SYMPOSIUM AA

Advances in Materials Theory and Modeling–Bridging Over Multiple-Length and Time Scales

April 16 – 20, 2001

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* Invited paper

TUTORIAL

ST AA: FUNDAMENTAL METHODS OF MULTIPLE LENGTH SCALE MODELING
Monday, April 16, 2001
9:00 a.m. - 4:00 p.m.
Golden Gate B2/B3

The purpose of this tutorial is to introduce the many facets of multi-length scale modeling. Because of the growing interest in the field of multiple length scale modeling, this tutorial will provide the attendees with a balanced description of the main facets of this field as applied in materials science. The tutorial will consist of four 45-minute lectures that will cover half a day, and the remaining time will be dedicated to a hands-on computer session where the attendees will have access to computers to run actual applications. The areas to be covered are the four fundamental areas that are required for multiple length-scale modeling: electronic structure theory, atomistic modeling (molecular dynamics and Monte Carlo methods), dislocation dynamics, and continuum level modeling. These lectures are meant to provide the attendees with a brief overview of the field and its challenges, and a detailed description of a particular method that will be utilized in the second part of the tutorial. The second half of the tutorial will be a hands-on session where personal computers will be used for the attendees to run illustrative examples in the four topical areas. There will only be a few computers, so attendees are encouraged to bring their laptops for use in the second part of the tutorial.

Instructors:
K.J. Cho, Stanford University
George Gilmer, Lucent Technologies
Hussein Zbib, Washington State University
R. Miller, University of Saskatchewan
Andrew Quong, Lawrence Livermore National Laboratory

SESSION AA1: MECHANICAL PROPERTIES, FRACTURE AND PLASTICITY
Chair: Ellad B. Tadmor
Wednesday Morning, April 18, 2001
Nob Hill C/D (Marriott)

8:30 AM *AA1.1
DISCRETE DISLOCATION PLASTICITY WITH FULLY ATOMISTIC DEFECT NUCLEATION. Ronald E. Miller, Department of Mechanical Engineering, University of Saskatchewan, Saskatoon, CANADA.

Several authors have presented approaches in which mesoscale plastic deformation is modelled by treating each dislocation explicitly as an elastic line defect (see, for example, Cleveringa *et al.*, *Acta Mat.* 45(8), pp. 3163-3179 (1997) and Kubin *et al.* in *Nonlinear Phenomena in Materials Science II*, ed. G. Martin and L.P. Kubin (1992)). These techniques serve as the ideal bridge between atomistic dislocation simulations and continuum plasticity. An important link which is missing between these mesoscopic models and the underlying atomistics is a complete picture of how dislocations are nucleated in the material, to wit, nucleation is normally treated phenomenologically using a critical value of the macroscopic state variables like local stress or strain. This talk will present a method for combining discrete dislocation plasticity with semi-empirical lattice statics calculations, whereby the regions of fully atomistic modelling serve as the nucleation sites for the dislocations. By allowing the nucleation of defects to be determined completely from atomistic considerations, the technique offers another important step towards a complete bridge between atomistics and continuum mechanics.

9:00 AM AA1.2
DISLOCATION DENSITY EVOLUTION OF BODY CENTERED CUBIC SINGLE CRYSTALS AT LOW TEMPERATURES: DISLOCATION DYNAMICS SIMULATION AND MODELING. Meijie Tang, Lawrence Livermore National Laboratory, Livermore, CA; Marc Fivel, GPM2, CNRS-INPG, Grenoble, FRANCE; Ladislas P. Kubin, LEM, CNRS-ONERA, Chatillon, FRANCE.

The plastic deformation of body centered cubic (bcc) single crystals at low temperatures is controlled by the thermally activated motion of the screw dislocations. For instance, the macro-yield stress is dominated by the effective stress to activate kink pairs and to move the screw dislocations. The strain hardening behavior depends on both the forest hardening behavior and the dislocation density evolution. Before the macro-yield stress is reached, the screw dislocations are essentially immobile and the edge or mixed dislocations move fast and leave behind elongated screw dislocations. The dislocation density increases significantly during this early stage, which affects the forest hardening during subsequent plastic deformation. A quantitative description is needed to describe the density evolution and its dependence on experimental conditions such as temperature and strain rates. A three-dimensional discrete dislocation dynamics simulation with an improved flux-balanced boundary condition is used to simulate the density evolution during the early stage at different temperatures. The numerical results are then analyzed and a model that relates the density evolution to its initial value and the experimental conditions is being developed.

9:15 AM AA1.3
MODELING PARTIAL DISLOCATIONS AT GRAIN BOUNDARIES USING FIRST PRINCIPLES CALCULATIONS AND THE PEIERLS-NABARRO MODEL. J.C. Hamilton, Istvan Daruka, J.A. Zimmermann, D.L. Medlin, Sandia National Laboratory, Livermore, CA; S.M. Foiles, Sandia National Laboratory, Albuquerque, NM.

We describe modeling of grain boundary partial dislocations at an aluminum sigma 3112 boundary. First principles calculations were used to determine the two stable symmetry-equivalent configurations of the grain boundary which exist far from the partial grain boundary dislocations. First principles nudged elastic band calculations were then used to determine the Peierls barriers associated with displacing the grain boundary between these two symmetry-equivalent configurations. Finally, a generalized Peierls-Nabarro model was used to obtain the partial dislocation widths from the calculated Peierls barriers. The calculated dislocation widths are in reasonable agreement with experimental TEM measurements. There are several novel features demonstrated by this theoretical analysis. One is that the dislocation core widths are very large ($\sim 40 \approx$) due to the very small Peierls barrier at the grain boundary. Another feature is that shearing the metal along the grain boundary causes translation of the grain boundary in a direction perpendicular to the boundary.

9:30 AM AA1.4
ALLOY HARDENING: COUPLING CONCENTRATION FIELD AND DISLOCATION DYNAMICS IN PHASE FIELD METHODS. David Rodney, Alphonse Finel, LEM (ONERA-CNRS), Chatillon, FRANCE.

We present a general formalism to incorporate dislocations into Phase Field methods. This approach couples the dynamics of the phase field (e.g. concentration field) to the dynamics of the dislocations. It is valid for any 3-dimensional anisotropic elastic media with any dislocation distribution. This new formalism extends the applicability of the Phase Field methods to the area of plastic properties of crystalline solids. We present an application to the study of hardening in a phase-separating FCC crystal. We investigate the influence of the dislocations on the phase decomposition as well as the effect of the decomposition on the dynamics of the dislocations and therefore on the plastic behavior of the material.

9:45 AM AA1.5
MODELING THE EFFECTS OF DISLOCATION-GRAIN BOUNDARY INTERACTIONS IN POLYCRYSTAL PLASTICITY: IDENTIFICATION AND CHARACTERIZATION OF UNIT MECHANISMS. M. de Koning, Lawrence Livermore Natl Laboratory, Univ of California, Livermore, CA; R. Miller, Univ of Saskatchewan, Dept of Mechanical Engr, Saskatoon, Saskatchewan, CANADA; V.V. Bulatov, Lawrence Livermore Natl Laboratory, Univ of California, Livermore, CA; F. Abraham, IBM Research Div, Almaden Research Ctr, San Jose, CA.

The quantitative modeling of polycrystal plasticity requires an atomistic-micro-meso scale computational approach that couples the physics of individual dislocations to the evolution of large collections of dislocations and, ultimately, to the aggregate behavior of grain microstructures under stress. As a first step in the construction of such a model one must understand the unit defect mechanisms that govern the behavior of the system at the atomistic level and provide the basis for the description on higher scales. In this paper we focus on one of the key issues in polycrystalline plasticity: the unit mechanisms involving the interactions between dislocations and grain boundaries (GB). Using a combination of large-scale molecular dynamics simulations based on an embedded atom potential and an analysis in terms of the line-tension model we identify and characterize the geometrical parameters that govern the occurrence of slip transmission, absorption, blockage, etc. in dislocation-GB interactions. The results provide a useful guideline for the development of quantitative micro-constitutive equations for dislocation-GB interactions to be used in meso-scale simulations of polycrystal plasticity.
This work is performed under the auspices of U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

10:30 AM *AA1.6
MULTISCALE MODELING OF PLASTICITY IN DYNAMIC
FRACTURE. <u>Robert E. Rudd</u> and James F. Belak, Lawrence
Livermore National Laboratory, Livermore, CA.

We study the nucleation and growth of voids in dynamic fracture with
an emphasis on the concomitant plastic deformation. The nanoscopic
mechanisms of this high strain-rate plasticity have not been studied
previously in detail. In this talk we focus on FCC materials such as
copper using molecular dynamics with an embedded atom model
potential. Multi-million atom molecular dynamics models have been
run to simulate systems consisting of a periodic box, filled with atoms
initially in a single crystalline or polycrystalline array. [1] These
models are extended, where appropriate, with concurrent multiscale
modeling techniques which embed the atomistic model in a finite
element model which runs concurrently to capture the long range
elastic fields. This minimizes the finite size effects associated with
dislocations interacting with the periodic image of the deformed
material. The atomistic simulations are used to characterize the
dislocation activity in the plastic zone surrounding voids growing
under tensile loading. A dilatational strain is applied that induces
void growth. We have studied the nucleation of dislocations that effect
the transfer of material associated with void growth. The dislocations
are naturally split into partials, and often appear in prismatic
dislocation loops, which facilitate outward transport of material to
accommodate the growing void. We further identify the character of
the most numerous dislocations and their associated glide planes. The
results are in agreement with experiment when account is taken of the
strain rate difference.
This work was performed under the auspices of the US Dept. of
Energy at the University of California/Lawrence Livermore National
Laboratory under contract no. W-7405-Eng-48.
[1] J. Belak, "On the nucleation and growth of voids at high
strain-rates", J. Comp.-Aided Mater. Design 5, 193 (1998).

11:00 AM AA1.7
TOPOLOGICAL CHANGES AT TRIPLE JUNCTIONS DURING
MICROSTRUCTURAL EVOLUTION: AN ATOMISTIC MODEL.
<u>Alessandra Satta</u>, Luciano Colombo, Istituto Nazionale per la Fisica
della Materia and Dipartimento di Fisica, Università di Cagliari,
Cittadella Universitaria, Monserrato (CA), ITALY; Fabrizio Cleri,
Ente Nuove Tecnologie, Energia e Ambiente, Divisione Materiali,
Centro Ricerche Casaccia, Roma, ITALY, and Istituto Nazionale per
la Fisica della Materia.

Topological changes in microstructures are strictly related to the
microscopic evolution of triple junctions[1]. The grain switching and
three-sided grain disappearance, usually called T1 and T2 proccesses
respectively, are here investigated via atomistic modelling. In
particular, both the evolution of a pair of neighboring triple-junction
and the stability of a three-sided grain insertion in a triple junction in
silicon are studied within the framework of Molecular Dynamics
simulations. The Stilliger-Weber interatomic potential and the
Environment Dependent Interatomic Potential (EDIP) schemes are
adopted for a comparative study. Constant-traction border conditions
are considered to ensure a proper embedding of the atomistic region
in a virtually infinite bulk continuum. Concerning the former case
study, T1, the profiles of internal and free energy barriers are
calculated by varying the distance between the triple junctions
vertices. Dealing with the latter topological event, T2, the critical
radius below which the three-sided inner grain becomes unstable is
given, together with an accurate description of the mechanisms
through which this instability sets in.
[1] S. Costantini, P. Alippi, L. Colombo, and F. Cleri, *to appear in*
Phys. Rev. B **63**, (2001).

11:15 AM AA1.8
CROSS-SLIP PATHS AND ENERGETICS IN Al AND Ag. Gang Lu,
<u>Nicholas Kioussis</u>, Department of Physics, California State University
Northridge, CA; Vasily Bulatov, Lawrence Livermore National
Laboratory, CA; Efthimios Kaxiras, Department of Physics, Harvard
University, MA.

We present a new semi-discrete variational approach which allows the
study of the stress states and energetics of dislocation cross-slip in
FCC metals. In the model the screw dislocation is allowed to spread
into two intersecting planes, namely the glide and the cross-slip
planes. Within the generalized Peierls-Nabarro formalism, the energy
of a given core structure is determined by the elastic interaction
between two continuously distributed dislocation densities and the
associated misfit energies integrated over the two planes. The
generalized stacking fault energy surfaces entering the model are
calculated from density functional theory. The optimal cross-slip path
and the associated cross-slip energy barrier are determined from
constrained minimization calculations, starting from different initial
core configurations. We find that screw dislocations in Al and Ag
follow different cross-slip paths characterized by very different

activation energy barriers. Our results are compared with
experimental and simulation data available in the literature.

11:30 AM *AA1.9
SIMULATIONS OF DISLOCATION PATTERNING AND STRAIN
HARDENING IN METALS. <u>B. Devincre</u>, R. Madec, D. Gomez-Garcia
and L. Kubin, Laboratoire d'Etude des Microstructures, CNRS-
ONERA, Chatillon Cedex, FRANCE.

Recent progress achieved in the understanding of the complex
relationship between dislocation patterning and strain hardening in
metals is presented. These results have been obtained by simulations
of dislocation dynamics in two and three-dimensions. On the basis of
a detailed analysis of dislocation properties at the microscopic scale,
it is shown that during the early stages of deformation, the increase of
dislocation density is directly related to the cross-slip mechanism.
Strain hardening and dislocation patterning are then strongly
correlated, since both derive from the storage of immobile dislocation
debris.

SESSION AA2: RADIATION-MATTER
INTERACTIONS
Chair: Tomas Diaz de la Rubia
Wednesday Afternoon, April 18, 2001
Nob Hill C/D (Marriott)

1:30 PM *AA2.1
MULTISCALE SIMULATION STUDY OF LASER ABLATION OF
ORGANIC MATERIALS. <u>Leonid Zhigilei</u>, Univ of Virginia,
Charlottesville, VA.

The interaction of laser pulses with organic matter leading to massive
material removal (ablation) from a target is a subject of scientific as
well as applied interest. Important practical applications include laser
surgery, matrix-assisted laser desorption/ionization (MALDI) of
biomolecules for mass - spectrometric investigations and surface
microfabrication of polymer thin films. The character of laser damage
to the irradiated sample, parameters of the ejected plume and the
dynamics of the ablation process are defined by interplay of processes
occurring at different time and length scales. The complex character
of the involved intertwined processes hinders an adequate analytical
formulation for a continuum description of the phenomenon whereas a
collective character of the laser ablation occurring at the mesoscopic
rather than molecular scale does not permit a direct application of the
atomistic simulation approach. We are developing a multiscale
computational model for dynamic simulation at atomic, mesoscopic
and continuum levels. The connection between the atomic-level and
continuum descriptions is provided by a novel breathing sphere model
for molecular dynamics (MD) simulation at mesoscopic/molecular
level. The breathing sphere model has advantage of both addressing
the effects of laser irradiation at a sub-micron resolution and yet
incorporating a realistic description of energy relaxation of individual
molecules internally excited by photon absorption. A combined MD -
finite element method approach as well as dynamic non-reflecting
boundary condition are used to simulate propagation of the
laser-induced pressure waves out from the MD computational cell
allowing us to focus our MD computational efforts on the areas where
active processes of laser-induced damage/ablation are occurring. The
essence of the computational approach and application of the model
to the analysis of different modes of cluster ejection and the resulting
cluster size distributions in the ablation plume will be covered in the
presentation. Further details and references can be found on web page
http://www.people.virginia.edu/ lz2n/Ablation.html.

2:00 PM AA2.2
MOLECULAR-DYNAMICS THERMAL-ANNEALING MODEL OF
LASER ABLATION OF SILICON. <u>Patrick Lorazo</u>, École
Polytechnique de Montréal, Département de Génie Physique et de
Génie des Matériaux et Groupe de Recherche en Physique et
Technologie des Couches Minces (GCM), Montréal, CANADA;
Laurent J. Lewis, Université de Montréal, Département de Physique
et Groupe de Recherche en Physique et Technologie des Couches
Minces (GCM), Montréal, CANADA; Michel Meunier, École
Polytechnique de Montréal, Département de Génie Physique et de
Génie des Matériaux et Groupe de Recherche en Physique et
Technologie des Couches Minces (GCM), Montréal, CANADA.

A molecular-dynamics thermal-annealing model (MADTAM) is
proposed to investigate the photothermal and photomechanical
processes involved in picosecond pulsed laser ablation of crystalline
silicon. A detailed description of the microscopic mechanisms arising
from irradiation of a Si(100) substrate with a single 308 nm Gaussian
laser pulse is embedded into a molecular-dynamics scheme. In
accordance with the thermal annealing model (TAM), the absorption
of photons causes the build-up of a dense gas of hot electrons and
holes relaxing primarily through carrier-phonon scattering within the

conduction and valence bands, respectively. Surface effects and the formation of a space charge layer (SCL) [J.R. Goldman and J.A. Prybyla, *Phys. Rev. Lett.* **72**, 1364 (1994)] are accounted for by explicitly including in the model the relaxation of carriers within surface states. Results for fluences in the range 0.01 to 1 J/cm^2 yield phenomena and time scales in good agreement with TAM. Above the predicted threshold fluence for ablation, F_{th}, the role of photothermal and photomechanical effects for material removal is analyzed for pulse durations from 10 to 100 ps; the results are compared with a recent MD study of organic solids in the thermal and stress confinement regimes [L.V. Zhigilei and B.J. Garrison, *J. Appl. Phys.* **88**, 1281 (2000)]. In addition, results for which surface effects have been neglected reveal that the latter are important to account for photothermal processes in picosecond laser ablation of silicon.

2:15 PM AA2.3
THE EFFECT OF INTERSTITIAL IMPURITIES ON RADIATION DAMAGE IN Fe: A MULTISCALE MODELING APPROACH. Jaime Marian, Brian D. Wirth, Tomas Diaz de la Rubia, Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, CA; J. Manuel Perlado, Instituto de Fusión Nuclear, Universidad Politécnica de Madrid, Madrid, SPAIN.

Irradiation of metals by neutrons and high-energy particles produces microstructure changes that result in significant degradation of material properties. High-energy displacement cascades generate large numbers of both isolated point defects and clusters of vacancies and interstitials. Point defect mobility, as well as defect cluster stability and mobility, play key roles in solute transport and the subsequent fate of defects and, hence, in the overall chemical and microstructural evolution under irradiation. In this work, we investigate the effect of interstitial impurities (C, O, N) on point defect mobility and subsequent solute and defect transport. Defect trapping efficiencies of interstitial impurities are obtained from ab-initio simulations using plane wave pseudopotential codes within the generalized gradient (GGA) approximation. Within a multiscale modeling framework, the electronic structure calculations of defect trapping energetics are incorporated into long-range kinetic Monte Carlo simulations of damage accumulation and microstructural evolution of irradiated α-Fe to quantitatively assess the effect of interstitial impurities. 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 and within the VENUS project (CSN/UNESA PCI) under contract P970530432.

