SYMPOSIUM D

New Advances in Materials Prediction

November 30 – December 3, 1999

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* Invited paper

SESSION D1: PREDICTIONS IN ADVANCED MATERIALS
Chair: John D. Joannopoulos
Tuesday Afternoon, November 30, 1999
Room 207 (H)

1:30 PM *D1.1
100% RELIABLE PREDICTOR OF p-DOPING IN II-VI SEMICONDUCTORS. James D. Chadi, NEC Research Institute, Princeton, NJ.

The structure for the ground state of the AX deep acceptor center in II-VI semiconductors is identified and the sign of its formation energy is found to be a highly reliable indicator of p-type dopability. Results from ab initio total-energy calculations on ZnS, ZnSe, ZnTe, and CdTe doped with N, P, As, or Sb show that the tendency for deep center AX formation arising from large-lattice-relaxation is strongly correlated with dopant inactivity in II-VI semiconductors. In some cases, vacancy formation is found to be energetically more effective in dopant compensation than AX centers.

2:00 PM D1.2
A COMPUTATIONAL INVESTIGATION OF INTERFACIAL SEGREGATION IN ZnO. H.S. Domingos, P.D. Bristowe, Cambridge University, Dept of Materials Science and Metallurgy, Cambridge, UK.

Polycrystalline ZnO is an electrically active material which exhibits non-linear conduction properties due to the presence of grain boundaries and impurities. These properties are commonly utilised in the manufacture of commercial varistors but the microscopic origin of the observed electronic behaviour is not clearly understood. In this paper we present a computational study of the phenomenon of grain boundary segregation in ZnO, which is thought to be the key underlying process. Three techniques are used: classical energy minimisation, quasi-harmonic lattice dynamics and total energy pseudopotential calculations. The study has focused on a series of [0001] twist boundaries and their interaction with two known varistor forming impurities: cobalt and barium. The classical calculations have shown how the propensity for segregation of these two impurities can be explained in terms of their relative atomic sizes and the local grain boundary structure. The lattice dynamics calculations have determined the influence of temperature on the segregation energies. The total energy pseudopotential calculations have focused on the effect of segregation on the electronic structure of one of the boundaries. In particular, the influence of impurity segregation on the local electron density distribution, Mulliken charges, bond orders and atomic structure has been studied. The result of all three approaches are compared, contrasted and rationalised in terms of the known physical properties of doped polycrystalline zinc oxide.

2:15 PM *D1.3
THE DELIBERATE DESIGN OF AN OPTO-ELECTRONIC MATERIAL. Tairan Wang

(ABSTRACT NOT AVAILABLE)

2:45 PM D1.4
ACCELERATING THE RATIONAL DESIGN AND SYNTHESIS OF NEW CRYSTALLINE AND AMORPHOUS OXIDES AND FLUORIDES. David Teter, Geochemistry Department, Sandia National Laboratories, Albuquerque, NM.

A set of accurate and transferable interatomic potentials for essentially all the possible oxides and fluorides in the periodic table has been developed by fitting to an extensive database of ab initio derived energy surfaces and experimental data. Combining these potentials with effective structure generation algorithms allows the rapid generation of realistic crystalline and amorphous structural models as a function of pressure, temperature and composition space. The energetics and physical properties of these models can be rapidly evaluated within the potential formalism, or evaluated with more rigorous ab initio methods. The application and results of this strategy to the development of materials for extreme-UV optical materials, fluoride glass host materials for rare earth ions, molecular sieves, fuel cells, and structural ceramics will be discussed.

3:30 PM D1.5
AB INITIO STUDIES OF BORON-NITRIDE HYDROGEN-STORAGE COMPOUNDS. Jens Kortus, Mark R. Pederson, Center for Comp. Mat. Sci., Naval Research Lab., Washington, DC.

If fuel-cell technologies are to succeed it will be necessary to determine a means for the safe transportation of hydrogen which implies an oxygen free environment. Borazan (BH_3NH_3) forms small molecular crystals which may be thermally activated in order to free the borazan molecules. The borazan molecules subsequently react further forming borazin ($B_3N_3H_6$) and molecular hydrogen. As such, borazan serves as an oxygen-free hydrogen storage compound which may have potential for use in fuel cells. To help guide and further understand the experiments on this material we have performed several ab initio investigations on the stabilities, reactivities and vibrational signatures of the molecular solid and gas phase structures. Our Raman and IR spectra of borazan molecules are compared to measured results in the solid. Also we predict heats of vaporization of the molecular solid and reaction energies for the gas-phase Borazan-Borazin hydrogen releasing reaction. In addition we will discuss several possible initial borazan-borazin reaction pathways and barriers to estimate the thermal stabilities of these compounds. Finally we examine the relative stability of the borazin end product. The inclusion of all degrees of freedom in this reaction, particularly zero point vibrations, and the use of the generalized gradient approximation within a density functional framework were key ingredients for understanding this system.

3:45 PM D1.6
AB INITIO STUDY OF COMPLEX MINERAL STRUCTURES. Victor Milman, Jim A. White, MSI, Cambridge, UK; Elena V. Akhmatskaya and Ross J. Nobes, FECIT, Uxbridge, UK; Bjoern Winkler, Chris J. Pickard, Inst. Geowissenschaften, Kiel, GERMANY.

The structure and electronic properties of a number of complex inorganic structures with more than 100 atoms in the unit cell have been studied at ambient conditions and under applied pressure. The study has been performed with the density-functional theory code CASTEP which uses pseudopotentials and plane-wave basis set. A systematic study of the compressibility of aluminosilicate garnets has been carried out, and the mechanism of polyhedral compression has been suggested. The effect of hydrogarnet substitution, $SiO_4 \Leftrightarrow (OH)_4$, on structure, stability and properties of pyrope and grossular is discussed. The dynamics and ordering of Mg in pyrope has been investigated via potential energy surface calculations. The structure, properties and relative stability of various polymorphs of klockmannite, CuSe, are analyzed and the driving force for the orthorhombic distortion has been identified.

4:00 PM *D1.7
THE REMARKABLE STRUCTURE AND PROPERTIES OF γ-ALUMINA. Karl Sohlberg, Stephen J. Pennycook*; and Sokrates T. Pantelides*, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; *also: Department of Physics and Astronomy, Vanderbilt University, Nashville, TN.

The structure and composition of γ-alumina have been debated for many years. We report a series of density functional theory calculations that reveal that γ-alumina is a series of compounds of the form $H_{3m}Al_{2-m}O_3$ and that H is mobile at elevated temperatures. Results for H diffusion, density as a function of H content, and OH vibrational modes are in excellent agreement with experimental data. We further show that the mobility and solubility of H make γ-alumina a "reactive sponge" that stores water molecules by breaking them apart. These reactions can account for several phenomena that occur on the surface, such as: 1) a massive reconstruction that eliminates the three-coordinated Al, as observed by ^{27}Al NMR, 2) formation of Pt trimers, as observed by atomic-resolution STEM, and 3) loss of porosity, as observed in automotive catalysis.

4:30 PM D1.8
ELECTRONIC AND STRUCTURAL STUDY OF STRESS DENATURATION OF ALPHA-HELICAL POLYALANINE. Joel Ireta, Arturo Rojo, Marcelo Galvan, Departamento de Quimica, Universidad Autonoma Metropolitana, Mexico, DF MEXICO; Joerg Neugebauer, and Matthias Scheffler, Fritz-Haber-Institute der Max-Planck-Gesellschaft, Berlin-Dahlem, GERMANY.

The electronic structure and conformational changes induced by uniaxial stress on an infinite alpha-helical polyalanine were studied with ab initio methodologies. It was found that in vacuum, the intrinsic response of the structure to mechanical deformations, as well as the transition from native to denatured state, are dominated by changes in the hybridization of the carbonyl bond. This kind of deformations might be present in a real experiment of protein denaturation by pressure.

4:45 PM D1.9
INTERACTION OF LIGHT WITH BIOLOGICAL MOLECULES. Robert Hamilton, Indrani Sinha, and Roland E. Allen, Texas A&M Univ., Physics Dept., College Station, TX.

Using the new technique of tight-binding electron-ion dynamics, we have performed simulations of the interaction of light with two biologically important molecules: chlorophyll, which is responsible for photosynthesis, and retinal, which is of central importance in vision. These simulations are a quite nontrivial extension of previous work on semiconductors and fullerenes, because of the size, chemical

composition, and more complex symmetries of the biological molecules. Despite these complexities, and the effect of rather ill-defined *in vivo* or *in vitro* environments, our results are consistent with existing experimental data. For example, our calculated absorption peak for chlorophyll lies in the red part of the visible spectrum, with a weak shoulder in the blue. The absorption has been studied as a function of wavelength, linear polarization, and circular polarization. Substantial linear and circular dichroism was observed for chlorophyll, and these effects were found to be strongly wavelength dependent. The calculations involve a new approach for simulating the electron dynamics in a molecule or material (electron-ion dynamics), in which the behavior of the electrons is determined by numerical solution of the time-dependent Schrødinger equation, using an algorithm which preserves probability. Several improvements in this technique were made in the present studies, based on considerations of stability and efficiency. In addition, a new approach was used for simulating the response of the electrons to a radiation field: the time-dependent Peierls substitution. This approach permits one to employ a semiempirical tight-binding Hamiltonian with no additional parameters. One need only multiply each of the original tight-binding matrix elements by a phase factor, which involves the time-dependent vector potential $A(t)$ and the difference $\vec{R}$ in the position vectors for each pair of atoms. The absorption of radiation was calculated by directly monitoring the energy absorbed by the molecule as the electrons were promoted to excited states. The successes of the present work imply that this general approach can be extended to other biological molecules, such as melanin.

SESSION D2: NEW PREDICTIVE DESCRIPTIONS OF MATERIALS

Chair: Efthimios Kaxiras
Wednesday Morning, December 1, 1999
Room 207 (H)

8:30 AM *D2.1
INTERATOMIC FORCE CONSTANTS AND MICROSCOPIC MODELS OF FERROELECTRICITY IN PEROVSKITE THIN FILMS AND SOLID SOLUTIONS. Karin M. Rabe and Philippe Ghosez, Yale University, Department of Applied Physics, New Haven, CT.

The full phonon dispersion relations of $SrTiO_3$, $BaTiO_3$, $PbTiO_3$ and $PbZrO_3$ in the cubic perovskite structure are computed using first-principles variational density-functional perturbation theory, with ab initio pseudopotentials and a plane-wave basis set. Examination of the interatomic force constants (IFCs) in real space, obtained by a transformation which correctly treats the long-range dipolar contribution, shows that most are strikingly similar, while it is the differences in a few key interactions which produce the observed differences in the phonon dispersions. This suggests the transferability of IFCs to more complex systems, such as thin films and solid solutions. In the present work, an atomistic model of a (001) perovskite thin film is constructed based on interatomic force constants from the bulk. A first-principles effective Hamiltonian is derived from this model to investigate the ground-state polarization and dielectric response of $PbTiO_3$ thin films. Under short-circuit electrical boundary conditions, (001) films of thickness well below d = 10 nm are found to support a stable perpendicular polarization, consistent with recent experimental observations. This analysis allows us also to propose a microscopic interpretation of the extrapolation length δ in the phenomenological Landau-Ginzburg theory of ferroelectric thin films. For the case of solid solutions, we compare the low-lying lattice dynamics predicted for $(Ba,Sr)TiO_3$ from the values of IFCs of the endpoint compounds with calculations for the intermediate virtual crystal and small ordered supercells. The derivation of the corresponding first-principles effective Hamiltonian and extension to Pb-containing perovskite systems is in progress.

9:00 AM D2.2
CARBON-SILICON COMPLEXES IN BULK SILICON: THEIR ROLES IN SILICON DIFFUSION. Jeongnim Kim, Ohio State Univ, Dept of Physics, Columbus, OH; Florian Kirchhoff, Ohio State Univ, Dept of Electrical Engineering, Columbus, OH; John W. Wilkins, Ohio State Univ, Dept of Physics, Columbus, OH; Michael Sternberg and Thomas Frauenheim, Univ of Paderborn, Paderborn, GERMANY.

We study the structure and dynamics of carbon defects in bulk silicon by using a self-consistent-charge density-functional-based tight-binding (SCC DFTB) approach.[1] Carbon is incorporated into bulk silicon on substitutional or interstitial sites. Substitutional carbon can also interact with silicon interstitials (Si_I) and form more stable C-Si_I complexes. The formation of stable C-Si_I complexes is suggested to deplete silicon interstitials available for boron transient enhanced diffusion (TED), thus reducing boron TED. Our SCC DFTB calculations find good agreement with first-principle caluclations for (i) the relative stability and (ii) the geometry of simple C-Si_I complexes containing one or two carbon atoms. We contrast the diffusion mechanism and the migration activation energy of silicon in the presence of C-Si_I complexes with those in pure silicon.
[1] D. Porezag *et al.*, Phys. Rev. B **51**, 12947 (1995); M. Elstner *et al.*, Phys. Rev. B **58**, 7260 (1998).
Supported by NSF and NRL component of the DoD CHHSI program. Computational aids are provided by OSC, NCSA and NPACI.

9:15 AM D2.3
CHARGE TRANSFER EFFECTS IN THE EMBEDDED ATOM METHOD THROUGH AN OPEN SYSTEM DENSITY FUNCTIONAL POINT OF VIEW. Steven M. Valone, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM; Susan R. Atlas, Department of Physics and Astronomy, Univeristy of New Mexico, Albuquerque, NM.

A preponderance of chemical processes and dynamical behaviors involve some degree of charge transfer. Yet very few classical potential energy surfaces deal directly with this process. One exception is the potential of Rick, Stuart and Berne [*J. Chem. Phys.* **101**, 6141 (1994)] which accounts for charge transfer effects to quadratic order in the charge transfer coefficients and uses the Sanderson principle of chemical potential equalization. Limitation to quadratic dependence is problematic for modeling true chemical behavior. The close association between the Embedded Atom Method (EAM) [*Phys. Rev. Lett.* **55**, 1564 (1983)] and density functional theory makes it possible to use some of its deeper results. Viewing EAM from an open-systems density functional point of view, we will present a derivation of EAM including charge transfer terms structurally identical to the original EAM forms and show how the requirement of chemical potential equalization can be used to construct the potential itself. Specifically the chemical potential, μ, determines the reshaping of the atom as it resides in the molecule, liquid or solid and most specifically determines changes to the background densities so fundamental to EAM:
$\phi \sim r^{(1/(\sqrt{(-2\mu)})-1)} \exp(-\sqrt{(-2\mu)}\, r)$
$n_{background} \propto \phi^2$
$\mu \sim \mu_{atom} + 2\,\omega\,\eta_{atom}$
where ω is the number of electrons being redistributed and η_{atom} is the hardness of the atoms. The above combines results from EAM, Perdew, Parr, Levy and Balduz [*Phys. Rev. Lett.* **49**, 1691 (1982)], and Parr and Pearson [*JACS* **105**, 7512 (1983)]. As the host system dissociates to atoms, $\mu \to \mu_{atom}$ as required since $\omega \to 0$ during this process.

9:30 AM D2.4
SIMULATIONS OF CHARGE STATES OF DEFECTS IN EXTENDED SYSTEMS. Peter A. Schultz, Sandia National Laboratories, Albuquerque, NM.

While first principles electronic structure simulations have become successful tools for the study of materials properties, the study of charged local defects in extended bulk systems has arguably lagged. The conventional approach for treating charged local defects in bulk using electronic structure methods invokes the supercell approximation and solves for an electrostatic potential withing periodic boundary conditions, and either approximates energies from the energy levels of the neutral system or treats the charged system explicitly by neutralizing the net charge in the cell with a flat density background. This artifice is demonstrated to incur errors that are potentially the size of the energy scale of typical interest: a band gap energy. I present results of a new method that treats the local electrostatic potentials correctly, and not via neutralization by jellium. The total defect distribution is divided into a local model density matching the charge (and multipole moments) of the defect, and a remaind

9:45 AM D2.5
A DENSITY FUNCTIONAL METHOD BASED ON LOCALIZED DENSITIES. L.L. Boyer, Naval Research Lab., Washington, DC; H.T. Stokes, Brigham Young Univ., Provo UT; M.J. Mehl, Naval Research Lab., Washington, DC.

The expression of total energy as a functional of density began originally with the density represented as a sum over localized "atomic-like" densities. Following this approach, we adopt a formulation of total energy that approximates kinetic energy due to overlapping densities using a Thomas-Fermi form, and apply a self-consistent proceedure to minimize the total energy, variationally, with respect deformations of the localized densities. Tabulated Slater functions are employed to account for radial deformations and spherical harmonic expansions are used to handle nonspherical distortions. The method, call self-consistent atmic deformation (SCAD), has been applied to compounds with ngative ions from V, VI and VII columns of the periodic table. Properties calculated include Born effective charges, dielectric constants and phonon frequencies.

10:30 AM D2.6
BOND-ORDER POTENTIALS FOR ATOMISTIC STUDIES OF THE STRUCTURAL AND MECHANICAL PROPERTIES OF L10 TiAl. S. Znam[1], D. Nguyen-Manh[2], V. Vitek[1] and D.G.Pettifor[2]. [1]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, [2]Department of Materials, University of Oxford, Oxford, UNITED KINGDOM.

