

SYMPOSIUM JJ

Modeling of Morphological Evolution at Surfaces and Interfaces

November 29 - December 2, 2004

Chairs

Jim Evans

Ames Laboratory and Dept. of Mathematics
Iowa State University
Ames, IA 50011
515-294-1638

Christine Orme

Chemistry and Materials Science Division
Lawrence Livermore National Laboratory
Livermore, CA 94550
925-423-9509

Mark Asta

Dept. of Materials Science & Engineering
Northwestern University
Evanston, IL 60208
847-491-5940

Zhenyu Zhang

Condensed Matter Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831
865-576-5346

Symposium Support

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Proceedings to be published online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume 859E
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

8:30 AM *JJ1.1/KK1.1/U1.1

Kinetic Critical Thickness for Quantum Dot Formation. Yuhai Tu and Jerry Tersoff, IBM Watson Center, Yorktown Heights, New York.

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 Stranski-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 heteroepitaxy. As the misfit strain is reduced (by varying the deposited alloy composition), 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 continuum 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 apparent critical thickness depends sensitively on composition, but only weakly on deposition rate. Our results confirm the insightful proposal of Cullis et al., that the key factor controlling the transition is the continuous increase of surface composition due to intermixing during growth. However, the specific kinetic mechanism is unanticipated and surprisingly simple.

9:00 AM *JJ1.2/KK1.2/U1.2

Microscopic View of InAs Quantum Dot Growth and Overgrowth. Klaus Kern, Nanoscale Science Department, Max Planck Institute for Solid State Research, Stuttgart, Germany.

Surfaces and interfaces not only determine to a large extent the properties of small-scale materials due to their high surface-to-volume ratio, they are also an ideal platform for the design, fabrication and device integration of nanostructures. Both top-down and bottom-up methods have been developed for the handling of matter at the molecular and atomic scale. The prime example for the bottom-up fabrication of nanostructures is the Stranski-Krastanov growth of semiconductor quantum dots (QD's), with the model systems Ge/Si(100) and InAs/GaAs(100). Although the self-organized growth of these nanostructures has been intensely studied for more than a decade and a number of important achievements have been obtained concerning their electronic and optical properties, a definite and coherent picture of the growth scenario is still missing. In this talk I will present a microscopic view of the growth and overgrowth of InAs quantum dots on GaAs(100) obtained by scanning tunneling microscopy. The atomic-scale experiments demonstrate that the shape and composition of the quantum dots are determined by the delicate interplay between thermodynamic and kinetic effects. Moreover, the STM measurements reveal that only two well-defined island shapes, pyramids and domes exist. Both structures are very similar to the island shapes observed in the Ge/Si system suggesting that pyramids and domes are universal island shapes, independent of specific material parameters. Also the overgrowth scenario that emerges from our measurements, in which the QD capping can be described as a backward transition from steeper domes to shallower pyramids, is material independent as long as the surface energy of the cap material is higher than that of the island material.

9:30 AM *JJ1.3/KK1.3/U1.3

Pattern Formation on Silicon and Silicon-on-Insulator. Max G. Lagally, Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

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 cause this layer, under appropriate conditions, to dewet, agglomerate, and self-organize 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 [3] and show how addition of Ge affects the energies and hence the pattern. The Si nanocrystal pattern formation can be controlled by lithographic patterning of the SOI prior to the dewetting process. The resulting patterns of electrically isolated Si