2:30 PM AA2.4
INITIATION OF CHEMISTRY IN MOLECULAR SOLIDS BY PROCESSES INVOLVING ELECTRONIC EXCITED STATES. Maija M. Kuklja and A. Barry Kunz, Department of Electrical and Computer Engineering, Michigan Technological University, Houghton, MI.

Over the years, investigations on explosive decomposition of materials have been investigated mostly in two directions. One is the physics of detonation waves describing macroprocesses. Second is the chemistry of explosives studying chemical reactions in terms of energetic barriers. Providing most of the understanding of the detonation theory, both approaches ignore solid-state effects. The lack of fundamental quantum-mechanical studies is easily realized when one recognizes that successful constructing of explosive/pyrotechnic devices was quite possible well before the technological methodology needed to understand such systems was available. In addition, there are the limitations of available computers and experimental techniques, coupled with the complexity of most useful energetic solids. The initiation of chemistry in energetic compounds is a complex process. Experiments indicate that very fast process (femtosecond range) of electronic excitation plays a key role in the initiation process. There is variety of initiation models proposed. However, the relationship between the defect structure, electronic excitations, and fast chemical processes in the detonation front is not yet established. In this study aimed at revealing this relationship, we analyze the initiation process from a solid-state physics viewpoint. The theoretical approach is based on band-structure calculations of perfect and defective RDX [CH_2N-NO_2]$_3$ high explosive under shock conditions. Specifically, we model an effect of the strong compression induced by a shock/impact wave on the crystal with and without edge dislocations. Based on the obtained conclusions, we developed a novel excitonic mechanism of initiation in explosives. Our theoretical predictions were tested experimentally using pulse radiolysis techniques at the time scale 10^{-10}-10^{-4} s and a laser initiation as a function of pressure. Besides the fundamental interest, the obtained results are of great practical importance for safety issues and also for a discovery of a very new perspective for the development of the modern initiation and detonation theory.

2:45 PM AA2.5
PULSE FREQUENCY EFFECTON NEUTRON DAMAGE IN

α-IRON: A KMC ANALYSIS. Manuel Perlado, Juan Prieto, Esteban Dominguez, Instituto de Fusion Nuclear, Universidad Politecnica de Madrid, Madrid, SPAIN; Dario Lodi, Dipartimento di Ingegneria Nucleare, Politecnico di Milano, ITALY; Tomas Diaz de la Rubia, Lawrence Livermore National Laboratory, Livermore, CA.

The pulsed nature of the irradiation and the high neutron dose are the critical factors in an Inertial Fusion Energy Reactors (IFE).The damage that structural materials suffer under these extremes conditions require a carefull study and assesment. The goal of our work is to simulate,trough the Multiscale Modelling approach,the damage accumulation in α-iron under conditions relevant to a IFE reactor. Multiscale Modelling approach is extended to second as a sequence of Molecular Dynamics (MD)and Kinetic Montecarlo (KMC). We discuss how the pulse frequency, 1Hz,10Hz,100Hz, and the temperature, 300K and 600K in our simulations,affect the damage production and accumulation. Results of the damage that this demanding environment can produce on a protected first structural wall exposed to 0.5-1 MeV average nuetron energy and on an unprotected wall where the average neutron energy is around 4-6 MeV will be presented A dose rate of 10^{-2} amd 10^{-1} dpa/s is considered, in order to compare these results with the ones computed in previous articles. A further comparison has been made with the damage produced by a continuous irradiation with similar average dose rate.

SESSION AA3: POLYMERS AND
MACROMOLECULES
Chair: Pablo Ordejon
Wednesday Afternoon, April 18, 2001
Nob Hill C/D (Marriott)

3:30 PM *AA3.1
LIVING POLYMERS: A COMBINED DENSITY FUNCTIONAL AND MONTE CARLO SIMULATION OF POLYCARBONATE. R.O. Jones, Institut für Festkörperforschung, Forschungszentrum Jülich, Jülich, GERMANY; P. Ballone, Dipartimento di Fisica, University of Messina, Messina, ITALY.

Polycarbonates, important thermoplastic engineering materials with favorable optical, thermal, and mechanical properties, can be produced by the ring-opening of cyclic oligomers. We have studied such reactions for bisphenol-A polycarbonate (BPA-PC) using a combination of density functional (DF) calculations and Monte Carlo simulations.
First, we use DF calculations to compute thestructural and energy changes accompanying the ring-opening reaction of the cyclic tetramer of BPA-PC with nucleophilic molecules, such as sodium phenolate NaOPh [1]. The "active site" after ring opening - here the Na atom - is at the end of the chain, and the successive reaction with other rings provides an example of a "living polymer". The results support experimental indications that the energies of reactants and products are essentially equal, so that the reaction is not enthalpy-driven. Furthermore, the calculated harmonic vibration frequencies show that the vibrational entropies of reactants and products are almost identical.
To identify the driving forces behind polymerization we have then performed Monte Carlo calculations using an idealized coarse-grained model, in which Lennard-Jones "particles", connected by harmonic springs and representing BPA-PC monomers, can interchange "covalent bonds" according to rules consistent with the reaction mechanism revealed by the DF calculations. Despite the exact equivalence in bonding strength and packing of oligomers and extended chains, the model favors - at equilibrium - a high degree of polymerization that is enhanced by increasing density and, to some extent, by increasing temperature. This results from the entropy associated with a polydisperse size distribution. We discuss the effect of dimensionality and the relation to crystallization, another entropy-driven phase transformation.
[1] P. Ballone, B. Montanari, R.O. Jones, J. Phys. Chem. A 104, 2793 (2000).

4:00 PM *AA3.2
COMPUTER MODELLING OF DENSE MACROMOLECULES. B. Dünweg, G. Besold, F. Müller-Plathe, K. Kremer, Max Planck Institute for Polymer Research, Mainz, GERMANY.

Recent improvements in simulation approaches to different polymer systems will be discussed. Special focus will be given towards dynamical properties of melts, networks, but also amphiphilic systems and block copolymers. The combination of a number of different techniques, ranging from atomistic force field simulations to semimacroscopic models of polymers will be used and where possible linked to each other.

4:30 PM AA3.3
ONE-MINUTE PRESENTATIONS OF THE AA4 EVENING POSTER SESSION.
Chair: Laurent Lewis, Universite de Montreal, CANADA.

SESSION AA4: POSTER SESSION
Chairs: Vasily V. Bulatov, Fabrizio Cleri, Luciano
Colombo, Laurent J. Lewis and Normand Mousseau
Wednesday Evening, April 18, 2001
8:00 PM
Salon 1-7 (Marriott)

AA4.1
LATTICE PARAMETER DEPENDENCE VERSUS COMPOSITION IN SEMICONDUCTOR ALLOYS: THE InGaAs CASE.
Claudio Ferrari, Nicola Armani, CNR Maspec Institute, Parma, ITALY; Elena Villaggi, INFM, Physics Department, Parma, ITALY; Gilberto Rossetto, Giovanni Carta, CNR Ictima Institute, Area della Ricerca di Padova, Padova, ITALY.

The measurements of the lattice parameter by means of X-ray diffraction methods in semiconductor alloys permits in principle a very accurate (10^{-4}) determination of the composition in a completely non destructive way. The method is based on the exact knowledge of the lattice parameter dependence versus composition. For a long time the Vegard law has been applied, assuming a linear dependence of the lattice parameter versus the stoichiometric coefficient x in alloys of type A_xB_{1-x}. Studies of the lattice parameter dependence of SiGe alloys [1] and, more recently of GaAlSb [2] and SiC evidenced deviations from the linear relationship of up to several percents of the total range near the stoichiometric value x=0.5. Several works based on different analytical techniques like Electron Probe Microanalysis, Rutherford Backscattering and X-ray fluorescence reported in the case of InGaAs alloy a linear dependence in the full range of composition from x=0 to 1 (see for instance Nakajima et al. [3]). In the present work a new method based on the measurement of X-ray absorption in the diffraction mode has been used to calculate the composition of a InGaAs/InP heterostructure grown by the Metal Organic Chemical Vapour Deposition Technique. Based on the known X-ray absorption coefficients of In, As and Ga for the CuKa wavelength, a deviation of 6% from the Vegard law toward higher In content has been found in the lattice matched InGaAs/InP alloy. Such result has been confirmed by Electron Probe Microanalysis measurements on standards prepared from InAs and GaAs fine ground crystals. The agreement with the theoretical prediction of Fournet et al. [5]and other models based on elastic distortion of atom bonds suggests that the deviation from linear relationship is a general behaviour in semiconductor alloys.
[1] J.P. Dismukes et al., The Journal of Physical Chemistry, 68, 1964, 3021.
[2] C. Bocchi et al., J. Appl. Phys. 86, 1999, 1298.
[3] K. Nakajima et al, J. Appl. Phys. 50, 1979, 4975.
[4] Hocking et al. J. Appl. Phys. 37, 1966, 2879.
[5] G. Fournet, le Journal de Physique et de Radium, 14, 1953, 374.

AA4.2
QTR *Ab initio* STUDIES OF STRUCTURAL AND OPTICAL PROPERTIES OF LAYERED HEXAGONAL GRAPHITE AND TRANSITIONAL METAL DICHALCOGENIDES: EFFECTS OF LITHIUM INTERCALATION. K.R. Kganyago and P.E. Ngoepe, Materials Modelling Center, University of the North, SOUTH AFRICA.

We present results of high pressure /QTRit Ab initio pseudopotential calculations of structural and optical spectra of LiC_6 and layered group IVA transitional metal dichalcogenides ZrS_2, TiS_2, HfS_2 and $LiTiS_2$. This procedure is used to systematically study the bulk moduli, compressibility along the c-axis, metallization in ZrS_2, TiS_2, HfS_2 systems and the effect of lithium intecalation on the latter including the optical spectra. We compare our results with experimental results.

AA4.3
EAM COPPER-TANTALUM POTENTIAL DEVELOPED WITH FORCE MATCHING METHOD. Youhong Li**, Donald J. Siegel*, James B. Adams**. **Department of Chemical and Materials Engineering, Arizona State University, Tempe, AZ. *Physics Department, University of Illinois, Urbana, IL.

Atomic potentials are useful for molecular dynamics simulations of large systems (millions of atoms). Following the EAM Tantalum potential we developed, a new Cu-Ta EAM alloy potential was constructed with force matching method. In addition to fitting the potential to the lattice constant, elastic constants, cohesive energy, and vacancy formation energy, we also fit the potential to thousands of forces calculated via DFT for a wide variety of structures including bulk structure at different temperatures, surfaces, and crystal defects, etc. Testing of the potential was also performed.

AA4.4
3D MINI-BAND FORMATION AND PHASE TRANSITIONS IN A QUANTUM DOT SUPERLATTICE. Olga L. Lazarenkova and Alexander A. Balandin, Univ of California at Riverside, Dept of Electrical Engineering, Riverside, CA.

Quantum dots (QDs) represent the ultimate case of spatial confinement for electrons. This creates an exciting opportunity for re-engineering of the optical, electronic, and thermal properties of many technologically important semiconductor materials through modification of their electronic states. Relative to a quantum well superlattice (QWS), a quantum dot superlattice (QDS) that consists of multiple arrays of regimented *coupled* quantum dots have many advantages in applications due to its modified density of electronic states, and relaxed optical selection rules. Although different types of QDS had already been fabricated using self-assembly techniques [1-2], little attention has been paid to theoretical description of electronic properties of such structures.- Here, we present a theoretical model for the electron band structure in a QDS. The coupling among quantum dots leads to a splitting of the quantized electron energy levels of single dots. The latter results in formation of three-dimensional (3D) electron mini-bands. Changing the size of quantum dots, inter-dot distance, barrier height and regimentation, one can control the electronic band structure of this artificial *quantum dot crystal*. Similar to real crystals, a QDS may manifest quasi- metallic or semiconductor properties depending on the relative position of Fermi level and mini-bands. At the same time, the metal-semiconductor phase transitions in the QDS can be controlled not only by doping, but also by proper modification of the DQS parameters, e.g. size, inter-dot distance, barrier height, etc., and application of an external field. A possibility of 3D mini-band design in QDS allows one to tune electronic and optical properties of nanostructured materials.
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[2]. K.L. Wang and A. Balandin, *Quantum Dots: Properties and Applications*, in Optics of Nanostructured Materials, ed. by V. Markel and T. George, (J. Wiley & Sons, New York, 2000) pp. 515-550.

AA4.5
TRANSMITTANCE QUANTITIES PROBABILITY DISTRIBUTIONS OF ELECTROMAGNETIC WAVES THROUGH DISORDERED SYSTEMS. Gabriel Cwilich, Fredy R. Zypman, Yeshiva University, New York, NY.

Waves propagate through disordered systems in a variety of regimes. Depending on the spatial dimensionality of the system there exists a threshold degree of disorder beyond which waves become localized and transport becomes restricted. The intensity I, of the wave transmitted through the sample has a dependence on the length L, of the sample that is characteristic of the regime. For example, I decays like $\frac{1}{L}$ in the diffusive regime. It is of current interest to characterize the transport regime of a wave, from statistical studies of the transmittance quantities through it Specifically, A.Z. Genack proposed that the probability distribution of the intensity could be used to characterize the localized regime. There is an ongoing debate on what deviations from the classical Rayleigh distribution are to be expected. In this numerical work we use scalar waves to obtain the intensity, transmission, and conductance of waves through a system with various degrees and qualities of disorder. We calculate the intensity, by setting an incoming plane wave towards the sample from a fixed direction. The outgoing intensity is then calculated at one point in space. This process is repeated for a collection of samples, belonging to the same ensemble, that is, chosen from the distribution that characterizes the disorder, and we construct the probability distribution of the intensity. In the case of the transmission we evaluate the field arriving to a series of points distributed in the far field, and repeat the same statistical analysis. In the case of the conductance we calculate the field at the same series of points for incoming waves in different channels. We will present the momenta of the distribution of the different transmittance quantities and their change with the degree of disorder. This work is supported by Yeshiva University.

AA4.6
DEEP LEVELS OF CLUSTERS FROM ANTI-SITE DEFECTS IN $ZnGeP_2$. Valerii Voevodin, Sergei Grinyaev, Siberian Physical-Technical Institute, Tomsk, RUSSIA.

Chalcopyrite semiconductor $ZnGeP_2$ is widely used in nonlinear optical devices, solar elements, detectors, modulators, filters, switches. The physical properties of threefold compounds essentially depend on the different defects, however the nature of thouse defects is investigated in considerably of a smaller degree in comparison with binary analogues. In the present work on the basis of methods of pseudo-potential and extended elementary cell (4*4*4) the research of deep levels in $ZnGeP_2$, connected with the point anti-site defects

$(\text{Zn}_{Ge}, \text{Ge}_{Zn}, \text{Zn}_P, \text{P}_{Zn}, \text{Ge}_P, \text{P}_{Ge})$ and them clusters containing up to 100 defects is carried out. The energy of levels of the localized states on of defects in a vicinity of the band gap ZnGeP_2 is determined, the distribution of them density of charge is constructed, probabilities of optical transitions are received. On the basis of results of account the interpretation of red shift of edge of fundamental absorption real ZnGeP_2, containing the clusters from the disordered zinc-blende-like phase is given.

AA4.7
AB-INITIO AND SEMIEMPIRICAL MODELLING OF CANDIDATE MATERIALS FOR HYDROGEN STORAGE. <u>F. Cleri</u> and M. Volpe, ENEA, Divisione Materiali, Centro Ricerche Casaccia, Roma, ITALY.

Materials science can give a determinant contribution to the solution of the problem of hydrogen storage for energetic applications. In fact, storage into a solid matrix could prove convenient with respect to the conventional techniques based on liquefation or compression of gaseous hydrogen. Several classes of materials are being actively investigated in this respect, both from the experimental and theoretical point of view. These can be roughly divided into two classes: (a) *adsorbers*, in which atomic or molecular hydrogen is attached to the free surfaces by either chemisorption of physisorption; such materials have huge values of specific surface, up to several thousands m^2/g, (b) *hydrides*, in which atomic hydrogen reacts with a host lattice to form a new hydride phase, which can have a different lattice stoichiometry, symmetry and volume. We present the initial results of computer simulations for disordered graphite and carbon nanotubes, both belonging to the (a) class, and for a group of metal hydrided among which LaNi_5 is the prototype, belonging to the (b) class. For carbon nanotubes we used a semiempirical tight-binding model for the C-H bonding interaction and Van der Waals classical potential for dispersion forces. We perfomed molecular dynamics simulations of the adsorption−desorption cycle of atomic and molecular hydrogen in simple nanotube−based systems. For graphitic carbon we performed ab-initio DFT-GGA calculations of H_2 molecules either in a perfect or defective graphite host lattice. For the LaNi_5−based hydrides we performed LDA energy−minimization to find optimal structures of the different hydride phases, and ab-initio molecular dynamics in the attempt to investigate hydrogen evolution under temperature from these systems.
Work performed in part under ENEA-ASI Fundamental Research Contract RIDR500110.

AA4.8
NOVEL MODEL FOR THE OPTICAL DIELECTRIC FUNCTION: APPLICATION TO HEXAGONAL GaN. <u>Y. Chan</u>, A.B. Djurivsić, and E.H. Li, Department of Electrical & Electronic Engineering, The University of Hong Kong, HONG KONG.

In this work we propose an analytical expression for the complex dielectric function which includes both discrete and continuum exciton effects. The model is based on the work of Elliott. The dielectric function models in the literature which are based on Elliott's work either do not take broadening into account properly (which leads to incorrect division by E^2 instead of $(Ei\Gamma)^2$ and singularity in zero, or discrete excitonic terms have been disregarded so that there are no terms depending on the exciton of order m. In this work, we start from the unbroadened expression for the dielectric function based on Elliott's work, and after accurate introduction of broadening we obtain the expression for the complex dielectric function. The proposed model has been applied to modeling the experimental data for the hexagonal GaN. We have obtained good agreement with the experimental data. The model assumes Lorentzian broadening in order to obtain dielectric function equations in analytically closed form. The agreement with experimental data can be improved further if adjustable broadening function is considered instead of a simple Lorentzain one. Lorentzian broadening assumption is valid only for weak exciton-phonon coupling and in absence of impurities, defects and crystal strain which give rise to Gaussian broadening. For very strong exciton-phonon coupling the broadening due to interaction with phonons can also be considered to be Gaussian, while intermediate coupling causes a mixture of Gaussian and Lorentzian broadening contributions. The exact form of the broadening function is unknown and it may even be sample dependent. However, a simple empirical approximation for adjustable broadening function can give significant improvement in accuracy and reduction of extended absorption tail below the absorption edge which is inherent to all models assuming Lorentzian broadening.