Bond-order potentials (BOP) is an order N, fully real space method that does not require use of periodic boundary conditions. The cohesive energy is composed of the bond energy that contains the angular dependence of the atomic interactions, an environment dependent central-force many-body term representing the overlap repulsion arising from the valence sp electrons, and a pair potential term representing short-range repulsions. A condition of charge neutrality at individual atoms is employed as an ersatz for self-consistency. These potentials have been constructed for Ti-Al alloys such that the bond part comprises the 3d (Ti) and 3p (Al) electron contributions to bonding. A transferable set of tight-binding parameters entering the bond part have been generated by first-principles calculations and incorporate the angular character of bonding arising from Ti-Al hybridization effects. The negative Cauchy pressures of γ-TiAl are adequately reproduced owing to inclusion of the environmentally dependent term. These potentials are tested by the following studies that have been made in parallel with ab initio calculations: Comparison of competing structures with the same stoichiometry, investigation of complex transformation paths between different structures, calculation of γ-surface and study of the structure of interfaces encountered in lamellar TiAl with L10 structure. Finally, these potentials are used a study of the cores of dislocations in TiAl.
This research was supported in part by the National Science Foundation grant no. DMR96-26344 (SZ and VV).

10:45 AM D2.7
A NEW METHOD FOR GENERATING ENVIRONMENTAL DEPENDENCE OF TIGHT-BINDING PARAMETERS.
D. Nguyen-Manh, D.G. Pettifor, Department of Materials, University of Oxford, Oxford, UNITED KINGDOM; V. Vitek, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA.

The environmental dependence of tight-binding (TB) potentials is shown to be crucial for the realistic atomistic simulation of materials (1,2). To date, the inclusion of environment-dependent effects has been modeled via an *empirical* function-that takes the same distance-dependent form irrespective of the angular character of the two-center TB bond integrals (2). We present a new derivation of the *analytic* form of the environment dependence that is angularly dependent by using the non-orthogonality matrix to screen the two-center intergrals. The method is based on the formalism recently developed for deriving analytic Bond Order Potentials (BOPs) (3) and is shown to reproduce the ab-initio screened LMTO bond integrals for bcc transition metals and their disilicides. These environmentally dependent bond integrals are currently being used in conjunction with BOPs to simulate defect behavior in these metallic systems.
This work is supported by the U.S. Department of Energy, BES, grant no. DE-FGO2-98ER45702.
1. D. Nguyen-Manh, D.G. Pettifor, S. Znam, V. Vitek, MRS Symposia Proceeding, MRS, Pittsburgh, vol. 491, (1998), 353.
2. H. Hass, C.Z. Wang, M. Fahnle, C. Elsasser, K.M. Ho, Phys. Rev. B, Vol. 57, (1998), 1461.
3. D.G. Pettifor, I.I. Oleinik, Phys. Rev. B., vol. 59, (1999), 8487.

11:00 AM D2.8
NEW ADVANCES IN SEMIEMPIRICAL TIGHT-BINDING APPROACH FOR CLUSTERS AND NANOSTRUCTURES.
Z.M. Khakimov, F.T. Umarova, N.T. Sulaymonov, D.S. Pulatova, Institute of Nuclear Physics, Tashkent, UZBEKISTAN.

Semiempirical tight-binding methods are traditionally used for a rather qualitative and separate estimation of spectroscopis properties and atomic structure of solids, defects and surfaces, but using different approximations in each case. Some progress in a quantitative estimation of energetics and geometry of atomic structures has become possible due to more recent advances in tight-binding total energy calculation schemes. However, reliability and applicability of these schemes are still limited by the fact that they don't take into account (i) charge redistribution effects (attempting sometimes only to prevent unphysical charge transfer between atoms or taking advantage of local charge neutrality conditions for specific systems such as hydrocarbons) and (ii) interactions of more distant atoms than the first-nearest-neighbors, and that (iii) individual properties of atoms are not involved properly or actually lost (destroyed) in parameterization procedures.
The semiempirical self-consistent tight-binding method developed by us (Comput. Mater. Sci. Vol. 3 (1994) p. 95) is free from these demerits and, unlike other tight-binding methods, enables one to calculate accurately configurational and spectroscopic energies of neutral and charged systems in the framework the same approximations. Reliability of the method have been demonstrated for point defects in Si (MRS Symp. Proc. Vol. 527 (1998) p. 369).
In this report we present the future development of this method with new parametrization, allowing to obtain stable and metastable structure and electronic properties (potential ionizations, electronic affinities, etc) of neutral and charged clusters of sp-elements (carbon, N,O, Si, Ge, etc) with acceptable accuracy. The results of application of the method incorporated into molecular dynamics simulation approach will be given for carbon, silicon, and their mixed clusters (molecules) and compared with corresponding ab initio calculation results. Simulation results of reactions between these clusters and their growth will be discussed. Here new technique is implemented for the integration of equation of motion, allowing to increase time steps of the integration with the least loose of its accuracy.

11:15 AM D2.9
TIGHT-BINDING HAMILTONIANS IN METALS: PHONONS, STACKING FAULTS, AND DEFECTS. Michael J. Mehl, Dimitrios A. Papaconstantopoulos, Naval Research Laboratory, Washington, DC; Florian Kirchhoff, Department of Electrical Engineering, Ohio State University, Columbus, OH.

Tight-binding total energy methods bridge the gap between highly accurate, but slow and memory consuming, first-principles density functional calculations and fast, compact, but less accurate atomistic potential methods. Over the past few years we have developed a highly accurate tight-binding method. The environmentally sensitive tight-binding parameters are determined by fitting to the band structures and total energies of a small number (10-30) of first-principles calculations. The resulting Hamiltonian is used to interpolate between these first-principles calculations, allowing highly accurate determinations of structural energy orderings, elastic constants, phonon frequencies, and surface energies. We have also developed computer programs which can use these parameters to do tight-binding molecular dynamics and to determine the electronic structure of a system. In this talk we show how these parameters can be used to calculate phonon frequencies over the entire Brillouin zone, determine vacancy and stacking fault energies, and present examples of MD simulation for metallic and covalently bonded systems. We will also discuss progress in dealing with binary systems.
This work is supported by the U.S. Office of Naval Research and the Department of Defense Common HPC Software Support Initiative (CHSSI) program. Computational support was provided by the Aeronautical Systems Center and Army Research Laboratory Major Shared Resource Centers.

11:30 AM D2.10
BAND STRUCTURE CALCULATIONS FOR DILUTE ALLOYS WITH APPLICATION TO GaAsN. N.A. Modine, E.D. Jones, A.A. Allerman, S.R. Kurtz, Sandia National Laboratories, Albuquerque, NM.

Ab initio determination of excited state properties for dilute alloys is a challenging endevour. Accurate treatment of the effects of the dilute species requires large computational unit cells, while conventional first principles band structure computations are limited to much smaller cells by an unfavorable scaling with system size. In some systems, a perturbative approach is a natural compromise, but in the GaAsN alloy, where incorporation of only 2 percent nitrogen reduces the band gap by about 0.5 eV, this can not be expected to give reasonable results. Traditional Kohn-Sham density functional theory calculations using the local density approximation (LDA) can be performed for the cell sizes of interest, but they are well known to give poor results for such properties as band gaps and band masses. We discuss a correction procedure for the LDA results which requires only a small amount of experimental input and gives results in good agreement with experiment for the pressure dependent band gap and conduction band mass of the GaAsN material. We also report our progress in the development of a truly first-principles approach to the problem based on the use of Hamiltonian-optimized localized orbitals to improved the scaling of the band structure calculations.

11:45 AM D2.11
NOVEL PROCEDURES FOR LATTICE POTENTIAL ENERGY PREDICTIONS OF IONIC SOLIDS. Leslie Glasser, Centre for Molecular Design, Dept of Chemistry, Univ of Witwatersrand, Johannesburg, SOUTH AFRICA; H. Donald Brooke Jenkins, Dept of Chemistry, Univ of Warwick, Coventry, UK.

Lattice energy is a central thermodynamic property in analysis of the stability of solids. Thus, an ability to predict lattice energy for stable, unstable, and even unknown solids is of considerable utility in dealing with materials properties and inorganic syntheses. We present a group of surprisingly simple methods for lattice energy predictions of ionic

solids, primarily relying on the fact that coulombic interactions predominate, especially for the more complex materials. These calculations yield lattice energies which are generally better than within 7% of more formally-calculated values. Indeed as a result of these back-of-the-envelope estimates, a new phase of inorganic chemistry prediction has begun(1). Firstly, we have extended(2) the well-known Kapustinskii equation for binary ionic solids to apply to complex ionic systems, by replacing the charge term by an ionic strength-related term. Only the chemical formula and ionic (or thermochemical) radii are required for this calculation. Thermochemical radii of over 400 simple and complex ions have been reported from this work(3). Secondly, we have extended Bartlett's linear correlation between lattice energy and the inverse cube-root of the unit cell volume from simple (1:1) ionic solids to a limited range of more complex materials(3,4) (again using the ionic strength-related term). This yields both effective and absolute single ion volumes for solids. Thirdly, we report a new linear energy/volume correlation which applies to some of the most complex ionic solids known (including minerals and superconductive materials), with lattice energies approaching 100 MJ/mol. This correlation relies only on the ionic strength and an electrostatic conversion term - with no empirical constants at all. (1) S Brownridge, I Krossing, J Passmore, HDB Jenkins, HK Roobottom, Coord. Chem. Rev., invited contribution, submitted. (2) L Glasser, Inorg. Chem., 1995, 34, 4935-6. (3) HK Basford, HDB Jenkins, J Passmore, L Glasser, J. Chem. Educ., in press. (4) HDB Jenkins, HK Roobottom, J Passmore, L Glasser, Inorg. Chem., in press.

SESSION D3: PREDICTION OF MECHANICAL PROPERTIES OF MATERIALS

Chair: Kyeongjae Cho
Wednesday Afternoon, December 1, 1999
Room 207 (H)

1:30 PM *D3.1
RAPID FRACTURE OF SILICON. Michael P. Marder, Department of Physics and Center for Nonlinear Dynamics, The University of Texas, Austin, TX.

Crystalline silicon provides an ideal setting to test the understanding of brittle fracture. Large single crystals of high quality are inexpensive, and atomic interactions of silicon have been more widely studied than for any other element. We have now succeeded in carrying out a careful comparison of theory and experiment for dynamic fracture. The theoretical work begins with scaling laws deduced from exact solutions of atomic fracture problems, and uses them to design molecular dynamics simulations. The experimental work builds upon techniques we originally developed to study rapid fracture of polymers, but with numerous refinements to accomodate the new difficulties posed by silicon. The comparison is barely satisfying even at a qualitative level. The difficulty appears to reside in the interatomic potentials employed for the molecular dynamics, which have largely been designed with thermal equilibrium in mind.

2:00 PM D3.2
SIMULATIONS OF DYNAMIC CRACK BRANCHING IN BRITTLE MATERIALS. Michael Falk, Harvard University, Division of Engineering and Applied Sciences, Cambridge, MA.

It has recently been observed that the velocity oscillations and surface features associated with high speed fracture in both PMMA and silica glass are closely correlated with crack branching.(Sharon,Gross and Fineberg, PRL v.74 p.5096; Sharon and Fineberg, Nature v.397 p.333) The branches seen in experiments appear when the crack is driven to speeds above approximately 40% of the Rayleigh wave speed. At these speeds the branch lengths are tenths of millimeters, orders of magnitude larger than the inhomogeneities in these materials. Simulations of brittle fracture in finite element models with cohesive zones between elements were performed in order to understand the branching process. The conditions under which multiple branches may co-propagate are investigated. Particular attention is paid to the effect of crack speed and loading on the process of crack tip splitting and the subsequent fracture path.

2:15 PM D3.3
DYNAMIC MULTISCALE SIMULATIONS OF FRACTURE IN SILICON. Noam Bernstein, Daryl Hess, Center for Computational Materials Science, Naval Research Lab, Washington, DC; Robert E. Rudd, Department of Materials, University of Oxford, Oxford, UNITED KINGDOM and SFA Inc, Largo, MD; Farid F. Abraham, IBM Research Division Almaden Research Center, San Jose, CA.

We present the results of multiscale simulations of fracture in silicon. Our method uses finite element continuum mechanics and empirical potential molecular dynamics to describe a crack propagating through a 0.4μm sized silicon sample. Regions near the crack are treated atomistically with molecular dynamics, while the far field stress and strain fields are described with continuum elasticity and finite elements. The two regions are dynamically coupled and evolve in time simultaneously. To simulate crack propagation we begin with a silicon slab with a thin crack loaded at a constant strain rate until the crack begins to propagate. We then fix the strain and continue the simulation with fixed system boundaries. We examine the behavior of the material at different applied strains, temperatures, and crystallographic orientations. While under some conditions we observe ductile fracture progressing via void formation and coalescence, in other cases we observe the emission of dislocations from the tip, which move along leaving behind a disordered region.

2:30 PM D3.4
MECHANICAL BEHAVIOR PREDICTIONS USING A NEW O(N) METHOD FOR MODELING AND SIMULATING THE MOTION OF A LARGE NUMBER OF DISLOCATIONS IN ANISOTROPIC MEDIA. Linyong Pang, David M. Barnett, Stanford University, Dept of Mechanical Engineering, Stanford, CA.

In this work an O(N) method is developed for calculating the interactions of a large number, N, of parallel straight dislocations in a solid whose linear elastic properties are of general anisotropy. The effect of anisotropy is accounted for by using a dislocation-dislocation interaction energy derived from the Stroh formalism for plane elastostatics. For simulations allowing the use of doubly periodic boundary conditions the interaction energy between an infinite dislocation wall and a single dislocation under conditions of general anisotropy is of more utility and has been developed by us; in combination with a fast multipole method (valid for anisotropy) and one-dimensional space partitioning, the extremely short-range nature of the dislocation-dislocation wall interaction force leads to a tremendously efficient and accurate computational scheme for determining equilibrium dislocation configurations as well as the kinetic evolution (via a non-linear velocity - Peach-Koehler force law) of dislocation motion in an O(N) scheme. The kinetic simulations also allow for dislocation generation and annihilation. As examples of the utility of the methods we have developed we present simulations of the dynamical evolution of dislocation patterns in copper single crystals with two active slip systems; these simulations can be carried far enough to provide evidence of dislocation (Mughrabi) cell formation. Other simulations in which the macroscopic strain rate is controlled using feedback methods allow us to generate the macroscopic stress-strain curve during both loading and unloading stages in a dynamic simulation involving over 20,000 dislocations in a basic computational cell (with periodic B.C.'s) and to track the total and mobile dislocation density as a function of strain. These numerical studies clearly indicate that such simulations provide a practical method for understanding and predicting dislocation pattern formation as well as post-yield behavior such as work-hardening.

3:15 PM *D3.5
HARD AND SOFT JUNCTIONS. Uzi Landman, Georgia Institute of Technology, Atlanta, GA.

(ABSTRACT NOT AVAILABLE)

3:45 PM D3.6
MOLECULAR DYNAMICS SIMULATIONS OF LUBRICANTS IN MECHANICAL TRANSMISSIONS. Hiroyuki Tamura, Hui Zhou, Yoshihisa Hirano, Seiichi Takami, Momoji Kubo, Akira Miyamoto, Tohoku Univ, Graduate School of Engineering, Dept of Materials Chemistry, Sendai, JAPAN.

Extreme properties are required for the lubricant molecules in the mechanical transmission so called traction fluids. The traction fluids must not only prevent wear of the contact surfaces but also efficiently transmit the mechanical power. Therefore, the traction fluid must be designed to transmit high frictional forces, in other words, they must have high traction coefficients. In the present study, the non-equilibrium molecular dynamics (NEMD) simulations have been performed to investigate the effect of the molecular architecture on the traction coefficient. The traction coefficient of benzene, cyclohexane, dicyclohexyl, cis- and trans-decalin molecules, which were confined between two solid surfaces, were calculated by shearing the confined films. The interaction in the molecules was approximated by the CVFF potential, and the temperature and normal load were maintained at 300 K and 1 GPa, respectively[1]. In the present simulations, the affinity of the solid surface is strong and so the slippage is observed at the inner parts of the confined films. The diffusion rate of the benzene molecules normal to the solid surfaces are found to be higher than the other molecules, while the cyclohexane rings tend to prevent the diffusion of the molecules. The traction coefficient of the cis-decalin is found to be higher than that of trans-decalin due to the bent molecular architecture. The highest traction coefficient is calculated for the dicyclohexyl molecules in agreement with the experimental measurements. Our NEMD

simulation revealed that the two connected cyclohexane rings of the dicyclohexyl molecules increase the shear resistance at the slippage interfaces in the confined film.
Reference: [1]Hiroyuki Tamura, Muneo Yoshida, Kenichi Kusakabe, Chung Young-Mo, Ryuji Miura, Momoji Kubo, Kazuo Teraishi, Abhijit Chatterjee, Akira Miyamoto, Langmuir (to be published).

4:00 PM *D3.7
MULTISCALE ELECTRONIC STRUCTURE MODELING OF DEFECTS AND INTERFACES. H.T. Johnson, Boston Univ, Dept of Aerospace and Mechanical Engineering; R. Phillips, Brown Univ, Div of Engineering.

There has been extensive experimental work in the areas of semiconductor nanostructure devices and microelectromechanical systems (MEMS) recently. In many of these submicron scale electronic materials applications, there is significant coupling between mechanical and electronic structure. In particular, heterogeneities such as dislocations and bimaterial interfaces are known to strongly affect this coupling. A multiscale modeling approach, which makes possible the direct probing of spatially varying electronic properties, is presented here for studying mechanical and electronic coupling at defects and interfaces. The approach involves the calculation of cohesive energy and forces throughout a body using semi-empirical tight binding atomistics. In nonuniform regions of a structure, individual atoms are considered explicitly. In uniformly strained regions of a structure, such as material that is remote relative to interfaces, spatial interpolation is performed so that only the energy and forces associated with particular, representative atoms are calculated directly. To obtain the tight binding based cohesive energy for a region of material, the site projected density of states is calculated in real space using an arbitrarily large set of moments of the density of states. These moments are constructed from components of the tight binding Hamiltonian, and a maximum entropy or Chebyshev polynomial technique is used to determine the statistically most likely density of states. As an example, the energetics of bimaterial interfaces in lattice mismatched materials are considered. The electronic properties effects of misfit dislocations are discussed. Results include minimum energy configurations of interfaces and spatially varying maps of density of states fields.

