Monte Carlo and Molecular Dynamics Investigations of the Thermal Conductivity in Stabilized Zirconia. Mathieu Fevre[1], Alphonse Finel[1] and Rene Caudron[1,2]; [1]Laboratoire d'Etude des Microstructures, ONERA-CNRS, Chatillon, France; [2]Laboratoire Leon Brillouin, CEA-CNRS, Gif-sur-Yvette, France.

Zirconia based oxides exhibit a large range of physical and mechanical properties, which make these compounds extensively used as engineering ceramics. Oxygen sensors, electrolytes, fuel cells, take their advantages of properties of fast ion conductors, chemical stability, and high toughness materials. Because of its low thermal conductivity (~2 W/mK), stabilized zirconia is also used as a thermal barrier in turbine engines for protecting blades from combustion gases. Finding compositions, whith the lowest thermal conductivity at high temperature, constitutes a necessary step to improve engines performances. Low conductivity in stabilized zirconia is due to the presence of defects in the system (structural vacancies on the oxygen sublattice, substitutional ions on the zirconium sublattice). Therefore, chemical correlations and strong local deformations take place and are strongly coupled. For yttria stabilized zirconia monocrystals, thermal conductivity at room temperature exhibits a minimum for 8mol.% Y2O3, and then increases with the doping concentration. This behavior has not been explained and physical mechanisms, which govern the intrinsic thermal conductivity in this oxide, are not clearly highlighted. The aim of this study is to model thermal transport properties in stabilized zirconia system as a function of doping concentrations and temperature, using a developed Monte-Carlo code for structural aspects in relation with local order measurements (neutron and X-ray diffuse scattering), and Molecular Dynamics simulations to compute the conductivity using a non-equilibrium approach. By this way, we have shown that the Monte Carlo approach is needed to reproduce local ordering between defects and that the simple rigid ions model, with a small number of parameters, gives good agreements concerning the microstructural properties as well as the thermal properties of yttria stabilized zirconia. Therefore, the same approach was used to explore the conductivity of Gd2O3-ZrO2, Nd2O3-ZrO2, Nb2O5-Y2O3-ZrO2 systems, and estimate the relevant parameters, which determine the absolute value of the conductivity.

8:45 AM KK10.2
Thermal Conductivity of Y_2O_3-doped ZrO_2 by Perturbed Molecular Dynamics. Masato Yoshiya[1], Akihiko Harada[2], Munetaka Takeuchi[3] and Hideaki Matsubara[1]; [1]Nanocoating Project Division, Japan Fine Ceramics Center, Nagoya, Japan; [2]Fujitsu Kyushu System Engineering Limited, Fukuoka, Japan; [3]Fujitsu Limited, Chiba, Japan.

Understanding and thereby lowering thermal conductivity by introducing nano-meter sized structural defects is a crucial issue for the development of the thermal barrier coating which is designed to protect hot components of gas turbine. Molecular dynamics (MD) calculations using a perturbation method were performed to evaluate the thermal conductivity of pure ZrO_2 and Y_2O_3 doped ZrO_2. It is found that the vibration of the oxygen ions dominates the overall thermal conductivity at low temperature. The contribution of the oxygen ions vibration to the thermal conductivity decreased dramatically with increasing temperature while that of the zirconium ions changed only slightly, resulting in an overall decrease in the thermal conductivity. Comparison with results from MD calculations using the mean field theory showed that scattering of phonons by yttrium ions is as large as that by oxygen vacancies in Y_2O_3 doped ZrO_2. This result implies that the thermal conductivity can be lowered by replacing yttrium ion by other trivalent ion without introducing vacancies further. Acknowledgment: This work was entrusted by NEDO as "the Nanotechnology Program / the Nanostructure Coating Project" promoted by METI, Japan.

9:00 AM KK10.3
First-Principles Study of Interfacial and Anti-phase Boundaries in Ni-Ni_3Al. C. Woodward[1,2], Axel van der Walle[1] and Mark Asta[1]; [1]Materials Science and Engineering, Northwestern University, Evanston, Illinois; [2]Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio.

Metallurgists have employed a combination of precipitation and solid-solution strengthening strategies in the Ni-based superalloys to optimize high-temperature materials performance. Current work hardening and strengthening models are often scaled by the energies of planar defect energies expected in these materials. For example, precipitation strengthening models are dependent on the relative magnitude of (100) and (111) Ni/Ni3Al interfacial boundary (IFB) energies and the (111) anti-phase boundary energy. Also, at high temperatures the L12 Ni3Al phase produces an increased yield stress through a dislocation cross slip process which is influenced by the relative magnitudes of the (111) and (100) anti-phase boundary energies. Finally, the width of the (100) Ni/Ni3Al IFB is a fundamental scaling parameter in models of the micro-structural evolution (e.g. the Phase Field model). We have used first-principles methods to investigate the magnitude and possible range in energy and structure of these planar defects. Also, we are investigating the free energies and composition profiles of these defects using Monte-Carlo calculations. This work is based on recent extensions to the Alloy Theoretic Automated Toolkit (ATAT). ATAT is incorporates suite of well-established computational methods that enable calculations of thermodynamic properties from first-principles.