AA4.9
THERMAL AND ELECTRONIC IN-PLANE TRANSPORT IN A QUANTUM DOT SUPERLATTICE. <u>A. Khitun</u>, University of California - Los Angeles, Electrical Engineering Department, Device Research Laboratory, Los Angeles, CA; A. Balandin, Department of Electrical Engineering, University of California - Riverside, Riverside, CA; J.L. Liu, K.L. Wang, University of California - Los Angeles,

Electrical Engineering Department, Device Research Laboratory, Los Angeles, CA; G. Chen, University of California - Los Angeles, Department of Mechanical and Aerospace Engineering, Nanoscale Heat Transfer and Termoelectricity Laboratory, Los Angeles, CA.

We present a theoretical model to describe thermal and electronic in-plane transport in a quantum dot superlattice. The model takes into account modification of electron and phonon transport due to spatial confinement caused by energy band discontinuity and acoustic impedance mismatch between the dot and host materials. Numerical calculations were carried out for a structure that consists of multiple layers of Si with regimented Ge quantum dots. Transport characteristics such as electrical conductivity, lattice and electronic thermal conductivities were calculated for different dot sizes and different dot concentrations. The obtained results show a significant decrease in both electric and lattice thermal conductivity due to the scattering on quantum dots. The simulation results for the lattice thermal conductivity are in a good agreement with available experimental data. The developed model provides analysis of the in-plane electronic and thermal properties of the quantum dot superlattice versus quantum dot size and dot arrangement.

AA4.10
ELECTRONIC AND OPTICAL PROPERTIES OF Si/SiO_2 SUPERLATTICES FROM FIRST PRINCIPLES. <u>Pierre Carrier</u>, Laurent J. Lewis, Univ. of Montreal, Dept of Physics, Montreal, CANADA; M.W. Chandre Dharma-Wardana, Institute for Microstructural Sciences, Ottawa, CANADA.

The observation of intense luminescence in Si/SiO_2 superlattices has lead to new theoretical research on silicon-based materials. We have performed first-principles calculations using three Si/SiO_2 superlattice models in order to examine their electronic structure and related optical properties. The first two models are derived directly from crystalline structures (diamond-like Si and β-cristobalite-like SiO_2 layers) and have simple interfaces. These models have been studied using the full-potential-linearized-augmented-plane-wave (LAPW) method, within the local-density approximation (LDA). The bandgaps are found to be indirect in both models and gap states are shown to exist in one of the models. In addition, optical absorption coefficients within the interband transition theory (excluding excitonic effects) have been calculated. The $\text{Si}(100)$-SiO_2 interface structure is shown to have dramatic effects on the optical behaviour. Following these observations, we have considered a more realistic, fully-relaxed model. The atomic positions have been derived from a $\text{Si}(001)$-SiO_2 interface study previously reported by Pasquarello, Hybertsen and Car [Appl. Surf. Sci. **104/105**, 317 (1996)]. The projector-augmented-wave (PAW) method under the LDA is used to perform the structural relaxation as well as band structure and optical calculations. A nearly direct bandgap is now observed. The role of confinement on the bandgap is studied by inserting additional silicon slabs into the supercell. It is shown that the bandgap decreases with increasing silicon slab thickness, as observed experimentally.

AA4.11
ATOMIC AND MOLECULAR HYDROGEN INTERACTION WITH GRAPHITE DEFECTS. Sara Letardi, Massimo Celino, Fabrizio Cleri, <u>Vittorio Rosato</u>, ENEA, Centro Ricerche Casaccia, Roma, ITALY.

The interaction between atomic and molecular hydrogen with perfect and defective graphite planes have been evaluated via first−principles molecular dynamics simulations. Defective graphite regions (with a single vacancy, a 5−7 ring pair) or partially folded graphite sheets have been used to mimic the relevant topological regions of a low-density disordered carbon structure, with the aim of understanding possible mechanisms of hydrogen trapping and their preferential sites.

AA4.12
DENSITY FUNCTIONAL BASED TIGHT BINDING STUDY OF IMPURITIES IN ULTRANANOCRYSTALLINE DIAMOND GRAIN BOUNDARIES. <u>Peter Zapol</u>, Larry A. Curtiss, Dieter M. Gruen, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; Michael Sternberg, Thomas Frauenheim, Department of Physics, University of Paderborn, Paderborn, GERMANY.

Nitrogen in ultrananocrystalline diamond (UNCD) films grown from hydrogen-poor plasmas leads to significant changes in morphology and electronic properties. In distinction from the conventional diamond growth process, hydrogen-poor argon plasmas are used to obtain diamond films with grain size as low as 3 to 15 nm. High-angle grain boundaries with rather high formation energy are believed to determine the properties of these films. Density-functional based tight-binding (DFTB) molecular dynamics simulations were performed for diamond high-energy high-angle (100) twist grain boundaries with N and H impurities to find out their effect on the grain boundary geometry and electronic structure. The $\Sigma13$ twist grain boundary was

found to adequately reproduce general properties of high-angle disordered grain boundaries. It is shown that N substitution in the grain boundaries is more favorable energetically than in the grain bulk by 0.5 to 2.5 eV/atom. We find that N in ultrananocrystalline diamond decreases the coordination of carbon atoms near the interface which leads to an increase in the density of carbon π and $\pi*$ electronic states. Hydrogen atoms tend to saturate dangling bonds and remove dangling bond related states from the band gap. Electronic levels associated with N and H atoms are discussed. Inverse participation ratios are calculated and localization of electrons is determined. Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

AA4.13
SIMULATING NON-EQUILIBRIUM TRANSPORT IN ELECTRONIC NANOSTRUCTURES. Peter P.F. Radkowski, III and Timothy D. Sands, Graduate Group in Applied Science and Technology University of California, Berkeley, CA.

The mechanisms for transporting heat and charge in electronic nanostructures are highly coupled. Analytical treatments of these highly nonequilibrium processes are hindered by the limitations imposed upon the Relaxation Time Approximation to the Boltzmann Transport Equation. An alternative approach to quantitatively describing coupled heat and charge currents is proposed. This discrete state approach combines the deterministic mechanisms of a traditional cellular automaton with the stochastic selection of scattering outcomes. An immediate advantage of this method relative to the Relaxation Time Approximation is that the nonequilibrium carrier distribution explicitly contributes to the scattering rate. This is important in the simulation of transport of carriers whose characteristic relaxation lengths exceed the nanoscale dimensions of the structure. In addition, the local nature of the simulation allows for an effective representation of defect scattering, including substitutional defects and interface states. Two case studies are presented. One case study considers the relative scattering effects imposed by polar and non-polar materials on an electron current in a confined nanostructure. The second case study considers the role of interface states on the phonon-mediated scattering of electrons. Implications are drawn regarding the simulation of hot electrons and phonons.

AA4.14
COMPUTER SIMULATION OF HYDRIDE PRECIPITATION IN BI-CRYSTALLINE ZIRCONIUM. X.Q. Ma, S.Q. Shi, C.H. Woo, The Hong Kong Polytechnic Univ, Dept of Mechanical Engineering, Hong Kong, HONG KONG; L.Q. Chen, The Pennsylvania State Univ, Dept of MS&E, PA.

The phase-field kinetic model is an effective model in describing the morphological evolution during phase transformation. It has been successfully applied to study the morphology of the second phase precipitation in many single crystalline materials. However, most of engineering materials are polycrystalline, therefore it is necessary to develop computational methods for polycrystalline materials. In this report, we present our preliminary study on γ-hydride precipitation in bi-crystalline zirconium. Zirconium and its alloys are important structural materials in nuclear industry. During services, these alloy gradually pickup hydrogen from environment. At a certain level of hydrogen concentration, hydride will form. Since the brittleness of the hydride, the mechanical properties of the material will degrade, and fracture initiation at hydrides may occur. It is believed that the critical conditions for fracture initiation at hydrides are controlled by the morphology and microstructure of hydride precipitates in the material. In our phase-field kinetic model, the structural and orientation difference of γ-hydride are represented by long-range structural order parameters (LRO). In the situation of single crystal zirconium, three LRO are needed to describe the orientation of the hydride. In bi-crystal zirconium, because of different crystal orientations of the two grains, six LRO were used, while in each grain only three LRO are non-zero. The driving force of hydride precipitation includes the following: the chemical free energy; the elastic accommodation energy; the interfacial energy between hydride and matrix; the free energy of grain boundary. Our 2D-simulation result shows that the grain boundary with high energy is preferred site for hydride nucleation, and when the two grains of the bicrystal have different orientation, the hydride precipitated in one grain will most likely stop grow at the grain boundary.

AA4.15
NEW POLARONIC-TYPE EXCITONS IN FERROELECTRIC OXIDES: NATURE AND EXPERIMENTAL MANIFESTATION. V.S. Vikhnin[1], R.I. Eglitis[2], E.A. Kotomin[2,3], S.E. Kapphan[2] and G. Borstel[2]. [1]A.F. Ioffe Physical Technical Institute, Saint-Petersburg, RUSSIA. [2]Universitaet Osnabrueck, Fachbereich Physik, Osnabrueck, GERMANY. [3]Institute of Solid State Physics, University of Latvia, Riga, LATVIA.

Charge Transfer Vibronic Excitons (CTVE) in ferroelectric oxides with mixed ionic-covalent type of chemical bonding are correlated pairs or/and triads of electronic and hole polarons. Ferroelectric oxides like KTN, SBN, PMN solid solutions, with properties important for applications, are good examples of such ionic-covalent bonding on the one hand, and rather strong charge transfer and not small vibronic interaction on the other. Here a review of recent theoretical and experimental investigations of new type excitons of polaronic type (CTVE) in ferroelectric oxides is presented. Computational analysis was performed by semi-empirical Hartree-Fock calculations using INDO method. A cluster approach was also used for description of phase transition aspects. Theory will be compared with luminescence, light absorption, and dielectric spectroscopy experiments. It is shown that: 1) CTVE and their clusters are autolocalized by strong self-consistent lattice distortion of vibronic origin; 2) a novel CTVE-phase is realized; 3) free CTVE obey triad structure, while the CTVE within clusters or CTVE-phase can be bipolarons; 4) recombination luminescence in $KTaO_3$ of free and trapped by oxygen vacancy CTVE are connected with *red* and *green* luminescence respectively; 5) CTVE clustering can explain an uncommon high temperature behavior of the fundamental absorption edge, as well as Cr-impurity effect in SBN. The studies confirm the CTVE concept for ferroelectric oxide materials.

AA4.16
FIRST PRINCIPLES SIMULATIONS OF PHASE STABILITY IN STOICHEOMETRIC AND DOPED LiMnO$_2$. Alex Landa, Chun-Chieh Chang, Prashant N. Kumta, Carnegie Mellon Univ., Dept. of MS&E, Pittsburgh, PA; Levente Vitos, Igor Abrikosov, Uppsala Univ., Physics Dept., Uppsala, SWEDEN.

There has been a significant interest in the area of lithiated transition metal oxides due to their use in lithium-ion batteries. In particular, the lithiated manganese oxide systems have drawn much attention because of the lower cost and more environmentally friendly nature of manganese as opposed to cobalt. However, the instability and the energetic of the transport reaction in LiMnO$_2$ system makes its use still very tenuous. Therefore, a prediction of the structural stability and the phase transitions in this system by means of modern first-principle theoretical simulation techniques is of considerable importance. In this presentation we report the results of our preliminary studies of LiMnO$_2$ in three most important crystal structures, the orthorhombic (Pmmn), the monoclinic (C2/m) and the rhombohedral (R$\bar{3}$m). Calculations were carried out by means of the recently developed exact muffin-tin orbital method (EMTO), and the effect of disorder was included within the coherent potential approximation (CPA). For ordered compound we reproduced the correct ground state, the antiferromagnetic Pmmn. The effect of doping was considered with the aim to predict an alloying element that stabilize the layered structure.
A.L., C.C. and P.N.K. gratefully acknowledge the support of Changs Ascending, Taiwan, DARPA and NSF for this research. I.A.A. and L.V. are grateful to the Swedish Natural Science Research Council and the Swedish Foundation for Strategic Research for financial support.

AA4.17
AUGER ELECTRON SPECTROSCOPY AND THE CALCULATION OF THE AUGER RECOMBINATION COEFFICIENT: IMPLEMENTATION WITHIN THE FLAPW CODE. S. Picozzi, A. Continenza, INFM - Dip. Fisica, Univ. L'Aquila, L'Aquila, ITALY; R. Asahi, Toyota Central R&D Labs., Inc., Nagakute, Aichi , JAPAN; W. Mannstadt, Fachbereich Physik, Philipps-Univeritat Marburg, Marburg, GERMANY; A.J. Freeman, Dept. of Phys. and Astron., Northwestern Univ., Evanston, IL; C.B. Geller, Bettis Atomic Power Laboratory, West Mifflin, PA.

We present ab-initio calculations of the $e-e-h$ (electron-electron-hole) Auger recombination coefficients in n-type doped semiconductors. The decay rate of the minority carriers (in this case, holes) are obtained from Fermi's golden rule (second order perturbation theory) where the relevant matrix elements take into account: i.) a Debye screening potential (whose screening length depends on temperature and carrier density); ii.) exchange as well as direct Coulomb contributions; iii.) electron-phonon coupling (according to Frohlich's Hamiltonian). The population of the states involved in the Auger transitions is fully considered through the Fermi-Dirac distribution function. The multiple integration of the Brillouin zone required in the evaluation of the Auger recombination rate is performed according to the scheme proposed by Sano and Yoshii[1]. The formalism has been implemented within the FLAPW[2]. code, with exact evaluation of the overlap matrix elements and of the screened Coulomb interaction (taking into account the q-dependence of the dielectric function). In order to overcome the shortcomings of the local density approach the screened-exchange formalism [3] was used to evaluate eigenvalues and wavefunctions for narrow gap semiconductors and to compare results

with available experimental data on InAs, InSb and GaAs.

[1] N. Sano and A. Yoshii, Phys. Rev. B **45**, 4171 (1992).
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AA4.18
COMPUTER MODELLING FOR SINGLE AND INTERACTING Li IMPURITIES IN $KTaO_3$. <u>R.I. Eglitis</u>, A.V. Postnikov and G. Borstel, University of Osnabrueck, Fachbereich Physik, Osnabrueck, GERMANY.

As was discovered by Yacoby and Just, Li ion substituting K in $KTaO_3$ gets spontaneously displaced off-center along one of six [100] directions. Previous theoretical studies of Li impurity in $KTaO_3$ have been either limited to small systems, or drastically influenced by the choice of parameters dealing with point charges or point dipoles, or those used e.g. in the shell model. In order to close the gap between empirical models and accurate *ab initio* schemes, we analyzed the relaxation of near neighbors to the Li impurity, and the impact of this relaxation on the reorientational energy barriers using the intermediate neglect of differential overlap (INDO) method. Moreover, we studied the effect of Li-Li interaction at different distances on the energetics and lattice relaxation, using the supercells containing up to 270 atoms. The Li-Li interaction energy as a function of Li-Li distance and orientation are calculated, including the lattice relaxation around Li-Li impurities. The supercell size effects are considered by comparing the results for $3 \times 3 \times 3$ and $6 \times 3 \times 3$ extended $KTaO_3$ supercells, which contain 135 and 270 atoms respectively. According to our calculations, the Li-Li interaction energies are smaller and less long-ranged than it was estimated from earlier shell model calculations.

AA4.19
CALCULATION OF EFFECTIVE BEHAVIOR IN FERRO-MAGNETIC RARE-EARTH-IRON ALLOYS FILLED FERROELECTRIC POLYMERS. <u>C.-W. Nan</u>, Department of MS&E, Tsinghua University, Beijing, CHINA.

Magnetoelectric effect characterized by a magnetic field inducing the electric polarization or an electric field inducing the magnetization have been known for over one century. So far, the magnetoelectric effect has been observed in about fifteen different crystal families (e.g., Cr_2O_3 and phosphates) and ferrite/piezoelectric ceramic composites. To be technologically viable, magnetoelectric materials must exhibit large magnetoelectric effect. However, among these known magnetoelectric materials which are brittle, particularly strong magnetoelectric effects, as initially dreamed of, have not yet been found. In this work, coupled magnetic-mechanical-electric effects involving linearly and nonlinearly coupling interactions in ferroic composites are investigated using a Green's function technique. We use the theory to suggest possible giant magnetoelectric effect in a ferroelectric poly(vinylidene fluoride-trifluorethylene) copolymer filled by giant magnetostrictive rare-earth-iron alloy, which is markedly larger than that in the best known magnetoelectric materials. In the meantime, the flexible composite is expected to exhibit large magnetostriction.

AA4.20
ANTISITE DEFECTS MODELING FOR SOME II-IV-V_2 - CRYSTALS. <u>Valeriy G. Voevodin</u>, Olga V. Voevodina, Siberian Physico-Technical Institute, Tomsk, RUSSIA.

There is no complete consent in an estimation of influence of antisite defects on properties of II-IV-V_2-crystals. At the same time there are the reasons to suppose that just these defects are responsible for an optical absorption in the transparency region of these crystals perspective for use in mid-IR nonlinear optics. The aim of the work was to obtain data on thermodynamic parameters and equilibrium concentrations of antisite defects as a stage of semi-empirical definition of the II-IV-V_2-crystals homogeneity regions. For equilibrium concentrations calculation a quasi-chemical model of antisite defects formation with allowance for Schottky and Frenkel defects was generated. Thermodynamic parameters were calculated based on Weiser's technique. Pauling's approach was used to estimate modification of a potential energy of a system owing to change of a chemical nature of atom in the site because of antisite formation. Using available experimental data and some semi-empirical approaches, the elastic constants and the energy modification because of a lattice strain were defined. Enthalpy of antisite defects formation as a sum of a chemical and a strain components was estimated. The neutral antisite defects equilibrium concentrations are represented on figures as the functions of liquidus temperatures and Gibbs triangle coordinates. Used models, approaches and initial parameters give the following. From six considered types of defects (A_B, A_C, B_C, C_A, C_B, B_A) the greatest concentration values about 10^{19} cm^{-3}) and, therefore, the greatest influence on properties of the crystals have defects connected with disorder in a cathion sublattice (A_B, B_A). The

problem of distinction of results obtained with use of different calculation models and approaches is touched upon. For $CdGeAs_2$ and $ZnGeP_2$ the calculation is compared with the results of the experiment on annealing in a vapour of volatile components.

AA4.21
CLASSICAL MOLECULAR-DYNAMICS STUDY OF ION-BOMBARDMENT-INDUCED DENSIFICATION OF SILICA THIN FILMS. <u>Alexis Lefèvre</u>, Laurent J. Lewis, Dept of Physics and Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), Université de Montréal, Montreal, Quebec, CANADA; Ludvik Martinu, Michael R. Wertheimer, Groupe de Recherche en Physique et Technologie des Couches Minces (GCM) and Engineering Physics Dept, École Polytechnique, Montreal, CANADA.

