SYMPOSIUM JJ
Modeling of Morphological Evolution at Surfaces and Interfaces

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* Invited paper
In heteroepitaxial growth of strained layers, the growing layer often remains planar up to some "critical thickness", at which point three-dimensional (3D) islands form. This Stranisi-Krastanov transition is of great practical importance. Many device structures require smooth planar layers, while conversely, 3D islands hold promise as self-assembled quantum dots. The transition from planar growth to islands poses a longstanding puzzle in the understanding of growth to islands. The "critical thickness" is observed to increase dramatically. Transition thicknesses as large as 10-30 atomic layers are seen for InGaAs on GaAs (001), and similar behavior is seen for GeSi on Si (001). We have simulated such strained-layer growth, using a computational model that consistently accounts for the alloy compositional degrees of freedom. Under generic assumptions, we find behavior closely resembling that seen experimentally. The surface remains flat up to some thickness at which islands suddenly form. This approach, called mean-field kinetic Monte Carlo, is sensitive to the alloy composition, but only weakly on deposition rate. Our results confirm the insight of Gullis et al., that the key factor controlling the transition is the continuous increase of surface energy due to increasing island density. However, the specific kinetic mechanism is universal and surprisingly simple.

Microscopic View of InAs Quantum Dot Growth and Overgrowth

The strain driven self-assembly of faceted Ge nanocrystals during epitaxy on Si(001) to form quantum dots (QDs) is by now well known. The strain field in the substrate was deduced using an exact solution for the strain field of a semi-infinite quantum dot. The strain field was used to calculate the energy of the islands formed on the substrate. The islands grow in a directed fashion, with the growth direction being determined by the strain field. The islands are faceted, with the facets being determined by the strain field. The strain field is also used to calculate the energy of the islands formed on the substrate. The islands grow in a directed fashion, with the growth direction being determined by the strain field. The islands are faceted, with the facets being determined by the strain field. The strain field is also used to calculate the energy of the islands formed on the substrate. The islands grow in a directed fashion, with the growth direction being determined by the strain field. The islands are faceted, with the facets being determined by the strain field. The strain field is also used to calculate the energy of the islands formed on the substrate. The islands grow in a directed fashion, with the growth direction being determined by the strain field. The islands are faceted, with the facets being determined by the strain field.

Pattern Formation on Silicon and Silicon-on-Insulator

The strain driven self-assembly of faceted Ge nanocrystals during epitaxy on Si(001) to form quantum dots (QDs) is by now well known. [1] We have also recently provided an understanding of the thermodynamic driving force for directed assembly of QDs on bulk Si (extendable to other QD systems) based on local chemical potential and curvature of the surface. [2] Silicon-on-insulator (SOI) produces unique new phenomena. The essential thermodynamic instability of the very thin crystalline layer (called the template layer) resting on an oxide can be measured under approximate conditions of zero stress, and self-organized into an array of Si nanocrystals. Using LEEM, we observe this process and, with the help of first-principles total-energy calculations, we provide a quantitative understanding of this pattern formation process. The pattern formed shows the facets of the island, and how they develop. The Si nanocrystal pattern formation can be controlled by lithographic patterning of the SOI prior to the dewetting process. The result is presented in a simple phase diagram. Then the kinetic process of deposition combined with morphological evolution by surface diffusion is simulated. It is found that configurations may arise.
that appear to be neither stable nor metastable according to a simple energetics analysis; free energy is reduced as islands translate in certain directions with a transition to a post-deposition configuration these configurations do not evolve kinetically. Such configurations are found to represent a novel metastable state wherein islands are locked in energetically unfavored sites because the kinetically preferred pathway is not accessible by the system. We report finite element simulations, we show that the self-limiting nature of trench growth is due to a competition between the elastic relaxation energy gained by the formation of a trench and the surface energy cost for creating the trench. Our simulations predict a linear increase of the trench depth with the island radius.

Energetics of Trench Formation Around Ge/Si Quantum Dots. Dhananjay Tulsiram Tambe and Vivek B. Shenoy; Solid Mechanics, Brown University, Providence, Rhode Island.

At high growth temperatures, the misfit strain at the boundary of a Ge quantum dot on Si(001) is relieved by the formation of a trench around the base of the island. The depth of the trench has been observed to saturate at a level that depends on the base-width of the island. Using finite element simulations, we show that the self-limiting nature of trench growth is due to a competition between the elastic relaxation energy gained by the formation of the trench and the surface energy cost for creating the trench. Our simulations predict a linear increase of the trench depth with the island radius.

Abstract Adsorbed on a solid surface, a molecule can migrate and carry an electric dipole moment. A nonuniform electric field can direct molecules on a dielectric substrate surface, beneath which an array of molecules can migrate and pattern under the combined actions of dipole moments, temperature gradient, growth or sublimation, electromigration).

The Quasicontinuum Monte Carlo method for simulating surface growth. Leonard M. Sander,1 Jason Devita1 and Peter Smerick2; 1Physics, University of Michigan, Ann Arbor, Michigan; 2Mathematics, University of Michigan, Ann Arbor, Michigan.

We have developed an algorithm for treating growth on surfaces which treats the adatoms as a continuous fluid, and the islands and steps as...
collections of discrete particles. The method gives an accurate account of shot-noise fluctuations by converting adatoms to solid one atom at a time. For the case of irreversible growth, we can treat fractal island shapes, multilayer growth, and the effect of Erlich-Schwoebel barriers, and nucleation. The algorithm can, in favorable cases, be faster than Kinetic Monte Carlo. For growth near equilibrium we need to treat attachment-detachment from the same footing. This is much more delicate than the irreversible case. We will discuss the issues that arise, and how we deal with them.

3:30 PM JJ2.4/KK2.4/U2.4

The difference-differential equations of step motion on crystalline surfaces below the roughening transition temperature are formulated for closed interacting steps of reasonably arbitrary shape in (2+1) dimensions. Among the major kinetic processes considered are the diffusional adatoms across terraces, and the attachment and detachment of adatoms at the step edges, with inclusion of the Ehrlich-Schwoebel barrier. Basic ingredients of the formulation are (i) the approximate solution of the Laplace equation for the adatom concentration on each terrace within the quasistatic approach via separation of the space variables into "fast" and "slow" ones and application of asymptotics, and (ii) an analytical expression for the step change in front a sufficient number of steps of (CS) interactions, which include local elastic dipole-dipole interactions as a special case. The continuum limit of the discrete step-flow equations is examined in detail, with particular emphasis on the case with next-neighbor interactions. This limit yields a nonlinear differential equation (PDE) of fourth order for the height profile, which accounts for both step stiffness and step-step interaction energy. The PDE is compared to the one derived from the standard surface-free energy considerations and is shown to reduce to the latter under certain local conditions on the step interactions. The role of longitudinal currents, which are parallel to the steps, is discussed.

3:45 PM JJ2.5/KK2.5/U2.5

Mesa structures fabricated on Si(111) surfaces have been experimentally found to develop step arrays with large spacing of the order of a micron or more after annealing at temperatures where sublimation becomes important. These are caused by transient ridges around the edges that initially develop during annealing and form a barrier to step motion before eventually breaking down. This produces a step distribution that can be approximated as an array of steps of the same sign with a sufficient number of wide terraces. The analysis of the evolution of such an array of steps presents new aspects from those associated with cases where the step train consists of nearly evenly spaced steps. We have done computer simulations using one dimensional Burton, Cabrera and Frank (BCF) theory with attachment-detachment and step-step repulsion for this configuration. The results suggest that under conditions where there is significant motion of the entire train of steps, the step-step repulsion for the evenly spaced terraces will persist for a long time. If we include a significant Ehrlich-Schwoebel effect, where the incorporation rate for adatoms from the lower terrace is higher than that for the upper terrace, the steps redistribute to form step density waves that become stable after a short time. With no Ehrlich-Schwoebel effect the steps tend to become uniformly spaced. The predicted distributions will be compared with the experimentally measured ones.

4:00 PM JJ2.6/KK2.6/U2.6
Self-ordering of Nano-facets on Vincal SIC(0001) Surfaces and Its Application to Heterogeneous Nanostructures. Satoru Tanihara, Kazunori Terada, Tomoyuki Miyamoto, Masahiro Fujii and Hideo Sugawara; RIHS, Hokkaido Univ., Sapporo, Japan.

Surface nanostructures by taking advantages of self-ordering or self-organization have been attracted much attention in nanofabrication of semiconductor or device structures. Periodically and spontaneously ordered semiconductor surfaces reveal significantly fine and spatially uniform patterns, which are beyond the lowest limit of electron beam lithography. Formation of step/terrace structures is typically observed on technical surfaces from the island on the semiconductor substrates such as Si and GaAs have been studied, both for device applications and for understanding of basic surface physics. Silicon carbide is a compound semiconductors which possess a wide bandgap and significant electronic properties. It is thus a promising semiconductor for the next generation of high power and high frequency electronic devices. Initially, we have investigated the step/terrace configuration on vicinal SiC(0001) surfaces after high temperature HR annealing and found that self-ordered nanostructures, consisting of pairs of (0001) and (11-2m), were generated. The origins of such periodic nanostructures were discussed in terms of equilibrium surface phase separation and surface elasticity theory followed by Marchenko et al [2]. Note here that the periodicity of such nanostructures on 4H and 6H-SiC surfaces is superior to other materials such as Si and GaAs. We believe this is due to its polytypic nature. In this presentation, we report such self-ordered nanostructures under various etching conditions and discuss possible control of surface nanostructures and also show an application to heterogeneous epitaxial system such as GaN nucleation on SiC. [1] H. Nakagawa, S. Tsuchiya, I. Suenobe, Phys. Rev. Lett. 91, 126107-126103 (2003) [2] M. Blakely and A. Y. Parshin, Sov. Phys. JETP 52, 1 (1980).

4:15 PM JJ2.7/KK2.7/U2.7

The growth of nano-crystalline islands on the surface of Stranski-Krastanow (SK) film-substrate systems by self-assembly is a promising technique for device applications. A critical issue in realizing the self-assembly technology is to control the sizes, the locations, and the shapes of the nano-structures of islands. In this talk we propose that the controlled self-assembly of nano-islands can be achieved by a novel scheme, namely the activated Stranski-Krastanow transition (ASKT) method. The basic idea of the ASKT method is to make simple pattern on the substrate that is in a special thickness range and then anneal the system to activate the self-assembly of the patterns into islands. The method can control the initial conditions, and by varying the geometry of the patterns, the method has the capability to produce different island structures. For example, changing the size, the aspect ratio, and the height of a rectangular pattern, the ASKT method can yield a two-by-two island array, a square ring with a single or multiple rings, and multiple wires. In addition, the feature length of the structures can be a small fraction of the pattern size, and the length can be tailored by adjusting the mismatch strain in the film without reducing the pattern size. Most importantly, the instability of the patterns against coarsening and shape transition, a common phenomenon that causes serious problems in device applications, can be avoided in the ASKT method. The theory of the ASKT method is presented in this talk together with three-dimensional numerical simulation that demonstrates the potential capability of the ASKT method.

4:30 PM JJ2.8/KK2.8/U2.8
Stability and Evolution of Nano-ripples on Crystalline Surfaces. Astrid RamaaRamanutram and Vivek B. Shenoy; Division of Engineering, Brown University, Providence, Rhode Island.