4:30 PM D3.8
CROSS-SLIP PATHS AND ENERGETICS IN Al AND Ag. Gang Lu, Nicholas Kioussis, California State University Northridge, Dept. of Physics, Northridge, CA; Vasily V. Bulatov, Lawrence Livermore National Laboratory, Livermore, CA; Efthimios Kaxiras, Harvard University, Dept. of Physics, Cambridge, MA.

A new semi-discrete variational approach is developed for the energetics of dislocation cross-slip in FCC metals. In the new model, we let screw dislocations spread into two intersecting planes, glide and cross-slip planes. Within the Peierls-Nabarro formalism, the energy of a given core configuration is then determined by the elastic interaction between two continuously distributed dislocation densities and the associated misfit energies integrated over the two planes. The Γ surfaces entering the model are calculated from the density functional theory. We find an optimal cross-slip path and the associated cross-slip energy barrier in a series of constrained minimization calculations, starting from different initial core configurations. It turns out that screw dislocations in Al and Ag follow different cross-slip paths characterized by very different activation barriers. Our results are compared with the experimental and simulation data available in the literature. Our approach can also be used to study more complicated dislocation reactions over different glide planes.

4:45 PM D3.9
THERMAL EXPANSION OF ANISOTROPIC MATERIALS – DENSITY FUNCTIONAL STUDY OF HIGH QUARTZ SYSTEMS. A.I. Lichtenstein, R.O. Jones, Institut für Festkörperforschung, Forschungszentrum Jülich, Jülich, GERMANY.

Thermal expansion is a basic property of any material and determines the ultimate usefulness of many ceramics. A low value of the volume thermal expansion over wide temperature ranges is essential, for example, for optical components (telescope mirrors, etc.) and cooktops, and it can be realized in practice only by highly anisotropic materials. The prediction of thermal expansion coefficients requires both an accurate description of the structure *and* the structural dependence of the phonon frequencies. We have applied the density functional (DF) formalism (LSD approximation) to calculate the thermal expansion in β-eucryptite (hexagonal $LiAlSiO_4$,the main component of most cooktops), which has a small volume thermal expansion over a temperature range from 300 – 1400 K and a structural phase transition at 755 K. Structural properties have been determined by combining DF calculations with molecular dynamics (Car-Parrinello method), and phonon properties using linear response within the DF perturbation theory. The calculations reproduce the measured changes in the lattice constants $[a(T) > 0, c(T) < 0]$ very well, and they identify the mechanism leading to contraction of the unit cell along the c-axis as T increases. We apply the same methods to β-quartz ("high quartz") and discuss the application to other systems.

SESSION D4: POSTER SESSION:
NEW ADVANCES IN MATERIALS PREDICTION: MECHANICAL AND DYNAMICAL BEHAVIOR, ADVANCED MATERIALS, AND NEW APPROACHES
Chair: T. A. Arias
Wednesday Evening, December 1, 1999
8:00 P.M.
Exhibition Hall D (H)

D4.1
FIRST-PRINCIPLE CALCULATIONS OF $(SiC)_{1-x}$ $(AlN)_x$ ALLOYS. Sung-Yool Choi, Mun Cheol Paek, ETRI, Micro-Electronics Technology Laboratory, Taejon, SOUTH KOREA.

There has been growing interest on the novel materials of wide band gap semiconductors including III-Nitrides and IV-column elements. The wide band gap semiconductor materials provide characteristic properties, which are preferentially adequate for anti-environmental or optoelectronic applications due to their unique electronic properties. It is well known the $(SiC)_{1-x}(AlN)_x$ alloys or solid solutions show very interesting properties such as indirect to direct band gap transition and tunable band gap according to the composition of the alloys. We report here first-principle pseudopotential calculations of structural and electronic properties of $(SiC)_{1-x}(AlN)_x$ alloys for several compositions as the first step of theoretical investigation of their interesting properties. Our investigation is based on the first-principle total energy and electronic structure calculations, including geometry optimization. On the basis of our calculations we predict optimized atomic structures of the alloys and discuss the electronic structures of them.

D4.2
FIRST PRINCIPLES CALCULATIONS FOR INTERMETALLIC Li-ION BATTERY INSERTION ELECTRODES. R. Benedek, M.M. Thackeray, Argonne National Laboratory, Argonne, IL; R. Prasad, IIT Kanpur, Kanpur, INDIA; L.H. Yang, Lawrence Livermore National Laboratory, Livermore, CA; A. Alavi, Queen's University, Belfast, UNITED KINGDOM.

Copper-tin intermetallic compounds with NiAs-like structures have recently been proposed as possible anode materials for Li-ion batteries. Experimental attention has been given to the $\eta\prime$ phase Cu_6Sn_5, which was found to undergo a topotactic phase transition with Li insertion to a cubic structure similar to that of Li_2CuSn (M. M. Thackeray, et al., Electrochem. Commun. 1, 115 (1999)). First principles calculations with the plane wave pseudopotential method are performed in the present work to elucidate atomic structure, electrochemical potentials and electronic properties of these systems. Calculations are presented for pristine $\eta\prime$-phase Cu_6Sn_5, a monoclinic system with four formula units per unit cell, and for $\eta\prime$-phase Cu_6Sn_5 with a single interstitial Li atom. The high-temperature η phase adopts the hexagonal NiAs structure. We calculate the relative energies of three hypothetical structures that accomodate the deviation from equiatomic composition in η-phase Cu_6Sn_5: interstitial Cu, antisite Cu and Sn vacancies. Calculations are also performed for cubic $Li_{2-x}CuSn$ with different Li contents ($0 \leq x \leq 2$).

D4.3
AB INITIO CALCULATIONS OF 3C-SiC (111) / Ti POLAR INTERFACES. Shingo Tanaka (SWING), Masanori Kohyama, Dept of Material Physics, Osaka National Research Institute, Ikeda, Osaka, JAPAN.

SiC is very important for high-temperature devices as well as high-performance structural ceramics. To fabricate SiC / metal interface with desirable electronic and structural properties is crucial for such applications of SiC. SiC / Ti system is the most important because Ti or Ti alloys are often used for such applications. First of all, it is essential to understand direct interfaces between SiC surfaces and Ti without reaction layers. Recently, atomic and electronic structures of the SiC / Ti interfaces as well as those of the SiC / TiC interfaces have been observed experimentally. On the theoretical side, however, there have been few ab initio calculations of the SiC / Ti interfaces. Recently, we performed *ab initio* calculations of the SiC (001) /Ti interfaces for the first time, and found that the adhesive energy and the Shottky barrier hight (SBH) greatly depend on the surfaces species of SiC. However, most experimental studies have been done to the SiC (111) / Ti or SiC(0001) Ti interfaces. In this paper,

we deal with SiC (111) / Ti interfaces using the technique of the first-principles molecular dynamics method. The stable configurations, adhesive energies and the SBH for the Si-terminated and the C-terminated interfaces are obtained. Results are compared with the experiments and our theoretical results of the SiC (001) / Ti interfaces. It should be noted that the 3C-SiC (111) / Ti interface can be regarded as models of the hexagonal SiC (0001) / Ti interfaces which are often dealt with experimentally. We examine the effects of the polar (111) surfaces as well as the effects of surface species on the adhesive energy, the SBH and the reactivity. And we discuss the methodology for the interface design of SiC / Ti system.

D4.4
INSULATOR-METAL PHASE TRASITION IN ENERGETIC MATERIALS. Maija M. Kuklja, A. Barry Kunz, Electrical Engineering Department, Michigan Technological University, Houghton, MI.

Energetic materials belong to a wide class of the technologically important organic molecular crystals. Most of them are composed of poly-atomic molecules having a complicated structure. There have been many theoretical and experimental advances in the understanding the macroscopic properties of these solids while microscale processes are still little understood. This is partly due to the complexity of the structure of energetics and partly due to the large velocity of detonation fronts (7km/s). Modern experimental techniques do not have enough time resolution to observe processes in the detonation fronts. Therefore, theoretical simulations are highly desirable. One of the most prominent mechanisms of detonation initiation suggested by J.Gilman is based on the idea of the optical gap closure during the shock propagating throughout the crystal, which undergo an electronic phase transition. As a result, the materials lose their transparency under high compression. In the preset study, the defect- and pressure-induced metallization in a solid $C_3H_6N_6O_6$ (RDX) were investigated by means of a first-principle, quantum-chemical method. The Hartree-Fock calculation scheme (CRYSTAL95) combined with the many-body perturbation-theory (LOPAS) permits us to simulate the atomic and electronic structure of a series of lattice defects such as a molecular vacancy, a vacancy dimer, an edge dislocation, a nano-crack, and a (210) surface in both equilibrium and highly compressed RDX. As a result, we can predict how the presence of defects in the crystal will affect the critical pressure for insulator-metal electronic phase transition. The obtained results compared with the relevant experimental data and are of great practical importance in particular, our conclusions provide useful insights for the predictions for sensitivity of explosive crystals to detonation initiation.

D4.5
FIRST-PRINCIPLES CALCULATION OF ELECTRONIC STRUCTURE OF $Ga_{1-x}Al_xN$ ALLOYS. Sudhir Kumar, Department of Physics, Institute of Engg. and Technology, M.J.P. Rohilkhand University, Bareilly, INDIA.

A full potential self-consistent linear muffin tin orbital (LMTO) calculation has been performed to predict electronic properties of the wide band gap semiconductors $Ga_{1-x}Al_xN$ alloys (for x=0.0, 0.25, 0.50, 0.75 and 1.0) and the random alloys have been investigated. The calculated direct band gap for random distribution of cation nearest-neighbour tetrahedral cluster in the $Ga_{1-x}Al_xN$ alloys for any arbitrary concentration x is seen to show a quite linear variation in agreement with the exeperiment. We observe a direct to indirect band gap crossover at x=0.59. The band gap is showing to be very small.

D4.6
Abstract Withdrawn.

D4.7
INTERFACIAL RELAXATION OF COBALT/COPPER SUPERLATTICES USING A FULL-POTENTIAL LMTO METHOD. D.L. Price, University of Memphis, Dept. of Physics, Memphis, TN; B.R. Cooper, University of West Virginia, Dept. of Physics, Morgantown WV.

Using the forces capability of our full–potential LMTO (Linear Muffin–Tin Orbital) electronic structure method, we have investigated the interfacial relaxation of small period cobalt/copper superlattices. In particular, we examine the effect of relaxation upon magnetic moments, and also consider the effect on calculated quantities of incorporating the generalized gradient approximation (GGA) within the method. The copper/cobalt multilayer system is an extensively studied giant-magnetoresistance material (GMR), and the study is motivated in part as a prelude to consideration of interdiffusion at the interface, and the related effects upon the magneto-resistance of these multilayer systems. We also investigate possible alternatives to the relatively expensive calculation of entirely accurate forces.

D4.8
KINETIC PARAMETERS AND DIFFUSION PATHS OF SILICON IN THE C54 AND C49 COMPETING PHASES OF $TiSi_2$. Paolo Raiteri, Marcella Iannuzzi, Leo Miglio, INFM and Dip. di Scienza dei Materiali, Univ. di Milano-Bicocca, Milano, ITALY; Massimo Celino, ENEA-Casaccia Research Center, HPCN Project, Roma, ITALY.

The formation of $TiSi_2$ metallizations in Integrated Circuits is usually obtained by solid state process which involves lattice or grain boundary diffusion of silicon atoms throughout silicide. A Ti layer is deposited on top silicon substrate, the silicide formation at the interface is then activated by thermal annealing and supported by Si upward diffusion through this growing layer. Since two competing phases are present it is interesting to understand if different diffusion rates and mechanisms are found, at least in the case of lattice diffusion. To this end molecular dynamics runs with an original tight binding potential are very instructive, as we predict that similar activation energies but rather different prefactors are present in the two phases. A correlation between the crystal structures and the different diffusion paths for the two phases is also drawn.

D4.9
PERIODIC FIRST-PRINCIPLES CALCULATIONS OF ORTHOBORIC ACID. Peter Zapol, Larry A. Curtiss, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; Ali Erdemir, Energy Technology Division, Argonne National Laboratory, Argonne, IL.

Periodic ab initio study for molecular crystal of orthoboric acid was performed. Orthoboric acid crystal has a layered structure with 28 atoms in the unit cell. Geometries of a two-dimensional layer and a three-dimensional molecular crystal were optimized. It was shown that intermolecular interactions within the layer are much stronger than interactions between layers. The latter are largely responsible for a number of technologically interesting properties of the boric acid. Lubricating properties of the boric acid are attributed to the weak interlayer bonding that permits easy mutual sliding of layers. Results of friction process modeling by total energy calculations with a relative shift of boric acid layers is compared to results of experimental friction studies. (Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.)

D4.10
GENERATING EAM TANTALUM POTENTIALS BY FORCE-MATCHING METHOD. Youhong Li, Department of Chemical, Bio and Materials Engineering, Arizona State University, Tempe, AZ; Donald J. Siegel, Physics Dept, Univ of Illinois, Urbana, IL; James B. Adams, Department of Chemical, Bio and Materials Engineering, Arizona State University, Tempe, AZ.

Tantalum is a promising material used as adhesion layer and barrier layer in copper metallization. To predict tantalum behavior in a materials system, one needs the tantalum potentials. However, tantalum potentials of high quality are still not available. In this paper, Force-Matching Method was used to generate EAM potentials for tantalum. Force Matching method, developed by Ercolessi F. and James B. Adams, incorporates the high quality data from ab-initio calculation for a variety of structures and important experimental data into the fitting process, resulting in potentials with excellent transferability. Several molecular dynamics calculations using the generated EAM tantalum potentials were performed and were compared to the previous calculations done by others as well as to the experimental data.

D4.11
DFT CALCULATIONS WITH PERIODIC BOUNDARY CONDITIONS USING GAUSSIAN BASIS SETS. Konstantin N. Kudin and Gustavo E. Scuseria, Chemistry Department, Rice University, Houston, TX.

When covalent bonding between first row atoms (B-F) dominates the structure of polymers, surfaces, and solids, Gaussian basis sets have significant advantages over plane waves. In this presentation, we will report on our recent implementation of energy and energy gradients (forces) of a Kohn-Sham density functional theory (DFT) program which yields linear scaling of computational time with respect to unit-cell size. The Coulomb contributions to the Hamiltonian matrix are computed in real space using the Fast Multipole Method (FMM). The DFT exchange-correlation potential and Hamiltonian diagonalization are treated by linear scaling techniques similar to those developed for the molecular case. Using FMM and the localized nature of Gaussian orbitals, we have also developed code for the analytic evaluation of energy gradients with respect to lattice dimensions (cell forces). As a result, atomic positions and lattice vectors can be optimized simultaneously. Redundant internal coordinates are employed for such optimizations. Representative calculations on the optimized structures and energetics of polymers

(polyacetylene, fluorinated polyacetylene, polymethineimine, PPV) will be presented using LDA, PBE, and VSXC functionals and different basis sets.

D4.12
MATERIALS PREDICTION USING THE ENVIRONMENT-DEPENDENT TIGHT-BINDING POTENTIALS. C Z. Wang, G.D. Lee, B.J. Min, Z.Y. Lu and K.M. Ho, Ames Laboratory-USDOE and Department of Physics, Iowa State University, Ames, IA.

Using the recently developed environment-dependent tight-binding potentials, we have performed extensive simulations to study the structures and properties of carbon and silicon based materials. Two examples will be discussed in this paper. In the first example, we have performed tight-binding molecular dynamics simulation to study laser-induced graphitization on the diamond (111) surface. Our simulations predict that under nanosecond or longer laser pulses, the diamond (111) surface will graphitize via formation of graphite-diamond interfaces. By contrast, the graphitization of the surface will occur in a layer-by-layer fashion under femtosecond laser pulses. The simulation results are consistent with experimental observations. In the second example, we investigate diffusion of silicon adatom and addimer on the Si(100) surface. Our studies discover several diffusion pathways with energy barriers lower than those of previously studied pathways. The predictions made by the tight-binding calculations are verified by ab initio calculations and are in good agreement with experimental data.

D4.13
A MICROSCOPIC DESCRIPTION OF STRONGLY CORRELATED ELECTRONS. Bernardo Barbiellini, Northeastern Univ, Dept of Physics, Boston, MA.

Individual particles provide an approximation to the theory of electron in solids which works well in various circumstances. For instance, the technological importance of semiconductors has given an enormous impetus to the energy band theory, which is based on the concept of Fermi Liquid. However, the evidence has been piling up that the Fermi liquid scheme fails for several materials such as the high temperature cuprate superconductors. We will use a variational theory for treating correlations in many electron systems which goes beyond the free fermion nodal structure. An electron pair wavefunction, called the generating geminal, is first constructed in terms of which the many-body wave function is obtained by taking an Antisymmetrized Geminal Product (AGP) over all pair configurations. For an infinite number of electrons, the AGP turns out to be a Resonating Valence Bond (RVB) state when the repulsion energy is large. According to P.W. Anderson it is usually not easy to calculate with the RVB states or to represent them. For instance the representation in term of the Gutzwiller projection is suggestive but not particularly useful computationally. In the AGP state, the Gutzwiller projection is already included since the generating geminal has a zero diagonal in the Wannier base expansion if the repulsion is large (i.e. the double occupancy is projected out). The computational complexity of the present scheme is comparable to Hartree-Fock calculations because the generating geminal has a diagonal expansion in the natural orbitals.