Ion-assisted processing of materials has become an efficient and widespread technique for thin-film fabrication at low deposition temperatures, as well as for controling properties such as film stress, defect concentration and packing density. However, the parameters − basically ion energy and flux − that lead to optimal film properties are difficult to determine. In particular, for amorphous solids, conventional characterisation methods probe structural modifications only over a limited length-scale. Therefore, a broad range of experiments is needed to provide adequate atomic-scale data to assess ion-beam effects. In this work, classical molecular-dynamics is used to investigate the densification process of amorphous silica thin-films deposited in a (simplified) ion-beam assisted deposition (IBAD) scenario. The atoms are assumed to interact through a three-body potential, where silicon is tetrahedrally coordinated to four oxygen atoms. Our model focuses on the roles played by collisions of incident SiO_2 particles on the densification process and on the annihilation/creation of defects at low initial energies (30 eV). Bond lengths, bond angle distributions, density, ring statistics and static structure factors of the grown layers are studied as a function of the flux ratio of energetic (30 eV) to thermal (1 eV) incident particles. We find that there exists an energy interval − about 10−15 eV per condensing SiO_2 − for which the growth results in a dense, low-defect concentration, low-stress amorphous structure, in agreement with the results of low-energy ion-beam experiments. We also find that densification proceeds through significant changes in the network topology at an intermediate length-scale (4-10 Å), as determined from an analysis of the ring structure, and manifest in an increase in amplitude of the first sharp diffraction peak. This leaves the structural "building block" of the network, the $Si(O_{1/2})_4$ tetrahedron, essentially unaltered.

AA4.22
IDENTIFICATION OF THE RELAXATION AND DIFFUSION PATHS IN MODELS OF AMORPHOUS SEMICONDUCTOR: AN AB-INITIO-ART APPROACH. <u>Yinglei Song</u> and Normand Mousseau, Ohio State University, OH.

An accurate description of relaxation and diffusion mechanisms is crucial to our understanding of the structural and dynamical properties of amorphous semiconductors and alloys. On the numerical side, a solution to this problem requires both an appropriate method for identifying these mechanisms and an interaction that can describe correctly the forces and energies far away from the equilibrium configuration. This can be achieved by combining the activation-relaxation technique (ART) with *ab-initio* calculations. ART, which has already been applied to a wide range of materials, is a method specifically designed to generate activated mechanisms in disordered and complex materials. We integrate this method into the local-basis self-consistent *ab-initio* SIESTA code of Ordejón *et al.*[1], providing a stable and efficient ab-initio-ART method. We discuss here some details of the integration of ART to the SIESTA code and present some preliminary calculations of activated mechanisms in *a*-Si using this approach.

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AA4.23
THE PROPERTIES OF THE ISOLATED ADSORBATE BY THE EMBEDDING METHOD. <u>Gian Paolo Brivio</u>, Mario Italo Trioni, Nicola Bonini, Universita' di Milano-Bicocca, Dipartimento di Scienza dei Materiali, Milano, ITALY.

Several surface science phenomena, for example the sticking process in the dynamics of adsorption or the tunnelling current of an adatom in a STM experiment, require the knowledge of the adiabatic electronic properties of a single isolated adsorbate interacting with a semi-infinite solid. Though ab initio calculations of adsorption are currently performed with the slab or supercell methods aiming at a very low coverage limit, neither of them can describe the correct boundary conditions of such systems and their continuum spectrum of

electronic states. On the other hand, the embedding method for the isolated adsorbate fulfils both mentioned properties. In such method, the Kohn-Sham equation for the Green function is solved self-consistently in the volume containing the impurity, and the solution is matched to the extended substrate one by an effective embedding potential. In this paper, after presenting the main equations of the embedding approach, we shall discuss new results for adsorption on simple metals, for which the detailed spectral analysis permitted by this method is essential. Namely: a) the residual resistivity ρ and the magnetic moment of $3d$ adatoms from a spin dependent calculation. In the former case a new behavior of ρ, as function of the adatom surface distance, is predicted. And we stress that ρ can only be computed when a truly semi-infinite solid is taken into account, while any translationally invariant method gives a vanishing ρ; b) The Auger CCV spectra induced by an impurity atom, located either in bulk, or just inside the surface or adsorbed on the surface. While the bulk results well reproduce the experimental ones, those calculated for an atom near the surface display different features to be used for the surface characterisation of such impurities.

AA4.24
MATERIAL PARAMETERS FOR ANALYTICAL AND NUMERICAL MODELLING OF STRAINED SiGe HETERO-STRUCTURE DEVICES WITH EMPHASIS ON HBTS.
Suresh C. Jain, Anupama Mehra, Stefaan Decoutere, Herman Maes, IMEC, Leuven, BELGIUM; Magnus Willander, Chalmers University of Technology, Department of Physics, Göteborg, SWEDEN.

SiGe heterostructures have acquired great importance in the recent years [1]. SiGe HBTs show better DC and AC characteristics than Si BJTs. SiGe quantum wires and quantum dots are used in optical devices. Modelling the performance of SiGe heterostructures require reliable values of effective masses of the charge carriers, Fermi energy and bandgap of the strained and doped SiGe. Both strain and doping reduce the bandgap considerably and increase the Fermi energy. Since valence band of Si and SiGe is warped and highly non-parabolic, values of the effective masses for p type SiGe depend on both dopant concentration and on the strain induced by Ge. We present detailed calculations of effective masses, bandgap reduction, and Fermi energy of strained and p-doped SiGe in this paper. The method we use is described in the book by Jain [1]. The calculations have been made for Ge concentrations in the range 0 to 30% and boron concentration in the range 1×10^{18} cm^{-3} to 3×10^{20} cm^{-3}. The results are presented in the form of graphs and as empirical expressions fitted to the calculated curves. The expressions are suitable for use in computer codes and for modelling device performance. To validate our calculated values we model the performance of the SiGe HBTs and compare the calculated and experimental results. The calculated values agree well with the experimental results. The method that we use can be applied to model other strained layer devices e.g. GaInAs heterostructures.
[1] S.C. Jain, A.H. Harker and R.A. Cowley, Philos. Mag. A 75 (6), 1461-1515 (1997); S.C. Jain, *Germanium−Silicon Strained Layers and Heterostructures*, Advances in Electronics and Electron Physics series, (Supplement 24) (Academic Press, Boston 1994); S.C. Jain, K. Pinardi, M. Willander, A. Atkinson, H.E. Maes, and R. Van Overstraeten, Semicond. Sci. Technol. 12, 1507 (1997); J.D. Cressler, IEEE-Transactions-on-Microwave-Theory-and-Techniques 46, 572-89 (1998); R. Shivaram, G. Niu, J.D. Cressler and E.T. Croke, Solid State Electronics 44, 559-63 (2000).

AA4.25
PREDICTING TRENDS IN METAL/CERAMIC INTERFACE ADHESION VIA FIRST-PRINCIPLES SIMULATION.
Donald J. Siegel, Univ. of Illinois at Urbana-Champaign, Dept of Physics, Urbana, IL; Louis G. HectorJr., General Motors Research and Development and Planning, Materials and Processes Lab, Warren, MI; James B. Adams, Arizona State Univ, Chemical and Materials Engeneering Dept, Tempe, AZ.

Metal/ceramic interfaces are essential for applications ranging from catalysis supports to microchip packaging. They present an interesting example of how atomic-scale phenomena (i.e., atomic and electronic structure) can directly effect macroscopic properties such as adhesion, wetting, and epitaxial growth. Recently, substantial progress has been made in understanding the adhesion properties of a range of metal overlayers on a small number of ceramic substrates. However, much less is known about how the properties of the ceramic affect adhesion. We present the first systematic study of variations in bonding, adhesion, and interface structure for a range of ceramics interfaced with Aluminum. We consider several metal-oxide ceramics (α-Me$_2$O$_3$, Me = Al, Cr, Fe) along with selected carbides (WC) and nitrides.

AA4.26
MODELING OF CHLORINE RELATED DEFECTS AND COMPLEXES IN ZnMgSe AND ZnCrSe SEMICONDUCTORS.

Yaxiang Yang, Leonid Muratov, Bernard R. Cooper, and Thomas H. Myers, West Virginia University, Dept of Physics, Morgantown, WV.

Because of the potential of optoelectronic applications, there is great interest in alerting the electronic and consequent optical properties of wide-band-gap semiconductors such as ZnSe and its alloys $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Cr_xSe$ (random alloys with a portion of the zinc replaced by magnesium or chromium) through the use of selected additives (dopants). Chlorine has turned out to be the most successful n-type dopant in ZnSe. In computations involving these materials there is a complication associated with the semi-core Zn $3d$ electrons that impairs the usual pseudopotential approach. Therefore we have used ab-initio full potential LMTO calculations to model native defects and chlorine-impurity-related defects and defect complexes in ZnSe, $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Cr_xSe$. We found that while the lattice relaxation around Mg and Cl atoms is not significant (nearest selenium atoms move less than 4% of the next-neighbor distance in both cases), the effects of lattice relaxation around the vacancies are much stronger (up 20% for the double positive Se vacancy). We showed that there is a strong tendency for formation of a defect complex between a chlorine impurity at the Se site and a vacancy at the neighboring Zn site. The formation energy of this complex decreases in the presence of magnesium. Our preliminary results show that the complex formation energy is 1.8eV lower in $Zn_{0.4}Mg_{0.1}Se_{0.5}$ than in pure ZnSe. A similar study of the ZnCrSe alloy is underway. In our calculations we used 32 and 64 atom unit cells. Lattice relaxation around defects was calculated using Hellman-Feynman forces. Use of multiple kappas and energy windows ensured a sufficiently rich basis. The results presented are compared with the most recent experiment results.

AA4.27
PLANE WAVE PSEUDOPOTENTIAL STUDY OF POINT DEFECTS IN URANIUM DIOXIDE. J.P. Crocombette, Section de Recherches de Métallurgie Physique, Commissariat à l'Energie Atomique Saclay, FRANCE; F. Jollet, T.N. Le, Centre d'Etudes de Bruyères le Châtel Commissariat à l'Energie Atomique, FRANCE; Th. Petit, Service d'Etudes et de Simulation du Comportement du Combustible, Centre d'Etudes de Cadarache, Commissariat à l'Energie Atomique, FRANCE.

A study on uranium and oxygen point defects in uranium dioxide using the ab initio plane wave pseudopotential method in the Local Density Approximation of the Density Functional Theoretical framework is presented. Norm conserving pseudopotentials are used to describe oxygen and uranium atoms. The uranium pseudopotential is specifically described and its validity is ascertained thanks to a detailed structural study of uranium dioxide and of three phases of metallic uranium (fcc, bcc and α). The free energies of formation of both intrinsic (Frenkel pairs and Schottky defect) and extrinsic (single vacancies or interstitials) defects are calculated. They are analyzed in the framework of the point defect model which is commonly used to assess defect concentrations in uranium dioxide and their variation with stoechiometry. From the obtained results, the ability of the point defect model to accurately reproduce defect concentrations in uranium dioxide is discussed.

AA4.28
ISOSTRESS MOLECULAR-DYNAMICS STUDY OF ELASTIC INSTABILITIES IN CRYSTALS. Jianhua Zhao, Dimitrios Maroudas, Frederick Milstein, Univ of California, Santa Barbara, CA.

Mechanical, geometric, and kinetic characteristics of crystal instabilities are revealed via isostress molecular-dynamics (MD) simulations according to the Lagrangian formulation of Parrinello and Rahman. Particular attention is given to the topics of (i) elastic instabilities at points of bifurcation (as predicted by elastic stability criteria of Hill and Milstein), (ii) post bifurcation phenomena leading to phase change or material failure, and (iii) crystal symmetry, which strongly influences the mechanical response and bifurcation behavior. Fluctuation formulae are used for computation of elastic moduli employed in assessments of elastic stability. Interatomic interactions are expressed by pair potentials that have been fit to experimental elastic moduli of metals. No special significance is placed on the specific forms of interatomic potentials, since our main concern is qualitative mechanistic understanding of stress-induced elastic instabilities in crystals. Although, the potentials do, in fact, yield large strain behavior in excellent qualitative agreement with more rigorous atomic models and experiment. The MD calculations are made over wide ranges of temperature and stress, for various modes of loading. Examples of computational results include isothermal, isostress, transformations from bcc to hcp structures under hydrostatic pressure and from fcc to hcp structures under uniaxial stress. Under hydrostatic pressure and [100] tensile loading, the transitions are found to originate with thermally activated elastic instabilities that are associated with vanishing or diminishing shear moduli. Various other modes of instability are also observed.

AA4.29
THEORETICAL MECHANICAL RESPONSE AND ELASTIC
STABILITY OF CUBIC METALS AT FINITE STRAIN IN THE
EMBEDDED-ATOM METHOD. Somchart Chantasiriwan,
<u>Frederick Milstein</u>, Univ of California, 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
transformation 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.

SESSION AA5: MULTI-RESOLUTION AND
MULTI-SCALE METHODS; MICROSTRUCTURAL
EVOLUTION
Chair: Ronald E. Miller
Thursday Morning, April 19, 2001
Nob Hill C/D (Marriott)

8:30 AM *AA5.1
APPLICATIONS OF REAL-TIME MULTIRESOLUTION
ANALYSIS FOR MOLECULAR DYNAMICS SIMULATIONS OF
INFREQUENT EVENTS. <u>David A. Richie</u>, Jeongnim Kim and John
W. Wilkins, Department of Physics, Ohio State University, Columbus
OH.

The simulation of defect dynamics (e.g., transient enhanced diffusion
of boron in the presence of silicon interstitials) is a technologically
relevant challenge for computational materials science. The dynamics
of defect structures in bulk unfolds as a sequence of thermally induced
structural transitions. Identifying and characterizing reaction paths,
as well as extracting dynamical quantities (e.g., diffusion constants) is
important for modeling the macroscopic properties of real materials.
Applying real-time multiresolution analysis (RTMRA) to various
dynamical quantities (e.g., atomic positions, local energies) using
simple Haar wavelets, we have developed a computationally cheap
data compression scheme to handle the massive data sets generated in
molecular dynamics (MD) simulations; data storage has been reduced
hundredfold with no loss of relevant information.
More importantly, the same RTMRA techniques are developed into a
sophisticated event detection scheme capable of solving three major
challenges to multiscale MD simulations, specifically, (1) identifying
metastable structures against the background of strong thermal
vibrations, (2) detecting infrequent events, e.g., structural transitions,
in the presence of strong thermal noise, and (3) accurately identifying
transition times to further enhance recently emerging MD acceleration
techniques.[1]
*Supported by NSF and DOE with computational resources of OSC,
NCSA and NERSC.
[1] A.F. Voter, Phys. Rev. Lett. **78**, 3908 (1997); Phys. Rev. B **57**,
R13985 (1998).

9:00 AM AA5.2
AN INTEGRATED MULTISCALE-MULTIPHYSICS MODEL OF
REACTOR PRESSURE VESSEL EMBRITTLEMENT.
<u>G. Robert Odette</u>, Dept. of Mechanical and Environmental
Engineering, University of California, Santa Barbara, CA; Roger E.
Stoller, Oak Ridge National Laboratory, Oak Ridge, TN; Brian D.
Wirth, Lawrence Livermore National Laboratory, Livermore, CA.

The continued safe operation of nuclear reactors and their potential
for lifetime extension depends on ensuring reactor pressure vessel
integrity. Reactor pressure vessels and structural materials used in
nuclear energy applications are exposed to intense neutron fields that
create atomic displacements and ultimately change material
properties. The physical processes involved in radiation damage are
inherently multiscale, spanning more than 15 orders of magnitude in
length and 24 orders of magnitude in time. This paper reports our
progress in developing an integrated, multiscale-multiphysics (MSMP)
model of radiation damage for the prediction of reactor pressure vessel
embrittlement. The key features of the fully integrated MSMP model
include: i) combined molecular dynamics and kinetic lattice Monte
Carlo simulations of cascade defect production and cascade aging to
produce cross-sections for vacancy, self-interstitial and vacancy-solute
cluster size classes for times on the order of seconds; ii) an integrated
reaction rate theory and thermodynamic code to predict the evolution
of nanostructural and nanochemical features for times on the order of
decades; iii) a micromechanics model to calculate the resulting
mechanical property changes.
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 and the U.S. Nuclear Regulatory Commission
under Contract No. NRC-04-94-049.

9:15 AM AA5.3
OBJECT-ORIENTED MULTISCALE MATERIALS SIMULATOR.
<u>Jeongnim Kim</u>, David A. Richie, John W. Wilkins, Ohio State
University, Dept. of Physics, Columbus, OH; Arthur F. Voter, Los
Alamos National Laboratory, Los Alamos, NM.

Atomistic simulations are crucial in identifying rate-limiting physical
processes and relevant energy and time scales to enhance the
predictive power of macroscopic modeling tools. Combinations of
improved classical and tight-binding Hamiltonians and recently
emerging algorithms capable of treating large length and time scales
provide opportunities to study the fundamental complexity of real
materials. We have developed OHMMS (Ohio Multiscale Material
Simulator) as an object-oriented framework for atomistic simulations
for a wide range materials science problems, reaching the length scale
of nanotechnology and the time scale of physical processes. Highlights
of the design principles and implementation include the integration of
different algorithms and the data structure requirements for atomistic
simulations. As an application, we discuss the growth of Si-interstitial
clusters studied using the parallel replica method[1] with classical and
tight-binding potentials.[2] The structural and dynamical properties of
Si-interstitial defects are key to predicting the temporal evolution of
dopant profiles in Si-based devices. We utilize the parallel replica
method to simulate infrequent events such as the diffusion of defects
without a prior knowledge of the complex dynamical system. The
growth mechanisms are modeled by the diffusion of an interstitial and
its capture by an existing interstitial cluster. The subsequent
structural transformations and diffusion of interstitial clusters are
simulated at various temperatures.
Supported by NSF and DOE with computational resources of OSC,
NCSA and NERSC.
[1] A.F. Voter, Phys. Rev. B **57**, R13985 (1998).
[2] T. Lenosky *et al.*, Phys. Rev. B **55**, 1528 (1997); Highly optimized
empirical potential model of silicon, T. Lenosky *et al.*, to be published
in Model. Simul. Mater. Sci. Eng.

9:30 AM *AA5.4
A MOLECULAR DYNAMICS APPROACH TO THE
QUASICONTINUUM METHOD. <u>Jens Jörgen Mortensen</u>, Jesper
Christiansen, Jakob Schiötz, Karsten W. Jacobsen, CAMP, Dept of
Physics, Tech Univ of Denmark, Lyngby, DENMARK; Chuin-Shan
Chen, Christopher R. Myers, Cornell Theory Center, Cornell
University, Ithaca, NY; Thierry Cretegny, Andrew Dolgert, James P.
Sethna, Lab of Atomic and Solid State Physics, Cornell University,
Ithaca, NY.