The relaxation of nano-ripples on metallic and semiconductor surfaces is studied using a nonlinear continuum approach that accounts for the formation and interaction energies of surface steps as well as the Ehrlich-Schwoebel barrier at step-edges. This method is used to model recent experimental studies of relaxation of a Cu(OOl) surface. The relaxation process is in the attachment-detachment kinetic regime at the temperatures of interest here. Ripples are seen to decay with the formation of step-free regions or facets which indicates that the instability of the steps plays an important role in the decay behavior. Although the ripples have a dominant spatial frequency or wavelength, our studies find that the decay behavior is not same as that of a sinusoid of a single wavelength. The inherent nonlinearity of the evolution equations leads to significant effects in the modes in the vicinity of the dominant wavelength. Numerical calculations that account for these coupling effects are in very good agreement with the experimental observations.

4:45 PM JJ2.9/KK2.9/U2.9
Dislocation Orientation Surface Dynamics on Solids. Sanjay V. Khare1,2, S. Kodambaka1,2, W. Swiec2,1, K. Ohmori1,3, J. Petrov1,2, and J. E. Grevello1,2; 1Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois; 2Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, Illinois.

Using low-energy electron microscopy, we investigate the near-equilibrium dynamics of surface-terminated dislocations. We observe, in real time, the thermally-driven self-organized surfaces of (100) elements that rapidly develop an ordered nanostructure. The nanostructure of the material was found to change significantly as the temperature of the specimen is increased, and the shapes of the dislocations observed at low temperatures, such as a spiral geometry, N2 partial pressure, annealing time, and temperature.
We find that $\omega$ is independent of the local environment and ambient, and decreases linearly with time. From the temperature-dependent $\omega$ data, we obtain an activation barrier of 4.8$\pm$0.5 eV for the growth of spiral spirals. This phenomenon, attributed to point-defect migration from the bulk to the surface along dislocation lines, is both qualitatively and quantitatively different from step curvature-driven surface diffusion, and "standard" Burton-Cabrera-Frank (BCF) spiral growth.\(^{1}\) Our results demonstrate that dislocation-mediated surface roughening can occur even in the absence of deposition or evaporation, and provide fundamental insights into mechanisms controlling nanostructural stability. We expect that this process is general and that it occurs in other materials.\(^{1,2}\) K. Kodambaka, S.V. Khare, W. Swiec, K. Ohmori, I. Petrov, and J.E. Greene, Nature 429, 49 (2004).

Mound Formation and Evolution during Ag/Ag(100) Homoepitaxy. Kyle Caspersen, Anthony Layson, Patricia Thiel, and Howard A. Stone; 1Department of Physics and Astronomy, Arizona State University, Tempe, Arizona; 2University of Sussex, Brighton, United Kingdom.

In models of nucleation and growth on surfaces, it has often been assumed that surface diffusion is isotropic; however, many cases are known (e.g. Ge clusters or silicide nanowires grown on Si(001)) where anisotropic diffusion appears to be important. Here we explore the effect of anisotropic diffusion on the formation and evolution of mounds (multilayer stacks of 2D islands) with rapid slope followed by a prolonged regime of steepening exceeding 1000ML (with roughening and coarsening at the same rate). The steepening regime is compressed at lower temperature. Atomic Force Microscopy has been used to observe mound topography evolution as a function of temperature, and experimental conditions. The formation of mounds is attributed to the degree of lattice mismatch between the two materials (above which islands continue to evolve. Since the oxidation of the (001) films is controlled by oxygen diffusion with only limited diffusion of copper, the oxidation barrier inhibiting downward transport of deposited atoms, and the oxidation rate is modeled using potential gradients for diffusion. Initially, simulation of atomistic segregation is performed by Yang's group have revealed the intricacies of the nucleation and growth of oxide islands on the surface of copper thin films with low index surface orientations. Nucleation and growth of oxide islands does not begin until after surface roughness is complete. For (001) surface thin films, the surface reconstruction is the oxygen "root 2" with 2 variants, the surface layer of copper has missing rows along only one of the [100] and [101] directions. The crystal structure of the oxide Cu$_2$O can be visualized as fcc copper with 1 oxygen located in each of the 2 tetrahedral interstices along 1 of the body diagonals. The orientation of oxide islands on the [001] substrate is cubic-on-cube with lattice mismatch of 15% at RT. The oxide islands are 3 dimensional extending above and below the surface of the substrate and morphologies are strongly temperature dependent, ranging from irregular convex polyhedra to nanorods to step pyramids. It is thought that the range in morphologies is due to the degree of lattice mismatch between the two phases due to thermal expansion. Based on kinetic data and rate theory it was determined that surface diffusion of oxygen controls nucleation and growth rates. Atomic Force Microscopy has revealed zones of copper depletion after oxidation and plateaus of copper after subsequent reduction near the oxide islands. TFOx (Thin Film Oxidation), an atomistic kMC simulation incorporating many of the aspects, has been developed to model copper oxidation and continues to evolve. Since the oxidation of the (001) films is controlled by oxygen diffusion with only limited diffusion of copper, the simulation represents the microstructure by modeling the deposition (O$_2$ diffusion, and nucleation of oxygen. Copper is left to "fill in the remainder" of the oxide structure. Homogeneous nucleation is modeled using random nucleation and/or diffusing atom collisions. Nucleation on substrate defects is simulated by randomly selected sites and/or "root 2" domain intersections as nucleation sites. Randomly selecting missing rows models the "root 2" domains allowing different diffusion rates parallel and perpendicular to the missing rows. The effects of strain and other intermediate range interactions on diffusion are modeled using potential gradients for diffusion. Initial condition parameters and gradients were based on theory and systematically adjusted to obtain a range of morphologies and kinetic data similar to experimental observations. The use of results from first principles MD simulations as inputs (activation energies, potentials, etc.) to TFOx is
planned to better relate the underlying physics to experimental results. TFOx, the essential background information and some results will be presented.

**J13.6**

**Morphological Evolution during Competitive Etching and Oxidation of Si(100) Surfaces**

Tai-Te Chen, Itaru Funahashi, Da-Jiang Liu, Cheol Cho, Mark Gordon and Jim Evans

1. Department of Physics And Astronomy, Iowa State University, Ames, Iowa; 2. Ames Laboratory -USDOE, Iowa State University, Ames, Iowa; 3. Department of Chemistry, Kyungpook University, Taegu, South Korea.

Exposure of a vicinal Si(100) surface to oxygen at around 550-600°C produces etching-mediated step recession, although occasional formation of growth centers produces pinning points for the recession steps. We develop an atomistic lattice-gas model for this process guided by input from ab-initio quantum chemistry analysis. The model accounts for the interplay between oxygen surface chemistry (adsorption, diffusion, oxide formation, and etching via SiO desorption) and the Si surface and step dynamics (anisotropic diffusion and aggregation of vacancies formed by etching with other or with steps, and Si attachment-detachment dynamics at steps incorporating anisotropic energetics). Kinetic Monte Carlo simulation of this model produces etch morphologies where receding steps retain qualitative features of their equilibrium morphology (alternating rough SB steps and smooth SA steps), although pinning greatly distorts equilibrium structure. These features are seen in Scanning Tunneling Microscopy studies by Peltz and coworkers.

**J13.7**

**A Multiscale Model of the Si LPCVD Process**

Carlo Cavallotti, Maurizio Rondanini, Maurizio Mais and Sergio Carra

Il Sito, Milano, Milano, Italy.

The Low Pressure Chemical Vapor Deposition of Si from SiH4 is an industrial process that can be used to deposit epitaxial Si at relatively low surface temperatures. Multiscale models are necessary in order to tune the operating conditions to improve the quality of the deposited materials. In this work we present a multiscale approach meant to describe the Si morphological evolution at different time and length scales. In its main features, our multiscale approach is organized as follows. The gas-phase elementary reactions as well as the surface reactions and diffusion processes which kinetic constants are not experimentally known are investigated with density functional theory, representing the surface with clusters of different dimensions. The reactor fluid dynamics and overall mass and temperature balances are solved with finite element method using the kinetic schemes developed with quantum chemistry. The morphological evolution of the film is investigated with 3D Kinetic Monte Carlo. Our KMC model explicitly considers the 2X1 surface reconstruction of the (100) surface, the contemporary presence of diffusing H and Si adatoms, the hydrogen recombintive desorption reaction and the adsorption of SiH4 and SiH2 radicals. Its capability to successfully predict the surface morphology of Si deposited through MBE as well as the temperature programmed desorption of H2 was demonstrated through comparison with experimental data. The KMC model is dynamically linked to the FEM model, where it appears as a Von Neumann boundary condition. The FEM and KMC models are solved iteratively until convergence is achieved. To improve convergence, the contribution of the KMC boundary condition to the FEM Jacobian was evaluated numerically. We found that the presence of a significant amount of hydrogen on the surface can greatly influence the surface morphology evolution. In particular, hydrogen can be considered as the principal responsible of the transition from an order terrace step flow growth regime, which prevails at high temperatures, to a disordered 3 dimensional growth regime. We have theoretically investigated the dependence of the growth morphology on temperature, pressure and gas phase composition (SiH4/H2 ratio) with the aim of determining the operating parameters window that can lead to the best film morphology. Finally it is also worth noting that our KMC simulations show that the hydrogen surface chemistry active at low temperatures is probably richer than expected, since the formation of a significant number of islands on the surface dramatically increases the concentration of steps and thus the variety of configurations by which two adsorbed H atoms can interact. We calculated the rate of some of the hydrogen desorption reactions that can take place at steps, which we identified as possible through the KMC simulations, using quantum chemistry.

**J13.8**

**First-Principles Study for Epitaxial Growth of Zinc-Blende CrAs on GaAs Substrates**

Ricchiro Mukose, Koichi Kusakabe and Naoshi Suzuki

Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.

The zinc-blende CrAs is known as a half-metallic material predicted theoretically. And in experiments, the thin films of it on GaAs substrates, and the multilayers of zinc-blende GaAs/CoAs are reported to be grown by molecular beam epitaxy (MBE) by many researchers have been interested in this new material and possible superstructures, especially in their magnetic properties. But theoretical studies for the growth mechanism of them are few. We investigate theoretically the growth mechanisms and estimate the growth conditions from the first principles, using the pseudopotential method. We calculate the total energies for many surface patterns consisted of Cr and/or As adatoms on GaAs substrates, using the slab model. The adatoms on the top several layers of the substrate are completely relaxed for the each pattern. We compare these calculated results and discuss theoretically the possibilities and experimental conditions for the MBE growth of these superstructures consisted of the zinc-blende CrAs and GaAs.

**J13.9**

**Analytic Bond-Order Potential for the Simulation of the Growth of Semiconductor Films**

Ralf Drautz, Duc Nguyen-Manh, Dewey A. Murdick, Xiaowang Zhou, Haydn N. G. Wedding and David G. Pettifor

1. Department of Materials, University of Oxford, Oxford, United Kingdom; 2. Cullum Science Centre, UKAEA, Oxfordshire, United Kingdom; 3. Department of Materials, Science and Engineering, University of Virginia, Charlottesville, Virginia.