9:15 AM KK10.4
Ab initio Modeling of C Segregation and Diffusion in Ni for MEMS Applications. Donald Siegel and John Hamilton; Sandia National Laboratories, Livermore, California.

Electrodeposited Ni alloys used in MEMS commonly contain organic additives which enhance alloy hardness via grain refinement. However, the (high-temperature) properties of these devices can also be adversely impacted by the segregation and diffusion of additive constituents at grain boundaries. Using large-scale Density Functional calculations, we address some of the fundamental aspects of C in bulk Ni and at a Ni Sigma 3 (112) tilt GB. We evaluate the heat of segregation of C interstitials to the GB a as a function of Ni magnetic state, and we find that segregation is favorable, up to a C coverage of 0.5 monolayer, regardless of Ni spin state. However, segregation is further enhanced in the ferromagnetic state, since C interstitials suppress Ni magnetism, and this effect is minimized when C resides at the GB rather than in the lattice. Employing the nudged elastic band method with a high density of images, we then evaluate the activation energies ΔE for C GB diffusion between segregation sites along three distinct pathways. Diffusion within the GB is predicted to be highly anisotropic. Migration parallel to the tilt axis should be relatively fast, as the calculated ΔE's are less than half the size found for lattice diffusion, while migration perpendicular to the tilt axis exhibits ΔE's comparable to lattice diffusion. For the most part, Ni ferromagnetism does not significantly alter diffusion energy barriers.

10:00 AM KK10.5
Accurate first-principle study of half-metallic ferromagnetism and structural stability of transition-metal pnictides and chalcogenides. Bang-Gui Liu[1], Wen-Hui Xie[1], Ya-Qiong Xu[1] and David G Pettifor[2]; [1]Institute of Physics, Chinese Academy of Sciences, Beijing, China; [2]Department of Materials, University of Oxford, Oxford, United Kingdom.

Half-metallic ferromagnets, especially those which are compatible with III-V or II-VI semiconductors, are seen as a key ingredient in future high performance spintronic devices, because they have only one electronic spin channel at the Fermi energy and, therefore, may show nearly full spin polarization at quite high temperature. Although zincblende phases of MnAs, CrAs and CrSb have been fabricated as epitaxial nanodots or ultrathin films, it has not been possible to grow the zincblende half-metallic ferromagnetic phases as high-quality layers or films thick enough. However, spintronic devices require these films or layers. Therefore, theoretical exploration for these materials are highly desirable. We studied systematically all zincblende phases of transition-metal pnictides and chalcogenides by using accurate full-potential density-functional method. We predicted the zincblende phases of MnBi and CrSb are excellent half-metallic ferromagnets. The half-metallic ferromagnetism of the zincblende CrSb phase is quite important because this phase has been fabricated. Furthermore, we proved that the zincblende phases of VTe, CrSe, and CrTe are the better half-metallic ferromagnets. They are not only low in energy with respect to the corresponding ground-state phases, but also mechanically stable against structural deformations, and therefore would be realized in the form of epitaxial films or layers thick enough for real applications. These half-metallic ferromagnetic phases should be useful in future spintronic applications because of their compatibility with the binary semiconductors. References: [1] Y-Q Xu, B-G Liu and D G Pettifor, Phys. Rev. B 66, 184435 (2002). [2] B-G Liu, Phys. Rev. B 67, 172411 (2003). [3] W-H Xie, Y-Q Xu, B-G Liu, and D G Pettifor, Phys Rev Lett, (accepted 2003).

10:15 AM KK10.6
Atomistic Simulations of Impurity Effects in Grain Boundary Migration. Mikhail I Mendelev[1], Seungwu Han[2] and David J Srolovitz[2]; [1]MAE, Princeton University, Princeton, New Jersey; [2]Princeton Materials Institute, Princeton University, Princeton, New Jersey.