We have implemented the quasicontinuum method which combines an
atomistic description of materials with a finite elements description.
In our case the atomistic description is an effective medium theory
potential, and the finite elements consist of tetrahedra with the
corners at atomic positions. Even for such a simple scheme there are
many technical issues, on which this presentation will focus, such as:
dynamic remeshing of the finite elements mesh (refinement and
coarsening) and the description of surfaces with reduced number of
degrees of freedom. Our implementation of the method is built on top
of an existing molecular dynamics code in such a way that existing
algorithms for force calculation and dynamics can be reused. Also
parallelization of the quasicontinuum code is taken care of in the
original molecular dynamics code. Applications of the method to
dislocations intersecting (111) surfaces in silver will be shown.

10:30 AM AA5.5
COMBINATION OF CONTINUUM AND ATOMISTIC
APPROACHES FOR THE STUDY OF DISLOCATION
NUCLEATION FROM ATOMIC SIZE SURFACE DEFECTS.
<u>Sandrine Brochard</u>, Pierre Beauchamp, Jean Grilhé, Laboratoire de
Métallurgie Physique, Futuroscope, FRANCE.

We have studied the nucleation of dislocations from atomic size surface defects: steps of different geometry and groove. By performing static atomistic simulations with semi-empirical potentials on f.c.c. crystals, it has been shown unambiguously that the surface defects are privileged site for dislocation nucleation: for a stress level well below the theoretical shear strength, dislocations are nucleated at the defect and glide in one of the dense plane in zone with the step. Before dislocation nucleation, an elastic shear, localized in the plane where nucleation will occur, is observed. The real dislocation forms when this localized shear reaches, at its maximum, the value where the crystal gets mechanically unstable, that is for a displacement of $\mathbf{b}/4$, $\mathbf{b}$ being the Burgers vector of the dislocation nucleated. This is comparable to the state defined by Rice as incipient dislocation at a crack tip, although quantitatively different. In order to explain the appearance of the localized elastic shear, the stress field in the neighborhood of the surface defect in a stressed crystal has been evaluated, in the frame of elasticity. This analysis shows that in the groove case the stress concentration induces a shear stress in the glide planes in zone with the groove direction, which can be directly linked to the elastic shear observed during the simulations. On the contrary, in the step case, elasticity shows that there is no local shear stress in the glide planes in zone with the step. For the step case, the origin of the shear is more indirectly linked to the stress concentration: by increasing the interplanar separation, the local stress makes shear easier in some planes. The assumption of an effect of the interplanar distance on the shear localization has been checked using an analysis based on the Frenkel model.

10:45 AM <u>AA5.6</u>
MULTI-SCALE SIMULATIONS OF SILICON ETCHING BY HALIDES: EFFECTS OF SURFACE REACTION RATES. <u>Matthias Kratzer</u>, Werner Steinhögl, Alfred Kersch, Tanja Sachse, Volker Höink, Infineon Technologies AG, MP TI SIM, München, GERMANY.

Simulation methods are increasingly used in microelectronics industry for the understanding and the optimization of surface patterning processes. We have investigated the reactive ion etching (RIE) of silicon by halides which is one of the key process steps in VLSI manufacturing. The feature evolution during etching is modeled using a two-dimensional cell based Monte-Carlo feature scale simulator. As input, the simulator requires the fluxes, the energy distributions, and the angular distributions of the wafer-incident particles as well as the relevant surface reaction rates. Thus, we have first applied a hybrid plasma sheath simulator[1] to get these properties of the impinging particles. The surface reaction rates, on the other hand, have been calculated separately by a molecular dynamics simulator using the Stillinger-Weber representation of the interatomic potential[2]. Parameters for the interaction of fluorine and chlorine with silicon have been taken from literature[3,4]. The Stillinger-Weber representation of a bromine and a silicon-bromine potential has additionally been developed since it was not yet available. Both potentials have been calibrated with $ab-initio$ calculations of molecule properties as well as cluster properties. Based on this model hierarchy of different length scales (from reactor scale down to atomic scale) we present calculated results for the etching of silicon by fluorine, chlorine, and bromine and discuss qualitative and quantitative differences of the feature evolution as a consequence of the different etching species. It turns out that the etch characteristics are strongly influenced by the particular reaction yield functions of the etching species.
[1] M. Kratzer et al.: submitted to J. Appl. Phys.
[2] F.H. Stillinger and T.A. Weber: Phys. Rev. B 31(8), 5262, 1985.
[3] P.C. Weakliem and E.A. Carter: J. Chem. Phys. 98(1), 737, 1993.
[4] H. Feil, J. Dieleman and B.J. Garrison: J. Appl. Phys. 74(2), 1303, 1993.

11:00 AM <u>*AA5.7</u>
IMPURITY EFFECTS IN MICROSTRUCTURAL EVOLUTION. <u>David J. Srolovitz</u>, Princeton University, Princeton, NJ.

The motion of grain boundaries and dislocations can be profoundly impacted by the presence of impurities, even when the impurity concentrations are extremely low. These effects become more pronounced as the impurity diffusivity increases. In this talk, I will discuss the determination of the heats of segregation to grain boundaries and dislocations via atomistic simulations, the force-velocity relations for grain boundaries and dislocations in the presence of diffusing impurities via kinetic Monte Carlo simulations and microstructural evolution via grain growth and dislocation patterning. Diffusing impurities give rise to striking non-linearities in defect mobilities, often changing mobilities by orders of magnitude relative to those in pure materials. The dimensionality of the defects is shown to be important. Based on the kinetic Monte Carlo results, we derive effective defect-defect interactions that can be used in large scale microstructural evolution simulations, in which the

concentration fields are not tracked. Finally, we examine the effects of impurities on non-steady defect motion.

11:30 AM <u>AA5.8</u>
LINKING ATOMIC SIMULATIONS TO MESOSCALE MODELS FOR MICROSTRUCTURAL EVOLUTION IN POLYCRYSTALS. Gregory N. Hassold, Department of Science and Mathematics, Kettering University, Flint, MI; Elizabeth A. Holm, Materials and Process Modeling, Sandia National Laboratories, Albuquerque, NM; Moneesh Upmanyu and David J. Srolovitz, Princeton Materials Institute, Princeton University, Princeton, NJ.

Grain boundary mobility and free energy influence microstructural evolution, texture development, and materials properties. Yet due to the large phase space involved, experimental characterization of boundary properties is minimal. In this study, molecular dynamics simulations of two-dimensional hairpin bicrystals were used to determine boundary energy and mobility as a function of crystallographic misorientation (tilt angle). These data provided the grain boundary properties used in mesoscale simulations of polycrystalline grain growth in tilt boundary systems. Regardless of their mobility, low energy boundaries are found to proliferate during grain growth, altering the microstructure and evolution kinetics dramatically. In contrast, when boundaries have uniform energy, anisotropic mobility does not alter the distribution of boundary types, the microstructure, or the kinetics of grain growth. Boundary energy, and not mobility, governs microstructural morphology and evolution. However, the strong preference for low energy boundaries is unique to systems with two-dimensional crystallography, such as tilt boundaries. In systems with full three-dimensional crystallography, specific misorientations are much harder to achieve, and low energy boundaries show much less enhancement during grain growth.

11:45 AM <u>AA5.9</u>
MODELING MACROSCOPIC ZEOLITE MEMBRANES FROM ATOMISTIC PRINCIPLES. <u>David S. Sholl</u> and Anastasios Skoulidas, Dept. of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA.

Zeolites are attractive as membrane materials in part because of their highly ordered pore structures. Current zeolite membranes are polycrystalline films 10-100 microns thick, far too large to be directly modeled using atomistic techniques. We have developed a multi-scale approach that provides predictions of macroscopic membrane performance using only the zeolite crystal structure and interatomic potentials as input. This approach relies on using atomistic Monte Carlo and Molecular Dynamics simulations to parameterize a continuum description of molecular transport through the membrane. We will describe extensive comparisons between our predictions and experimental measurements of methane and tetraflouromethane through silicalite membranes. Our study also provides information on the long-standing controversies surrounding experimental measurements of Fickian and tracer diffusivities in zeolites by giving an extensive set of systems where we compute both of these quantities simultaneously. We will describe how our methods can be generalized to other applications of molecular transport in nanoporous materials and how we are using our methods to screen candidate materials for high temperature gas separations.

SESSION AA6: NEW METHODS FOR MATERIALS
SIMULATION
Chair: Robert O. Jones
Thursday Afternoon, April 19, 2001
Nob Hill C/D (Marriott)

1:30 PM <u>*AA6.1</u>
DIELECTRIC POLARIZATION OF MATERIALS: A MODERN VIEW. <u>Raffaele Resta</u>, Università di Trieste, INFM and Dipartimento di Fisica Teorica, Trieste, ITALY.

The concept of macroscopic polarization is the basic one in the electrostatics of dielectric materials: but for many years this concept has evaded even a precise microscopic definition, and has severely challenged quantum−mechanical calculations. Textbooks usually visualize a polarized dielectric as an assembly of discrete microscopic polarization elements, à la Clausius−Mossotti. From this viewpoint, the macroscopic polarization looks like trivial matter. Unfortunately, the electronic distribution inside a real material is continuous, and often quite delocalized: the partition of the valence charge into localized contributions is highly nonunique. The concept of dielectric polarization in condensed matter has undergone a genuine revolution in recent years (1992 onwards). It is now pretty clear that—contrary to a widespread incorrect belief—macroscopic polarization has nothing to do with the periodic charge distribution of the polarized crystal: the former is essentially a property of the *phase* of the electronic wavefunction, while the latter is a property of its *modulus*.

An outline of the modern theory, based on a Berry phase, will be presented. Experiments invariably address polarization derivatives (permittivity, piezoelectricity, pyroelectricity,...) or polarization differences (ferroelectricity), and these differences are measured as an integrated electrical current. The modern theory addresses this same current, which is cast in terms of the phase of the electronic wavefunction. I will then present a few implementations of this theory in a first−principle framework, using state−of−the−art ingredients. Applications have concerned various phenomena (ferroelectricity, piezoelectricity, and lattice dynamics) in several materials. Actual calculations are in spectacular agreement with experiments, and have provided thorough understanding of the behavior of dielectric materials.

2:00 PM AA6.2
AB-INITIO CALCULATION OF THE OPTICAL PROPERTIES OF BN(110) SURFACE. Giancarlo Cappellini, Guido Satta, INFM-Dept. of Physics, University of Cagliari, Cagliari, ITALY; Maurizia Palummo, Giovanni Onida, INFM-Dept. of Physics, University of Rome "Tor Vergata", Rome, ITALY.

We compute the optical properties of the (110) surface of cubic Boron Nitride within first-principle DFT-LDA scheme. Starting from the surface electronic structure calculation, the imaginary part of the theoretical dielectric function and the Reflectance Anisotropy Spectrum (RAS) have been calculated [1]. The results are analyzed in comparison with those obtained by some of the authors for the better known Gallium Arsenide (110) surface [2]. This permits us to study in details the influence of ionicity on the surface relaxation, the surface states character, and the surface optical spectra [2,3]. Detailed comparisons with existing data relative to the surface under present study [3,4] and to the GaN(110) surface are also given [5].
[1] O. Pulci, G. Onida, R. Del Sole, A.I. Shkrebtii, Phys.Rev.B Vol.58, 1922 (1998).
[2] A. Filippetti, V. Fiorentini, G. Cappellini, A. Bosin, Phys. Rev. B Vol.59, 8026 (1999).
[3] U. Grossner, J. Furthmüller, Phys. Rev. B Vol.58, 1722 (1998).
[4] R. Miotto, G.P. Srivastava, A.C. Ferraz, Surf. Science Vol.426,75 (1999).
[5] C. Noguez, Phys. Rev. B Vol.62, 2681 (2000).

2:15 PM AA6.3
MOLECULAR-DYNAMICS SIMULATIONS OF MAGNETIC STRUCTURES IN METALLIC SYSTEMS. Ralf Meyer, Laurent J. Lewis, Département de Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), Université de Montréal, Montréal, CANADA.

The competing magnetic interactions in itinerant magnets like Fe, Cr, Mn, and their alloys quite often exhibit rather complex magnetic structures which are the subject of experimental as well as theoretical investigations. Using a recently proposed method [1], the magnetic structures of such systems are determined at temperatures $T > 0$ K with the help of molecular-dynamics simulations. In these simulations the equations of motions of local magnetic moments at the sites of a perfect crystal lattice are solved. Problems can arise from the lack of rotational invariance in the original formulation of the method. We, therefore, suggest a calculational procedure which inherently retains the rotational symmetry of the model. Results of the application of this method to fcc Fe and Fe-Ni alloys are presented.
[1] Y. Kakehashi, S. Akbar, and N. Kimura, Phys. Rev. B 57, 8354 (1998).

2:30 PM *AA6.4
EXACT METHOD FOR THE SIMULATION OF COULOMBIC SYSTEMS BY SPHERICALLY TRUNCATED, PAIRWISE 1/r SUMMATION. Dieter Wolf, Materials Science Division, Argonne National Laboratory, Argonne, IL.

An exact, physically transparent method permitting the evaluation of the Coulomb energy in ionic systems by spherically truncated direct summation over the 1/r Coulomb pair potential is discussed. The method is based on the observation that the problems encountered in determining the Coulomb energy by pairwise, spherically truncated 1/r summation are a direct consequence of the fact that the system summed over is practically never neutral. A simple method is developed that achieves charge neutralization wherever the 1/r pair potential is truncated and results in the convergence of the problem. This enables the extraction of the Coulomb energy, forces and stresses from a spherically truncated, usually charged environment in a manner that is independent of the grouping of the pair terms. The close connection of this novel approach with the Ewald method is demonstrated and exploited, providing an efficient method for the simulation of even highly disordered ionic systems by direct, pairwise r-1 summation with spherical truncation at rather short range. The method is validated by simulations of crystals, liquids and interfacial systems, such as free surfaces and grain boundaries.

3:30 PM *AA6.5
NANOTUBE MATERIALS MECHANICS. K. Cho, Stanford Univ, Dept of Mechanical Engineering, Stanford, CA.

Carbon nanotubes (CNTs) are promising new materials for nanotechnology applications due to their unique materials properties. Single-wall CNTs (SWNTs) can be semiconducting or metallic depending on the chirality and diameter of the tube, and these diverse electronic properties open a new possibility of developing novel nanodevices through a chirality control and chemical functionalization of nanotube surfaces. Current status of experimental control and fabrication of CNT devices is not well developed yet, and much of the microscopic processes of nanotube growth, functionalization, and physical properties are not well understood, either. To realize the full potential of CNTs as nanodevice materials, it is very important to develop a mechanistic understanding on how to control their physical properties, and the atomic scale modeling, both molecular dynamics and quantum simulations, will play an important role in elucidating the atomic scale processes. Using the density functional theory (DFT), tight-binding (TB), and molecular dynamics (MD) methods we have investigated diverse electronic, chemical, and mechanical properties of nanotubes. Our findings include plasticity mechanism of CNTs [1], chemical sensor applications [2], chemical doping of CNTs [3], and electro mechanics of nanotubes [4]. We will discuss these findings and ongoing research projects on nanotube modeling. Supports: NASA
[1] D. Srivastava, M. Menon, K. Cho, Phys. Rev. Lett. 83, 2973 (1999).
[2] J. Kong et al., Science 287, 622 (2000).
[3] S. Peng, K. Cho, Nanotechnology 11, 57 (2000).
[4] S. Peng, K. Cho. J. Appl. Mech. (submitted).

4:00 PM AA6.6
INTRINSIC DUCTILITY OF FCC & BCC METALS. C.R. Krenn[1,3], D. Roundy[2,3], J.W. Morris Jr.[1,3] and Marvin L. Cohen[2,3]. [1]Univ of California at Berkeley, Dept of Materials Science. [2]Univ of California at Berkeley, Dept of Physics. [3]Lawrence Berkeley National Lab, Materials Sciences Division, Berkeley, CA.

All available *ab initio* calculations of the ideal shear and tensile strengths of defect free crystals show that fcc metals will fail via a shear instability, whereas bcc metals can fail either in a shear or tensile mode. These results suggest that although true cleavage will never occur in fcc metals, bcc metals will be "conditionally" brittle at low temperatures. The ratio of the ideal shear and tensile strengths also offers a measure of the intrinsic ductility of a material and implies that the addition of nickel to iron based bcc alloys will lower the tendency for cleavage in these alloys.

4:15 PM AA6.7
DEVELOPMENT OF AN AB-INITIO MODEL OF THE LATTICE THERMAL CONDUCTIVITY IN SEMICONDUCTOR NANOWIRES. Jie Zou, Univ of California at Riverside, Dept of Electrical Engineering, Riverside, CA; Alexander A. Balandin, Univ of California at Riverside, Dept of Electrical Engineering, Riverside, CA.

Quantum wire arrays as well as other nanostructured materials have recently been proposed for applications in electronic, optoelectronic and thermoelectric devices [1]. Thermal management of electronic and optoelectronic devices based on semiconductor nanostructures presents significant difficulties due to increase in power dissipation per unit area and variety of size effects that complicate acoustic phonon transport at nanoscale. Development of an accurate theoretical description of heat transport in nanostructured materials is also important for optimization of thermoelectric devices. In this talk, I will present an ab-initio model for phonon heat conduction in a semiconductor nanowire with lateral dimensions comparable to the phonon mean free path. It is based on the solution of phonon Boltzmann equation and rigorously takes into account (i) modification of the acoustic phonon dispersion due to spatial confinement, and (ii) change in the non-equilibrium phonon distribution due to scattering from rough boundaries and interfaces. The role of point defects, impurities, dopants, free carriers and surfaces on phonon relaxation processes is analyzed. The difference in thermal conductivity values obtained with the exact phonon density-of-states and the Debye approximation is investigated. A method to generalize the boundary conditions for lattice vibration modes from the two limiting cases, e.g., free-surface and clamped-surface, is also discussed. The value of thermal conductivity in a silicon nanowire and its dependence on temperature and interface quality predicted on the basis of our model are in good agreement with available experimental data.
[1]. A. Balandin, et al., Optoelectronic Properties of Quantum Wires, in Optics of Nanostructured Materials, edited by V. Markel and T.F. George, (J. Wiley and Sons, New York, 2000), pp. 467-514.

4:30 PM AA6.8
ONE-MINUTE PRESENTATIONS OF THE AA7 EVENING
POSTER SESSION.
Chair: Normand Mousseau, Ohio University, OH.

SESSION AA7: POSTER SESSION
Chairs: Vasily V. Bulatov, Fabrizio Cleri, Luciano
Colombo, Laurent J. Lewis and Normand Mousseau
Thursday Evening, April 19, 2001
8:00 PM
Salon 1-7 (Marriott)

AA7.1
RECONSTRUCTION OF MULTISCALE PHASE MORPHOLOGIES
FROM CORRELATION FUNCTIONS. M.G. Rozman, Marcel Utz,
Institute of Materials Science and Department of Physics, University
of Connecticut, Storrs, CT.