D4.14
HIGHLY OPTIMIZED EMPIRICAL POTENTIAL MODEL OF SILICON. Thomas J. Lenosky, Babak Sadigh, Eduardo Alonso, Vasily V. Bulatov, and Tomas Diaz de la Rubia, Lawrence Livermore National Laboratory, Livermore, CA; Arthur F. Voter, Joel D. Kress, Theoretical Division, Los Alamos National Laboratory, Los Alamos NM; David F. Richards and James B. Adams, University of Illinois at Urbana-Champaign, Urbana, IL.

We have fitted an empirical potential for silicon using a generalized modified embedded atom (GMEAM) form. This form is similar to an embedded atom potential, except that the local density also contains a three-body term similar to the Stillinger-Weber form. We parametrized the GMEAM using five cubic splines, each with 10 fitting parameters, and fit the parameters to a large database using the force-matching method. GMEAM provides a reasonable description of energetics for all atomic coordinations from the dimer (Z=1) to fcc (Z=12). The GMEAM model is fit to accurately reproduce phonons and elastic constants, as well as point defect energetics. It provides a fairly good description of both the 30 and 90 partial dislocations, and accurately predicts the reconstruction energy for the 2 by 1 reconstruction of the (100) surface. These examples illustrate that GMEAM may be useful for many previously intractable problems. GMEAM is computationally very inexpensive, allowing very large systems to be studied.
This work is performed under the auspices of the U.S. Department of Energy and Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

D4.15
GENERALIZATION OF EQUIVALENT CRYSTAL THEORY (ECT) TO INCLUDE ANGULAR DEPENDENCE. John Ferrante, NASA-Lewis, Cleveland, OH; Fredy R. Zypman, University of Puerto Rico, Humacao, PR.

ECT's basic idea rests in the proven fact that the total ground state energy of a quantum system is a functional of the density. So ECT requests that the density be the same for both the real lattice and the equivalent defect-free lattice, at the atomic site under consideration. That provides a value for the equivalent lattice parameter aeq at that site. The energy from that site is obtained by using the Universal Binding Energy Relation (UBER) curve, which provides binding energy as a function of average atomic separation (in this case lattice parameter). The total energy is obtained as the sum of the individual site energies. In this work, we generalize ECT without loosing its original flavor, that is, we keep the assumption that the electron density must remain the same for both the real and the equivalent crystal. However, here we consider that the real crystal may experiment a shear stress in addition to the hydrostatic compression or expansion. In this new framework the equivalent crystal at an atomic site will be assigned two (instead of just one) parameters: the equivalent lattice parameter, and the tilt angle with respect to a given direction in space. To go from the ground state, to the equivalent lattice, we slide and shrink (or expand). The sliding and shrinking parameters are obtained from two equations: the monopole and dipole term of the charge distribution at each site is assumed to be the same for both the real and the equivalent crystal. We apply the method to obtain improved results for transition-metal surface energies.

D4.16
FIRST PRINCIPLE MOLECULAR DYNAMICS CALCULATION OF ALUMINUM GRAIN BOUNDARY EMBRITTLEMENT PROMOTED BY CALCIUM IMPURITY. Guanghong Lu, Akira Suzuki, Ryoichi Yamamoto, Department 4th, Institute of Industrial Science, University of Tokyo, Tokyo, JAPAN; Akira Ito, SDK HD Research & Development Center, Ichihara, Chiba, JAPAN; Masanori Kohyama, Department of Materials Physics, Osaka National Research Institute, Ikeda, Osaka, JAPAN.

It has been reported[1] that Ca as impurity in Al-Mg alloy tends to segregate in grain boundaries and thus induces embrittlement. We therefore chose Ca as impurity and Al as host metal to present the first principle molecular dynamics (FPMD) calculation based on density functional theory (DFT) and local density approximation (LDA). We gave an 84-atoms model with Al Σ9[110] tilt grain boundary, in which 4 of 8 atoms were substituted by Ca impurity atoms. The pseudopotentials of Al was given based on Troullier and Martins[2], and that of Ca was given based on Hamann, Schlüter and Chiang[3]. The calculated pseudopotentials were used then to test equilibrium lattice parameter and bulk modulus. The results were within the error. The most stable atom construction, valence charge density and local density of states (LDOS) of Al grain boundary with and without Ca impurity atoms was calculated, respectively. The results shows that due to Ca segregation in the grain boundary, Al atoms around Ca atom is away from Ca atom. The charge density over the grain boundary decreases, and the range of lower charge density region caused by Ca segregation extends along the whole grain boundary. However, between other Al atoms along the most-closely-packed lattice direction, the charge density increases. According to the results above and combining the results of Sodium segregation in aluminum grain boundary we reported, we presented a new model on the mechanism of grain boundary embrittlement for embrittling elements of group I and II in the periodic table . [1] K. Horikawa, et al., Scripta Materialia 39, 860 (1998) [2] N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993(1991) [3] D. R. Hamann, M. Schlüter and C. Chiang, Phys. Rev. Lett. 43, 1494(1979)

D4.17
BENDING STIFFNESS OF NANOMETER-SIZED BEAMS AND PLATES. Ronald Miller, Department of Mechanical Engineering, University of Saskatchewan, CANADA.

Structures like carbon nanotubes and nanometer-sized beams and plates can now be fabricated through a variety of techniques. Further, recent experiments have directly measured the elastic bending stiffness of such structures. In the present paper, atomistic simulations are carried out to compute the elastic properties of beams and plates in bending. The goal of the calculations is to study the change in elastic properties as the cross-sectional dimensions of the structures approach the atomic scale. The results show a clear size effect in the elastic properties of these materials, whereby the stiffness of the material is reduced with decreasing cross-section. Simulations are performed for both FCC Al (using the Embedded Atom Method) and diamond structured Si (using the Stillinger-Weber Model). The simplicity of the model used for the FCC Al allows for analytic calculations that shed light on the nature of the elastic size effect and

the effect of the non-uniform strain fields brought about by bending. The simulations of Si demonstrate the importance of the size effect in open, covalently bonded materials.

D4.18
HYDROGEN AT INTERSTITIAL SITES AND VACANCIES IN IRON: FIRST-PRINCIPLES STUDY. Yoshitaka Tateyama, Tsuyoshi Miyazaki, Takahisa Ohno, National Research Inst for Metals, Tsukuba, JAPAN.

In this paper we study (1) hydrogen states at interstitial sites and (2) the role of hydrogen in vacancy formation and aggregation in pure iron, aiming at understanding elementary processes in hydrogen embrittlement. We have carried out first-principles calculations of a supercell (Fe_{54}:H) with considering deformation of the lattice. The interstitial hydrogen state, the first problem, has not yet been settled due to experimental difficulty in direct detection of hydrogen and its low solubility in iron. We have calculated the potential energy surfaces (PES's) of hydrogen at the interstitial sites. Detailed information of the local lattice deformation induced by hydrogen and the change of electronic states of the host is also obtained. We have further employed quantum-mechanical calculations for the hydrogen nucleus using the above PES's. Based on the results of the vibrational energies and their eigen functions of the nucleus, the quantum effect and the probable location (distribution) of hydrogen are discussed. For the second issue, thermal desorption experiments have recently suggested that hydrogen enhances the formation of monovacancy in iron. This might be crucial for an initial process of the void formation related to hydrogen embrittlement. We have calculated the total energies and the optimized structures for several possible configurations of hydrogen atoms around a monovacancy and a divacancy. On the basis of these results, we discuss the effect of hydrogen on the formation of vacancies and their aggregation.

D4.19
PRESSURE-INDUCED STRUCTURAL TRANSFORMATIONS IN METALS: MECHANICAL STABILITY CRITERIA AND MOLECUALR-DYNAMICS SIMULATIONS. Jianhua Zhao, University of California, Santa Barbara, Dept. of Chemical Engineering and Dept. of Mechanical and Environmental Engineering; Frederick Milstein, University of California, Santa Barbara, Dept. of Mechanical and Environmental Engineering and Materials Dept.; Dimitrios Maoudas, University of California, Santa Barbara, Dept. of Chemical Engineering, Santa Barbara, CA.

The structural stability of crystalline solids under stress is a topic of both fundamental interest, in understanding the mechanical response of materials, and of technological importance, in modifying materials structure and properties. The study of stress-induced structural transitions in perfect crystalline solids provides understanding of more complex stress-induced dynamics in various problems of materials failure. This work examines the influence of pressure and temperature on the domains of both thermodynamic equilibrium and mechanical stability, as well as the dynamics of transitions between phases, for cubic and hexagonal close packed (hcp) crystal structures. The interatomic interactions are described by empirical potential energy functions parameterized for studies of crystal elasticity at finite strain; the crystalline models exhibit the experimental values of elastic moduli and atomic volumes of selected metals at zero pressure. Detailed monitoring of structural response under loading is carried out based on isostress molecular-dynamics (MD) simulations following the Lagrangian formulation of Parrinello and Rahman. The results are discussed and analyzed within the framework of rigorous criteria for elastic stability of cubic crystals under pressure P, which may be expressed as $\kappa(P)>0$, $\mu(P)>0$, and $\mu'(P)>0$, where κ is the bulk modulus, and μ and μ' are the independent shear moduli. One particularly noteworthy result is the transition, from the body centered cubic (bcc) structure to the hcp structure, that is found to occur in association with the vanishing of the shear modulus μ of the bcc structure. Since this transition is accompanied by symmetry breaking, it is necessarily inhomogeneous; the MD simulations exhibit a pressure- and temperature-dependent dynamic shearing of the (110) planes, which remain remarkably rigid during transformation and transform into the (0001) planes of the hcp crystal. Throughout this transformation process, the pressure is maintained strictly hydrostatic and constant.

D4.20
AB INITIO STUDY OF THE TENSILE STRENGTH AND FRACTURE OF GRAIN BOUNDARIES IN SiC. Masanori Kohyama, Osaka National Research Institute, Dept. of Material Physics, Ikeda, Osaka, JAPAN.

It is essential to investigate the structure and properties of grain boundaries in order to develop high-performance SiC ceramics. Especially, it is of great imortance to understand the mechanical properties of SiC grain boundaries. First of all, it is crucial to clarify the behavior of grain boundaries under various tensile or shear stresses. Currently, *ab initio* calculations based on the density-functional theory can be applied to such complex problems using the recent computational techniques. We have performed the *ab initio* tensile tests [1] of the coincidence tilt grain boundaries in cubic SiC, and clarified the tensile strength and fracture through the behavior of atoms and electrons. We have dealt with one non-polar interface and two kinds of polar interfaces of the Σ=9 boundary. Polar interfaces contain either C–C or Si–Si wrong bonds, and non-polar interface contains both kinds of wrong bonds. In the tensile tests, the supercell is stretched in a small increment, and all the atoms are relaxed according to the Hellmann-Feynman forces. This cycle is iterated untill interfaces are broken. From the calculated energy–strain and stress–strain curves, the Young's modulus, the maximum tensile strength, the fracture energy, and the fracture toughness of each interface have been obtained. The features of bond breaking and the associated changes in the electronic structure have been analyzed in detail. We analyze the effects of the C–C and Si–Si wrong bonds on the mechanical properties and discuss the methodology of the interface design for optimized mechanical properties of SiC ceramics.
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D4.21
DYNAMICS OF DISLOCATIONS AND CRACKS: INSTABILITIES AND PATTERN FORMATION. Robin L.B. Selinger, Ming Li and John M. Corbett, Catholic Univ., Physics Dept., Washington, DC.

Using molecular dynamics simulation, we explore dynamics of dislocations and cracks in geometries where they exhibit morphological instability. We perform simulations of dislocation pair annihilation and annihilation of a dislocation at a crack tip, to look at instabilities as predicted in [1], caused by a positive gradient in the driving stress. We also perform simulations of crack propagation along a weak interface in three dimensions under mode I loading. When perturbed by heterogeneity in the fracture toughness of the interface, the crack shows initiation and propagation of non-dispersive crack front waves as predicted by Morrissey and Rice [2]. Random heterogeneity in the fracture toughness also causes the dynamic crack to roughen and become self-affine.
[1] Ming Li, Brian B. Smith, and Robin L. B. Selinger, Phys. Rev. Lett. 82, 2306 (1999). [2] J. W. Morrissey and J. R. Rice, J. Mech. Phys. Sol. 46, 467 (1998).

D4.22
MOLECULAR DYNAMICS STUDY ON ANOMALOUS ELASTIC PROPERTIES OF β-CRISTOBALITE IN CRYSTALLINE SiO_2. Hazime Kimizuka, Hideo Kaburaki, Japan Atomic Energy Research Institute, Center for Promotion of Computatinal Science and Engineering, Tokyo, JAPAN; Yoshiaki Kogure, Teikyo University of Science & Technology, Yamanashi, JAPAN.

Cristobalite, a low density polymorph of silicon dioxide (SiO_2), shows an anomalous elastic property of negative Poisson ratio, which results in a transverse expansion under the uniaxial extension. We have successfully derived a complete set of elastic stiffness constants of cristobalite for a wide range of temperatures (300-1,800K) including the α-β transition by the equilibrium molecular dynamics (MD) method using the fluctuation formula. The number of atoms in the system is 576 (containing 48 unit cells), and we use periodic boundary conditions. The Nosé-Hoover and Parrinello-Rahman isothermal-isobaric ensemble was applied to calculate the structures of the reference states. We have employed the nonempirical pair-wise potentials of Tsuneyuki *et al.*(TTAM) and Beest *et al.* derived by cluster calculations of potential energy surfaces using the *ab initio* method. We have found that cristoballite shows a negative Poisson ratio over this temperature range, and that mechanisms are different for the low temperature α-phase and the high temperature β-phase, respectively. In particular, the structure of the high temperature β-phase is found to be stable dynamically, in which the site of oxygen is disordered and a framework of SiO_4 tetrahedra shows a twist with a bend at the oxygen connection point. We have also found in the cubic β-phase that the elastic constant C_{44} is extremely close to C_{11} rather than C_{12}. This leads to a remarkable property that longitudinal and transverse velocities coincide for the acoustic wave propagating along [100] direction. Microscopically, we predict that the softening of C_{11} occurs due the cooperative motions of SiO_4 tetrahedra.

D4.23
STUDY OF THE 90° PARTIAL DISLOCATION IN SILICON. Karin Lin, Dept. of Physics, University of California, Berkeley, CA Division of Materials Science, Ernest Orlando, Lawrence Berkeley National Laboratory, Berkeley, CA; D.C. Chrzan, Dept. of Materials Science and Mineral Engineering, University of California, Berkeley, CA and Division of Materials Science, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA.

The 90° partial dislocation in Si is studied using a periodic array of

dipolar cells with both Tersoff potentials and isotropic elasticity theory. The total energy is calculated as a function of the parameters characterizing the dipolar unit cell. Comparison of the results from both techniques demonstrates that isotropic elasticity theory describes reasonably well the total energies predicted by the Tersoff potentials. Further, the comparison allows one to extract numerical values for the the dislocation core radius as well as the effective shear modulus. It is suggested that calculations of this type offer a means to connect *ab initio* results with larger scale continuum dislocation dynamics techniques. This research is supported by the Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences Division under contract No. DE-AC03-76SF00098.

D4.24
IDEAL YIELD STRENGTHS OF FCC METALS UNDER MULTIAXIAL LOADING. C.R. Krenn, D.C. Chrzan and J.W. Morris, Jr., Dept of Materials Science and Mineral Engineering, University of California at Berkeley, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

The embedded-atom method (EAM) is used to calculate a multiaxial yield surface for the homogeneous shear of defect free crystals of a number of FCC metals. Specifically, we calculate the minimum yield stresses for shear failure under uniaxial tension and compression, biaxial tension and compression, and simple shear. The effects of triaxial stress states are examined with superimposed hydrostatic stresses. The critical resolved shear stresses required for shear vary significantly with the applied stress state, but this variation can be rather simply modeled using elasticity theory. These models will allow ab-initio simulations of ideal shear strengths and dislocation dynamics to be more accurately incorporated into continuum plasticity codes. Phonon spectra at finite temperatures are also analyzed to monitor incipient lattice instabilities.

D4.25
THEORETICAL MECHANICAL RESPONSE AND ELASTIC STABILITY OF CUBIC METALS AT FINITE STRAIN IN THE EMBEDDED-ATOM METHOD. Somchart Chantasiriwan, Frederick Milstein, Univ of California Santa Barbara, Depts of Materials and Mechanical Engineering, Santa Barbara, CA.

The theoretical mechanical response of a variety of body centered cubic (bcc) and face centered cubic (fcc) metals, to unconstrained uniaxial loadings, coaxial with principal symmetry directions, is studied at finite strain, in the framework of embedded-atom method (EAM) calculations. Results include path dependent computations of potential energy, stress, strain, elastic moduli, elastic stability, and branching or bifurcation of crystal structure at the termination of a stable range. Connexions are made between potential stress induced phase transformations and the location and nature of secondary branch paths. For example, the character and/or existence of a phase transition may depend on whether stress increases or decreases with strain on a secondary path, at a branch point; this, in turn, depends not only on the second order moduli at the branch point, but also on the third and fourth order moduli. The EAM models used in this work were formulated to reproduce, identically, empirical values of the three second-order elastic moduli and the six third-order elastic moduli and thus the linear (harmonic) and nonlinear (anharmonic) response of the metals is represented in the computations. The mechanical behavior, including theoretical strength, is strongly influenced by crystalline symmetries and bifurcation phenomena. Characteristic anisotropies, both at infinitesimal and at finite strain, are associated with each of three subgroups, i.e., the fcc metals, the bcc alkali metals, and the bcc group-V and group-VI transition metals. The behavior of bcc Fe is intermediate to that of the bcc alkalis and that of the group-V and group-VI transition metals.

D4.26
EFFECTS OF CELL IRREGULARITY ON THE ELASTIC PROPERTIES OF 2D RANDOM FOAMS. H.X. Zhu, A.H. Windle, Univ of Cambridge, Dept of Materials Science, Cambridge, UK.