The presence of impurities can alter the mobility of grain boundaries in metals by several orders of magnitude. It is extraordinarily difficult to separate the effects of individual impurities on grain boundary migration through experiment since truly pure metals do not exist (ppm levels of impurities can greatly alter boundary properties) and because metals always contain a wide range of impurities. Therefore, experimental data on the impurity drag effect cannot be analyzed without the aid of supplementary atomistic computer simulation. In the present work, we studied the effects of Fe impurities on grain boundary motion in Al. The first step was to construct appropriate interatomic potentials. Potentials for pure Al and Fe were fitted to perfect crystal properties (lattice parameter, unrelaxed vacancy formation energy end elastic constants), interstitial formation energies, liquid density and forces in a liquid configuration obtained from the first principles calculations. These potentials provide good agreement with crystal and defect data, liquid diffraction data and melting points (the latter two were not included in the fits). The cross-potential for alloys were fitted to lattice parameters and formation energies of Al-Fe compounds and forces in a liquid configuration obtained from first principles calculations. The second step was to simulate the stress-driven motion of flat boundaries in pure Al using molecular dynamics (MD). Thirdly, we examined the effect of Fe impurity atoms on the same boundaries in Al. The segregation isotherms and the heats of segregation were determined using Monte Carlo simulations. Then the diffusivity of Fe in bulk Al and on the boundary was estimated using MD. Finally, we performed MD simulations of the motion of grain boundaries in Al containing several Fe atoms. The Fe atoms substantially slowed the boundary migration. The simulation results were compared with classical models of the impurity drag effect and the experimental data on grain boundary motion in Al.

10:30 AM KK10.7
Combining Ab-Initio Computations with Experiments for Designing High Energy-Density Electrode Materials for Advanced Lithium Batteries. Shirley Ying Meng[1], Yin Wei Tsai[2], Bing Joe Hwang[2], Yi Li[3,1] and Gerbrand Ceder[4,1]; [1]Advanced Materials for Micro- & Nano- System Programme, Singapore-MIT Alliance, Singapore, Singapore; [2]Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan; [3]Department of Materials Science, National University of Singapore, Singapore, Singapore; [4]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Density Functional Theory has been used successfully to predict and

rationalize the properties of materials. The ability to do property prediction and optimization, while tremendously useful, leaves materials synthesis, processing and optimization, as the bottleneck in materials development. In an effort to shorten the design cycle of advanced materials we have integrated ab initio computations with experimental research in all phases of the development of electrodes for rechargeable Li batteries. An initial search with Density Functional Theory to sort through potential cathode materials based on their Li intercalation potentials and electronic structure identified certain Fe-containing compounds as good substitutes for current battery materials. Crystal structure predictions and calculated mixing enthalpies were used to guide the synthesis conditions and explain experimental results. Motivated by the first principle calculation results, LiNi1/3FezCo1/3-zMn1/3O2 (0=<z=<1/3) cathode materials were synthesized by a sol-gel method. X-ray photoelectron spectroscopy was used to confirm the electronic behavior predicted with the first principles methods. This approach has produced competitive electrode materials with very few iteration steps in the design cycle. We believe that such direct integration of ab initio methods with experimental research holds promise for significantly shortening the development cycle of materials.

10:45 AM KK10.8
Molecular Dynamics Simulation for Structure and Dynamics of Interstitials in Metals. Yoshiaki Kogure[1], Toshio Kosugi[1], Masao Doyama[1] and Hideo Kaburaki[2]; [1]Environmental Materials, Teikyo University of Science & Technology, Uenohara, Yamanashi, Japan; [2]Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki, Japan.

A large number of mechanical relaxation peaks have been observed in the temperature dependence of high frequency ultrasonic attenuation and internal friction in crystals. The defects responsible to the peaks are interstitials, impurity pairs, impurity-interstitial pairs and so on. These defects accompany a non-spherical strain field and respond to the external shear stresses. The temperature dependence of internal friction and elastic modulus change are used to be analyzed on the basis of phenomenological anelasticity model developed by Nowick et al., in which the point defect strain per unit concentration is called as "the elastic dipole". Recently, Granato has developed the interstitialcy model (1992) and the model has successfully been applied on thermal and mechanical phenomena of glass and liquid, in which the dynamical characters of the interstitials play essential role as an elementary process. To investigate the fundamental mechanisms of internal friction by interstitials in Cu and Al crystals, a molecular dynamics simulation has been performed. Several potential functions are adopted to express the atomic interaction. An embedded atom method potential developed by present authors is also used in the calculation. The atomistic displacement and the elastic field around the self or mixed interstitials in Cu and Al crystals are calculated under the periodic or free boundary conditions. Then the relaxation strength and the relaxation time for the interstitials are estimated. The interaction between point defects through the strain field is also important, that may cause a distribution of relaxation time and a glass-like behavior. The effects of temperature on the structure and the dynamics of point defects are also investigated by the simulation under constant temperature conditions.