The reconstruction of representative structural models of multiphase
media from spatial correlation functions is a problem of fundamental
importance. It arises in the interpretation of data from scattering
experiments, which directly measure correlation functions, but also in
the generation of model microstructures, which is a prerequisite for
the prediction of properties. We propose a novel algorithm for
restoration, based on stochastic optimization, which is several orders
of magnitude faster than previous approaches. While the achievable
spatial resolution has been previously limited by computational cost,
this increase in efficiency makes it possible to treat multiphase
systems that contain two or more widely different structural length
scales. Like previous approaches, our algorithm is based on stochastic
optimization. The speedup is realized by a fast update of correlation
functions after localized changes of the microstructure, along with a
new optimization strategy. We present results of reconstruction of
several physical multiphase systems, including triblock copolymers.

AA7.2
THE CHEMISTRY OF CRACKING IN ALUMINUM: MERGING
FIRST PRINCIPLES CALCULATIONS OF TRACTION VS.
SEPARATION RELATIONS WITH CONTINUUM MODELS.
Robin L. Hayes, Emily A.A. Jarvis, Emily A. Carter, UCLA, Dept. of
Chemistry and Biochemistry, Los Angeles, CA; Olivier Nguyen,
Michael Ortiz, Caltech, Dept. of Aeronautical Engineering, Pasadena,
CA.

Continuum mechanics, used to study crack formation and other
defects in materials under stress, generally ignores chemistry-induced
effects on the mechanical behavior of solids. Typically, parameters
appearing in laws governing a material's mechanical behavior are
chosen somewhat arbitrarily. We are initiating studies to provide
details for such constitutive laws from atomic scale first principles
calculations. Aluminum is an important engineering metal used in a
variety of applications, like airplane fuselages, and understanding its
behavior under stress is essential. In air, ductile aluminum readily
oxidizes to form a self-limiting brittle outer oxide layer 20-30 $\mathring{A}$ thick.
The oxidation of Al will effect its mechanical strength at the surface,
and hence it may be critical to account for such chemical effects in a
continuum mechanics simulation of crack growth. In this study, we
use Density Functional Theory (DFT) to calculate the dependence of
the crystal energies of Al and α-Al$_2$O$_3$ upon tensile stress applied
perpendicular to the fcc (111) and basal (0001) planes, respectively.
We introduce a region of vacuum (the "crack") into the periodic cell
and allow the outer surface layers to relax. By fitting the energy vs.
introduced crack, we can derive the traction (force per unit area) vs.
separation relation utilized in continuum models. Typically, the
Universal Binding Energy Relation is used, but we find this is
adequate only for the unrelaxed structures. Instead, a different
relation is needed to represent the relaxed structures. Thus, crack tip
velocity, related to extent of relaxation, will dictate which form of the
traction curve is appropriate. While the DFT work of adhesion is
reasonable, the critical separation ($\mathring{A}\approx$) and critical stress (GPa), are
found to be $\sim$7 and $\sim$1-2 orders of magnitude larger, respectively,
than typical values used in continuum models. Methods to bridge the
apparent discrepancy in the scales are considered.

AA7.3
Abstract Withdrawn.

AA7.4
A MOLECULAR ORBITAL STUDY ON THE OPTICAL
PROPERTIES OF FLUORESCENT DYES. Su-Jin Park, Seung-Hoon
Choi, Dae-Yup Shin, Han-Yong Lee, Ho-Kyoon Jung, Corporate R&D
Ctr, Samsung SDI Co. Ltd., Suwon, KOREA; Jung-Sik Kim, Jin-Kyu
Lee, School of Chemistry and Molecular Engr, Seoul Natl Univ, Seoul,
KOREA; Sung Soo Park, Seeyearl Sung, Kyoung Tai No, Computer
Aided Molecular Design Research Ctr, SoongSil Univ, Seoul, KOREA.

Nile Red (NR), fluorescein and 4-(dicyanomethylene)-2-methyl-6-(p-
dimethylaminostyryl)-4H-pyran (DCM) are well-known fluorescent
laser dyes and their luminescent characteristics have been studied for
the organic light emitting device (OLED) application. Even though a
wealth of experimental and theoretical approaches on optical
properties of these dyes is available, however, systematic studies on
the substituents effect of their derivatives have not been thoroughly
investigated. We carried out some calculations and experiments to find
the simple and easy way to predict the substituent effects on these
dyes, in order to make efficient red luminescent dopant materials.
Relationship between the molecular structure and optical properties
were calculated by ab initio and semiempirical calculation methods
such as DFT/AM1/PM3 and INDO/S for the geometry optimization
and for the information of electronic transition, respectively. Since the
result of these calculations was comparable with several experimental
results, these semiempirical molecular orbital calculation methods
could be used as a powerful prediction tool for optical properties of
the luminescent molecules. It was also found that the absorption
maximum and the oscillator strength of molecules strongly depended
on the molecular dipole moment, especially for the molecules having
both strong electron donor and acceptor groups.

AA7.5
PREDICTION OF SOLVATOCHROMIC SHIFT OF
FLUORESCENT DYES USING REGRESSION AND NEURAL
NETWORK TECHNIQUES. Seung-Hoon Choi, Su-Jin Park, Dae-Yup
Shin, Han-Yong Lee, Ho-Kyoon Jung Corporate R&D Center,
Samsung SDI Co. Ltd., Suwon, KOREA; Seung Hee Lee, Jin-Kyu Lee,
School of Chemistry and Molecular Engineering, Seoul National
University, Seoul, KOREA; Sung Soo Park, Seeyearl Sung, Kyoung
Tai No, Computer Aided Molecular Design Research Center, SoongSil
University, Seoul, KOREA.

In order to investigate the relationship between the solvatochromic
shift and the intrinsic properties of fluorescent dyes, a novel series of
4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-
pyran(DCM) derivatives was studied by computer aided molecular
design. Molecular orbital calculations such as AM1/PM3 and
INDO(S) were used for the geometry optimization and for the
information of electronic transition, respectively. SCRF calculation
was also performed to consider the medium polarity with the virtual
solvent having the dielectric constants from 1 to 80 with the interval of
10. Based on the calculated optical properties under various solvents,
quantitative structure-property relationship study on solvatochromic
shift was carried out using genetic algorithm and artificial neural
network technique. It was found that the variations of the polarity of
medium induce the remarkable changes in absorption band positions
and intensity. The absorption intensity (oscillator strength) as well as
the position of absorption maxima seems to be strongly correlated
with the molecular properties, such as dipole moment and energy
band gap of DCM derivatives. From these calculated results, it is
possible to guess how much the position of absorption maxima of
fluorescent dyes will shift as the function of solvent polarity. And
these calculations could also provide some clues to understand the
differences between photoluminescence and electroluminescence due to
the chemical environments around the luminescent molecules.

AA7.6
COUPLED ATOMISTIC–MESOSCOPIC MODELLING OF
POLYCRYSTALLINE PLASTICITY. F. Cleri and G. D'Agostino,
ENEA, Divisione Materiali, Centro Ricerche Casaccia, Roma, ITALY;
A. Satta and L. Colombo, INFM and Dipartimento di Fisica,
Universita di Cagliari, Monserrato, ITALY.

Modelling the complex interplay of phenomena contributing to plastic
deformation in a polycrystalline microstructure is one of the most
challenging subjects of materials science. Even discarding impurity
effects, voids and inclusions, still a number of possible processes are
competing in the different ranges of temperature, external strain and
strain rate. We present the latest results of our stochastic mesoscale
model [1,2], which includes dislocation plasticity at different levels of
sophistication and grain–boundary plasticity resulting from
(diffusion–mediated) grain sliding. The ultimate goal is to describe
the crossover between dislocation–mediated and interface–mediated
plasticity in a real microstructure, whose most spectacular evidence is
the so–called inverse Hall–Petch effect. The technical implementation
of the model is also briefly discussed. Moreover, we describe how
atomic–level simulations do represent an integral part of the
mesoscopic modelling, both to supply the qualitative behavior of
physical parameters and to identify the relative importance of the
various microscopic events leading to microstructural evolution, some
of which still to be addressed experimentally.
[1] F. Cleri, Physica A282, 339 (2000).
[2] F. Cleri and G. D'Agostino, MRS Fall Meeting 2000, Proceedings
of the Symposium "Influences of Interface and Dislocation Behavior
on Microstructure Evolution", in press. Work performed in the

framework of the INFM-FORUM Interdisciplinary Research Project "MUSIC".

AA7.7
A SIMULATION STUDY OF TRACER DIFFUSION CONCENTRATION PROFILES RESULTING FROM THE TRANSITION FROM DISLOCATION PIPES TO GRAIN BOUNDARY SLABS. Irina V. Belova and Graeme E. Murch, University of Newcastle, Dept. of Mechanical Engineering, New South Wales, AUSTRALIA.

We are concerned with the consequences on effective diffusion of the transition from high diffusivity regularly spaced dislocation pipes to high diffusivity grain boundary slabs. Of special interest is how the linear dependence of the logarithm of the tracer concentration on penetration distance (characteristic of dislocation pipes) transforms to the 6/5 dependence (characteristic of grain boundary slabs). We map the problem onto a grid which is subsequently explored by Monte Carlo random walk methods. We also analyse the effective diffusivity of the system.

AA7.8
EVALUATING EFFECTS OF NANOSTRUCTURAL NUANCES ON BULK MECHANICAL PROPERTIES OF NaCrE USING 3D FINITE ELEMENT MODELING. Dinesh R Katti, Kalpana S. Katti, Jingpeng Tang, North Dakota State University, Civil Engineering, Fargo, ND; Jeffrey M. Sopp, Mehmet Sarikaya, University of Washington, MS&E, Seattle, WA.

Nacre, the inner layer of seashells is a structural biocomposite with exceptional mechanical properties. Nacre consists of layered composite structure with organic and inorganic layers. The organic layers in the composite play a significant role in the mechanical response of nacre to stresses. In addition the role of nanoscale interfacial phenomena is also critical for the resulting macroscopic behavior. In our previous work, three dimensional finite element models of nacre were constructed to design 'brick and mortar' micro-architecture of nacre to study influence of nonlinear response of organic component. Nanomechanical properties such as hardness and elastic moduli are measured using nanoindentation techniques. These properties were applied to mesoscale finite element models of nacre. In this work, the role of nanoscale structural nuances is quantitatively evaluated. Specifically, influence of inorganic-inorganic contacts through the organic layer on bulk properties of nacre are quantitatively related to response of nacre under tensile and compressive loading. In addition our new 3D finite element models more accurately represent the symmetry and nanoarchitecture of nacre. The multiscale approach in our study involves incorporation of experimentally obtained nanoscale parameters into meso-macroscale numerical models.

AA7.9
PRESSURE INDUCED RAPID RESOLIDIFICATION IN METALS. F.H. Streitz, Lawrence Livermore National Laboratory, Livermore, CA.

A molten metal compressed to sufficiently high pressure will resolidify. The nature of this solidification in the limit where compression is very sudden is simulated in Cu by means of temperature and pressure controlled molecular dynamics using a modified Sutton/Chen potential. Temperature is controlled during the simulation by the use of a Langevin thermostat, while hydrostatic pressure is controlled using Andersen's algorithm. The process of resolidification under compression is seen in the simulations to be rather different than the related process of freezing − the former is a process characterized by the gradual localization of atoms, while the latter process is characterized by large scale cooperative rearrangement of atoms. The effect of different thermostat algorithms on the resulting dynamics will also be discussed.
Work performed under the auspices of the U.S. DOE by LLNL under contract W-7405-ENG-48.

AA7.10
MODELING OF SOL-GEL TRANSITION WITH LOOP NETWORK FORMATION AND ITS IMPLICATIONS ON MECHANICAL PROPERTIES. Hang-Shing Ma, Princeton Univ, Dept of Chemical Engr, Princeton, NJ; Jean-H. Prévost, Princeton Univ, Dept of Civil and Environmental Engr, Princeton, NJ; Rémi Jullien, Université Montpellier II, Lab de Sci des Matériaux Vitreux, Montpellier, FRANCE; George W. Scherer, Princeton Univ, Dept of Civil and Environmental Engr/Princeton Matls Inst, Princeton, NJ.

Certain classes of sol-gel transition have been modeled as diffusion-limited cluster-cluster aggregation (DLCA). Like other existing aggregation algorithms, DLCA produces excessive dangling branches on the resulting network which underestimates the rigidity of gels. The "dangling bond deflection" (DEF) algorithm was developed to simulate spatial fluctuation of the dangling branches

under thermal energy. Collision and sticking of two dangling branches within the same cluster turns these branches into a loop. Combination of the DLCA and DEF algorithms create networks which possess extensive loop structure and negligible dangling mass. Assuming that the interparticle bonds behave mechanically as beam elements, the finite element method (FEM) was applied to deform the networks and calculate their moduli from the strain energy absorbed. The networks are substantially stiffened by the loop structure, and successfully reproduce the empirical scaling relationship between linear elastic modulus and density exhibited by real aerogels. No experimental techniques permit a direct examination of connectivity in the gel network, but FEM can reveal the spatial distributions of the load-bearing structures from the realistic gel models created by the DLCA and DEF algorithms. The gel structure can be represented by the "blob-and-link" model, in which blobs refer to dense, rigid collections of particles, interconnected by tenuous links of particle chains. When the network is deformed, only these few weak links contribute to the stiffness, leaving the blobs unstrained. The gel modulus drops significantly as porosity increases because more particles reside in the blobs and fewer particles carry the strain. Plastic compression of the gel models is also simulated by breakage of the heavily strained bonds and formation of new bonds between the approaching blobs. The mechanical behavior of the networks is compared with the experimental data obtained from hydrostatic compression of aerogels in a mercury porosimeter.

AA7.11
PERCOLATION THROUGH THE VOID SPACE OF BED OF RANDOMLY PACKED PARTICLES OF DIFFERENT SIZES. Daniel P Riley, Irina V Belova and Graeme E. Murch, The University of Newcastle, Dept of Mechanical Engineering, Callaghan, NSW, AUSTRALIA.

We are concerned with the problem of determining the percolation characteristics of the void space of a bed of randomly packed spherical particles of different diameters. We prepare the randomly packed bed using a global minimization of a very loosely packed randomly generated distribution of particles with a highly repulsive core to emulate hard spheres. The density of the bed is in agreement with that prepared by other methods. A very fine grained grid is mapped into the randomly packed bed of particles. This grid is explored with independent particles using Monte Carlo random walk methods and the scaled diffusivity/conductivity of the void space is determined as a function of various system parameters such as relative packing density.

AA7.12
Abstract Withdrawn.

AA7.13
SCREENING DOPANTS TO Cu INTERCONNECTS BY MODELING. Chun-Li Liu, MOTOROLA ADVANCED SYSTEMS RESEARCH LABORATORY, MESA, AZ.

Desirable additives to Cu have been sought using modeling and simulation as an alternative tool to experiment. We have designed a virtual simulation procedure to cover several important aspects in screening a potential dopant to Cu with the assumption that grain boundary (GB) diffusion is dominant for Cu electromigration performance. The procedure determines dopant segregation to GB, bulk diffusion, dopant and Cu self-diffusion at GB, and effect of dopant's presence on Cu diffusion at GB. Defect formation and migration energies as well as the activation energies were calculated using state of the art ab-initio method. Two primary mechanisms for a dopant to be effective were identified, namely stuffing and dragging mechanisms. For stuffing mechanism dopants occupy the GB interstitial sites and block the fast diffusion pathway for Cu. In the case where Cu atoms occupy the GB interstitial sites, dopants segregate to the nearby sites and drag the fast diffusing Cu. Early electromigration experimental results have confirmed model prediction for one of the several dopants identified so far. The mean time to failure (MTTF) has increased more than 60%-150% with a dopant concentration as low as 0.01at% in Cu and the resistivity increase can be controlled below 15% compared to undoped Cu. Further implication of the selected dopants acting as potential barrier layers and improving interface adhesion will also be discussed briefly.

AA7.14
DUAL SCALE SIMULATION OF GRAIN GROWTH USING A MULTI PHASE FIELD MODEL. Ingo Steinbach, Markus Apel ACCESS e.V. RWTH-Aachen GERMANY.

The kinetics of grain growth in multicrystalline materials is determined by the interplay of curvature driven grain boundary motion and interfacial stress balance at the vertices of the grain boundaries. A comprehensive way to treat both effects in one model is given by the Time Dependent Ginzburg Landau model or Phase Field Model. The paper presents the application of a Multi Phase Field

model, recently developed for solidification processes [1..3], to grain growth of a multicrystalline structure. The specific feature of this Multi Phase Field Model is its ability to treat each grain boundary with its individual characteristics dependent on the type of the grain boundary, its orientation or the local pinning at precipitates. This pinning effect is simulated on the nanometer scale resolving the interaction of an individual precipitate with a curved grain boundary. From these simulations an effective pinning force is deduced and a model of curvature dependent grain boundary mobility is formulated accounting for the pinning effect on the mesoscopic scale of the grain growth simulation. 2-D and 3-D grain growth simulations are presented and the relevance to real grain growth processes is discussed.

[1] I. Steinbach et al. Physica D 94 (1996) pp 135.
[2] J. Tiaden et.al. Physica D 115 (1998) pp 73.
[3] I. Steinbach, F. Pezzolla Physica D 134 (1999) pp 385.

AA7.15
PHASE FIELD SIMULATIONS OF RAPID DENDRITIC GROWTH WITH STRONG INTERFACE KINETICS. <u>Andrew M. Mullis</u>, Department of Materials, University of Leeds, Leeds, UNITED KINGDOM.

Dendrites are the most commonly encountered growth mode when a metal is solidified from its undercooled melt and are frequently observed in casting and welding processes. Although the initial dendritic structure can be modified by subsequent thermomechanical processing, many final properties of the material, such as toughness and corrosion resistance, may be sensitive to the details of the original dendritic microstructure. Recent studies by a number of authors have shown that virtually all the important characteristic of dendritic growth can be scaled, in an undercooling independent manner, by the tip radius, R. Such quantities include primary trunk radius, secondary arm spacing and amplitude, area and volume of the dendrite and the secondary arm envelope, arc length along the dendrite and fractal dimension. It has previously been universally found that in the solidification of pure metals, R decreases monotonically with increasing undercooling. However, in this presentation we will discuss the results of phase field simulations which indicate that this may not be true in systems with strong interface kinetics. As growth velocity increases we find that a transition from diffusion limited growth to kinetic limits growth occurs and that this transition is delineated by a minimum value of R. Further increases in undercooling (or equivalently growth velocity) lead to a slow increase in R. Using parameters appropriate to pure Ni we find that this transition would occur at a growth velocity of 18 m/s. We also find that within the kinetically dominated growth regime the onset of sidebranching moves rapidly towards the dendrite tip, destroying the self-similarity observed at lower undercoolings.

AA7.16
MOLECULAR MODELING OF THE DIELECTRIC SATURATION IN A PROTON EXCHANGE MEMBRANE PORE. <u>Reginald Paul</u>, University of Calgary, Dept of Chemistry, Calgary, AB, CANADA; Stephen J. Paddison, Computational Materials Group, Motorola Inc, Los Alamos, NM.