In this talk we outline the derivation of classical interatomic potentials by making two well defined approximations within density functional theory. In a first step we show that a simple tight binding (TB) model, in which the bond integrals are calculated from first principles, gives a good description of sp-valent systems such as C, Si or GaAs. We next sketch the derivation of classical analytic bond-order potentials (BOPs) by coarse grain the TB electronic structure in terms of moments of the local density of states. The required σ and τ bond orders quantify the single, double, triple and conjugated bonds in hydro-carbon systems and lead to a good treatment of radical formation. We demonstrate that analytic BOPs are able to describe bond formation and breaking and to accurately predict structural energy differences for varying bandfilling in quantitative agreement with TB calculations. This allows to treat sp-valent elements and their compounds within the BOP framework. We discuss the current development of BOPs for modeling the MBE growth of semiconductor films.

**J13.10**

**Modeling of Time Evolution of the Microstructure of V02(B) Films Deposited on Glass by MOCVD**

M.B. Sahana, G. Wadley and David G. Pettifor


The thin films of V02(B), a metastable polymorph of vanadium dioxide, grown at 370°C for 90 minutes on glass substrates by metalorganic chemical vapor deposition (MOCVD) using vanadyl(acac)2 as a source and SnO2 as a dopant were observed to form a complex microstructure comprised of ordered ensembles made up of strongly (001) oriented platelets. The growth of highly oriented platelets is driven by surface energy minimization and by the anisotropy in the crystal structure of V02(B). The distinctive microstructure of these films prompted us to carry out an investigation of the morphological evolution of V02(B) films grown at 370°C, as a function of the duration of deposition. The evolution of this microstructure is an oscillatory phenomenon, as manifested in the differential growth rate and the smoothness of film morphology, both as a function of deposition time, i.e., the microstructural evolution leads to stages in film growth, wherein the emergence of numerous platelets roughens the film surface and raises surface energy. This rising surface energy creates instability in film morphology, which is overcome by a net negative growth rate at certain stages in the growth process. During such a stage, even as the flow of reactants into the growth chamber continues, the film deposited hitherto deposited deposited some of its mass. This process results in a smoothening the film surface, thus reducing its surface energy, and correcting the instability caused by surface roughness. This roughening-shedding-smoothening of the film morphology is repeated as a function of the deposition time, i.e., the oscillatory evolution of film microstructure does not appear to have been reported to date. Hence, a growth model considering the minimization of the total surface energy of a growing film has been developed to explain qualitatively the intriguing evolution of microstructure of MOCVD-grown V02(B) films on glass.

**J13.11**

**Molecular dynamics study on the asymmetric intermixing behavior of Co-Al and Co-Cu multilayer**, Sang-Pil Kim, Seung-Suck Yoo, Seung-Cheol Lee, Kwang-Ryeol Lee, and Yong-Chae Chung

1. Future Technology Research Division, Korea Institute of Science & Technology, Seoul, South Korea; 2. Department of Ceramic Engineering, Hanyang University, Seoul, South Korea.
For the development of thin film muliplayer devices such as MRAM or GMR/TMR sensors, atomic scale intermixing at the interface should be controlled in a systematic manner. In the present work, we employed classical molecular dynamics simulation to investigate the atomic scale intermixing at room temperature during thin film deposition in Co-Al and Co-Cu systems. These two systems were chosen due to their significantly different thermodynamic characteristics. Each system has a stable intermetallic phase of CoAlB2 structure while Co-Cu system is almost immiscible at room temperature. In spite of the difference, both systems exhibited asymmetric intermixing behaviors. Atomic intermixing occurred when Co was deposited on Al or Cu substrate. When Al or Cu were deposited on Co substrate, no atomic intermixing was observed at room temperature unless the kinetic energy of the deposited atom was much larger than a few eV. The asymmetric intermixing was discussed in terms of the deposition kinetics. As the deposited atom approaches to the substrate, the deposited atom is inevitably accelerated by the interatomic potential between the deposited atom and the substrate atoms. Intermixing occurred only when the increase in kinetic energy due to the acceleration near substrate is sufficiently large to overcome the energy barrier of intermixing.

**JJ3.12**


The surface of a solid under stress is unstable if there is mass exchange and transportation along the surface. A notch on the surface can be a preferred site for crack nucleation. This work studies the evolution of a single notch under stress and reaction. The surface is represented by a family of curves with many degrees of freedom, and the elastic field is solved using complex conformal mapping method. In the numerical simulations, the notch either deepens immediately and forms singular tip, or becomes perfectly flat after long time; or flattens first, staying in a slowly evolving stage for a long time, then nucleates new surface instability and finally forms sharp tip, or becomes flat first, then forms a bump on the surface. Under certain condition, the time for nucleate a crack for a deep and sharp notches under stress can be longer than a smooth and shallow notch under the same condition. In the simulations, the effects of sign of stress, strain energy, surface energy, and chemical driving force are addressed in detail.

**JJ3.13**


The morphological stability of thin wires is important in electronic materials processing. As a first step in understanding the stability, we studied the linear stability of a freely-suspended thin wire with strong circumferential surface energy anisotropy. Wires of triangular and square cross-section of various shapes are considered. These shapes are modeled by a recently developed delta-function model of facets, which can easily control the degree of anisotropy. The stability of the wire depends on the equilibrium shape of the wire and on the tangential wave number of the perturbation. When the wire is circular, it is susceptible to Rayleigh's capillary instability. Deviation from circularity stabilizes the wire first and further deviation will destabilize the wire. These conclusions also hold for cylindrical cavities. [1] Xin, T. and H. Wong, "A delta-function model of facets," Surface Science 487, L529-L533 (2001).

**JJ3.14**

Phase-field model for epitaxial growth of islands and nanostripes. **Yu Yan Mei** and **Liu Bang-Gui**; Institute of Physics, CAS, Beijing, China.

We develop a novel phase-field model for the epitaxial growth of islands and nanostripes in order to span large spatial and time scales of practical engineering interests. A local phase-field variable, varying in the real space for distinguishing the substrate and different epitaxial atomic layers, is introduced to describe formation and aggregation of epitaxial features. The evolution of this phase field is determined by a time-dependent Ginsburg-Landau-like equation coupled to a diffusive transport equation of adatoms. The limited interlayer diffusion is taken into account according to the Schwoebel barrier. The atomic detachment is included into the model for the reverse growth and for the growth on top of islands in the submonolayer regime[1], this model reproduces both the scaling laws of island density and experimental size and spatial distributions of islands. For island growth in the multilayer regime[1], this phase-field model reproduces essential features of such experimental images concerned. Accurate coarsening and roughening exponents of the mounds are obtained. On a stepped substrate[2], this model reproduces the hybrid growth of islands on terraces and nanostripes at the substrate steps. Furthermore, this model describes the self-organized formation of a regular array of nanostripes, as a result of ripening, during the post-deposition annealing at elevated temperatures. Compared with atomic models and mean-field models, the phase-field model not only can span larger space and time scales while containing the elemental atomic kinetic of epitaxy, but also can provide a fine visualized morphology of epitaxial features. [1] Y. M. Yu and B. G. Liu, Phys. Rev. E 69, 021601 (2004); [2] Y. M. Yu and B. G. Liu, submitted to Phys. Rev. B.

**JJ3.15**

How does a dendrite choose its orientation? **Alan Kara** and **Tomokazu Hashimoto**; Physics, Northeastern University, Boston, Massachusetts.

Solidification dendrites typically grow along <100> directions in metallic systems with an underlying cubic symmetry. Other growth orientations, however, are possible and even commonly observed in Al alloys. This raises the question: how does a dendrite choose its orientation? The answer to this question is investigated using phase-field simulations of dendritic evolution in two and three dimensions. We find that the usual assumption that dendrites grow along directions that coincide with maxima of the interface free energy is incorrect. For a truly anisotropic second harmonic expansion of the anisotropic solid-liquid interfacial free energy, we find that dendrites grow along crystallographic directions that coincide very roughly in three dimensions with maxima of the interface free energy. For small anisotropies, the anisotropic phase-field model reproduces the hybrid growth of islands on terraces and nanostripes at the substrate steps. Furthermore, this model describes the self-organized formation of a regular array of nanostripes, as a result of ripening, during the post-deposition annealing at elevated temperatures. Compared with atomic models and mean-field models, the phase-field model not only can span larger space and time scales while containing the elemental atomic kinetic of epitaxy, but also can provide a fine visualized morphology of epitaxial features. [1] Y. M. Yu and B. G. Liu, Phys. Rev. E 69, 021601 (2004); [2] Y. M. Yu and B. G. Liu, submitted to Phys. Rev. B.

**JJ3.16**

Simulation of Dendritic Solidification With Moving Solids. **Jong-Kyu Yoon**; School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

Simulating dendritic solidification with solids carried by a moving fluid is the key to understanding microstructural evolution in metallic systems with an underlying cubic symmetry. Other growth orientations, however, are possible and even commonly observed in Al alloys. This raises the question: how does a dendrite choose its orientation? The answer to this question is investigated using phase-field simulations of dendritic evolution in two and three dimensions. We find that the usual assumption that dendrites grow along directions that coincide with maxima of the interface free energy is incorrect. For a truly anisotropic second harmonic expansion of the anisotropic solid-liquid interfacial free energy, we find that dendrites grow along crystallographic directions that coincide very roughly in three dimensions with maxima of the interface free energy. For small anisotropies, the anisotropic phase-field model reproduces the hybrid growth of islands on terraces and nanostripes at the substrate steps. Furthermore, this model describes the self-organized formation of a regular array of nanostripes, as a result of ripening, during the post-deposition annealing at elevated temperatures. Compared with atomic models and mean-field models, the phase-field model not only can span larger space and time scales while containing the elemental atomic kinetic of epitaxy, but also can provide a fine visualized morphology of epitaxial features. [1] Y. M. Yu and B. G. Liu, Phys. Rev. E 69, 021601 (2004); [2] Y. M. Yu and B. G. Liu, submitted to Phys. Rev. B.

**JJ3.17**

Morphology and resistance evolution during single asperity contact. **Ji Hee Kim**; PI-Ryung Chae; David J. Srolovitz; and Jong-Kyu Yoon; School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; School of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; School of Advanced Materials Engineering, Keokuk University, Seoul, South Korea.

Electrochemically actuated microswitches are common features of a wide range of Micro-Electro-Mechanical Systems (MEMS) devices. For example, a cantilever beam can be pulled repeatedly into contact with the substrate to create a high (radio) frequency electrical device. Since the surfaces are invariably rough, electric current begins to flow when asperities on the two surfaces come into contact. Such asperities suffer both elastic and plastic deformation when the surfaces are forced together. They also evolve as a result of adhesion and capillarity forces via surface diffusion. The electric current density through these very small contacts may be very large, giving rise to...
additional morphology evolution through electromigration. In this presentation, we will discuss the morphology evolution that occurs as a result of the defect limited diffusion of the electromigration. We model morphology evolution within the framework of the phase field model starting from the elastic adhesive asperity contact shape. The electromigration flux is determined by solving for the local electric potential and assuming that the atom flux is proportional to minus the electric potential gradient. We examine the shape of the evolving contact and the contact resistance as a function of applied voltage, contact density and asperity size. We have used geometrically perfect conical geometry. The asperities, the regions of large curvature are smoothed, the neck sizes increase and contact resistance falls rapidly. After this initial capillarity dominated regime, the evolution is dictated by the electromigration flux. This leads to further conical development and a conical dome dominates in the contact resistance. At the same time, a smooth trench develops near the asperity on the anode side.