Mechanical models of foams are usually based on idealised unit cell structures. A significant disadvantage of the unit cell modelling approach is that it does not account for the natural variations in microstructure which are typical for most foam structures. Our objective was to investigate how the cell irregularity affected the elastic properties of 2D random foams. We constructed periodical random 2D samples with different degrees of irregularity, and performed finite element analysis (FEA) to determine the effective elastic properties. The geometrical properties were investigated for those 2D random foams , and were related to the elastic properties. The results indicate that, the more irregular the 2D random foams, the bigger the variations in cell size and cell structure, and the larger the foam effective moduli. This finding can serve as a guider in practical applications.

D4.27
MOLECULAR DYNAMICS SIMULATION OF MICROCRACK RECOVERY. Guo Hui Zhou, Wu Yang Chu, Dept of Mater Physics, Univ of Sci and Tech Beijing, Beijing, CHINA.

Molecular dynamics simulation showed that a microcrack in aluminum crystal could recover when applied compressive stress or heating temperature exceeded a critical value, and dislocation emission and motion accompanied recovery of microcrack. Similar to propagation of microcrack, the resistance of microcrack recovery is $2\gamma+r_p$. The critical temperature of microcrack recovery related to the orientation of the crack plane, and the microcrack in the slip plane was most easy to recover. If there were some dislocations, the critical temperature of recovery could be greatly decreased. Therefore, releasing plastic deformation energy is one of the driving forces for microcrack recovery.

D4.28
PLASTIC AND FRACTURE PROPERTIES OF SOLIDS. Valery P. Kisel, Institute of Solid State Physics, Chernogolovka, Moscow District, RUSSIA.

The remarkable finding of this work is the universal correlation between the starting stresses of different stages of plastic flow and fracture at various scale lengths of observations (internal friction, deformation photoluminescence and etch pit technique [1], macroscopic yield stress and the starting stresses for the first microcrack or macrocrack nucleations in bulk and in fiber or impurity inclusion, etc.), in single or polycrystalline samples, disordered, composite or polymer materials, adhesive films, superconductors and semiconductors, ceramics, etc. under different tests and environments. This universal scaling of stresses points to the controlling role of the deformation stress and to the same mechanisms of plasticity in the strict chain of deformation stages: dislocation motion and multiplication, dislocation cross-slip, climb and full stop, cell and grain boundary origin and the first micro-crack nucleation, then microcrack coalescence into macrocracks (macrofracture) and the formation of fracture surfaces in matrix, adhesive films and second phase particles. It is the change in dislocation cross-slip parameters versus deformation stress that explains the above scaling and deformation structures up to fracture: at low stresses and high temperatures, in extremely pure samples or at low stress rates the wavy or diffuse slip originates the so-called ductile mode of fracture; at high deformation stresses and low temperatures, in impure crystals and disordered (polymer) structures, at high stress rates the straight slip lines promote the so-called brittle fracture mode: the smooth surfaces with atomic-scale cleavage steps,kinks, river patterns, vacancy clusters or microdimples, etc. 1. Kisel, V. P., Mater. Sci. Engn., 1993, 164A, p.356.

D4.29
AB-INITIO AND TIGHT BINDING STUDIES OF DEFECTS AND INTERFACES IN NICKEL-COPPER SYSTEM. Leonid S. Muratov, Bernard R. Cooper, West Virginia Univ, Morgantown, WV; Madhu Menon, Univ of Kentucky, Lexington, KY; Antonis N. Andriotis, Inst of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklio, GREECE; David L. Price, Univ of Memphis, Memphis, TN.

Defect formation and interaction energies, as well as point defect interactions with a planar copper - nickel interface, have been studied using a combination of tight-binding molecular dynamics (TBMD) and full-potential $ab-initio$ calculations. This provides an informative test of our technique designed to accurately model lattice relaxation effects extending a number of interatomic distances away from the impurity. The Ni_xCu_{1-x} system provides a good testing ground for comparisons of completely $ab-initio$ and semi-empirical approaches. In addition, Ni is ferromagnetic; therefore magnetic effects can be studied. Parameters for the semiempirical TBMD were obtained by fitting to reproduce band structures and total energies of small (1-4 atoms) unit cells calculated with our full-potential linear combination of muffin-tin orbitals (FPLMTO) program. Results of TBMD for the relaxed structure around point defects were compared to relaxation calculations using FPLMTO method augmented with Hellman-Feymann forces in 32-atom unit cells. Such a direct comparison allowed us to refine our TBMD scheme and justifies its use for other defect systems. Furthermore, comparison to results for larger unit cells and symmetry-unrestricted relaxation calculations demonstrated the inadequacy of the 32-atom unit cell for accurate considerations of magnetization and some other aspects of the lattice relaxation around point defects. Clearly, TBMD calculations for defect interaction and extended defect simulations require cells with at least several hundred atoms.

D4.30
FIRST-PRINCIPLES CALCULATIONS OF POINT DEFECTS IN ALUMINUM. Karin Carling, Goran Wahnstrom, Dept of Applied

Physics, Chalmers University of Technology, Goteborg, SWEDEN.

Aluminum is one of the most important commercial metals with a number of important properties: low weight, high strength, good conductivity for electrons and heat, and it is simple to form and shape. We find aluminum in various products from soft-drink cans to airplanes. Point defects, although microscopic, can change the macroscopic properties of a material. Vacancies and interstitials effect diffusion rates which are important for phase transformations including the first stages of nucleation and growth of precipitates. To increase our knowledge about point-defects we calculate the formation energies and volumes for single vacancies, di-vacancies and interstitials in bulk aluminum and compare out results with recent experiments. The entropy of a system is an important thermodynamic property. We determine the change of the force constant induced by a single vacancy, di-vacancy or an interstitial and thereby we can estimate the change in entropy. According to Hehenkamp the di-vacancy can be the explanation for the anomalies in the Arrhenius plot[1]jpcs55:hehenkamp. Our calculations use a first-principles code based on density functional theory. It is implemented with a plane-wave basis set, pseudopotentials and periodic boundary conditions (supercells). The local density approximation, some tests are made with the generalized gradient approximation, is used for the exchange-correlation function.
(1) T. Hehenkamp, J. Phys. Chem. Solids **55**, 907 (1994).

D4.31
INCREASED TRANSFERABILITY OF EMBEDDED ATOM METHOD POTENTIALS USING DENSITY FUNCTIONAL THEORY. Lesser Blum[1], Ilya Grinberg[2], Marc D Legault[1], Andrew Rappe[2], Fredy R Zypman[1]; [1]University of Puerto Rico, PR, [2]University of Pennsylvania, PA.

During the last decade, the Embedded Atom Method (EAM) has been successfully applied to the calculation of energies of various atomic systems. However, there are limitations in the applicability of EAM bulk-determined potentials to systems with far-from-bulk configurations, such as clusters and surfaces.
To improve EAM applicability, we present potentials with increased transferability by obtaining a parametrization of them that includes off-bulk conditions [A]. Typical implementations of EAM are done by fitting the EAM functions to experimental data such as lattice parameter, lattice structure, elastic constants, and sublimation energy. These properties sample an extremely narrow region of configuration space around the bulk equilibrium. *Ab initio* methods can be used to obtain reliable information of configurations inaccessible to experiments.
In this work, we use the Density Functional Theory calculations using accurate pseudopotential [B] to increase the properties database. We apply these ideas to improve the previous [C] ruthenium EAM potentials, and then use them to calculate surface relaxation and reconstruction.
[A] Y Mishin, D Farkas, MJ Meho, DA Papaconstantopoulos, Phys Rev **B59**, 3393 (1999)
[B] NJ Ramer and AM Rappe, Phys Rev **B59**, 12471 (1999)
[C] L Blum, MD Legault, FR Zypman, Modeling and Simulation of Microsystems, 1999
Acknowledgments: This work has been supported by the National Science Foundation (DMR 9872689) and the Department of Energy (DE-FG02-98-ER-45729 and subcontract from UNM).

D4.32
VIBRATIONAL PROPERTIES OF CARBON IMPURITIES IN CRYSTALLINE SILICON. Xiao Yan Zhu, Jae Yon Kim, Young Hee Lee, Eun-Kyung Suh, Chonbuk National University, Semiconductor Physics Research Center, Chonbuk, SOUTH KOREA; Alexander Sieck and Thomas Frauenheim, Universität-GH Paderborn, Fachbereich Physik, Theoretische Physik, Paderborn, GERMANY.

$Si_{1-x}C_x$ alloys have been grown by molecular beam epitaxy and further characterized by Raman spectroscopy fourier transformed infrared spectroscopy and density-functional-based self-consistent-charge tight-binding calculations. The origin of experimentally observed carbon-induced vibrational peaks near 475, 605, and 800 cm^{-1} are analyzed based on the theretical calculations. The stability, vibrational frequencies, lattice relaxations, and energy gap variances of substitutional, interstitial single carbon and dicarbon complexes in crystalline silicon are calculated. The substitional carbon is energetically the most stable configuration and induces severe lattice relaxations of nearest neighbor Si atoms and several new vibrational peaks, in good agreement with the observed Raman shifts. We also find some other stable carbon complexes. All carbon complexes induce severe lattice relaxations and the related vibrational peaks, although some do not show high frequency peaks. We conclude that the peak near 475 cm^{-1} originates from the lattice relaxations of Si atoms up to second nearest neighbors from carbon impurities in all cases. The relative populations of these impurities with different growth temperatures and the annealing effects are further discussed in conjunction with experimental observations.

D4.33
DIFFUSION OF 2-D Pd_7 CLUSTER ON Pd(111) SURFACES THROUGH MOLECULAR DYNAMICS SIMULATIONS.
E.Z. da Silva and A. Antonelli, Instituto de Física "Gleb Wataghin", UNICAMP, Campinas-SP, BRAZIL.

Structure and diffusion of a small 2-D Pd7 cluster on Pd (111) surface have been studied using constant temperature Molecular Dynamics (NVT-MD) implemented using Nosé-Hoover dynamics. The interatomic interacion is modeled by a many-body potential derived within the second moment aproximation to the tight-binding model fitted to first principles calculations in bulk Pd. The surface is simulated with a 9 layer slab of 64 atoms each, with the two bottom layers fixed to simulate the semi-infinite solid and periodic boundary conditions on the plane of the surface. The results NVT-MD simulations at temperature T = 800 K show that the cluster diffuses over the surface. Many diffusion events occur, mainly without change of shape, the cluster diffuses mantaining its symmetrical form. Nevertheless, distortion events do occur in a short time interval with subsequent recomposition of the original shape. The intermediate distorted states are short lived and, therefore, would probably not be seen in the experiments. The migration mechanism is mainly row glinding for the compact symmetrical cluster. One row of atoms glides over the surface, and subsequently the other rows are pulled by this leading row, all this process (concerted row) happens in a very short interval of time as compared with the time scale for diffusion events. On the other hand, during the time interval that the cluster is distorted, the migration mechanism is more complex and more frequent. Many diffusion processes occur, namely, edge gliding, single atom movements, and concerted row. The results highlight basic atomistic mechanisms underlying the diffusion processes of symmetric 2D clusters on metal (111) surface.

D4.34
SIMULATION OF DIFFUSION MECHANISMS IN ORDERED COMPOUNDS. Y. Mishin and D. Farkas, Dept of Materials Science and Engineering, Virginia Polytechnic Institute, Blacksburg, VA.

Atomic mechanisms of diffusion in ordered intermetallic compounds are more complex, diverse, and different from those in pure metals and disordered alloys. Vacancy jumps in compounds are strongly correlated and occur in a way that to preserve the average degree of order. We consider typical diffusion mechanisms in triple-defect and antisite-disorder compounds. Such mechanisms include sublattice self-diffusion, sublattice antisite diffusion, cyclic mechanisms, and the anti-structural bridge mechanism. For each mechanism, methods by which the diffusion coefficient can be calculated are discussed. For most mechanisms, such calculations are based on kinetic Monte Carlo (KMC) simulations. KMC offers the most efficient way of taking into account the strong jump-correlation effects in compounds. In some cases also analytical methods, such as the mean-first-passage time theory, can be successfully applied. The input data for both KMC and analytical methods include the equilibrium point-defect concentrations and the vacancy jump frequencies. Methods and models available for calculating these quantities are analyzed. Examples of diffusion calculations in different compounds are shown, and the results are compared experimental data. In some cases, such comparison allows us to identify the dominating diffusion mechanism.

D4.35
TRACE ELEMENT DIFFUSION IN BULK NiAl: EFFECTS OF ELECTRONIC STRUCTURE ON DIFFUSIONAL ACTIVATION ENERGY. Sonali Mukherjee, Bernard R. Cooper, West Virginia Univ, Dept of Physics, WV; D.L. Price, University of Memphis, Dept of Physics, TN.

The use of NiAl as a high temperature material is hindered due to its limited ductility. Experiments have pointed out the dependence of dislocation motion in NiAl on self-diffusion of Ni. This opens up possibilities of mechanically blocking dislocation movement with the addition of trace elements with higher diffusional activation energy. To that end, we have studied the factors determining the diffusional activation energy of typical trace elements like Cr, Mo, and Nb in NiAl using LDA based total energy calculations along with Feynman-Hellman forces. We find that the size of the trace elements plays the dominant role in determining the diffusional pathway and the activation energy. Cr and Mo atoms follow the same diffusional pathway, namely atomic exchanges wit h a Ni vacancy, with the activation energy increasing with the trace element size from Cr to Mo. However, with further increase in trace element size to Nb, the diffusional pathway changes with a dramatic increase in the activation energy. Although Nb has similar valence as compared to Cr and Mo, we find that Nb diffusion via a Ni vacancy is not possible. This is because it entails Nb occupation of a Ni vacancy; and this gives an

energetically unstable configuration due to the large size of Nb and its compression by the nearest neighbor Al atoms. Furthermore, Nb diffusion via an Al vacancy is also rendered impossible because of the high Al vacancy formation energy in NiAl. Consequently, Nb undergoes a cyclic diffusion process, with Nb and Al atoms moving in a concerted fashion so as to avoid formation of an Al vacancy. This increases the activation energy dramatically. The large increase in the diffusional activation energy of Nb is borne out in experiments which show a drastic increase in the stress required for the same deformation rate in NiAl with Nb as trace element as compared to Cr and Mo.

D4.36
C INCORPORATION MECHANISMS ON Si(001) INVESTIGATED BY AB-INITIO CALCULATIONS. Chun-Li Liu, Len Borucki, Tushar Merchant, Matt Stoker and Anatoli Korkin, Computational Technologies Laboratory, Motorola, Los Alamos, NM.

It is critical to fully incorporate C substitutionally in SiGeC films for heterobipolar transistor (HBT) applications. Extensive experiment has been conducted by many research groups to identify the favorable deposition and growth conditions for maximum substitutional C incorporation and to elucidate the incorporation mechanisms. We report the results of our ab-initio investigations for C incorporation on Si(001). Energy of C adsorption at different surface and under surface sites and energy barriers of C diffusion on Si(001) will be presented. Incorporation mechanisms of both substitutional and interstitial C are proposed based on the atomic picture obtained. Our results agree with and explain several of experimental findings.

D4.37
THERMAL PROPERTIES OF DI-INTERSTITIAL DEFECTS IN SILICON AND THEIR ROLE IN THE GROWTH OF EXTENDED INTERSTITIALS DEFECTS. Jeongnim Kim, Wilfried G. Aulbur and John W. Wilkins, Ohio State University, Dept of Physics, Columbus, OH; Florian Kirchhoff and Furrukh S. Khan, Ohio State University, Dept of Electrical Engineering, Columbus, OH.

We propose a di-interstitial model for the P6 center commonly observed in ion implanted silicon. The di-interstitial structure and transition paths between different defect orientations can explain the thermally activated transition of the symmetry of the P6 center from low-temperature C_{1h} to room-temperature D_{2d}. The activation energy for the defect reorientation determined by *ab initio* calculations is 0.5 eV in agreement with the experiment. We have also determined possible migration processes for di-interstitial diffusion by constant temperature molecular dynamics simulations using a tight-binding potential. We obtain an energy barrier 0.7 ± 0.1 eV for the di-interstitial migration. Larger interstitial clusters that share the same di-interstitial defect as building block also have a positive binding energy. Our di-interstitial model establishes a link between point defects and {311} defects, supporting the growth model by interstitial nucleations. Supported by the DoD CHSSI program and by NSF. Computational aids are provided by OSC, NCSA and NPACI.

D4.38
PREDICTING DOPANT BEHAVIOR IN SILICON WITH KINETIC LATTICE MONTE CARLO. Marius M Bunea, Boston Univ, Dept of Physics, Boston, MA; Scott T. Dunham, Boston Univ, Dept of Electrical and Computer Engineering, Boston, MA.

Kinetic lattice Monte Carlo is used to span the time and distance scales between atomistic processes and macroscopic diffusion in silicon. The behavior of a dopant flux in a vacancy gradient is investigated using a lattice model with transition rates based on recent ab-initio results for dopant-vacancy interaction. We find significant differences from the pair diffusion model, particularly at high temperatures. We also analyze the influence of these results on the time evolution of an implanted dopant profile as revealed from current process modeling models.

D4.39
VACANCY AND DIVACANCY CONTRIBUTION TO THE DIFFUSION COEFFICIENT OF TRANSITION METALS. Fredy R. Zypman, Dimaries Nieves, University of Puerto Rico, Humacao, PR; Oscar Loera, University of Texas, San Antonio, TX.