The transport of water and hydronium ions plays a very important part in the operation of membranes in fuel cells. Recent theoretical work carried out with a view to model this transport has shown the importance of the charged groups on the interior surface of the pores. In this and in all other model calculations the permittivity of the pore interior plays a very crucial role. Generally the commonly accepted value of the permittivity for bulk water is adopted, but it is evident that this can not be correct since the presence of charged groups on the pore wall would produce a dielectric saturation effect. In this paper we present a theoretical calculation of the pore permittivity using the methods of statistical thermodynamics. The calculation commences by writing a classical mechanical Hamiltonian for water molecules in a pore. This Hamiltonian includes pair-wise interactions between the water molecules and interactions with the electrical field generated by the charged pendant groups located on the pore walls. The pendant groups are modeled as a periodic lattice of negatively charged rings located on the cylindrical pore wall and separated by from each other by a fixed lattice length. From the Hamiltonian the partition function and Helmholtz free energy are calculated as a power series in the pendant group field. The power series is summed using the method of Pade approximants. Finally the permittivity is obtained as a function of the location within the pore by computing a functional derivative of the Helmholtz free energy with respect to the pendant group field magnitude. The results of our calculation show that in the center of the pore, far away from the pendant group charges, the permittivity acquires the value of bulk water but as the pore walled is approached saturation effects become evident.

AA7.17
MULTISCALE MODELING OF FERROELECTRIC MATERIALS.

Yi-Chung Shu, National Taiwan University, Instititive of Applied Mechanics, Taipei, TAIWAN.

We present a multiscale approach to investigate large electrostrictive strain in ferroelectric materials with potential to enhance and enlarge the current spectrum of applications that are interest in the design of sensors and actuators. This is motivated by the most recent theoretical analysis and experiment demonstrating the feasibility of attaining large strain (0.9%) with Barium Titanate, a very common ferroelectric. This large strain is already an order of magnitude larger than that attainable with the commonly used piezoelectric materials. Our approach to study ferroelectric ceramics is based on the multiscale modeling. A ceramic is approached at three distinct length scales °V the length scale of specimen, that of individual grain and that of the ferroelectric domains. Using this framework, we examine the domain patterns and the macroscopic behavior of ferroelectric materials. A large strain ferroelectric is obtained by applying combined electromechanical loading that allows a cyclic change in the domain pattern. A possible low-energy path that allows domain switching is proposed and a novel configuration that yields very large electrostriction in electromechanical devices is also identified here.

AA7.18
BROWNAIN DYNAMICS SIMULATION OF THE MICRO-STRUCTURE AND RHEOLOGY OF DENSE COLLOIDAL SUSPENSIONS. <u>Andrew M. Mullis</u>, Department of Materials, University of Leeds, Leeds, UNITED KINGDOM.

Dense colloidal suspension are structured fluids displaying extremely complex rheological properties, which can include both shear thinning and shear thickening. The ability to predict the rheological properties of such suspension is of fundamental importance in the processing diverse materials such as of ceramic slurries, pharmaceuticals, paints and foodstuffs. One route to understanding such systems is the technique of Brownian Dynamics (BD). Brownian Dynamics is a particle dynamics technique in which hydrodynamic interactions between the particles are restricted to calculating the Stokes drag. The model is particularly successful in calculating the behaviour of suspensions of strongly interacting particles, where the rheology of the suspension is dominated by interparticle forces such as Coulombic attraction/repulsion. Simulations containing thousands of particles are feasible meaning that such simulations can yield statistical information about the level of structure in the fluid. Brownian Dynamics thus spans several length scales relating interparticle forces to the microstructure of the suspension and hence the bulk rheological properties of the slurry. In this presentation we will give an overview of the technique illustrated by simulations of a dense (75% volume fraction solid) suspension of repulsively electrostabilized particles. Such suspension are observed to undergo a shear thickening transition with increasing applied shear, related to an order-disorder transition in the microstructure. This sequence is reproduced in the simulations with progressive loss of order being observed as the applied shear is increased. The level of order can be characterised by various particle distribution statistics. Depending upon the size and range of the stabilizing electrostatic forces the predicted shear thickening transition may be continuous or discontinuous (step-wise).

AA7.19
NANOPATTERNS FORMED WITH ANISOTROPIC PHASE BOUNDARY ENERGY. <u>Wei Lu</u>, Zhigang Suo, Princeton University, Mechanical and Aerospace Engineering Department and Princeton Materials Institute, Princeton, NJ.

A thin binary epilayer on a substrate often exhibits intriguing phase separation behaviors. The phases may self-organize into a regular pattern, such as an array of periodic stripes, a lattice of dots or squares, and the size of the phases is in nanoscale. It is a process involves phase separation, phase coarsening, and phase refining. The competition of these forces determines what patterns will form and the size, spatial ordering and shape. Anisotropy is important in that it breaks the symmetry of the system and induces direction preference. Hence it may considerably change the patterns formed. In this paper, we focus on the anisotropy of phase boundary energy. In our continuous phase field model, phase boundary is represented by the gradient of concentration. Phase boundary energy is a function of the magnitude of the gradient as well as the orientation. Based on the model, we simulated the formation and evolution of nanopatterns with various degree of anisotropy. Numerical simulations reveal a very strong effect of phase boundary energy anisotropy on the pattern.

AA7.20
DIFFUSION IN THE PRESENCE OF GRAIN BOUNDARIES: A VARIABLE LENGTH SCALE SIMULATION METHOD. <u>Irina V. Belova</u>, Graeme E. Murch, The University of Newcastle, Dept of Mechanical Engineering, Callaghan, NSW, AUSTRALIA.

We are concerned with the behavior of the effective diffusivity and

tracer concentration profiles in the presence of high diffusivity parallel grain boundary slabs and much lower diffusivity grains. We attack this problem by mapping a grid onto the phenomenologically conceived system and explore this grid with independent particles using Monte Carlo methods. The grid has a variable spacing so that diffusion on vastly different length scales can be addressed in the same problem by rescaling the jump distances and therefore the jump frequencies on the grid. This allows the determination of the detailed structure of the tracer concentration contours in the vicinity of the grain boundaries even in the situation of large grain boundary spacing. We examine several well-known models for grain boundary diffusion.

AA7.21
MULTISCALE MODELING OF ULTRASHALLOW JUNCTION FORMATION FOR SEMICONDUCTOR DEVICES.

Gyeong S. Hwang and William A. Goddard, III, Materials and Process Simulation Center, Beckman Institute, California Institute of Technology, Pasadena, CA.

Multiscale modeling has emerged as a powerful tool for the study of materials science and engineering. We have applied this method to uncovering complex phenomena occurring during ultrashallow junction processing in which a time-scale ranges from picoseconds (e.g., migration of single vacancies and Si self-interstitials) to tens of seconds (e.g., doping profile evolution). This systematic approach further allows developing a predictive description of doping profiles for a wide range of process conditions. We present our simulation model in which we combine (i) quantum mechanics simulation of the fundamental atomic-level processes, (ii) kinetic Monte Carlo (MC) simulation of relatively long time-scale defect-dopant clustering and dissolution, and (iii) continuum-level simulation of doping profile evolution. We will also discuss the advantage and disadvantage of kinetic MC and continuum models in describing defect-dopant dynamics, as well as time-acceleration schemes implemented in these macro-scale simulations.

AA7.22
LINKS BETWEEN CRYSTALLOGRAPHIC TEXTURE AND GRAIN BOUNDARY CHARACTER DURING GRAIN GROWTH.

Elizabeth A. Holm, Materials and Process Modeling, Sandia National Laboratories, Albuquerque, NM; Gregory N. Hassold, Department of Science and Mathematics, Kettering University, Flint, MI; Mark A. Miodownik, Department of Mechanical Engineering, King's College London, London, UNITED KINGDOM.

Designing materials processing routes to optimize materials properties requires understanding the relationships between crystallographic texture, grain boundary character, and thermomechanical history. In order to study the development of texture and boundary character during annealing, three-dimensional crystallography and realistic boundary properties were incorporated into a Monte Carlo model for grain growth. Systems with similar initial microstructures but different textures exhibit markedly different behavior during microstructural evolution. Microstructures with random textures evolve in a normal fashion. The grain size distribution is statistically equivalent to that of isotropic grain growth, and growth kinetics follow the usual power law. While texture remains random in these systems, the boundary character distribution evolves to a steady state that favors low misorientation angle boundaries. To first order, the increase in low angle boundaries is geometrical; changes in triple junction angles cause low energy boundaries to lengthen, but their frequency does not increase. In contrast, microstructures with a strong single component texture develop four grain junctions and highly curved grain boundaries. The grain size distribution is skewed toward small grains, and both the texture and the misorientation distribution continually sharpen. Formation and growth of clusters of low mobility boundaries causes growth to slow, which may explain some experimentally observed low grain growth exponents. While often seen in experiments, abnormal grain growth did not occur in these simulations.

AA7.23
SIMULATION OF MICROSTRUCTURAL EVOLUTION DURING SINTERING UNDER AN APPLIED STRESS.

Michael Braginsky and Veena Tikare.

We present a numerical simulation of sintering based on a kinetic, Monte Carlo model, known as the Potts model. This model has previously been applied to study simple sintering in a single-phase, single-component, system that undergoes microstructural evolution by curvature-driven grain growth, pore migration by surface diffusion, vacancy formation and annihilation. In this work, we extend this model to include the effect of applied stress on microstructural evolution during sintering. This is important for systems undergoing differential sintering due to any number of reasons, including non-uniform packing of the powder. We are going to introduce the model and present numerical results showing the influence of stress

state on the developing microstructure. Finally, the capabilities and limitations of this model will be discussed.

AA7.24
SIMULATION MODEL OF KINETICS OF DEFECT COMPLEX FORMATION FOR ORDERED STRUCTURES.

Maria Ganchenkova, Andrei Nazarov, Moscow Eng Phys Inst, Dept of Materials Science, Moscow, RUSSIA.

Formation and migration of defect complexes play important role in diffusion processes in condensed matters. In one's turn, kinetics of complex formation is defined by mutual influence of defects ash-forming this complex on local diffusion characteristics of each other. In basis of present work it is laid the idea to take into account the influence of defect interaction on their diffusivities in full measure. Defect interaction leads to activation barrier change of an atom jump. Singularity of developed approach is logically checked combination of two types of methods. When the distance between two defects is small, the values of activation barriers of atom jumps calculate with help of molecular static method. But for the case of the lager distances we use developed approach, which allows to take into account the influence of elastic field on jump rate. Into the framework of this approach, it was obtained the expression for calculation of activation barrier change of atom jump in arbitrary direction. According to this expression the activation barrier value depends on the deformation tensor components, initial local atomic configuration near the jumping atom and saddle-point configuration. The components of deformation tensor are determined by anisotropic elastic field generated by another defect. Based on obtained values of activation barriers we calculate the probabilities of atom jumps in arbitrary directions for different defect configurations. It allows us to realize the kinetics Monte-Carlo method for defect complex migration. As results of the simulation we can determine an average binding energy of defects and their diffusion coefficients. This approach was applied to the ordered structure of B2-type for the case of two interactive vacancies. The results show the formation of dynamic pair of these vacancies and their migration as tight complex, what confirm realization in such structures of Dynamic Pair mechanism.

AA7.25
SIMULATION OF DIFFUSION UNDER PRESSURE IN B2-TYPE ORDERED STRUCTURE.

Maria Ganchenkova, Andrei Nazarov, Moscow Eng Phys Inst, Dept of Materials Science, Moscow, RUSSIA.

There are discrepancies between results of theoretical study of diffusion and results of diffusion experiments in B2-type ordered structures. In particular, theoretical calculations give the large value of the activation barriers for the next nearest-neighbour jumps. However, the QMS and NRS measurements indicate that vacancy jumps into the next nearest-neighbour sites are preferable. Probably, it arises from fail to take into account the correlative motion of defects in the most of the theoretical works. One of the causes of the defect correlative migration is the effective interaction between the different defects. We simulate the effect of interaction of defects on their diffusivities. Our results indicate that for such structures NNN-jump is preferable for certain defect configurations and allow to introduce a new diffusion mechanism called Dynamic Pair mechanism. The features of it are a dynamic pair generation and lesser effective activation energy of diffusion than one for other known mechanisms. One of the methods, which allow choosing the diffusion mechanism from the several variants, is the study of the pressure influence on diffusion coefficient. We developed a general approach to calculate the activation volume for different mechanisms in solids. Based on it we built the model, which allows us to calculate migration volume for elementary diffusion jump for the different jump type and different local atom environments. If diffusion coefficient can be expressed from set of jump rate, then for each of these rates we can evaluate the migration volume with the help of the developed model. Thus this way allows us to obtain the dependence of diffusion coefficient on pressure in different systems. We investigated mentioned dependence for the different ordered systems. For the case of migration of tight vacancy pair, which takes place in B2-type ordered structure, it is obtained nonlinear pressure dependence of diffusion coefficient logarithm.

AA7.26
A MASTER EQUATION APPROACH FOR THE CURRENT-VOLTAGE DEPENDENCE OF THIN CONJUGATED POLYMER FILMS.

José A. Freire, M.G.E. da Luz, Dongge Ma, I.A. Hümmelgen, Departamento de Física, Universidade Federal do Paraná, BRAZIL.

The charge carrier transport in conjugated polymer films sandwiched between metallic electrodes is described by means of a one-dimensional master equation where the hopping rates are given by thermally activated jumps over barriers separating trapping sites of

same energy. An applied electric field along the chain reduces the barrier height leading to a field-dependent mobility, $\mu(E) \sim \sinh(E)/E$. We exactly derive the current-voltage characteristics of such a system assuming that the injected carriers generate space charge effects inside the polymer. We find an excellent agreement with the experimental data for different types of conjugated materials and compare our model with other models that predict $\exp(\sqrt{E})$ for the field dependent mobility.

AA7.27
DEFECTS CLUSTERS ACCUMULATION IN α-IRON. MULTISCALE MODELLING ASSESSMENT OF IONS IRRADIATION EXPERIMENT. Jose Manuel Perlado, Dario Lodi, Juan Prieto, Esteban Dominguez, Instituto de Fusion Nuclear, Universidad Politecnica de Madrid, Madrid, SPAIN; Dario Lodi, Dipartimento di Ingegneria Nucleare, Politecnico di Milano, Milano, ITALY; Jaime Marian, Tomas Diaz de la Rubia, Brian Wirth, Lawrence Livermore National Laboratory, Livermore, CA.

We present results of a Multiscale analysis of the damage induced in α-iron samples irradiated with ions to be compared with similar experiments. The aim of this work is, to develop full computational system to assess damage in reactor pressure vessel steel and internal components, inside an international collaboration.In this framework the actual goal is to value the reliability of Molecular Dynamics and Kinetic Montecarlo models in comparison with analogous experiments. The considered variables are : the dose, the temperature, the percentage of impurities and the effect of the geometrical distribution of the irradiation. We have therefore simulated the irradiation of a iron sample, irradiated with a dose rate of 0.05 dpa/s for two differents temperatures and keeping in count two possible manners of irradiating the sample. The first one simulating a double side irradiation and the second considering that all the dose is introduced for one side. The final magnitude to be compared with the experiments will be expressed in terms of visible clusters concentracion. A different behavior is conducted from vacancies and interstitial clusters whith a large influence due to impurities effetct. Visible clusterare are in the form of interstitial clusters which nature needs to be fully understood depending on the irradiation procedure.

AA7.28
Abstract Withdrawn.

AA7.29
BCC DISLOCATION DYNAMICS SIMULATIONS USING THE PARANOID CODE. L.K. Wickham, Lawrence Livermore National Lab, Livermore, CA; K.W. Schwarz, IBM T.J. Watson Research Center, Yorktown Heights, NY.

We show results of 3D linear elastic dislocation dynamics simulations for BCC materials, using the PARAllel Nodal IBM Dislocation Code. For example, we analyze behaviors of junction-containing dislocation clusters under stress. This includes tracking effects of line tension on motion and breakup of junctions in these clusters, and looking at how the behavior of one link can affect others nearby. We also look at effects of moderate- and large-sized jogs on the motion of screw dislocations. We show self-multiplication behaviors both in large simulations with periodic boundary conditions and in smaller runs with higher spatial resultion, which we used to check assumptions of simple models.

AA7.30
ATOMISTIC SIMULATION OF KINKS FOR 1/2 a <111> SCREW DISLOCATIONS IN TA. Guofeng Wang, Alejandro Strachan, Tahir Cagin and William A. Goddard, III, Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA.

The structure, formation energy and mobility of kinks for 1/2a<111> screw dislocation in Tantalum have been investigated via low temperature molecular dynamics with a new, first principle based, Embedded-Atom-Model (EAM) potential. We studied a/3<112> kinks using a simulation cell containing four dislocations in a quadrupolar arrangement. We imposed periodic boundary conditions in the directions perpendicular to <111> and fixed the boundaries in the <111> direction. We find that two, energetically equivalent, core configurations for the 1/2a<111> dislocation lead to 16 distinguishable kinks. The different mismatches of core configurations along <111> direction lead to variations in kink formation energy. We propose an interpretation of these variations based on a detailed structure and energy analysis. We also calculate the activation energy for dislocation motion via double kink mechanism from a dipole annihilation simulation. We facilitate the nucleation of a double kink by introducing a vacancy on the path of one of the dislocations. We find that the migration energy for dislocation motion via double kink formation is 0.016 eV/b, which is more than four times lower than 0.073 eV/b associated with a straight, perfect dislocation moving collectively.

SESSION AA8: MULTI-TIMESCALE METHODS AND APPLICATIONS
Chair: David J. Srolovitz
Friday Morning, April 20, 2001
Nob Hill C/D (Marriott)

8:30 AM *AA8.1
LONG TIMESCALE SIMULATIONS OF SURFACE PROCESSES WITHIN HARMONIC TRANSITION STATE THEORY USING THE DIMER METHOD. Graeme Henkelman and Hannes Jónsson, Dept. of Chemistry, University of Washington, Seattle, WA.

We have used the Dimer method (1) to search for various possible transitions from a given initial state and then used a kinetic MC algorithm to select between the different transition and advance time in order to simulate long timescale dynamics of island formation and diffusion on an Al(100) surface. Typically a few tens of dimer searches suffice to find the relevant processes in a system of a few hundred atoms. Comparison with other methods for finding saddle points will be given (2). The Al islands diffuse primarily by concerted substitutional processes.
(1) G. Henkelman and H.Jónsson, 'A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives' it J. Chem. Phys. **111**, 7010 (1999).
(2) G. Henkelman, G. Jóhannesson and H. Jónsson, 'Methods for Finding Saddle Points and Minimum Energy Paths', Progress on Theoretical Chemistry and Physics, ed. S.D. Schwartz (in press) (Kluwar Academic Publishers, 2000).
available at
http://students.washington.edu/graeme/research/saddle/review/review.html

9:00 AM *AA8.2
A NOVEL APPROACH FOR THE DETERMINATION OF ACTIVATION BARRIERS FOR PHYSICAL PROCESSES. E.B. Tadmor, Technion-Israel Institute of Technology, Dept of Mechanical Engineering, Haifa, ISRAEL.