**J3.18**
Modelling the Stability of TiO₂ Nanoparticles in Acid and Base. Amanda S. Barnard 1, 2, Peter Zapol 1, 2, and Larry A. Curtis 3, 2
1Center for Nanoscience Materials, Argonne National Laboratory, Argonne, Illinois; 2Chemistry Division, Argonne National Laboratory, Argonne, Illinois; 3Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

An important aspect in the use of nanometer sized titanium dioxide for advanced photochemical applications is the precise control of the size, phase and morphology of the nanoparticles in solution. The pH of the solution is widely used to manipulate such properties at the nanoscale. If a thermodynamic model is used to describe nanoparticles as a function of size and shape to theoretically investigate the effects of pH on titanium dioxide nanoparticles, with special attention given to the size dependence of the anatase to rutile transition phase, then an input for the model is the electronegativity functional of the solution. Calculations have been used to accurately determine surface energies and surface tension of low index stoichiometric surfaces of anatase and rutile under hydrogen rich and hydrogen poor conditions. The results indicate that the anatase phase is stabilized in acidic solutions while the rutile phase is stabilized in basic solution, and that pH may also be used to control the nano-morphology. This work has been supported by the U.S. Department of Energy, BES-Chemical Sciences, under Contract W-31-109-ENG-38.

**J3.19**
Kinetics of Interface Impurity Segregation Including the Effect of Nucleation and Growth of Islands of Segregated Atoms. Eduard Feldman 1 and Tetyana Melnik 2
1Matematicas, Universidad Popular Autonoma del Estado de Puebla, Puebla, Mexico; 2Electronic Properties of Metals, Donetsk Physics and Engineering Institute, Donetsk, Donetsk, Ukraine.

Segregation of impurity atoms to grain boundaries, other interfaces and surfaces is a well known phenomenon in solids. Many physical and mechanical properties of materials are controlled by impurity segregation. A classical example is embrittlement of grain boundaries in copper-base alloys, containing Bi in ppm range. It is necessary to know both energy levels and kinetics of the segregation for a correct understanding of segregation-property relationships. The progress in the description of the segregation kinetics is connected to the development of realistic models, which consider inter-atomic interaction within a segregation layer. In this report we considered the segregation of mutually attractive atoms towards an interface including the effect of nucleation and growth of islands of segregated atoms within the segregated layer. The Gorskii-Bragg-Williams modelling and the resulting Fowler noether are the most simple one possible in order to deal with interacting atoms. It is studied the kinetics of the average impurity concentration on the interface in case when surface segregation is thermodynamically metastable. It is shown that the average impurity concentration becomes more complicated and can include long period of intermediate non-equilibrium states with concentrations, different from the equilibrium value. Their duration is determined by evolution of this island-like structure. The range of parameters (temperature, bulk impurity concentration) are established where these phenomenon can occur. The main stages of the segregation combined with redistribution of impurities along nonhomogeneously filled interfaces are analyzed and the duration is evaluated. The authors knowledge no special experiments aimed at the detection of nonhomogeneous segregation caused by 2D decomposition are present in the literature. However, impressive progress in the development of new experimental techniques, e.g. analytical electron microscopy methods, with a better spacial resolution and higher elemental sensitivity will provide better possibilities for direct experimental observation of such mentioned phenomenon.

**J3.20**
On the Nucleation, Localization and Stabilization of Coarse Slip Bands. Chehung Wei 1 and John L. Bassani 2
1Mechanical Engineering, Tsinghua University, Taipei, Taiwan; 2Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania.

Localized deformation is widely observed during plastic flow of single- and poly-crystalline metals as well as metal-matrix composites. Within the setting of continuum theory, where crystallographic slips (shears) provide the kinematical mechanism for plastic flow, we have shown that fine secondary slips contribute significantly to overall hardening behavior and also play an important role in the nucleation and stabilization of localized modes of deformation. One such example is the evolution of coarse slip bands (CSBs) in ductile FCC single crystals. A bifurcation calculation is used to predict the evolution of localized deformation in the growth of very small imperfections. A physically-based hardening model which captures a wide range of phenomena is shown to be essential for the predictions of CSBs. The initial rapid growth of shear strains in the bands is associated with the suppression of secondary slip in the band that results from equilibrium and compatibility conditions. Eventually, secondary slips are activated to stabilize the localization, essentially by a forest hardening mechanism. Since the orientation of the tensile axis affects secondary-slip activity, it also affects localized deformation.

**J3.21**
Influence of Strain from an Embedded Particle on the Microstructural Evolution of a Thin-Film System. Steve Policastro 3 and Nitin Singh 2
1University of Virginia, Charlottesville, Virginia; 2Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

Three dimensional simulations in an elastic half-space are used to examine the influence of an embedded particle on the chemical decomposition and microstructural evolution of a stressed, binary thin film located on a non-decomposing substrate. Phase evolution is governed by a Cahn-Hilliard equation where the variational derivative of the free energy defines the driving force for diffusion in the elastically anisotropic system. The strain field from the embedded coherent inclusion and the heteroepitaxial strain is shown to influence strain-free evolving microstructure in the thin film through the elastic interaction between the misfit strain of the buried inclusion and the compositional strains in the film. This work was supported by the NSF Materials Research Science and Engineering Center, "The Center for Nanoscopic Materials Design" at the University of Virginia.

**J3.22**
Nucleation and growth of drugs and other crystalline solids on self-assembled monolayers on gold. Branko Zubic, Adam L. Wilbur and John C. MacDonald; Department of Chemistry & Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.

We currently are investigating whether nucleation and growth of crystals of drugs and other crystalline solids can be induced and controlled using self-assembled monolayers (SAMs) on gold as substrates. Our strategy is to crystallize drugs such as acetaminophen and barbital (diethylbarbituric acid) in particular because these drugs crystallize in several different polymorphic forms. We also have examined the crystallization behavior of bis(imidazolium 2,6-dicarboxypyridine) metal(II) complexes on these substrates. Goals of this research include determining the following: (1) if crystals of these compounds will nucleate and grow selectively on SAMs, (2) if nucleation occurs preferentially on surfaces functionalized a certain type of adsorbate, (3) whether polymorphism can be controlled on different surfaces and (4) whether crystals grow oriented on specific faces (lattice planes). The results of this research are presented.

**SESSION JJ4: Solidification: Atomistic and Continuum Modeling**
Chair: Mark Astar
Tuesday Morning, November 30, 2004
Room 201 (Hynes)
8:30 AM **JJ4A1**
Anisotropic Free Energies of Crystal-melt Interfaces.
James Robert Morris 1, Ruslan Davidakov 2, Mikhail Mendelev 3 and David J. Srolovitz 3
1Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; 2Department of Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania; 3Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

We currently are investigating whether nucleation and growth of crystals of drugs and other crystalline solids can be induced and controlled using self-assembled monolayers (SAMs) on gold as substrates. Our strategy is to crystallize drugs such as acetaminophen and barbital (diethylbarbituric acid) in particular because these drugs crystallize in several different polymorphic forms. We also have examined the crystallization behavior of bis(imidazolium 2,6-dicarboxypyridine) metal(II) complexes on these substrates. Goals of this research include determining the following: (1) if crystals of these compounds will nucleate and grow selectively on SAMs, (2) if nucleation occurs preferentially on surfaces functionalized a certain type of adsorbate, (3) whether polymorphism can be controlled on different surfaces and (4) whether crystals grow oriented on specific faces (lattice planes). The results of this research are presented.
Mathematics, University of Leicester, Leicester, United Kingdom; 3Dept. of Mechanical & Aerospace Eng., Princeton University, Princeton, New Jersey.

In the past several years, there have been significant advances in approaches to calculating the free energy of crystal-melt interfaces from simulations. However, there has been large discrepancy in previous calculations, current approaches can not only predict accurate values, but can resolve the anisotropies in the values on the order of 1-2%. We demonstrate these approaches, in particular the fluctuation approach applicable to rough interfaces, and compare the results. For the Lennard-Jones system, the results are in very close agreement; whereas the hard-sphere results give smaller values than in previous calculations. For more realistic models of Al, we show that different potentials have very different values, which are correlated with the liquid structure. We also include recent results for purely repulsive potentials, of the form 1/r^6. This research has been sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle. We also acknowledge funding from the Dept. of Energy’s Computational Materials Science Network project, “Microstructural Evolution Based on Fundamental Interfacial Properties,” and computer time from the Dept. of Energy’s National Energy Research Scientific Computing Center.

9:00 AM *J14.2 Molecular Dynamics Simulations of Solid-Liquid Interface Mobility in FCC and BCC Metals. Jeffrey J. Hoyt1, Mark D. Asta2, Doyun Sun1 and A. Karma1, 1Sandia National Laboratories, Albuquerque, New Mexico; 2Dept. of Materials Science & Engineering, Northwestern University, Evanston, Illinois; 3Physics Dept., East China Normal University, Shanghai, China.

The crystal-melt interface mobility plays an important role in controlling the morphology and growth kinetics of dendrites. The mobility is typically characterized by the kinetic coefficient, \( \mu \), defined as the constant of proportionality between the interface undercooling and the solidification velocity. Using molecular dynamics simulations and interatomic potentials of the embedded atom form, we have computed the kinetic coefficient in several FCC and BCC pure metals. With the exception of BCC metals growing along [100], the crystallization rates and their dependence on crystallographic growth direction are well described by a density functional theory based model due to Mikheev and Chernov. The discrepancy in the BCC case stems from an anomalously large solid-liquid interface width observed for the [100] orientation. In addition, we have computed the kinetic coefficient in a binary alloy, namely the B2 ordered NiAl system. For NiAl a low value of \( \mu \) and a pronounced asymmetry between solidification and melting rates is observed.


We extend the density functional based phase field approach to describe fcc crystal growth. The density functional is constructed using a simple phenomenological two-peak liquid structure factor that yields a free energy minimum corresponding to a fcc crystal structure. As an example of application of this functional, we study equilibrium density profiles across the crystal-melt interface. The spatial variation of spacing between density peaks for different crystal faces are found to be in good qualitative agreement with the results of previous molecular dynamics simulations. We also examine the relationship between the anisotropy of the interface kinetic coefficient and the underlying crystal structure in the context of this model.


The composition dependence of the magnitude and associated crystalline anisotropy in the crystal-melt interfacial free energy is of primary importance in determining alloy solidification rates and morphologies. To date the most detailed information concerning crystal-melt interfacial properties has been derived from atomistic computer simulations. This work has focused primarily on elemental systems, and far less is known about alloys. We are using Metropolis Monte-Carlo techniques to determine how the equilibrium interfacial solute adsorption depends on size and energy mismatch through a survey of model Lennard-Jones binary alloys. These simulations also provide the starting point for fluctuation simulations to examine how the interfacial free energy and its associated anisotropy depend on composition.

10:00 AM *J14.5 Nucleation and polycrystalline growth in phase field theory. Laszlo Granasy1, Tamas Puza1, James A. Warren2 and Jack F. Douglas2; 1Research Institute for Solid State Physics and Optics, Budapest, Hungary; 2Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, Maryland;

A phase field theory of crystal nucleation and polycrystalline growth is presented. The model is tested for crystal nucleation in the hard sphere system. It will be shown that evaluating the model parameters from molecular dynamics simulations, the phase field theory predicts the nucleation barrier accurately. The formation of spherulites is discussed in an extension of the model that incorporates branching with definite orientational mismatch induced by a metastable minimum in the orientational free energy. The mechanism of polycrystalline growth is the quenching of orientational defects (grain boundaries) into the solid due to a reduced ratio of rotational and translational diffusion coefficients expected at high undercoolings. It will be demonstrated that a broad variety of spherulitic patterns can be recovered by changing only a few model parameters (anisotropy, free energy of metastable minimum, branching angle, orientational mobility).