Early experimental work on the diffusion of Copper and Zinc [1] established vacancy as the principal mechanism of atomic diffusion. Typically, diffusion coefficients are obtained by setting a system for which the diffusion equation can be easily solved, and the concentration of a diffusing specie measured. On the other hand, there exist well accepted theoretical efforts that propose models to explain thermally activated diffusion [2] in terms of the enthalpies of formation and jump rates of the processes involved. Their validity relies on the assumption that those quantities can be independently obtained. It turns out that it is not possible to experimentally *measure* the enthalpies of formation, and jump rates of specific processes, as each process cannot be simply isolated from the others. However, these quantities can be independently *calculated* from newly developed theories during the last decade. One such theories is the second moment expansion of the Tight Binding method (SMTB), which was proven equivalent to Finnis-Sinclair and works well in predicting cohesive and defect energies in transition metals [3]. SMTB, thus, provides a framework in which to check the validity of earlier diffusion models against experiments. In this work we present results for Copper. We calculate enthalpies of formation of vacancies and divacancies, as well as their activation enthalpies. In addition, we calculate the jump rate of both defects, by evaluating the phonon spectra when the defect is in its stable and in its metastable spatial configuration.
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D4.40
MICROSTRUCTURE AND MULTISCALE MODELING OF PIEZOELECTRIC MATERIALS: THE DEPENDENCE OF MACROSCOPIC RESPONSE TO MICROSTRUCTURAL VARIABLES. R. Edwin Garcia, W. Craig Carter, Massachusetts Institute of Technology, Cambridge, MA.

While the piezoelectric response of a homogeneous phase may be understood through either empirical or first principles calculations, the macroscopic response of a polycrystalline piezoelectric material is not directly amenable to direct analysis. In a polycrystal, the microscopic state of stress will depend on geometrical effects such as grain size and grain morphology as well as the degree of crystallographic alignment (texture). Furthermore, the microscopic stress state will also depend on the existence of residual stresses from processing and whether microscopic defects develop, either as a result of processing or from subsequent polarization. Prediction of macroscopic response requires a model which incorporates all pertinent spatial and crystallographic aspects of microstructure and allows coupling between fields indirectly through coupled single crystal material properties. We examine the role of microstructure in polycrystalline piezoelectric materials by combining finite element techniques with image and orientation data from real microstructures. We will attempt to characterize the effect of texture and morphology with a reduced set of microstructural parameters and test our results against direct calculation. We will demonstrate a technique for the direct numerical predictions of microstructural effects on the effective average stiffness and piezoelectric coefficients under isothermal conditions.

D4.41
PREDICTION OF METALLIC GLASS FORMATION IN THE Ni-Mo SYSTEM BY MOLECULAR-DYNAMICS SIMULATION. Q. Zhang, W.S. Lai, B.X. Liu, Tsinghua University, Dept of Materials Science and Engineering, Beijing, CHINA.

A realistic n-body potential in a Finnis-Sinclair formalism [1] is constructed for the Ni-Mo system [2] based on those calculated physical properties from first principle. Employing the potential, molecular-dynamics simulation is performed to investigate the possibility of metallic glass formation in the Ni-Mo system characterized by a small negative heat of formation and small size difference, which have beenconsidered to be unfavored for solid-state amorphization [3]. It is found that solid-state amorphization can take place in the Ni-Mo multilayers upon annealing at medium temperatures even down to 350°C and is initiated with a crossing-interface atomic migration, resulting in a planar growth of an interlayer with amorphous structure [4]. It should be noted, however, when the multilayers consist of the close-packed planes, the interfacial reaction is frustrated, as the coherent interfaces serve as a barrier preventing interfacial rewaction. Kinetically, the growth of the amorphous layer is found to follow exactly a square-root t law, indicating that solid-state amorphization is indeed governed by a diffusion-limited-reaction. It is also observed that the growing speed towards Ni is greater than that directed to the Mo lattice. To determine the glass-forming composition range of the system, the relative stability of the Ni- and Mo-rich solid solutions is compared with their corresponding amorphous states with increasing the Mo and Ni contents, respectively. Two critical solid solubilities are found to be of 21% Mo in Ni and 25% Ni in Mo, below which amorphous states are favored versus their crystalline counterparts. These result suggest that the composition range for metallic glass formation of the system is within 21-75% Mo. We present, in this paper, the detailed simulation results and a comparison with experimental observations.
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D4.42
DYNAMICAL PROPERTIES OF UNDERCOOLED Ni_3Al. Pierre Lombardo, Didier de Fontaine, University of California at Berkeley, Berkeley, CA; Jeffrey J. Hoyt, Mark Asta, Sandia National Laboratories, Livermore, CA; Babak Sadigh, Lawrence Livermore National Laboratories, Livermore, CA.

We have investigated the dynamical properties of the liquid alloy Ni_3Al in the undercooled region, using molecular dynamics simulation and embedded atoms potentials. With decreasing temperature the dynamical structure factor as a function of time develops a plateau region, a result which is consistent with mode coupling theory. At large undercoolings, 900-1100 K, the liquid exhibits dynamical heterogeneities where clusters of mobile Ni atoms are identified. The dynamical heterogeneities are consistent with experimental observations in polymer systems and in a model Lennard-Jones system. In addition, the calculated diffusion coefficient vs. temperature has been used to predict a dynamical critical temperature for Ni_3Al. Finally, at very low temperatures (< 800 K) crystallization is observed in the MD simulations at relatively short times. This work was supported by the U. S. Department of Energy, Office of basic Energy Sciences, Materials Science Division, under contract number DE-AC04-94AL85000.

D4.43
PREDICTING THE PROPERTIES OF SOLVATED SYSTEMS USING NONLOCAL DENSITY FUNCTIONAL THEORY AND PARALLEL COMPUTING. Laura J. Douglas Frink, Andrew G. Salinger, Sandia National Laboratories, Albuquerque, NM.

Solvated systems are composed of small fluid (or solvent) molecules and large surfaces, macromolecules, or porous media. Such systems abound in nanotechnology (e.g. zeolites and self-assembled systems) and biology (e.g. solvated protein-DNA interactions). These systems are difficult or impossible to treat with traditional molecular dynamics (MD) simulation methods due to the wide disparity between the equilibration time of the fluid and the equilibration time of the surfaces or macromolecules. One way to overcome this bottleneck of the MD is to formally separate the degrees of freedom of the surfaces from those of the suspending solvent. The resulting statistical thermodynamics for inhomogeneous fluids revolves around the surface free energy, and typical quantities of interest (adsorption, potentials of mean force, entropy, etc.) are defined by derivatives of the surface free energy, and can be calculated independently via sum rules. The problem to be solved is thus reduced to finding the equilibrium density d

D4.44
STRUCTURE, VIBRATIONS, AND REACTIONS IN POLYCARBONATE SYSTEMS. P. Ballone, R.O. Jones and B. Montanari, Forschungszentrum Julich, Julich, GERMANY.

The favorable optical and mechanical properties of bisphenol A polycarbonate (BPA-PC) have made it one of the most important polymers in production. The microscopic basis of some properties, such as its high impact resistance, are not well understood, and this has led to numerous simulations of polycarbonate materials. We have applied density functional (DF) theory (with the PBE approximation for exchange and correlation) to a series of molecules related to PC, from fragments of the monomer to polymeric rings. Structures are determined by combined MD/DF calculations, and the vibrational properties by diagonalizing the dynamical matrix. The results agree well with available experimental data, and provide a database for studying and extending empirical force field models. We have also studied the reactivity of the largest molecular analogs (cyclic tetramers, with 132 atoms) in the presence of smaller species (phenol, Li- and Na-phenoxides, 13 atoms) that are used in the polymerization reaction. The calculations show that the carbonate group provides a docking site for the positive end of polar species (i.e., Li- and Na phenoxides), giving rise to stable complexes ($\Delta \sim 10$ kcal/mol) that are connected by low energy paths to a variety of different chemical species known to arise during polymerization. The DF calculations provide important parameters (reaction barriers, characteristic vibrational frequencies for different chemical species, etc.) that are useful in interpreting experimental measurements.

D4.45
PROTON TRANSPORT ALONG A WATER WIRE IN THE PRESENCE OF AN ELECTRIC FIELD. M. Elstner, T. Kaxiras, Department of Physics, Harvard University, Cambridge MA; S.M. Lee, Y.-H. Lee, Department of Physics, Jeonbuk National University, Jeonju, KOREA; T. Frauenheim, Department of Physics, University of Paderborn, Padeborn, GERMANY.

The fast translocation of protons in liquid water, ice or through biological transmembrane channels can not be explained by a diffusion of hydronium ions. The proposed mechanism for proton transport through 'water wires' [1] involves a two-step process of propagation of so called ionic and orientational defects along a hyrogen-bonded chain of water molecules: The first step constitutes the motion of an ionic defect, which involves the hopping of the protons along the chain between two energetically degenerate postitions at neighboring oxygen atoms. This step has been shown by computer simulations to be a barrierless process that occurs on the picosecond timescale. The second step contitutes the propagation of an orientational defect, which involves sucessive rotations of water molecules along the chain. This step has a high activation barrier and therefore might be the rate limiting step in the proton transfer process. We apply a self-consistent charge density functional based tight-binding (SCC-DFTB) method [2] to study ionic and orientational defects in water molecule chains in the presence of an external electric field. We estimate the mobilities of both defects and determine the threshold electrical field for the reorientation process. For biologically relevant field strenghts we find that the reorientation step can also become a fast process occuring on the picosecond timescale. [1] J. F. Nagle, H. J. Morowitz, Proc. Natl. Acad. Sci. USA 75 (1978) 298. [2] M. Elstner, D. Porezag, M. Haugk, J. Elsner, Th. Frauenheim, G. Seifert, S. Suhai, Phys. Rev. B 58, 7260 (1998). M. Elstner, D. Porezag, G. Jungnickel, T. Frauenheim, S. Suhai, and G. Seifert, Mat. Res. Soc. Symp. Proc. 491 (1998) 131 M. Elstner, D. Porezag, G. Seifert and Th. Frauenheim Mat.Res.Soc. Symp. Proc., 538 (1999), 541

D4.46
AB-INITIO MODELING OF STRESS-MEDIATED DIFFUSION IN SILICON. Wolfgang Windl, Murray S. Daw, Matthew Laudon, Motorola, Inc., Computational Materials Group, Austin, TX, and Los Alamos, NM; Aaron D. Lilak, Dept of Electrical Eng, SWAMP Center, Univ of Florida, Gainsville, FL.

The continued shrinkage of silicon device dimensions and increasing complexity of device processing has led to an increase in stress levels in the active regions of silicon devices. As a consequence, the diffusion kinetics of the implanted dopants and the defect concentrations are expected to change in the strained areas.
In this talk, we present a methodology to model stress-mediated diffusion based on input from first principles calculations. For the latter, special care has been taken to minimize the errors introduced by finite-size supercells and the known band-gap problem in density-functional calculations. Also, for the first time, we present calculations of the anisotropic formation volumes for Si self-interstitials, vacancies, and dopants as a function of the Fermi level. These numbers are implemented into a continuum model and used to examine stress-mediated diffusion.

D4.47
LIQUID-LIKE TO SOLID-LIKE STRUCTURAL TRANSITION FOR NARROWLY CONFINED ALKANE FILMS. S.T. Cui,[1,2] P.T. Cummings[1,2] and H.D. Cochran[2,1]; [1]Department of Chemical Engineering, University of Tennesse, Knoxville, TN; [2]Chemical Technology Division, ORNL, Oak Ridge, TN.

When a fluid is narrowly confined within spacing comparable to the molecular dimension, its structural, thermodynamic and rheological properties can be very different from those of the corresponding bulk fluid. Surface force apparatus (SFA) experiments have found that when fluids are confined between molecularly smooth mica surfaces, the fluid develops solid-like behavior. This is manifested by the ability of the film to sustain a finite stress, a phenomenon typically associated with solids. The phenomenon is still not well understood theoretically. We describe a comprehensive molecular dynamics simulation study that demonstrates the solidification behavior for narrowly confined alkane films at ambient temperature and pressure. The system was initially in the disordered liquid-like state. As the system is equilibrated with volume rescaled to produce approximately the ambient pressure, the confined film underwent a transition to an integer number of well-ordered layers. On decreasing the spacing between the confining walls, the film is better ordered with larger crystalline volumes. Constant external shear stress is applied to the films where three and six molecular layers form. We find that the film exhibits solid-like behavior including a yield stress. The magnitude of the yield stress roughly corresponds to that found in experiments. The yield stress for the three-layer film is significantly higher than that of the six-layer film, showing an increased solidity when the film is more narrowly confined. The same trend has also been observed in experiments.

SESSION D5: PREDICTION OF ELECTRONIC PROPERTIES OF MATERIALS
Chair: Andrew M. Rappe
Thursday Morning, December 2, 1999
Room 207 (H)

8:30 AM *D5.1
CHEMISTRY AND ELECTRONIC STRUCTURE OF Ti - PTCDA CONTACTS: AN AB INITIO MOLECULAR DYNAMICS STUDY. Amedeo Palma, CNR-ICMAT, Monterotondo S. (RM), ITALY; Alfredo Pasquarello, IRRMA, EPFL, Lausanne, SWITZERLAND; Roberto Car, Princeton Univ, Dept of Chemistry and Materials Institute, Princeton, NJ.

Contacts to organic semiconductors are of great importance for optoelectronic devices. In this work we present a theoretical investigation on the interaction of Ti atom(s) with the organic semiconductor 3,4,9,10 perylenetetra-carboxylic dianhydride (PTCDA) by ab initio molecular dynamics in the Car-Parrinello scheme, using ultrasoft pseudopotentials and the Perdew-Wang (PW) generalized gradient approximation (GGA) to the exchange-correlation functional. The calculated PTCDA structure, in a monoclinic cell subject to periodic boundary conditions, reproduces the known crystalline structure within an average error of less than two percent. The HOMO level of PTCDA shows pi character and is delocalised on the perylene and carboxylic groups. Our calculations show that, in the most stable structures, Ti atoms chemically react with the oxygen of the carboxylic group of PTCDA and form an additional bridge-type bond with the perylene ring of a PTCDA molecule located on a different layer. We find that, as a consequence of the chemical bonding between Ti atoms and the PTCDA molecular subunits, electron states are induced in the gap above the HOMO level of the organic semiconductor, in good agreement with photoemission spectroscopy (PES) data. The presence of these gap states can explain the observed ohmic nature of the contacts for reactive metals. Finally, we also calculate the C(1s) core level shifts, including core hole relaxation, for both PTCDA and Ti-PTCDA systems.

9:00 AM D5.2
CARRIER POCKET ENGINEERING APPLIED TO "STRAINED" Si/Ge SUPERLATTICES TO DESIGN USEFUL THERMOELECTRIC MATERIALS. T. Koga[a], X. Sun[b], S.B. Cronin[b], M.S. Dresselhaus[b,c]. [a]Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA; [b]Department of Physics, and [c]Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA.

The recently proposed concept of Carrier Pocket Engineering is applied to the strained Si/Ge superlattices to design materials with a large thermoelectric figure of merit ZT. Considering the coupling between the Si and Ge layers at both Δ- and L- points in the Brillouin zone and including the effect of the reduced lattice thermal conductivity $\kappa_{\rm ph}$ for the whole superlattice, the thermoelectric figure of merit ZT for this system is calculated. The results show a large increase in ZT relative to the values for the corresponding bulk Si and bulk Ge. In addition, the lattice strain effect due to the lattice mismatch at the Si/Ge interfaces provides another degree of freedom which can be used to control the conduction band structure of the superlattice in this system. We explore various geometries and structures to optimize ZT for the whole (3D) superlattice. The resultant ZT calculated for the symmetrized Si(20Å)/Ge(20Å) superlattice grown on a (111) oriented $Si_{0.5}Ge_{0.5}$ substrate is 0.96 at 300 K (which is more than a factor of 100 enhancement relative to the corresponding value for bulk Si) and ZT is further shown to increase significantly at elevated temperatures. It is noted that such a superlattice structure is actually obtainable using the current MBE technology. Some preliminary experimental results are also shown to compare with the theoretical results.
We would like to thank Prof. G. Chen, Prof. K. Wang and Dr. G. Dresselhaus for valuable discussions and inputs. We gratefully acknowledge support from ONR under MURI subcontract #205-G-7A114-01, and from the US Navy N00167-98-K-0024.

9:15 AM D5.3
PHONONS AND STATIC DIELECTRIC CONSTANT IN $CaTiO_3$ FROM FIRST PRINCIPLES. Eric Cockayne, Benjamin P. Burton, NIST, Ceramics Division, Gaithersburg, MD.

$CaTiO_3$ has a static dielectric constant that extrapolates to a value greater than 400 at zero temperature. We investigate the origin of this large dielectric response on a microscopic level via first principles plane-wave pseudopotential density functional calculations. All zone center phonons and Born effective charges are determined for $CaTiO_3$ in its low temperature 20-atom per cell orthorhombic phase. We obtain the ionic contribution to the dielectric tensor on an ion-by-ion basis and mode-by-mode basis. The dielectric response is dominated by low frequency ($\nu \sim 100\,{\rm cm}^{-1}$) polar optical modes in which cation motion opposes oxygen motion. We compare these results with those for related systems.

9:30 AM D5.4
MICROSCOPIC POLARIZATION CURRENTS IN DIELECTRICS. Paolo Umari, IRRMA, Lausanne, SWITZERLAND; Raffaele Resta, University of Trieste, ITALY.

We address the very basic issue of what happens, at a microscopic level, inside a polarized dielectric. We show that the complete information about electronic polarization is embedded in the microscopic polarization density $\mathbf{P}_{\rm ind}(\mathbf{r})$: this is a vector field, for which we provide a quantum–mechanical expression. Previous studies in the literature have addressed the induced electronic *charge* density (alias the divergence of our vector field) where the most relevant information is obliterated. An useful interpretation of the polarization density comes from imagining that the perturbation (such as an applied field) is adiabatically switched on in time: $\mathbf{P}_{\rm ind}(\mathbf{r})$ is then the microscopic current flowing through the sample while the perturbation is switched on. We present results for the case study of Si, whose (unperturbed) valence charge defines a continuous network of bonds. When a field is switched on, most of the polarization (pseudo)current $\mathbf{P}_{\rm ind}(\mathbf{r})$ flows within narrow channels along the bonds, and steers to keep clear of the core regions: the basic feature is that the current percolates across the material. This is in sharp contrast with a Clausius–Mossotti picture, where charge is displaced only within the cells, without crossing the cell boundaries.