A novel method for determining transition paths and activation barriers between known physical states has been developed. The method uses a continuous path expansion to characterize the path instead of the discretized approaches common to other methods such as the elastic band method. The method has several advantages when compared to existing approaches: (1) Use of a continuous description of the path obviates the need for artifacts such as numerical springs which are needed to keep the replicas on discretized paths together. (2) The method can directly minimize the barrier across the path and not an integral along the path as in other approaches. This is important because there are many examples where the path with the minimal integral is not the path with the minimal barrier. (3) The method lends itself to global minimization schemes like the parallel tempering method allowing for the determination of the globally minimal transition path. The method has been used to calculate the activation barriers for a variety of processes including adatom diffusion on surfaces, polarization switching in ferroelectrics and the mutation of DNA molecules involving the tunneling of hydrogen atoms.

9:30 AM AA8.3
A HIERARCHICAL SCHEME FOR THE PREDICTION OF GAS PERMEATION THROUGH MICROPOROUS MATERIALS. Canan Tunca, David M. Ford, Texas A&M Univ, Dept of Chemical Engineering, College Station, TX.

Classical molecular simulation techniques have become an important tool for developing an understanding of the transport of adsorbed molecules in microporous materials. However, the prediction of transport rates is often limited by the time scales currently accessible to molecular dynamics simulations. In the past, transition-state theory (TST) formalisms combined with stochastic dynamics techniques have successfully addressed the time scale problem; however, most of this work was confined to the case of a single adsorbate at infinite dilution in the microporous material. Building on this past work, we have developed a scheme for modeling transport in systems with arbitrary adsorbate loadings. Multidimensional TST is used to calculate "hopping rates" of adsorbate molecules between neighboring cages in the solid matrix. The TST rates are determined as functions of the occupancy of the neighboring cages as well as the primary cage, and they are then dynamically corrected using short-time molecular dynamics runs. We then employ all of this fundamental rate information to perform stochastic dynamics simulations of molecular transport, which can access very long time scales. Furthermore, we have moved beyond equilibrium diffusivity calculations, using a dual-control volume concept to directly model permeation under a chemical potential gradient. In this talk, we evaluate the results of this approach for the specific cases of methane and xenon permeating through zeolite ZK-4 under pressure gradients.

9:45 AM <u>AA8.4</u>
CHARACTERIZATION OF THE ACTIVATION-RELAXATION TECHNIQUE : RECENT RESULTS ON LENNARD-JONES CLUSTERS AND AMORPHOUS SILICON. Rachid Malek, Yinglei Song, <u>Normand Mousseau</u>, Ohio University, Dept. Physics and Astronomy, Athens, OH; Gerard T. Barkema, Universiteit Utrecht, Theoretical Physics, Utrecht, THE NETHERLANDS.

The activation-relaxation technique (ART) is a method for finding saddle points in high-dimensional energy landscapes. ART has already been applied to a wide range of materials including amorphous semiconductors, Lennard-Jones glasses, and proteins. In spite of its successes, a number of fundamental questions remain to be answered regarding the biases associated with its sampling of the saddle points. We present here results of a detailed analysis of the biases on Lennard-Jones clusters and in amorphous silicon. We focus in particular on the biases of the method in sampling saddle points, the completeness of the sampling and the sensitivity of these quantities to variations of the different parameters.
This work is supported in part by NSF DMR-9805848.

10:30 AM <u>AA8.5</u>
DIFFUSION AND CLUSTERING MECHANISMS IN Si AND Ge. <u>Blas Pedro Uberuaga</u>, Graeme Henkelman, Hannes Jónsson, University of Washington, Dept of Chemistry, Seattle, WA; Scott Dunham, University of Washington, Dept of Electrical Engineering, Seattle, WA; Wolfgang Windl, Motorola, Austin, TX.

As semiconductor devices become smaller and smaller, being able to accurately model such properties as dopant profiles and defect concentrations become correspondingly more important. In order to model elemental and defect profiles, the atomic scale processes governing diffusion and clustering must be well understood. Diffusion describes the transfer of material from one spatial location to another, while clustering is a mechanism that inhibits diffusion by rendering diffusers immobile. We have conducted theoretical investigations within the framework of density functional theory to gain a better understanding of the important clustering and diffusion mechanisms in bulk Si and Ge systems. We have calculated the complete diffusion constant, including both the activation energy as well as the entropies that determine the diffusion prefactor. An important part of this work has been an effort to correct the errors inherent in periodic cell density functional calculations in order to be able to make more quantitative predictions about these systems.

10:45 AM <u>AA8.6</u>
A KINETIC STUDY OF HYDROCARBONS REACTIVITY ON PALLADIUM CATALYSTS THROUGH A DFT APPROACH. <u>Valeria Bertani</u>, Carlo Cavallotti, Maurizio Masi, Sergio Carrá, Dipartimento di Chimica Fisica Applicata, Politecnico di Milano, Milano, ITALY.

Heterogeneous catalysts, consisting of one or more metals dispersed on a support, are widely used in different fields of chemical industry and consequently a large number of investigations are carried out to improve their operating life and selectivity. Although in this last decade the characterization techniques of catalyst surfaces have become more and more accurate, they are still insufficient to understand completely the mechanisms underlying catalyst behavior, essentially because there is a gap between analytical and operative conditions. Due to this fact, and thanks to the increase in computer speed, quantum chemistry calculations are by now successfully performed to investigate the reactivity of catalysts. In this work, palladium clusters have been chosen to represent a typical supported heterogeneous catalyst and their interaction with hydrocarbons has been investigated theoretically. The calculations were performed through density functional theory and the Becke-Lee-Yang-Parr hybrid (B3LYP) functional was adopted to calculate exchange and correlation energy. An effective core potential basis set (ECP on core electrons and Dunning/Huzinaga on outer electrons) was found sufficiently accurate to reproduce experimental data. Clusters containing up to seven Pd atoms were considered and their interaction with hydrogen, methane and ethane and their fragments was analyzed. After having determined structure and energy of the most relevant species, a kinetic study of the system was performed. Transition states structures and energies were calculated through quantum mechanics and kinetic constants were derived from a statistic thermodynamic approach. On the basis of such information, a kinetic model that accounts for ethane transformations and carbonaceous deposit formation was derived. Finally the kinetic scheme was embedded in a plug flow reactor model and simulations were performed to test the validity of the developed mechanism. In this way information obtained at the atomic scale were adopted to study phenomena occurring on the much higher reactor scale.

11:00 AM <u>*AA8.7</u>
CHANGING SHAPES IN THE NANOWORLD. <u>Pablo Jensen</u>,

Nicolas Combe and Jean-Louis Barrat, Département de Physique des Matériaux, UMR CNRS, Université Claude Bernard Lyon-1, Villeurbanne Cédex, FRANCE.

What are the mechanisms leading to the shape relaxation of three dimensional crystallites? This is a fundamental question for the understanding of the morphology of nanostructured films (Ref 1). After a brief introduction to the history and advantages of Kinetic Monte Carlo simulations, I will show (Ref 2) how these can help understanding the relaxation mechanisms. Specifically, I'll deal with simulations of fcc clusters which show that the usual phenomenological theories of equilibration, via atomic surface diffusion driven by curvature, are verified only at high temperatures. Below the roughening temperature, the relaxation is much slower, kinetics being governed by the nucleation of a critical germ on a facet. The energy barrier for the nucleation linearly increases with the size of the crystallite, leading to an *exponential* dependence of the relaxation time.
1. P. Jensen, Rev. Mod. Phys. **71**, 1695 (1999).
2. N. Combe, P. Jensen and A. Pimpinelli, Phys. Rev. Lett **85**, 110 (2000).

11:30 AM <u>AA8.8</u>
Abstract Withdrawn.

11:45 AM <u>AA8.9</u>
DIFFUSION UNDER STRESS: THEORY AND SIMULATION. Maria Ganchenkova, <u>Andrei Nazarov</u>, Moscow Eng Phys Inst, Dept of Materials Science, Moscow, RUSSIA; Alexander Mikheev, IP Bardin Central Res Inst of Ferrous Metallurgy, Dept of Metal Physics, Moscow, RUSSIA.

Some times ago a new approach was suggested by us to resolve the problem of the influence of elastic stress on the vacancy jump rate for atomic diffusion in crystals. It was based on assumption that as the stress fields can alter the surrounding atom configuration the height of the activation barrier is altered. The change of activation barrier was obtained to depend on displacement field, symmetry of crystal, atom structure near point defects and pair potential. Knowing this change it is possible to calculate the jump rate. The expression for the vacancy flow was obtained with help of the "hole gas" method, using jump rate. Then this method was applied to the influence of stresses upon the diffusion fluxes in binary systems. In the approximation of regular solid solutions the expressions for the fluxes of components and vacancies under stress were obtained. In these nonlinear equations, influence of deformation tensor component on diffusion flux is determined by coefficients depending on atom interaction. Some evaluations for mentioned coefficients were made for different cases in approximation of rigid lattice. Now we have developed model for calculation of these coefficients into the framework of molecular static method taking into account atom environment as near the defect as for the saddle-point configuration. This approach gave the possibility to investigate the influence of uniform pressure on diffusion. In cases of pure metals and binary alloys the expressions for migration and formation volumes were obtained and the calculation for some BCC and FCC metals were made. Now we have built a general approach to calculate the activation volume for different mechanisms in solids. It allows, in particular, to study pressure influence on diffusion in ordered structures. Apart from it, it was studied the influence of concentration stresses on interdiffusion and redistribution of interstitial atoms near the crack orifice.

SESSION AA9: LARGE-SCALE AB-INITIO
CALCULATIONS
Chair: Luciano Colombo
Friday Afternoon, April 20, 2001
Nob Hill C/D (Marriott)

1:30 PM <u>*AA9.1</u>
LARGE SCALE ATOMISTIC ELECTRONIC STRUCTURE CALCULATIONS OF NANOSTRUCTURES. Lin-Wang Wang, NERSC, Lawrence Berkeley National Laboratory, Berkeley, CA.

Developing theoretical tools to describe accurately the electronic structures of nanosystems containing 10^3-10^6 atoms is one major challenge facing the nanostructure science. The sizes of these systems are too small for effective mass like continuum models to be quantitatively accurate, and too large to apply ab initio methods. Recently, accurate million atom calculations become possible [1] due to new computational algorithms and the use of massively parallel computers. In these calculations, the single electron Hamiltonian is obtained nonselfconsistently, based on the information of small ab initio calculations or experimental data. Like in a conventional ab initio calculation, the Hamiltonian is described by pseudopotentials and the wavefunction is expanded in planewaves. The resulting

Hamiltonian is then solved [using the folded spectrum method (FSM)] only for a few eigenstates relevant to the physical properties we are interested in. We will discuss the possible ways to use the selfconsistent charge densities from small system ab initio calculations to construct the large system Hamiltonians. This is intended to introduce ab initio elements in this approach, thus makes it more reliable. Examples will be presented for CdSe quantum dots, GaAsN and InGaN alloys.

[1] L.W. Wang, J. Kim and A. Zunger, Phys. Rev. B 59, 5678 (1999).

2:00 PM AA9.2
DEFECTS ENERGETICS IN β - SiC. J.M. Perlado, M. Salvador, Instituto de Fusion Nuclear, Universidad Politecnica de Madrid, Madrid, SPAIN; L. Malerba, SCK-CEN, Mol, BELGIUM; L. Colombo, Universita degli Studi Cagliari, Monserrato, Cagliari, ITALY; T. Diaz de la Rubia, Lawrence Livermore National Laboratory, Livermore, CA.

The knowledge of the defects energetics, is a key issue for the diffusion of defects. These parameters for SiC will be used in simulations by Kinetic MonteCarlo (KMC). The convenience of using Tight-Binding Molecular Dynamics (TBMD) comes from uncertainties in calculations performed with classical MD. However, the basic knowledge of damage in SiC is not well know, and more studies are needed. The displacement damage has been systematically studied using molecular dynamics code MDCASK (DENIM/LLNL) with the Tersoff potential. The values are reliable for our studies in high energy cascades displacement, amorphization by damage accumulation, and basic damage phenomena. However, through our preliminary results and those of the other authors, it is concluded that the defect energetics from our classical MD for some key structures in SiC have not a good agreement with available results from *ab initio* or experiments. In any case, results with Tersoff potential demonstrated better agreement than those with other potentials, and some new results will be presented here. Because of the previous reasons, we consider a new step in our research to look for development of TBMD as a better model and first approximation, instead of more expensive *ab initio* calculations. We will present a new discussion on those calculations using TBMD. Results with *ab initio* analysis in small volumes are mostly exacts. By using TBMD, we have a less expensive model than *ab initio*, but more reliable than classical MD because the level of the parametrization is upgraded to the basic level of the generation of the potential. The application of the model to Si and C has given good results. However, its application to SiC has not yet been effective. In this work it we will present a criticism about the model for SiC with better and necessary improvement and preliminary results.

2:15 PM AA9.3
NOVEL SOLID STATE HYBRID QM/MM EMBEDDING INVESTIGATION INTO METHANOL SYNTHESIS OVER COPPER SUPPORTED ON ZnO CATALYSTS. Samuel A. French, S.T. Bromley, A.A. Sokol, C.R.A. Catlow, The Royal Institution of Great Britain, London, UNITED KINGDOM; J. Kendrick, S. Rogers, ICI Strategic Technology Group, Wilton, UNITED KINGDOM; P. Sherwood, CLRC Daresbury Laboratory, Warrington, UNITED KINGDOM.

The development of methodology allowing new theoretical approaches and computational tools for the investigation of heterogeneous catalytic reactions has been pursued utilising hybrid QM/MM embedding techniques. Such techniques have previously been developed in solid-state physics to treat point defects in ionic solids, most notably the ICECAP model. Here we further extend this approach to the surfaces of polar solids typified by metal oxides. This model has been incorporated into a programming shell, CHEMSHELL, which realises a number of alternative hybrid QM/MM techniques, mostly intended for chemical applications, using modern multi-processing computer facilities. The simulation of the active sites of metal supported on metal oxide catalysts requires the application of computationally expensive high-level electronic structure techniques, particularly, to model the interaction between reacting molecules and the active site of the support. Our investigation of the industrially relevant synthesis of methanol from the feed gas $CO/CO_2/H_2$ over Cu active sites supported by a ZnO surface has focused on: i) The development of a viable model for the active site. Initially the models used were the catalytically relevant reconstructed (0001) and (000-1) polar surfaces of ZnO. Copper clusters in various electronic states have been introduced and used as active sites for adsorption. ii) Various physi- and chemisorption scenarios for major reactants and products. Full geometry optimisation of the adsorbing species and a large region of surface has been performed to study the important surface-to-adsorbate interactions as well as coadsorbate interactions. iii) Characterisation of transition states. The rate-determining step for the methanol process is the hydrogenation of CO_2 adsorbed to the surface. We have investigated the dissociation of H_2, before then introducing CO_2, and analysed the subsequent transition to formate. The QM treatment employs density functional

theory making use of recent hybrid functionals, and the MM portion utilises the shell model.

2:30 PM AA9.4
MULTISCALE MODELING OF STRESS-MEDIATED DIFFUSION IN SILICON—AB INITIO TO CONTINUUM. Wolfgang Windl, Neil N. Carlson, and Michael P. Masquelier, Computational Materials Group, Motorola, Inc, Austin, TX, and Los Alamos, NM; Matthew Laudon, Axiowave Networks, Inc, Marlborough, MA; Murray S. Daw, Dept of Physics and Astronomy, Clemson University, Clemson, SC.

In this paper, we present the development of a complete methodology to simulate the effects of general anisotropic nonuniform stress on dopant diffusion in silicon with special focus on the involved first-principles calculations. The macroscopic diffusion equation is derived from microscopic transition state theory; the microscopic parameters are calculated from first principles; a feature-scale stress-prediction methodology based on stress measurements in the relevant materials as a function of temperature has been developed. The developed methodology, implemented in a continuum solver, is used to investigate a TiN metal gate system. A compressive stress field is predicted in the substrate, resulting in an enhancement in lateral boron diffusion. This enhancement, which our model attributes mostly to solubility effects, is in good agreement with experiment.

2:45 PM AA9.5
DISLOCATION CORE STRUCTURES IN BCC-METALS. Sóren L. Frederiksen and Karsten W. Jacobsen, Center for Atomic-Scale Materials Physics, Department of Physics, Technical University of Denmark, DENMARK.

The structures and energies of $\frac{1}{2}\langle 111 \rangle$ screw dislocations in the BCC-metals Fe and Mo are studied using Density Functional Theory. The $(1\bar{1}0)$ and the $(2\bar{1}\bar{1})$ γ-surfaces along the $\langle 111 \rangle$-direction are calculated and the structures of the two important configurations ("hard" and "easy") of the screw dislocation are determined. Our results show non-degenerate core structures which spread symmetrically across the $(1\bar{1}0)$-planes. The displacement field is affected by the twinning-antitwinning asymmetry. The energy barrier for dislocation motion is discussed.

3:30 PM *AA9.6
LINEAR SCALING DFT CALCULATIONS WITH NUMERICAL ATOMIC ORBITALS. Pablo Ordejón, ICMAB-CSIC, Barcelona, SPAIN; Jose M. Soler, Emilio Artacho and Javier Junquera, Universidad Autónoma de Madrid, SPAIN; Daniel Sanchez-Portal, University of Illinois, IL; Alberto Garcia, Universidad del País Vasco, Bilbao, SPAIN; Julian Gale, Imperial College, London, UNITED KINGDOM.

In the context of linear-scaling methods for electronic structure and molecular dynamics calculations, we have developed a fully first-principles DFT method able to deal with systems with an unprecedented number of atoms with a modest computational workload. The feature that distinguishes the method from other common DFT approaches is the use of numerical-atomic-orbitals as basis set. The rest of the approximations (such as pseudopotentials, DFT functionals, and grid integration) are common to other well established approaches. The development of special techniques to optimize the handling of the numerical-atomic-orbitals, makes the method, implemented in the it Siesta code, particularly efficient. Linear-scaling techniques are incorporated to allow the treatment of systems with a very large number of atoms. The method has allowed us to study a wide variety of problems involving nanoscale atomic aggregates, such as nanoclusters, nanotubes, biological molecules, adsorbates in surfaces, etc. We will present here a review of the method and some selected applications.

4:00 PM AA9.7
ROUND-TABLE DISCUSSION
BRIDGING OVER MULTIPLE LENGTH AND TIME SCALES
Panel:
Srolovitz, Tadmor, Rudd, Jonsson
Moderators:
Vasily Bulatov, Lawrence Livermore National Laboratory, Livermore, CA; Fabrizio Cleri, Centro Ricerche Casaccia, Roma, ITALY.