11:00 AM J14.6 Modelling the Crystal Size Distribution for Nucleation and Growth Kinetics in 2D. David T. Wu, Mechanical Engineering, Yale University, New Haven, Connecticut.

For crystallization by the nucleation and growth mechanism, the crystalline fraction transformed is a function of time in the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model, but except for special cases in 1D, there is no exact theory for the time-dependent crystal size distribution on account of impingement. I present an analysis for the time-dependent size distribution and a method for its construction via superposition of appropriate weight functions.

11:15 AM J14.7 Growth Front Nucleation: A Mechanism for Polycrystalline Growth. James A. Warren1, Laszlo Granasy1, Tamas Puza1 and Jack Douglas2; 1NIST, Gaithersburg, Maryland; 2RISSPO, Budapest, Hungary.

The formation of a polycrystal is usually considered to occur either by the impingement of nucleating grains in a liquid (equiaxed grains), or via the nucleation of columnar grains on a surface. In this presentation we consider the formation of a polycrystal via a third mechanism: growth front nucleation. This model of growth manifests when new orientations nucleate on the front of a growing crystal, yielding a densely branched morphology, where the classical effects of surface energy anisotropy are disrupted by the nucleation process. We develop a phase field model to describe the phenomenon, and demonstrate that this type of growth can be initiated by either static or dynamic heterogeneities in the solidifying system. We examine several types of growth forms, reexamine some older experiments, and examine prospects for models of this phenomenon in three dimensions.

11:30 AM J14.8 Phase Field Modeling of Microstructural Evolution in Polycrystalline Columnar Materials. Ming Tang1, W. Craig Carter1 and Rowland M. Cannon2; 1Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; 2Lawrence Berkeley Laboratory, University of California, Berkeley, California.

The microstructural evolution of polycrystalline columnar materials was modeled with the phase-field method. The model naturally takes into account various evolution mechanisms such as grain boundary motion and grain rotation. The model is found to be in parallel to Cahn’s critical point wetting model[1], and grain boundary prewetting transitions occur at elevated temperatures. The transitions could be either first order or continuous, depending on the grain misorientation. Grain boundary phase diagrams are constructed from the modeling. Grain rotation is an important grain growth mechanism for nanocrystalline materials, but the rotation rate is affected by the grain boundary status (dry or pre-melted). In addition, grain boundary migration and grain rotation, a third possible grain growth mechanism via grain melting/re-solidification was found. Pre-melted grain boundaries could cause small grains to be melted below the bulk melting point. The nearby larger grains then achieve a growth by re-solidifying the local melt. [1] J.W. Cahn, J. Chem. Phys. 66, 3667 (1977).
Surface morphology and internal atomic structure of Cu nanoparticles are investigated by means of molecular dynamics simulation. An embedded atom method potential function developed by the present authors is adopted in the simulation. Two kinds of model samples of copper nanoparticles are prepared for the simulation. These are polycrystalline and amorphous-like particle. Each particle consists of 5000 - 20000 atoms, and sizes are 5 - 8 nm in diameter. In the simulation the polycrystalline nanoparticle is formed by cooling the molten state slowly and then by annealing the particle. Several methods of annealing procedure are tried to obtain a configuration with minimum configuration energy, and the results are compared. Thus obtained particles are rather irregular polyhedrons compared to the natural nanoparticles, and large portion of surfaces are composed of non-planar faces, such as corner, edge, and dislocation. Surface morphology of the simulated nanoparticles are characterized in relation to surface energy. The amorphous-like particles of pure copper can be realized by quenching the molten states, but it turned out to be impossible in the case of copper-alloys because of the altered mechanical behavior of the porous overlay. Porosity formation generally requires that the driving force to remove the more chemically active element of the alloy exceeds some threshold (known as the critical potential). Even though this threshold has been well characterized in both controlled experiments in electrochemical cells and kinetic Monte Carlo simulations, the mechanism of porosity formation remains elusive. No fundamental theory free of fit parameters is yet available to predict the critical potential. This talk describes a phase-field approach to simulate the nanomorphological evolution of the alloy/electrolyte interface during dealloying. A diffuse interface model is developed motivated by a plausible set of mechanisms of non-spherical, self-similarly growing crystals. We then examine the evolution of nonplanar surfaces. Specifically, we detail the impact of competition between two surfactant additives, a deposition-rate accelerating additive and a leveling additive, on the concentration of the more noble element forming the porous structure. Even though this model is a considerable simplification of the underlying electrochemistry, it reproduces the salient features of nanoporosity formation observed experimentally and makes simulations of realistic three-dimensional pore structures computationally accessible. Results pertaining to the dynamical mechanism of porosity formation and to the dependence of the critical potential on characteristic length and time scales of the problem are discussed in the context of previous theories and experiments.
critical flux for self-similar growth, in the sense that the symmetry of the crystal remains unchanged. This suggests that in experiments, small oscillating critical flux will yield large fluctuations of self-similar growth. Shape perturbations may either grow or decay. However, at long times there is nonlinear stabilization even though unstable growth may be significant at early times. Interestingly, this stabilized flow depends on the existence of internal limiting shapes. That is, we find that the morphologies of the nonlinearly evolving crystals tend to limiting shapes that evolve self-similarly and depend only on the flux. A number of limiting shapes exist for each flux (the number of possible shapes depends on the flux), but only one is universal in the sense that a crystal with an arbitrary initial shape will evolve to this shape. By performing a series of simulations, we construct a phase diagram that reveals the relationship between the applied flux and the achievable symmetries of the limiting shapes. Finally, we use the phase diagram to design a protocol by which the compact growth of crystals with desired symmetries can be achieved.

4:30 PM J15.6


Grain boundary structure and properties depend on five distinct crystallographic variables: three to describe the relative orientation of one grain with respect to the other and two to describe the boundary plane. The evolution of polycrystalline structures may depend on the anisotropy in grain boundary mobility, grain boundary free energy/twistiness, efficiency with which the boundary absorbs defects, and the degree of anisotropy in the mobility of the grain boundary as a function of temperature. We discuss methods to reveal the anisotropy of the quantity that describes how quickly a particular boundary migrates in capillarity-driven situations and how quickly a particular boundary migrates in capillarity-driven situations (i.e., the reduced mobility) as a function of the grain boundary mobility and the grain boundary anisotropy. By combining these results with the pure boundary mobility extracted in stress-driven boundary migration, we determine the grain boundary stiffness as a function of boundary inclination. This approach can be used to determine the entire space of reduced boundary mobility and stiffness as a function of all five bicrystallographic parameters.

4:40 PM J15.7

Faceting and Structural Transformations in Asymmetrical Grain Boundaries. Juan Anthony Brown and Yuri Mishin, School of Computational Sciences, George Mason University, Fairfax, Virginia.

Faceting and other structural transformations at grain boundaries (GBs) can play a significant role in materials properties and are not well understood on the fundamental level. We use copper as a model material to study structural trends, structural phase transformations and faceting in a series of Sn11 [100] symmetrical tilt GBs with various inclination angles. Molecular statics and dynamic simulations in conjunction with an embedded-atom potential are applied to study the structures of the boundaries over the entire range of inclinations at temperatures from 0 K to almost the melting point. The structures of the boundaries may or may not exhibit faceting behavior and other structural effects depending on the temperature. The low-temperature faceting behavior is consistent with the polar plot of GB energy and the relevant Gibbs-Wulff construction. Overall the results are in agreement with available experimental data and can be rationalized in terms of interfacial thermodynamics.

4:15 PM J15.8

Grooving of a Grain Boundary by Evaporation-Condensation below the Roughening Transition. Howard Alvin Stone, Michael Aziz and Dionisios Margolis, Engineering & Applied Sciences, Harvard University, Cambridge, Massachusetts; Department of Mathematics, MIT, Cambridge, Massachusetts.

The development of surface grooves at grain boundaries that intersect a planar surface is analyzed in this work. The evolution occurs below the thermodynamic roughening transition by evaporation-condensation processes. The dynamics are described by a one-dimensional nonlinear partial differential equation. This equation has a similarity solution that produces a self-similar groove profile described by a nonlinear ordinary differential equation. An analytical approximation is constructed which is in excellent agreement with the numerical solution. The depth and width of the groove varies as t^{1/2}, where t is time, analogous to the classical results valid above the thermodynamic roughening temperature. In addition, the approximate analytical solution provides an explicit relation between the groove width and the dihedral angle.

4:30 PM J15.9


A vertical grain boundary intercepting a horizontal free surface forms a groove to reduce the combined surface energy of the system. We study grooving by surface diffusion with anisotropic surface energy. A recently developed delta-function model of facets is used to describe the surface energy with three or four fold symmetry. It is found that the groove forms follow a similarity law. The self-similar groove profile is solved numerically by a shooting method. Even with strong anisotropy, the groove profile can be smooth if the exposed surface orientations do not include a facet orientation. The smooth self-similar groove shape is the same as an isotropic groove, but the size is reduced by a factor that depends on the degree of anisotropy. This induces a large error on the value of surface diffusivity if the isotropic model is used for an anisotropic system [1]. In this talk, we will describe how to correct for this error [1]. Xin, T. and H. Wong, "Grain-boundary grooving by surface diffusion with strong surface energy anisotropy," Acta Materialia 51, 2305-2317 (2003).

4:45 PM J15.10


We have developed a novel, computationally efficient reaction rate theory based on the Wooten-Winer-Weire (WWW) algorithm to study transformations between amorphous and crystalline phases in network forming materials. Different phases are treated in terms of atomic ring distributions, and the transformation between the phases is considered to be due to conversion of one set of rings into another. Using this approach we have studied the collapse of amorphous regions in thin crystalline films. We found that an amorphous region is emitted by motion of low-energy facets, while its collapse is due to the mobility of the high-energy facets. The approach is easily transferable to realistic network and non-network materials and can be applied to studying these crystalline embedded amorphous systems, which are of potential interest for the phase-change data storage. (This research is funded by Hewlett-Packard Laboratories, Palo Alto, USA.)
the incoming molecule and the surface. I show that for many proteins this barrier is due to the necessity to destroy the solvent shell around the protein molecules. I show that the destruction of this shell is also a major component of the energy and entropy effects of crystallization and the intermolecular interaction barrier that it causes drastically modifies the phase diagram of the protein solution. For an ultimate test, I present results with insulin, a protein, which crystallizes in the presence and absence of acetone, a reagent known to break water structures at hydrophobic surfaces. These tests show that in the presence of acetone, the insulin step kinetic coefficient is of order of a few 0.1 mm/min; i.e., slower than the kinetic coefficients of small molecule substances. Molecular dynamics simulations support the conclusion that acetone accelerates the destruction of the solvent shell around the insulin molecules. The overall conclusion of these results is that of the many factors that lead to slow protein crystallization, the most significant is the contribution of the solvent structures around the hydrophobic patches on the surface of the protein molecules. J. Amer. Chem. Soc. 122, 156 (2000); Proc. Natl. Acad. Sci. USA 97, 4277 (2000); Proc. Natl. Acad. Sci. USA 100, 752 (2003); Phys. Rev. Lett. 84, 1330 (2000); Acta Crystallogr. D 58, 1611 (2002); Biophys. J. 85, 9365 (2003); Phys. Rev. Lett 90, 225503 (2003); J. Am. Chem. Soc. 125, 11684 (2003).