10:15 AM *D5.5
CARBON NANOTUBES: NUCLEATION, ELONGATION, AND POST-SYNTHESIS TUNING OF ELECTRONIC PROPERTIES VIA STRETCHING AND SQUASHING. Vincent H. Crespi, Paul E. Lammert, Peihong Zhang, Ctr for Mater Phys and Dept of Phys, Penn State Univ, University Park, PA.

Carbon nanotubes provide both fascinating fundamental one-dimensional physics and opportunities for electronic and structural applications. I will discuss (1) a new model of nanotube nucleation starting from a multilayered graphitic patch, (2) the determination of growth temperatures for multiwalled tubes from analysis of thermal fluctuations locked into the structure of tapered ends, and (3) methods of tuning the electronic properties of nanotubes through (3a) bond rotations induced via plastic deformation or ion bombardment and (3b) collapse of nanotubes into ribbons, wherein the new couplings between adjacent surfaces can reversibly induce bandgaps in tubes which are metallic when uncollapsed.

10:45 AM D5.6
INTERPLAY BETWEEN MECHANICAL DEFORMATION AND ELECTRONIC PROPERTIES OF CARBON NANOTUBES. Lei-Liu, Chakram S. Jayanthi, Shi-Yu Wu, Dept of Physics, University of Louisville, KY; Hong Jie Dai, Dept of Chemistry, Stanford University, CA.

Bending of carbon nanotube produces regions of increased curvatures. Increase of curvature induces stronger π- σ interactions, thus leading to sp^2 to sp^3 rehybridization. Bending of single-walled nanotubes (SWNT) from elastic deformation to buckling is modelled using the order-N non-orthogonal tight-binding molecular dynamics [C.S. Jayanthi, S.Y. Wu, J. Cocks, N.S. Luo, Z.L. Xie, M. Menon, and G. Yang, Physical Review B 57, 3799 (1998)]. The local density of states (LDOS) in the bent region is calculated using the real space Green's function method [S.Y. Wu, J.A. Cocks, C.S. Jayanthi, Phys. Rev. B49, 7957 (1994)]. The interplay between the mechanical deformation and electronic properties of single-walled nanotube is analyzed by studying the variation in the LDOS along the bent region. Specifically, we find a transition from a semimetal to a semiconducting behavior for a (5,5) SWNT.
This work was supported by the NSF(DMR-9802274).

11:00 AM D5.7
AB INITIO STUDY OF ATOMIC AND ELECTRONIC STRUCTURES OF Si-Al INTERFACE. Umesh V. Waghmare, E. Kaxiras, Harvard University, Cambridge, MA.

We study the stability of thin Al films with different structures corresponding to limiting coverages on a Si substrate, using first-principles calculations. We considered structures of the Al film which are commensurate with the atomic structure of the Si (111) 1×1 surface and structures which preserve the Al bulk features on an appropriate supercell of the substrate. Due to mismatch in lattice constants of Al and Si, we explore possible defects in some of these structures. We examine how the variation in atomic structure and defects at the interface affect the electronic states and in particular the formation of Schottky barriers of different height.

11:15 AM D5.8
PREDICTING COMPOSITIONAL PHASE TRANSITIONS IN FERROELECTRICS USING THE VIRTUAL CRYSTAL APPROXIMATION. Nicholas J. Ramer, Andrew M. Rappe, University of Pennsylvania, Department of Chemistry and Laboratory for Research on the Structure of Matter, Philadelphia, PA.

In this work, we present a new method for modeling disordered solid solutions, based on the virtual crystal approximation. Throughout condensed matter, solid solutions provide unique properties which are inaccessible in pure materials. In particular, the latest generation of single-crystal ferroelectrics are based on binary, ternary and more recently quaternary oxides. These materials exhibit a frequency-dependent dielectric constant; the so-called relaxor behavior. While experimental studies of these materials have furthered device applications, theoretical work has been limited due to compositional disorder in these materials. Standard electronic structure modeling approaches of materials with compositional disorder necessitate an increased repeat distance, and such superlattice studies focus on a small subset of possible structural configurations. The virtual crystal approach is a tractable way of studying configurationally disordered systems; the potentials which represent atoms of two or more elements are averaged into a composite atomic potential. We report results employing a new virtual crystal approach which uses the designed nonlocal pseudopotential approach to provide unprecedented accuracy in characterizing the virtual atom orbital energies. We apply our method to predict the rhombohedral-to-tetragonal compositional phase transition in $Pb(Zr_xTi_{1-x})O_3$ under uniaxial stress. This is the first time that a first-principles virtual crystal approach has been used to determine compositional phase transitions in complex ferroelectric oxides.

11:30 AM D5.9
USING TIGHT-BINDING FITTING FOR SENSITIVE FERMI SURFACE INTEGRATIONS. I.I. Mazin and D.A. Papaconstantopoulos, Center for Computational Material Science, Naval Research Lab, Washington, DC.

The standard technique for evaluating Brillouin zone integrals in the band structure calculations is the linear interpolation tetrahedron method, where the zone is broken into microtetrahedra and all k dependent functions are linearly interpolated within them. The convergence is rapidly deteriorated when the functions in questions themselves include electronic velocities or masses, which involve derivatives of one-electron energies. Examples of the physical calculations which are particularly prone to this problem include Hall coefficient (masses), transport and tunneling properties (velocities) in supercells (where large number of band crossings makes numerical differentiation unstable), electronic Raman scattering, and others. We have used the NRL tight binding fitting program, which allows selection for fitting of a group of bands in a given energy range, to accurately fit the bands near the Fermi level, after which the velocities can be obtained analytically with the same accuracy as the band fitting itself. Then the integration in question converges much faster; besides, lower computational cost of tight binding schemes allows using a finer mesh, when needed. We illustrate all this on various physical examples.

11:45 AM D5.10
THEORETICAL AND EXPERIMENTAL ANALYSIS OF THE STABILITY OF Sr SILICATES. Alex Demkov, Peter Fejes, Semiconductor Product Sector, Motorola, Inc., Mesa, AZ; Jamal Ramdani, Jimmy Yu, Ravi Droopad, Jun Wang, Jerry Hallmark, and William Ooms Physical Sciences Research Laboratories, Motorola, Inc., Tempe, AZ.

The rapid scaling of the CMOS structure drives us to search for alternative high dielectric constant gate materials. Transition metal perovskite crystals have recently attracted significant attention due to the newly discovered possibility of their epitaxial growth on a Si (001) substrate. MBE was used to form a silicate template (few monolayers (1-2)) of silicate using the solid state reaction between SrO and SiO_2 at high temperature with proportions 1 to 1. The silicate showed an ordered structure, 2x1 by RHEED, matching the Si 2x1 surface. High quality $SrSiO_3$ was grown on this surface. We will report on some of the physical characteristics of thin STO on Si. Several $SrSiO_3$-Si samples exhibit an ultrathin (1.5 nm) interfacial layer. HRTEM, together with PEELS was utilized to investigate the structure and chemical nature of this interface. We use ab-initio density functional calculations to study the geometric and electronic structures of Sr, SrO, quartz, and a number of $SrSiO_4$ and $SrSiO_3$ silicates reported in the literature. The calculations were carried out in the local density approximation (LDA) employing ultra-soft pseudopotentials and a plane wave basis set. The cohesive properties of the bulk materials are determined in good agreement with experiment when available. Possible solid state reactions resulting in the formation of interfacial silicates and possible ways of their subsequent decomposition are suggested. Our results are in qualitative agreement with the available thermochemical data. Using theoretically generated model structures of the interface we simulated HRTEM and RHEED images and compare them with experiment.

SESSION D6: PREDICTIONS OVER LARGE LENGTH AND TIME SCALES
Chair: Kyeongjae Cho
Thursday Afternoon, December 2, 1999
Room 207 (H)

1:30 PM *D6.1
PUSHING MOLECULAR DYNAMICS SIMULATIONS PAST THE MICROSECOND BARRIER. Arthur F. Voter, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM.

The molecular dynamics (MD) simulation method is a powerful approach for investigating materials properties. Once an interatomic potential is assumed, most any property (in principle) can be investigated with microscopic detail. However, while impressive strides have been made in the accessible size scales (now a billion atoms), the time scale has been limited by the sequential nature of the integration algorithm.
For a system of a few hundred atoms interacting with a fast empirical potential such as the embedded atom method, more than a month of simulation time is required to reach one microsecond, even on the very fastest computers, parallel or not. This "microsecond barrier" places a severe restriction on the study of processes such as surface growth, grain boundary diffusion, and radiation damage annealing, in which activated events on the time scale of microseconds and longer can be crucial to the dynamical behavior. Presently, these systems are usually studied using artificially high driving forces (e.g., temperature or stress) to observe activity on the nanosecond time scale, or via kinetic Monte Carlo, in which activated mechanisms are assumed rather than observed. Both of these methods run the risk of misrepresenting the true system behavior.
I will discuss an alternative approach to this problem. Exploiting the infrequent-event nature of these systems, we have derived accelerated dynamics methods that directly extend the simulation time into the microseconds and beyond. For example, the parallel replica method, in which the simulation time enhancement (per wall-clock time) is proportional to the number of processors, makes no approximations beyond that of infrequent events. Having virtually no overhead, it should also be well suited to first-principles simulations. The hyperdynamics method, which assumes that transition state theory holds (known to be a good approximation in the solid state), offers acceleration factors of hundreds and more in favorable cases. Finally, the temperature-accelerated dynamics, which makes the additional approximation of harmonic transition state theory, looks particularly promising. These methods can be used in combination for multiplicative gain. I will discuss the current state of the art in the development and application of these methods, and the obstacles preventing us from reaching even longer time scales.

2:00 PM D6.2
PARALLEL TEMPERING ALGORITHM FOR THE DETERMINATION OF LOWEST-BARRIER TRANSITION PATHS. I. Pickholtz, E.B. Tadmor, Technion - Israel Institute of Technology, Dept of Mechanical Engineering, Haifa, ISRAEL.

Determination of transition paths plays an important role in bridging scales from fundamental processes in materials to their macroscopic response. Given a particular fundamental process, such as the hopping of an interstitial atom from one site to the next or the cross-slip of a screw dislocation from one glide plane to another, it is necessary to determine the lowest energy barrier for the process, i.e. its activation energy. In addition, details of the transition path itself may be of interest from a physical standpoint. Determination of the transition path with the lowest energy barrier is a problem of global minimization. Such problems have been notoriously difficult to solve in the past and continue to pose great difficulties. Current implementations are based on Simulated Annealing techniques which can be quite efficient, but often require a significant amount of tuning to individual problems. An alternative approach based on the recently introduced Parallel Tempering algorithm is proposed. In this approach a collection of identical replicas of the investigated transition path are generated. Each replica is set at a different temperature and allowed to evolve as in a standard Monte Carlo simulation with moves accepted or rejected according to the Metropolis rule. In addition, the replicas themselves are swapped according to the same rule. In this manner, higher-temperature replicas aggressively explore a large proportion of phase space, while the low-temperature replicas guard the best path identified to date. The approach has proven to be very effective in a variety of applications and has the additional advantage of being readily parallelizable for concurrent computing. We demonstrate the efficiency of the method by applying it to a variety of

test cases including a study of the transition paths associated with polarization switching in piezoelectric $PbTiO_3$, an end-member of the technologically important family of ferroelectric materials $PbZr_xTi_{(1-x)}O_3$ (PZT).

2:15 PM D6.3
REVERSIBLE-SCALING: FREE ENERGY AS A FUNCTION OF TEMPERATURE FROM A SINGLE ATOMISTIC SIMULATION. Maurice de Koning, Sidney Yip, Dept of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, MA; A. Antonelli, Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Unicamp, Campinas, Sao Paulo, BRAZIL.

A common approach to the evaluation of the temperature dependence of free energies by Monte Carlo (MC) or molecular dynamics (MD) simulations is the integration of the appropriate free-energy derivative with respect to temperature. While this approach provides 'exact' results, it is computationally very intensive since the numerical integration requires a set of independent simulations, carried out at different temperatures. Due to the high computational cost of this procedure, considerable effort has been devoted toward the development of more efficient techniques. Important examples include the histogram analysis methods and the cumulant expansion approach which enable the calculation of free energies as a function of temperature from a single simulation. While these techniques represent a significant efficiency gain compared to the integration procedure, the temperature range over which the free energy can be covered accurately is limited. We present a new method that is not subject to such limitations and allows extremely efficient and accurate determination of free energies as a function of temperature from a single constant temperature MC or MD simulation. The Reversible-Scaling (RS) technique is based on a combination of the scaling of the potential energy function of the system of interest and the adiabatic switching technique. This combination leads to a highly optimized technique that permits the determination of the free energy as a function of temperature from a single constant temperature MD or MC simulation, without relying on limiting approximations. The applications presented here demonstrate the capabilities of the new approach and indicate that, given its accuracy and remarkable efficiency, the RS technique should be useful for free-energy calculations based on sophisticated modeling schemes such as tight-binding and *ab initio* MD.

2:30 PM D6.4
SPEEDING UP AB INITIO MOLECULAR DYNAMICS BY SEMI-EMPIRICAL POTENTIALS. G.J. Ackland and C. Verdozzi, Department of Physics, The University of Edinburgh, UNITED KINGDOM.

We present a method which mixes ab-initio and ab-initio parametrised semi-empirical potentials, to reduce the computational effort in ab-initio hybrid Molecular Dynamics (AIMD). One of the main merits of the method is to allow for longer MD runs, due to an alternation of abinitio and (computationally inexpensive) atomistic potentials. Semi-empirical(SE) potentials are generated on the fly by a fit to the ab-initio forces, to switch from ab-initio to semi-empirical segments of the evolution trajectories. To accept/reject a SE segment, SE and AIMD nuclear forces are compared at the end of it, and in case of rejection, the segment is regenerated by AIMD, to restart the hybrid approach at the new end of it. To characterise the approach, we i) compare pairs of model potentials of different functional form, one of them to be considered ab-initio; ii) present tests with AIMD trajectories.

3:15 PM *D6.5
QUANTUM DYNAMICS IN NANOPORES: MODELING PROTON TRANSFER IN ZEOLITES WITH SEMICLASSICAL TRANSITION STATE THEORY. Justin Fermann, Chandra Saravanan, Cristian Blanco and Scott M. Auerbach, Univ of Massachusetts, Depts of Chemistry and Chemical Engineering, Amherst, MA.

Proton transfer is thought to be the key initiating step for virtually all catalyzed reactions in acidic zeolites. Unfortunately, very little is known theoretically about the quantum dynamics of proton transfer in zeolites, largely because of the complexity of both the structure and dynamics calculations. We have applied a reliable semiclassical transition state theory that requires a minimum of ab initio information, making it especially suitable for applications involving complex materials. We have performed a series of ab initio calculations to parametrize the dynamics theory, on both cluster and periodic models of zeolites. We find that quantum tunneling is an important process for temperatures as high has 300 K and above.

3:45 PM D6.6
DETERMINING PATHWAYS FOR BORON-DEFECT CLUSTERING IN Si MATERIALS USING BOTH ATOMIC-SCALE AND CONTINUUM LEVEL APPROACHES. Weiwei Luo, Paulette Clancy, School of Chemical Engineering, Cornell University, Ithaca, NY.

There is considerable current interest in determining the most important boron clusters following ion implantation of boron, due to the importance of boron as a p-dopant and its problematical TED during subsequent annealing steps. Much of the focus has been on the B_4I cluster for which there is some indirect evidence of its importance. However, the path by which such a cluster might be form is unclear. A B_4I boron-defect cluster could be formed by the interconnection of mobile B-I pairs (i.e. BI to B_2I_2 to B_3I_3 to B_4I_4), or by incremental capture of boron atoms (from BI to B_2I to B_3I to B_4I), or by other as yet unspecified routes. We investigate the relative probability of the two routes to B_4I production, described above, via tight-binding studies. Statics calculations were used to calculate the formation and binding energies of all the B_mI_n species mentioned above. Molecular Dynamics simulation of key B_mI_n clusters was used to probe their subsequent fragmentation. During ion implantation, a large number of Si self-interstitials are created. As a results, there are enough mobile boron interstitials to allow the precipidation of boron atoms along the path from BI, B_2I_2, B_3I_3 and B_4I_4. Our results suggest that this is a relatively favorable energetic route compared to the incremental capture of boron atoms. The subsequent annealing processes drastically reduce the concentration of Si interstitials. As near equilibrium concentrations of Si self-interstitials are reached, B_2I, B_3I and B_4I become more viable. MD simulations capture the dynamics of B_4I_4 dissolution under appropriate annealing conditions. Finally, we shall show how atomic-scale information from LDA and tight-binding calculations of diffusion in solids can be used directly in a continuum PDE solver, here Stanford's ALAMODE, to assess the relative importance of mechanistic pathways and dopant-defect species.

4:00 PM *D6.7
AB-INITIO STUDIES OF GOLD NANOSTRUCTURES. Daniel Sanchez-Portal[1], M. Beltran[2], K. Michaelian[3], I. Garzon[3], Pablo Ordejon[4], Alberto Garcia[5], Javier Junquera[6], Emilio Artacho[6], and Jose M. Soler[6]; [1]Department of Physics and Materials Research Laboratory University of Illinois, Urbana, IL; [2]Inst. de Materiales, Univ. Nacional Autonoma de Mexico, Mexico D.F., MEXICO; [3]Inst. de Fisica, Univ. Nacional Autonoma de Mexico, Mexico D.F., MEXICO; [4]Institut de Ciencia de Materials de Barcelona (CSIC), Barcelona, SPAIN; [5]Departamento de Fisica Aplicada II, Universidad del Pais Vasco, Bilbao, SPAIN; [6]Dep. de Fisica de la Materia Condensada, Inst. Nicolas Cabrera, Univ. Autonoma, Madrid, SPAIN.