9:00 PM *J16.3 Surface freezing and the kinetics of the isotropic-smectic phase transition. Zeevamin Dugie, Rowland Institute, Harvard University, Cambridge, Massachusetts.

We study the kinetics of the isotropic-smectic phase transition in a colloidal rod/polymer mixture by visualizing individual smectic layers. First, we show that the bulk isotropic-smectic phase transition is preceded by a surface freezing transition in which a quasi-two-dimensional smectic phase wets the isotropic-nematic interface. Next, we identify a two-step kinetic pathway for the formation of a bulk smectic phase. In the first step a metastable isotropic-nematic interface is formed. This interface is wettet by the surface induced smectic phase. In the subsequent step, smectic layers nucleate at this surface phase and grow into the isotropic bulk phase.

9:30 PM J16.4 Simulating Vapor Deposition of Polymer Thin Films. Yiping Zhao and Wade Bowie, Physics and Astronomy, University of Georgia, Athens, Georgia.

Recently there has been increasing interest in vacuum deposited polymer thin films because they have become more technically important for micro-electronic interconnects, organic electronics, and biotechnology. Due to the different chemical nature of the polymers, the growth mechanisms of polymer thin films will be very different from those of inorganic films. For vapor deposition polymerization of linear chain polymers, both condensation and diffusion of monomers occur. The monomers can be consumed by two chemical reactions: first, initiation, in which new polymer molecules are generated; and second, propagation in which existing polymer molecules are extended to higher molecular weights. Despite these two chemical reactions, the monomer diffusion and polymer chain relaxation can be considered as two other natural mechanisms for the morphology formation. The nature of the linear chain polymer has confined the bonding sites of the polymer and the monomer can only bond to the active (end) sites of a polymer, or another monomer. Therefore the grown polymer chain will form an entangled or an overhanging configuration, which will block the space it covered from the access of other incoming monomers. Here we have constructed a simple 1D dimension model by considering shadowing effect, bonding limitation and monomer bulk diffusion, to simulate linear polymer thin film growth under vapor deposition polymerization. The simulation shows that the polymer chain length, the width of the growth front, the film thickness, as well as the interfacial depth between the film and substrate increase as a function of the ratio of diffusion coefficient to deposition rate \( G \), while the density of the polymer film decreases with \( G \). These results qualitatively agree with some existing experimental results. Acknowledgement: Work supported by NSF.

9:45 PM J16.5 Abstract Withdrawn

SESSION J17: Epitaxial Thin Film Growth: Strain Effects and Instabilities

Chair: Xiangrong Wang
Wednesday Morning, December 1, 2004
Room 201 (Hynes)

8:30 AM J17.1 First-Principles Calculations of Strain Dependent Thermodynamic and Kinetic Parameters in Ge/Si(100).

Matthew J. Beck, Axel van de Walle, Mark D. Asta and Peter W. Voorhees; Materials Science and Engineering, Northwestern University, Evanston, Illinois.

Quantitative modeling of morphological evolution in Stranski-Krastanov epitaxial growth requires a knowledge of the dependence of surface thermodynamic and kinetic parameters upon strain state. These properties are known to be strongly coupled to the detailed surface structure, and are, therefore, highly sensitive to strain-induced surface structure modifications. We present results of first-principles calculations of the strain dependencies of surface structure, energetics, and diffusion barriers for complex dimer vacancy line reconstructions observed in the Ge/Si(100) wetting layer system. The implications of these results for morphological development in Ge/Si(100) thin film growth are discussed based upon continuum-level analyses employing the first-principles calculated parameters.

8:45 AM J17.2 Atomistic Modeling and Experimental Observations of Simultaneous Plastic and Elastic Relaxation in 3D-dislocated Ge Islands on Si(001). Anna Marzegalli 1, Francesco Montemelã, Armando Rastelli 1, Hans van Kaster 3 and Leo Miglio 3; 1INFN and L-NESS, Dipartimento di Scienza dei Materiali, University of Milano-Bicocca, Milano, Italy; 2INFN and L-NESS, Dipartimento di Fisica, Politecnico di Milano, Polo Regionale di Como, Como, Italy; 3Max-Planck-Institut fur Festkorperforschung, Stuttgart, Germany.

Atomistic simulations based on Tersoff potentials are used to investigate strain relaxations in dislocated Ge islands on Si(001). Detailed information about the elastic energy and strain fields, as well as the overall formation of the dome-shaped island growth along the [110] direction, is obtained. Intriguing features closely related to experimental observations appear. In particular, our theoretical calculations provide an explanation for STM and AFM images showing inhomogeneous dome-shaped island growth along the [110] direction, triggered by dislocation nucleation in the so-called "cyclic growth" phenomenon.

9:00 AM J17.3 First-Principles Studies of Growth and Structural Properties of Surfaces.Kalman Varga 1,2, Ligen Wang 3, Sokrates Pantelides 4; 1Condensed Matter Theory Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2Department of Physics, University of Nebraska, Lincoln, Nebraska; 3Department of Physics, University of Tennessee, Knoxville, Tennessee.

The formation and stability of low dimensional surface structures are strongly influenced by various quantum effects e.g. confinement, rebonding, reconstruction, or Friedel oscillation. First-principles total energy calculations based on density functional theory have been well developed as accurate methods to predict, at the atomic level, the energy, structure and other properties of surface nanostructures. In this talk we present our first-principles study of Ge film growth on Si(001) as a prime example for a system where realistic atomic description is indispensable. In the study of the Stranski-Krastanov growth of Ge on Si(001) we have shown that the observed critical layer thickness can only be explained by the inclusion of the Ge dimer buckling and the (2x2) superstructure on the Ge top layer. Calculations that assume to preserve the (2x1) reconstruction of the Si surface in the growth front of Ge predict island formation already after 1 or 2 monolayer of Ge. In contrast, the inclusion of the dimer buckling and the the (2x2) superstructure as the first strain-relieving mechanisms leads to delayed islanding, predicting the critical thickness to be equal to the experimental value of 3-4 monolayers.

9:30 AM J17.4 Atomic Simulation of Stress Evolution in the Early Stages of Volmer-Weber Growth. Chien-Wei Pao 1,2, Mikhail I. Molokeev 1,2 and David A. Muller 2; 1Polytechnic Institute of New York, University of Science and Technology of Materials, Princeton University, Princeton, New Jersey; 2Department of Mechanical & Aerospace Engineering, Princeton University, Princeton, New Jersey.

Wafer curvature experiments show that during Volmer-Weber growth, the stresses in the islands are compressive; the magnitude of which increases as the islands grow. The origin of these stresses is speculative. We performed a series of hybrid quantum-mechanical/molecular dynamics simulations of the growth of islands on an amorphous substrate that confirm that compressive stresses form and increase as the islands grow. To identify the origin of this effect, we perform a series of simulations as a function of island/substrate bond strength. Stronger interfacial bonding leads to smaller wetting angle and larger compressive stresses. Weaker bonding leads to slipping at the island/substrate interface and islands that are nearly stress-free. These observations are consistent with experimental

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results in which stronger interfacial bonding leads to larger compressive stresses in the islands and smaller film thicknesses at which the interfacial development of tensile stresses during film growth occurs.

9:45 AM 117.5
Contrasting Growth Modes of Mn on Ge(100) and Ge(111) Surfaces: Subsurface Segregation versus Interdiffusing, Wenguang Zhu1,2, Hanno Weitinger3,1, Enge Wang2, Efthimios Kaxiras3 and Zhenyu Zhang1,3,4,1 Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; 2International Center for Quantum Studies and Institute of Physics, Chinese Academy of Sciences, Beijing, China; 3Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee; 4Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Boston, Massachusetts.

Based on first-principles total energy calculations within Density Functional Theory (DFT), we show that a low dose of Mn on Ge(100) initiates in a novel subsurface growth mode, characterized by easy access to, and strong preference for, interstitial sites located between the two topmost Ge layers. Strikingly, such a "subsurtactant action" is preserved even during epitaxial growth of additional Ge layers, analogous to the well-known phenomenon of surfactant action. In contrast, along the (111) orientation, Mn can easily diffuse into the bulk via interstitial sites. These results are discussed within the context of dopant control and delta-doping in dilute magnetic semiconductors.

10:30 AM 117.6
Ab Initio Modelling of Self-Assembled Pattern Growth in Heteroepitaxial Alloy Films with Long-Range Elastic Interactions, Vidvuds Ozolins1, Tejodher Muppidi1 and Mark D. Asta2; 1Materials Science & Engineering, UCLA, Los Angeles, California; 2Materials Science & Engineering, Northwestern University, Evanston, Illinois.

Formation of two-dimensional (2D) nanoscale patterns (stripes and disks) has been observed in several surface alloy systems composed of bulk-compatible species. These unusual 2D structures occur due to a competition between attractive short-range clustering tendencies and repulsive long-range elastic forces. We will present a theoretical framework that accurately incorporates structural energies obtained from first principles non-structure methods. The central role in this formalism belongs to a Fourier transform of long-ranged pair interactions between surface atoms, which include both alloying and elastic strain effects. Our formulation enables rapid screening for new alloy/substrate systems with strong energetic tendencies to form long-period ordered patterns. This method can be efficient coupled with kinetic Monte Carlo simulations, enabling studies of dynamical pattern evolution during epitaxial growth. Finally, we outline efficient strategies for dealing with long-range elastic interactions in ultrathin 2D films based upon site elimination strategies developed in the context of the renormalization group. Applications to metallic alloy films and rare-earth dilute nanowires on Si(100) will be shown.

11:00 AM 117.7
Interfacial States and Far-from-equilibrium Transitions in the Epitaxial Growth and Erosion on (110) Crystal Surfaces, Artem Levandovsky1, Leonardo Golubovic1 and Dorel Moldovan2; 1Physics, West Virginia University, Morgantown, West Virginia; 2Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana.

We theoretically discuss the far from equilibrium interfacial phenomena occurring in the multilayer homoepitaxial growth and erosion on (110) crystal surfaces. As evidenced by experiments, these rectangular symmetric faceted layers exhibit a wide variety of interfacial non-equilibrium interfacial structures, such as the rippled one-dimensionally periodic states that are not present in the homoepitaxial growth and erosion on the high symmetry (100) and (111) crystal surfaces. Within a unified continuum model for interface dynamics, here we elucidate this multitude of novel states on (110) surfaces as well as the transitions between them. In particular, by analytic arguments, numerical simulations, and by bridging of length scales, we find two distinctive transitions, driven by the combination of the first two phenomena, as well as an additional transition between two types of rippled states on (110) surfaces. We discuss variously intermediate states and surface modulations in crystal growth and study the

interfacial state recently revealed in the epitaxial growth on Al(110) surface. Also, we predict the existence of striking interfacial structures that, usually, carry with them a large fraction of the total energy of the resulting surface currents of ad-atoms. These results are analogues to the well-known phenomenon of surfactant action. In contrast, along the (111) orientation, Mn can easily diffuse into the bulk via interstitial sites. These results are discussed within the context of dopant control and delta-doping in dilute magnetic semiconductors.

11:45 AM 117.10
Large-Scale Simulations of Evolving Faceted Surfaces, Scott Norris and Stephen Watson; Northwestern University, Chicago, Illinois.

We will present a scheme for efficiently performing large-scale simulations of evolving faceted surfaces. Hundreds of thousands of facets may be simulated in a few days, allowing detailed statistical analysis. In prior work, the piecewise-affine nature of the surface has been exploited, and per-facet evolutions derived using matched asymptotic analysis. Thus, each facet is moved as a unit, and the resulting system has a computational complexity similar to a system of ODEs. Since simulation time scales as \( O(\text{number of facets}) \) instead of \( O(\text{domain size}) \), the method is ideally suited to studying coarsening behavior, where the number of facets ranges over orders of magnitude in time. The price of this simplification is the need to detect and implement a variety of topological changes which occur as the system evolves. For any symmetry group, there exist four classes of events, grouped by detection method. Identifying, detecting and performing these events is the main difficulty posed by the method. Fortunately, this difficulty is conceptual; i.e. once worked out, these events do not significantly affect computational time. The main benefit of the method is speed, and the ability to easily extract detailed statistical data from the system. In particular, it can quickly extract scale-invariant distributions of shape, size, and topological configuration for coarsening problems. It can also track the evolution to this scale-invariant state. In this talk, we will outline the method, spend considerable time discussing topological events and their implementation, and present comparative results for the problem of driven growth under a variety of symmetry groups.
Two-dimensional shape relaxation. Atomistic and continuum modeling have been used strongly suggests that translation of the whole cluster is the actual surface exhibits a row like structure with bridging oxygens which are bonded to the bridging oxygens. In the case of the 38 atom which are bonded to the bridging oxygens. In the case of the 38 atom cluster, the cluster morphology is altered from that for a free cluster. This may well account for the different catalytic properties of small clusters. We next used nudged elastic band calculations to find the activation energy for diffusion of such clusters by simultaneous translation of the whole clusters. The results were in excellent agreement with the measured activation energies for diffusion. This strongly suggests that translation of the whole cluster is the actual diffusion mechanism. We believe these results represent a definite experimental and theoretical confirmation of a previously unexpected diffusion mechanism for supported metal nanoparticles.

Mechanisms by which adsorbates decrease mass flow, it is often observed that adsorbates increase mass transport. Little is known about the underlying mechanisms of this phenomenon. One proposal is that adsorbates react with the substrate to form mobile species. For example, calculations show that Cu-Si clusters, compared to Cu adatoms, have a much higher formation energy but not a much higher diffusion barrier and are responsible for the enhanced surface self-diffusion on Cu(111) with trace amount of S [1]. Nevertheless, where such clusters form and how the mass transport kinetics is affected have not been addressed. We propose a new model of surface mass transport that takes into account the enhanced surface self-diffusion on Cu(111) with trace amount of S [1]. This model is based on a combination of atomistic and continuum modeling. We have used first principles calculations in order to address several important questions. We determined by the diffusion and sintering of clusters, consequently it is critically on their size. The size distribution of such 3D clusters is observed for a range of cluster sizes from about 5 to about 50 atoms. Atom tracking also allows for careful measurements of diffusion rates as a function of cluster size and temperature. These measurements reveal a very interesting result, namely that the clusters diffuse by rounding barrier, also have effects. Additionally, some details of atomistic processes, such as kink rounding barrier, also have effects.

First Principles Calculations of Pd Cluster Diffusion on TiO2 (110). John C. Hamilton, Lani Sanders, A. K. Davey and B. S. Shawbridge, National Laboratory, Livermore, California; 2S industry, Livermore, California; 3Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, California.

Pd nanoclusters supported on TiO2 are a commonly used supported catalyst. The catalytic activity of these nanoclusters depends critically on their size. The size distribution of such 3D clusters is determined by the nucleation and sintering of clusters, consequently it is critical to understand the process of cluster diffusion. To this end, we present a combined experimental and theoretical investigation of cluster morphology and diffusion on TiO2(110). The TiO2(110) surface exhibits a row like structure with bridging oxygens which protrude above the surface and define the rows. Atom tracking STM reveals that Pd clusters diffuse along the rows. This is clearly observed for a range of cluster sizes from about 5 to about 30 atoms. Atom tracking also allows for careful measurements of diffusion rates as a function of cluster size and temperature. These measurements reveal a very interesting result, namely that the clusters diffuse by hopping over distances of roughly 3 Angstroms, which is the unit cell size of the substrate in the diffusion direction. This suggests that the clusters are hopping as a unit, rather than by Pd atoms running around the surface of the cluster. In addition to this provocative result, the diffusion rate is found to be largely independent of cluster size up to a cluster size of about 30 atoms. The activation energy for diffusion is measured to be about 0.5eV. We have used first principles calculations in order to address several important questions. We started by calculating probable cluster shapes for 13 atom and 38 atom clusters. In spite of the dramatic size difference, both 13 and 38 atom clusters have a face with a 7 atom hexagon of Pd atoms many of which are bonded to the bridging oxygens. In the case of the 38 atom cluster, the TiO2 surface does not change the cluster morphology from that expected for a free cluster. In the case of the 13 atom cluster, the cluster morphology is altered from that for a free cluster. This may well account for the different catalytic properties of small clusters. We next used nudged elastic band calculations to find the activation energy for diffusion of such clusters by simultaneous translation of the whole clusters. The results were in excellent agreement with the measured activation energies for diffusion. This strongly suggests that translation of the whole cluster is the actual diffusion mechanism. We believe these results represent a definite experimental and theoretical confirmation of a previously unexpected diffusion mechanism for supported metal nanoparticles.


Many studies have shown that adsorbates can significantly modify surface mass transport. While it is easy to imagine atomic blocking mechanisms by which adsorbates decrease mass flow, it is often observed that adsorbates increase mass transport. Little is known about the underlying mechanisms of this phenomenon. One proposal is that adsorbates react with the substrate to form mobile species. For example, calculations show that Cu-Si clusters, compared to Cu adatoms, have a much higher formation energy but not a much higher diffusion barrier and are responsible for the enhanced surface self-diffusion on Cu(111) with trace amount of S [1]. Nevertheless, where such clusters form and how the mass transport kinetics is affected have not been addressed. We propose a new model of surface mass transport that takes into account the enhanced surface self-diffusion on Cu(111) with trace amount of S [1]. This model is based on a combination of atomistic and continuum modeling. We have used first principles calculations in order to address several important questions. We determined by the diffusion and sintering of clusters, consequently it is critically on their size. The size distribution of such 3D clusters is observed for a range of cluster sizes from about 5 to about 50 atoms. Atom tracking also allows for careful measurements of diffusion rates as a function of cluster size and temperature. These measurements reveal a very interesting result, namely that the clusters diffuse by rounding barrier, also have effects. Additionally, some details of atomistic processes, such as kink rounding barrier, also have effects.
nucleation, growth and coalescence and attachment/detachment of
adatoms to/from island boundaries or terrace steps. A key feature of
these processes is the existence of nucleation barriers at which the kink
sites at which new atomic units are incorporated into the crystal.
In this talk, we develop a phase-field (Cahn-Hilliard type) model to
simulate the motion of steps including diffusion, attachment kinetics,
edge-diffusion and attachment energy of adatoms across step boundaries.

We propose and study an alternative continuum description of
the morphological relaxation of crystal surfaces below the roughening
transition, in which the dependent variable is the step position as a
function of the properly scaled step number and time, in place of the
usual height and slope profiles. In order to demonstrate the
advantages of this approach, we focus on axisymmetric surfaces
(circular steps) with step energetics that account for step line tension
and local elastic dipole-dipole step interactions, and consider the
combination of growth of adatoms across terraces with the
attachment and detachment of atoms at steps. The continuum limit of
the step-flow equations yields a new PDE for the step position, where
the influence of the step kinetics and energetics is characterized by
dynamic boundary conditions. We study the behavior of the solutions
to this PDE both analytically and numerically (for a wide range of
values of these parameters and time), and identify regions in the
parameter space (or time domain) where this behavior can be
dramatically different. We compare these results with previously
reported classifications of step behavior, in particular those of pure
diffusion-limited (DL) or pure attachment-detachment limited (ADL)
behaviour where a single parameter takes two extreme values. We also
place emphasis on the dynamic conditions required for the formation
of step bunches, when the traditional continuum approach becomes
questionable or breaks down. In our approach the step bunches give
rise to shock-like solutions and, hence, may in principle be treated
within our continuum description.

4:45 PM J18.9
A New Monte Carlo Model for Simulations of Surface Dynamic,
Ramon M.V. Murty, E2O Communications, Inc.,
Woodland Hills, California.

Monte Carlo simulations have provided tremendous insight into the
evolution of surface morphology during epitaxy, erosion and
annealing. The Monte Carlo model consists of an elaborate set of rules
for the motion of atoms that must satisfy detailed balance. First
principles calculations have shown that the barriers for atomic motion
are site-dependent depending on their neighborhood. In a
convventional Monte Carlo model on a lattice, the activation barrier for
an atom jump is determined solely by its coordination in the
initial and final sites. It will be shown that such a model places severe
restrictions on the energetics (and elastic field) of the system. For instance, on a square
lattice with nearest-neighbor interactions, the energy of the first
in-plane bond must be equal to the third in-plane bond to satisfy
detailed balance. A new Monte Carlo model will be discussed where
there are no restrictions on the energetics. In this model, the
activation barrier is determined not only by the moving atom but also
the neighboring atoms whose coordination is effected. A method
based on adatom and vacancy distribution on a vicinal surface will be
described that allows for quick identification of violations of detailed
balance in Monte Carlo models. Finally, the new model is used to
study the adatom and vacancy density in equilibrium with a
two-dimensional island growth model that predicts that the growth is
controlled by the excess free energy of the island edge due to curvature is accommo-
dated by a combination of changes in the adatom and vacancy densities.

8:45 AM J10.2
Diffusion in Potential Fields: Time-Dependent Capture on
Radial and Rectangular Substrates, John A. Venables and Pu Yang;
Physics and Astronomy, Arizona State University, Tempe, Arizona;
Physics and Astronomy, University of Sussex, Brighton, United
Kingdom.

In rate equation models of nucleation and growth on surfaces, it has often been assumed that the energy surface of the substrate is
flat, that diffusion is isotropic, and that capture numbers can be
calculated in the diffusion-controlled limit. Following previous work
[1,2] we lift these restrictions analytically, and illustrate the results
using a discrete FFT method of solving for the 2D time-dependent
diffusion field of ad-particles, which has been implemented in
Matlab6.5. A general substrate energy surface is included by
transformation of the field [1-3]. The method can work with any
boundary conditions, but is particularly clear for periodic boundary
conditions, such as might be appropriate following nucleation on a
regular (rectangular) array of defects. The method is instructive for
visualizing the potential and diffusion fields, and for demonstrating the
time-dependence of capture numbers in the initial stages of deposition
and annealing. Applications to strained clusters and nanowires, in the
case of growth on Si(001), are ongoing, and the latest results will be

9:00 AM J10.3
Quasicontinuum Monte-Carlo Simulation of Surface Growth,
Jason P. DeVita, Leonard M. Snader and Peter Smereka;
Physics, University of Michigan, Ann Arbor, Michigan;
Mathematics, University of Michigan, Ann Arbor, Michigan.