Gold clusters and atomic-size contacts are central in some of the most active areas of nanodevice research. We study the structure and properties of these nanostructures by means of density functional calculations, in the local density or generalized gradient approximations. We use a Troullier-Martins norm-conserving pseudopotential in the Kleinman-Bylander form. The atomic basis functions are constructed from numerical solutions of the atomic pseudopotential, and they are constrained to be zero beyond a cutoff radius. Multiple-zeta and polarization functions are also included to achieve an accuracy comparable to that of a plane-wave basis set. The basis functions are projected on a real space grid in order to calculate the electron density and the Hartree and exchange-correlation potentials and matrix elements. Other matrix elements, like those of the kinetic energy and nonlocal pseudopotentials are tabulated as two-center integrals.
We find [1] that the most stable structures of intermediate-size gold clusters are amorphous. This is specially surprising in the case of 'magic' cluster sizes, for which very compact ordered structures exist. We show how the analysis of the local stress can be used to understand the physical origin of this amorphization. We find that the compact ordered structures, which are very stable with pair potentials, are de-stabilized by the tendency of metal bonds to contract at the surface, because of the decreased coordination. The amorphous structures are also favored by the relatively low energy associated to coordination and bond-length disorder in metals. Although these are general properties of metallic bonding, we find that they are specially important for gold, and we predict some trends in the tendency of metal clusters to present amorphous structures. In the case of nanocontacts, we find [2] that gold monatomic wires exhibit a spinning zigzag structure, offering an explanation for the very long bonds apparently observed [3]. Unlike the directional covalent bonds of most chainlike molecules, metal bonds are nondirectional and lead to compact structures. However, we find that zigzag gold chains of monatomic width are (meta)stable even as free-standing clusters, capable of holding its chainlike shape. This unexpected metallic-wire stiffness, which prevents the wires from collapsing, stems from the transverse quantization in the wire, as shown in a simple free electron model.
[1] I. Garzon et al, Phys. Rev. Lett. 81, 1600 (1998).
[2] D. Sanchez-Portal et al., cond-mat 9905225.
[3] H. Ohnishi, Y. Kondo, and K. Takayanagi, Nature 395, 780 (1998).

4:30 PM D6.8
Abstract Withdrawn.

4:45 PM D6.9
A COMBINED LINEAR SCALING QUANTUM MECHANICAL AND MOLECULAR MECHANICAL METHOD FOR LARGE BIOLOGICAL SYSTEMS. M. Elstner, E. Kaxiras, Harvard University, Dept. of Physics, Cambridge, MA; H. Liu, W. Yang, Duke University, Dept. of Chemistry, Durham, NC; T. Frauenheim, University of Paderborn, Dept. of Physics, GERMANY.

We present a combined quantum mechanical and molecular mechanical method (QM/MM). For the QM part, we apply the self-consistent charge density functional based tight-binding (SCC-DFTB) method in combination with the divide and conquer (DC) approach developed by the Yang group. The SCC-DFTB method is based on a second order expansion of the DFT total energy functional with respect to a reference density, where the matrix elements are determined within a confined LCAO basis in a two-center representation [1]. The DC approach makes use of a partition function to divide the electron density into subsystem contributions, which can be determined seperately, and a common Fermi energy for the total system ensures the proper normalization of the electron density [2] This leads to a linear scaling for the solution of the generalized eigenvalue problem of the SCC-DFTB method. This work is based on an earlier implementation for a semiempirical quantum chemistry method by Liu and Yang [3]. We present test calculations for the SCC-DFTB/MM and the DC/SCC-DFTB methods and report first applications of the DC/SCC-DFTB/MM approach, where we simulate large biological molecules in aqueous solution, which is treated within the MM approach. [1] M. Elstner, D. Porezag, M. Haugk, J. Elsner, Th. Frauenheim, G. Seifert, S. Suhai, Phys. Rev. B 58, 7260 (1998). M. Elstner, D. Porezag, G. Jungnickel, T. Frauenheim, S. Suhai, and G. Seifert, Mat. Res. Soc. Symp. Proc. 491 (1998) 131 [2] W. Yang, Phys. Rev. Lett. 66, (1991) 447 [3] H. Liu, W. Yang (to be published)

SESSION D7: PREDICTION OF SURFACE PHENOMENA
Chair: Andrew M. Rappe
Friday Morning, December 3, 1999
Room 207 (H)

8:30 AM *D7.1
VIBRATIONAL DYNAMICS OF ADSORBED METAL SURFACES. Steven P. Lewis and Michael V. Pykhtin, Univ of Georgia, Dept of Physics & Astronomy, Athens, GA; Andrew M. Rappe, Univ of Pennsylvania, Dept of Chemistry, Philadelphia, PA; Eugene J. Mele, Univ of Pennsylvania, Dept of Physics & Astronomy, Philadelphia, PA.

When molecules adsorb on a metal surface, there emerge new vibrational modes associated with fluctuations of the molecule-surface bond. These modes are typically low in frequency compared to internal molecular vibrations, and thus they play an integral role in numerous thermally activated surface processes. This is especially true of the frustrated translations, which are usually lowest in energy. This talk will report on a theoretical investigation [1-4] of the vibrational dynamics of frustrated translations for molecular overlayers on metal surfaces. Our research shows that vibrational coupling to the substrate phonons generally dominates the frustrated-translational relaxation dynamics. In addition, this coupling mechanism leads to a long-range indirect interaction between adsorbates. As a result, collective motion and structural order within the overlayer drastically affect the dynamical behavior, even for very low adsorbate densities. We predict vibrational lifetimes that are in excellent quantitative agreement with experiment for very diverse overlayer conditions, including ordered and disordered overlayers, as well as high and low surface coverage. [1] S. P. Lewis and A. M. Rappe, Phys. Rev. Lett. 77, 5241 (1996).
[2] S. P. Lewis, M. V. Pykhtin, E. J. Mele, and A. M. Rappe, J. Chem. Phys. 108, 1157 (1998).
[3] M. V. Pykhtin, S. P. Lewis, E. J. Mele, and A. M. Rappe, Phys. Rev. Lett. 81, 5940 (1998).
[4] S. P. Lewis and A. M. Rappe, J. Chem. Phys. 110, 4619 (1999).

9:00 AM D7.2
SO_x ADSORPTION ON MgO SURFACES. W.F. Schneider, K.C. Hass, J. Li, Ford Motor Company, Dearborn, MI.

The chemisorption of small molecules on metal-oxide surfaces is a problem that impacts many areas of technology and provides significant challenges for both theory and experiment. The binding modes of molecules such as SO_x are especially complicated because of reactions with surface O that lead to the formation of surface sulfites and sulfates. Poisoning of alkaline-earth oxides by these complexes is a major impediment to the development of NO_x traps for controlling vehicle emissions. The present work reports density functional theory predictions (based on planewave pseudopotential calculations) for the structures, binding energies, and vibrational frequencies of SO_x adsorbates on ideal and defective MgO(100). Comparisons are made to infrared spectroscopy data on MgO powders exposed to SO_2 under varying conditions of surface preparation, O_2 concentration, and temperature. The combination of first-principles predictions and spectroscopic measurements greatly enhances our understanding of the complex surface chemistry of MgO.

9:15 AM D7.3
MODELING OF SURFACE CHEMICAL REACTIONS IN THE PLASMA DEPOSITION OF SILICON THIN FILMS. Shyam Ramalingam, University of California, Santa Barbara, CA; Stephen P. Walch, NASA Ames Research Center; Eray S. Aydil, University of California, Santa Barbara, CA; Dimitrios Maroudas, University of California, Santa Barbara, CA.

Hydrogenated amorphous and nanocrystalline silicon films grown by plasma-enhanced chemical vapor deposition are used widely for electronic, optoelectronic, and photovoltaic device manufacturing technologies. A major challenge in modeling plasma deposition of silicon films is both the identification and the quantitative prediction of the energetics and kinetics of surface chemical reactions. Such reactions occur when chemically reactive radicals originating in the plasma impinge on the silicon surface during the deposition process. In this presentation, we focus on the reactions of the silyl (SiH_3) radical with crystalline and amorphous silicon surfaces; SiH_3 is considered as the dominant deposition precursor from silane-containing plasmas. Our analysis combines nanosecond-time-scale molecular-dynamics (MD) simulations based on an extended Tersoff potential with ab initio pseudopotential calculations based on density-functional theory (DFT). MD simulations of radical impingement on silicon surfaces are used primarily for chemical reaction identification. The reactions are analyzed subsequently both by quenching the MD trajectories to obtain the corresponding energy landscapes and by targeted quantitative studies of reaction paths based on DFT calculations. Special emphasis is placed on MD simulations of hydrogenated amorphous film deposition on H-terminated Si(001)-(2×1) surfaces assuming that SiH_3 is the only deposition precursor. Reactions leading to radical adsorption, dissociative adsorption, and surface migration have been identified. In addition, abstraction by the impinging SiH_3 radicals of surface H has been found to follow an Eley-Rideal mechanism. Additional important reactions for deposition that have been identified include formation of disilane on the deposition surface and disproportionation reactions between two adsorbed SiH_3 radicals. The energetics of all of these reactions have been analyzed and the corresponding reaction paths have been obtained. Finally, the surface hydride coverage of the MD-deposited films is compared with experimental measurements. The theoretical results are found to be in good agreement with the experimental data.

9:30 AM D7.4
SURFACE CHEMISTRY FROM FIRST-PRINCIPLES: DISSOCIATIVE CHEMISORPTION OF Cl_2 ON Al(111). Nicola Marzari, Naval Research Laboratory, Washington DC; and George Mason University, Fairfax, VA.

Ab-initio molecular dynamics simulations are an established and very successful tool that can be used to study the energetics and thermodynamics of comparatively large systems, while retaining the accuracy of a full quantum-mechanical treatment. Recent algorithmic advances allow to extend this approach to metallic systems, at a computational cost still comparable to that of semiconductors or insulators. We report here the first study of a chemical reaction at a metal surface performed with full ab-initio molecular-dynamics simulations at finite temperature. The trajectories of Cl_2 molecules impinging on a thermalized Al(111) surface have been studied using a $11\times11\times27$ $\AA$ supercell and an aluminum slab modeled with 8 layers of 16 atoms, separated by ~ 11 $\AA$ of vacuum. The trajectories have been followed for an average of 1ps each, and different initial conditions for the orientation of the molecule and the point of first impact have been probed. The highly exothermic reaction leads in all cases to dissociative chemisorption. The energy released is often transferred directly into the kinetic energy of the adsorbed species, leading to a large translational motion of the isolated Cl atoms on the surface ("cannonball" dissociation). The transferral of charge and the filling of bonding or antibonding orbitals can be followed during the simulations, highlighting the interplay of chemical and kinetic effects. The latter are enhanced by aluminum and chlorine having comparable atomic masses.

9:45 AM D7.5
ATMOSPHERIC CORROSION OF COPPER: FIRST-PRINCIPLES PSEUDOPOTENTIAL CALCULATIONS OF SOLID-STATE TRANSPORT PROCESSES IN COPPER METAL, OXIDES, AND SULFIDES. Jeffrey S. Nelson, Sandia National Laboratories, Albuquerque, NM.

The kinetics of oxidation and sulfidation of copper depends in part on solid-state transport processes through multi-layer metal-oxide-sulfide thin films. In this presentation we will discuss the role of copper cation vacancy diffusion in the Cu-Cu2O-Cu2S system. The activation energies (sum of formation (Ef) and migration energies (Em)) of Cu cation vacancies in metallic Cu , Cu2O, CuO, and Cu2S were calculated using the first-principles pseudopotential method within density functional theory. Excellent agreement with experiment is found for Cu (Qcalc=2.3 eV, Qexp=2.2 eV) and Cu2O (Qcalc=1.7 eV, Qexp=1.8 eV), but the calculated value Qcalc=0.8 eV for the Cu2S layer is substantially greater than Qexp=0.3 eV. Interestingly, the calculated migration energy (Em=0.3 eV) is close to Qexp for Cu2S. Experimentally it is known that Cu2S materials are p-type semiconductors due to Cu atom deficiencies, and compositions ranging from Cu1.8S to Cu2S can be obtained depending on synthesis conditions. Because of the large number of cation vacancies in non-stoichiometric Cu2S, the activation energy is smaller (i.e., closer to Em) since the vacancies do not have to be thermally generated. Based on the idea that Cu cation diffusion is a critical mechanism determining the corrosion rate, we performed a calculation of Al anti-site defects in Cu2O to examine whether an impurity could act as a trap for vacancy diffusion, thereby slowing down the corrosion process. If an Al or In atom is substituted for a Cu atom in Cu2O, the antisite (AlCu)2+ will be a double-positively charge site, with the potential to bind two negatively charged Cu vacancies (Vcu)-. Our calculations indicate that the Al impurity is able to bind copper cation vacancies, in agreement with recent experimental measurements. Finally, the results of our calculations will be compared to existing experimental data and models of atmospheric corrosion of copper.

10:30 AM *D7.6
DOUBLE-JUMPS IN ADATOM DIFFUSION. Joachim Jacobsen, Haldor Topsoe A/S, Lyngby, DENMARK; Karsten Jacobsen, Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, Lyngby, DENMARK; James P. Sethna, Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY.

We study the rate of activated motion over multiple barriers, in particular the correlated double–jump of an adatom diffusing on a missing-row reconstructed Platinum (110) surface. We develop a Transition Path Theory, showing that the activation energy is given by the minimum–energy trajectory which succeeds in the double–jump. We explicitly calculate this trajectory within an effective-medium molecular dynamics simulation. A cusp in the acceptance region leads to a $\sqrt{T}$ prefactor for the activated rate of double–jumps. Theory and numerical results agree.

11:00 AM D7.7
MONTE CARLO STUDY OF SURFACE EVOLUTION AND FILM THICKNESS UNIFORMITY IN STACKS. Victor Sapozhnikov, Recording Head Operations, Seagate Technology, Minneapolis, MN.

Our 3D Monte Carlo model, with deposition and diffusion taking place in parallel, has been used to simulate stack growth. We have studied the evolution of film surface roughness during deposition of a film upon another, with different mobility of atoms. We showed that when a higher-diffusivity film is being deposited upon a lower-diffusivity film, the roughness first decreases at all scales and then increases at larger scales (due to the development of long-wavelength oscillations) but shows no or little increase at smaller scales. The effect of roughness on stack properties depends significantly on the degree of roughness correlation between the neighboring interfaces. We have analyzed the evolution of roughness correlation with film growth and its dependence on the growth conditions and the morphology of the surface upon which the film is deposited. The correlation decays faster when the mobility of the top-film atoms is higher than that of the bottom-film atoms, and slower when it is lower or equal to the atom mobility in the bottom film. Thus, one can control the roughness correlation by varying the deposition and growth conditions. We also studied thickness uniformity in films deposited upon a surface with a non-zero roughness (e.g., upon the surface of a previously deposited film). The simulation suggests that up to several atomic layers, the thickness is more uniform for lower-diffusivity films and only later (as the film grows) for higher-diffusivity films. Thus, to grow more uniform thin films one may have to reduce the mobility of the film atoms (or increase the deposition rate).

11:15 AM D7.8
MAGNETICALLY DRIVEN DISTORTION IN THE Sn/Ge AND Pb/Ge SURFACES. C. Stephen Hellberg and Steven C. Erwin, Naval Research Laboratory, Washington, DC.

Electrons at the Sn/Ge(111) and Pb/Ge(111) surfaces form a narrow band, indicating that correlations between electrons are important. We study these surfaces with a hybrid first-principles approach: We use density functional calculations to derive a Hubbard Hamiltonian for the surface electrons, and we solve this Hamiltonian with exact diagonalization. In the region of applicability to Sn/Ge and Pb/Ge, we find the Hamiltonian has a structurally distorted ground state with 1/3 magnetization. The distortion agrees qualitatively with that observed by STM and surface x-ray diffraction. Magnetism in these surfaces has not yet been probed experimentally.

11:30 AM *D7.9
SURFACE OPTICAL ANISOTROPY FROM *AB INITIO* CALCULATIONS. W.G. Schmidt, Department of Physics, North Carolina State University, Raleigh, NC.

Reflectance anisotropy spectroscopy (RAS) is becoming an increasingly important tool for *in situ* control of semiconductor processing with real-time feedback. The understanding and interpretation of the measured spectra, however, has been hampered by relatively slow theoretical progress. We studied InP and GaP(001) growth structures as model systems. Their optical properties were calculated using a massively parallel real-space multigrid technique [1] and *ab initio* pseudopotentials. Our results agree well with experiment, notably with respect to the stoichiometric changes induced by different surface preparations. We identify two distinct sources for the optical anisotropy: (i) highly structure-dependent features are caused by transitions involving electronic surface states, and (ii) derivative-like oscillations at the bulk critical point energies arise from transitions between surface-modified bulk wave functions. The latter are nearly independent from the actual surface structure. The agreement between the calculated and measured spectra is further improved by applying quasi-particle corrections obtained from numerically efficient, simplified GW calculations [2]. The combination of converged *first-principles* calculations with an approximate treatment of many-particle effects allows the reliable identification of "structural fingerprints" in the optical spectra, paving the way for the exploitation of their rich technological potential.
Work done in collaboration with EL Briggs, J Bernholc and F Bechstedt.
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[2] F Bechstedt, R Del Sole, G Cappellini, L Reining, Solid State Commun.**84**, 765 (1992).