We will describe an algorithm for simulating surface growth which
combines continuum and discrete methods. Atoms which are part of
an island are treated as discrete particles, while adatoms are treated
as a continuous probability density. The evolution of the adatom field,
with discrete boundary conditions, determines the growth of the island
edges. Atoms are added as whole particles, allowing for shot-noise
fluctuations. For irreversible growth, our model compares favorably to
standard KMC, for both submonolayer and multilayer growth.

9:15 AM J10.4
Kinetic Monte Carlo Simulations of the Development of Various
Cu2O Island Morphologies during Oxidation of Cu(100) Thin Films,
Xueqin Han, Richard J. McAfee and Judith C. Yang;
Materials Science and Engineering, University of Pittsburgh,
Pennsylvania.

In this talk we describe a phase-field model for the nucleation and
growth of Cu2O islands during oxidation of Cu(100) thin films. The
model is formulated as a variational problem which ensures valid-
ity of the free energy functional. The model parameters are chosen
such that the obtained phase-field solution reproduces the experi-
mentally observed island nucleation and growth. The model allows
for a quantitative comparison of the growth rates of Cu2O islands
under different temperatures. We show that the growth rate is
quadratically dependent on the oxidation temperature. The
model predictions are in excellent agreement with experimental data.
Surface oxidation processes play critical roles in environmental stability, high temperature corrosion, electrochemistry and catalysis. Thin oxide films, formed by direct reaction between metal surfaces and gaseous O2, are also widely used as sensors, dielectrics, and corrosion inhibitors. Because of its importance, many experimental and theoretical studies have been done to investigate this process using various techniques, differing in their approach. The initial oxidation kinetics is a striking property for large surfaces and is governed by surface diffusion, and shadowing effects. To model the transition from nano-scale processes and island morphology variation under different experimental conditions, a combined application of potential functions and anisotropic sticking probabilities is necessary. We focus on the oxide island morphology changes during oxidation. As the temperature increases the lattice mismatch decreases due to differences in thermal expansion. The strain energy associated with the introduction of oxide and substrate mismatch is changing the energy balance across all of the interfaces of the island. In the TFOX model, the effect of interface energy is modeled using anisotropic probabilities of atoms attaching to islands. Potential energy gradients in the TFOX model are sensitive to the surface diffusion of oxygen due to strain and other mechanisms that act over distances greater than one lattice parameter are also used. The combined application of potential functions and anisotropic sticking probabilities has successfully led to various island morphologies and their evolution which have also been observed in the experiments.

9:30 AM J10.5
Enhanced Layer Coverage of Thin Films by Oblique Angle Deposition, Tansel Karabacak, Gwo-Ching Wang and Toh-Ming Lu; Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York.

The nucleation and island growth characteristics of oblique angle deposition with substrate rotation have recently attracted interest due to the formation of novel 3D nanostructures by a physical self-assembly process. In this study, we present the results of a Monte Carlo simulation work that explores the layer coverage evolution of thin films during oblique angle deposition. The simulations accounted for oblique incidence flux, shadowing effect, surface diffusion, and substrate rotation. Layer coverage and ratio of average volume to average island size values are reported for the initial stages of island growth from submonolayer thicknesses up to a few nanometers. Our results show that, at small deposition angles and at limited or no rotation, the average island size increases as the island nucleation rate is faster in lateral directions that results in the enhanced layer coverage. This is due to the sides of the islands can be exposed to the incident flux more effectively at small deposition angles. On the other hand, normal incidence and high oblique angle depositions give poorer layer coverages due to the slower growth rates in lateral directions. This work is supported by the NSF.

9:45 AM J10.6
Evolution of the Shape of Patterned GaAs Surfaces During Epitaxial Growth, Anders Ballestad,1 R. Kumaran,1 Bayo Lau,1 J. H. Schmidt,1 T. Tiedje,1-2 and M. Whitwick1; 1Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada; 2Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada.

Continuum models have been shown to describe the shape of GaAs (100) surfaces during vapor deposition rather well in the limit of low surface slopes (<5%) [1]. These models break down for the surfaces with larger slopes that are of interest for lateral pattern formation and device fabrication. It was recently shown that several popular nonlinear growth equations fail to reproduce the features observed in regrown on patterned surfaces, including in particular an amplitude overshoot [2]. We have investigated the morphology changes that occur during the growth of semiconductor surfaces with a range of surface slopes, using a combination of in-situ optical monitoring, ex-situ characteristic and theoretical modeling. From observations of the topography of films grown on random and lithographically patterned GaAs (110) surfaces, we conclude that there is a slope dependent force which acts to drive deposited adatoms downhill. Microscopically, this effect could be caused by inverted Ehrlich-Schwoebel barriers at step edges that favor downhill adatom migration, or by other mechanisms such as downhill diffusion or step edge knock-out. The downhill drift leads to a second order linear Edwards-Wilkinson (EW) term in the growth equation. We use this concept to develop a new mathematical description of the shape of surface crystal structures during growth. This includes much more accurate dynamics of adatoms explicitly and their coupling to the surface height through incorporation. The model includes adatom diffusion, island nucleation, step attachment/detachment, and preferential downhill drift at step edges [3]. It gives excellent agreement with the complex surface shapes that are observed in regrown on patterned GaAs surfaces as a function of layer thickness and growth temperature for surface slopes up to 50%. The model is highly nonlinear and predicts layer thickness plateaus for step edges [3]. It correctly predicts the amplitude overshoot reported in Ref. [2] as well as the asymptotic behavior for low slopes [1]. Using perturbation theory we find that in the limit of low surface slopes the model reduces to a KPZ-like equation, $\dot{h}(x,t) = \nabla \cdot (\nabla h(t)) + \eta(t)$, in which the coefficients can be expressed in terms of microscopic physical parameters and are flux dependent, as observed experimentally.


10:30 AM J10.7
Molecular Dynamics Simulation of Low- and High-Temperature Molecular Beam Epitaxy and GaAs(001) Surface Phase Reconstruction, Davew A. Murdiek,1 Xiao-wang Zhou,1 H. Schmid,2 T. Tiedje,2 and M. Whitwick; 1Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada; 2Department of Materials Science & Engineering, University of Virginia, Charlottesville, Virginia; 3Department of Materials, University of Oxford, Oxford, United Kingdom.

The evolution of epitaxial GaAs and (Ga,Mn)As thin films under UHV conditions during far-from-equilibrium growth are studied using classical molecular dynamics (MD). A variety of literature interatomic potentials and their parameterizations are evaluated for their ability to model bulk, surface, and vapor deposition properties. Of the known 7 potential formats and 10 parameterizations of GaAs only a few are capable of being used in MD vapor deposition simulation. In addition to these empirical potentials recent advances in analytic bond order potentials are also discussed. Results of the molecular beam epitaxial simulations are reported in regard to film morphology as a function of substrate temperatures ranging from 500-1000 K and As/Ga flux ratios between 1 and 20. The low-temperature growth conditions hold particular interest due to its application to spintronic devices, such as (Ga,Mn)As. The reduced temperature during deposition limits transition metal dopant clustering and segregation during growth. We also address the problems of surface reconstructions of the GaAs(001) surface and propose a solution. Surface phase diagrams will be shown and a new method for stabilizing experimental surface reconstructions within classical MD environments are presented. Both success and current limitations are discussed with the goal of improving interatomic potentials for the study of grown thin films and surfaces in equilibrium and during growth. We gratefully acknowledge the support of DARPA/ONR grant no. N00014-99-1-0999, Carey Schwartz and Julie Christodoulou program managers.

10:45 AM J10.8
The Effect of Hydrogen Passivation Surface and Particle Size Ratio on Silicon Nanoparticles Coalescence, Takumi Hoya,1,2 and Michael R. Zachariah1,2; 1Process Measurements Division, NIST, Gaithersburg, Maryland; 2Mechanical Engineering and Chemistry, U of Maryland, College Park, Maryland.

Understanding a fundamental formation mechanism of nanoparticles growth and controlling primary particle size as well as extent of agglomeration when grown from the gas-phase are the primary challenges in the use of nanoparticles. In this talk we present a possibly mathematical model to describe the particle coalescence. Here the sintering of (1) hydrogen terminated silicon surface slowing the process and (2) non-equal-size silicon nanoparticles have been studied, and results are compared with molecular dynamics simulations. Nanoparticles of the size between 2 and 6 nm at 1000 and 1500 K were considered with a re-parameterized Kirkendall-Dullin-Stillerling empirical passivation potential. The hydrogen passivation surface completely changes and slows the beginning of the sintering process. In addition, the presence of hydrogen atoms reduces surface tension of the particle about 40 to 50%, and this also slows the formation of spherical shape, which is the rest of the sintering process. The model is able to describe both initial induction period and the standard coalescence period. It presents that the effective surface tension decreases with increasing hydrogen coverage, making it harder for particles to coalesce. When the extent of coverage is below 60%,
the normalized effective surface tension decays exponentially with the extent of coating. Above about 67%, the normalized effective surface tension decreases even more rapidly. The change in decrease corresponds to the appearance of the induction period, which is the energy needed not only for the repulsion, but also for relocation of surface hydrogen and silicon atoms. For particles with coverage of 75% or less the final temperatures of the particles are essentially equivalent. While at higher surface coverage the rise in temperature is tempered. Moreover, the characteristic coalescence times of unequal sized silicon nanoparticles decrease with decreasing the ratio of two particle sizes (smaller/larger) when final particle sizes are the same. The mathematical model describes this nature satisfactory.

11:00 AM J10.9
Steering Effect on the Growth Instability of Cu on Cu(11 17).
Jikeun Seo1, Hye-Young Kim2 and Jae-Sung Kim2; 1Division of General Education, Chodang University, Muan, South Korea; 2Physics, Sook Myung Women’s University, Seoul, South Korea.

Steering effect, modification of the trajectories of incident atoms through interaction with atoms on substrate, results in non-uniform deposition flux during the growth of thin films. Especially when the deposition is made at grazing incidence, steering effect is most dramatically manifested as dynamically broken symmetry in the shape of islands.[1] Recently, we reproduced such experimental observation by employing modified kinetic Monte Carlo (KMC) simulation that incorporated molecular dynamic (MD) simulation for the description of deposition event.[2] In the present presentation, we applied the modified KMC simulation to find how the steering effect affects the growth instability of Cu on a vicinal surface, Cu(11 17). We find the deposition flux shows noticeable dependence on deposition angle. Such angle dependence is translated into the dependence of growth instability on deposition angle. Deposition at grazing incidence always enhanced the instability by making growth front rougher and meandering width smaller compared with the deposition at angles near normal to the sample surface. For all deposition angles, however, steering effect increased the growth instability compared with the case where it is absent. The instability caused by steering effect is attributed to the increased deposition flux near downward step edge, which in turn increases the step Erlich Schwoebel barrier effect and the net current toward upward step edge. Such localized and increased current has more chance to be trapped to protruding edges of the growth front while flowing from the downward step edge to the upward step edge, and enhances the growth instability of steps.[1] S.V. Dijken, L.C. Joritsma, and B. Poelsema, Phys. Rev. Lett. 82, 4038 (1999). [2] J. Seo, S.-M. Kwon, H.-Y. Kim, and J.-S. Kim, Phys. Rev. B 67, 121402(R) (2003).