nanocrystals can in turn be used as a template for growth of nanostructures, such as carbon nanotubes. [4] We show that this growth is controlled by the flow dynamics, and possibly by electrostatics. Growth of heteroepitaxial films on SOI brings with it unique defect generation mechanisms, associated with the Si-oxide interface, that may, in fact, result in the elimination of patterns found for growth on bulk Si. We fabricate thin membranes and free-standing structures to investigate the effect of added uniaxial stress on adatom diffusion and the nucleation and coarsening of 2D and 3D structures on this surface. Finally, nanopattern formation on Si using etching techniques results in unexpected wetting behavior. Aspects of the work were supported by DOE and by NSF. In conjunction with B. Yang, F. Liu, P. Rugheimer, D. Savage, M. Roberts, P. Zhang, V. Joshkin, M. Marcus, and M. Eriksson. 1. Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Letters **65**, 1020 (1990). 2. B. Yang, F. Liu, and M. G. Lagally, Phys. Rev. Letters **92**, 025502-1 (2004). 3. Bin Yang, Pengpeng Zhang, M.G. Lagally, Guang-Hong Lu, Minghuang Huang, and Feng Liu, submitted to PRL. 4. B. Yang, M.S. Marcus, H. F. Tang, P.P. Zhang, Z.W. Li, B.J. Larson, D.E. Savage, J.M. Simmons, O. M. Castellini, M.A. Eriksson, and M.G. Lagally, submitted to Appl. Phys. Letters.

10:30 AM JJ1.4/KK1.4/U1.4

KMC Computations of Strained Heteroepitaxy in 3 Dimensions. Peter Smerka¹, Giovanni Russo², Leonard Sander¹ and Jason Devita¹, ¹University of Michigan, Ann Arbor, Michigan; ²University of Catania, Catania, Italy.

We study the evolution of strained heteroepitaxial films in 3 dimensions using an atomistic model due to Orr, Kessler, Snyder and Sander. This model consists of a SOS type model with nearest and next nearest neighbor bonds. The elastic effects are considered using a ball and spring model with nearest and next nearest neighbor bonds. The strain field in the substrate was deduced using an exact solution which can be efficiently evaluated using Fast Fourier Transforms. Our results show that when the elastic effects are small the films grows in a layer-by-layer fashion. However, when the elastic effects become strong we observe either mound formation or trench type structures depending on the deposition rate.

10:45 AM JJ1.5/KK1.5/U1.5

The Effect of Inhomogeneous Diffusion on the Formation of Quantum Dots. Christian Ratsch, Raffaello Vardavas, Xiaobin Niu and Russel Caflisch; Mathematics, UCLA, Los Angeles, California.

The simulation of the formation and self-organization of quantum dots is a major goal in modeling efforts of epitaxial growth. An anisotropic, spatially varying diffusion constant can lead to preferred island nucleation in certain regions. Such an anisotropic, inhomogeneous diffusion field can be achieved, for example, by burying defects (or other structures) underneath the surface: the inhomogeneous strain field leads to an inhomogeneous potential energy surface, and thus to an inhomogeneous diffusion field. We will show that under the right conditions, nucleation occurs preferentially along certain geometric lines, with all islands being approximately the same size. In addition, there are large denuded zones on the surface without any islands in it. Our results were obtained with an island dynamics model that employs the level-set technique. This approach is particularly well suited for this problem, as both, a spatially varying diffusion field, as well as microscopic events on vastly different time-scales can easily be implemented in our model, without extra computational cost.

11:00 AM JJ1.6/KK1.6/U1.6

On the mechanisms guiding epitaxial island assembly on topographically patterned substrates. Robert V. Kukta, Mechanical Engineering, Stony Brook University, Stony Brook, New York.

A method of self-assembling quantum dot domains that promises substantial flexibility and control is strained layer growth on topographically patterned substrates. Prior to growth, features are introduced on the substrate by a method such as lithography and ion-etching. These features guide morphological development by providing preferred sites for islands to nucleate and grow. While it is known from experiment that the arrangement of islands on patterned substrates is affected both by energetic and kinetic phenomena, the nature of these effects has not been well characterized. There have been few analytical efforts to understand where islands form and why and how they develop at particular sites. It is the purpose of this paper to offer some new insight. A continuum-level model is used where the free energy of system is assumed to consist of surface free energy and strain energy. Energetics is first addressed to understand which sites are most favorable for islands, depending on factors as substrate shape, lattice mismatch between the film and substrate materials, surface energy, and the amount of material deposited. 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 energetic analysis; free energy is reduced as islands translate in certain directions. Yet even with a lengthy post-deposition anneal 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 pathway admitted by surface diffusion requires evolution through states of higher free energy. It is demonstrated that a critical island size exists for this metastability to occur. Small islands tend to be mobile and able to move to minimum-energy sites, whereas large islands tend to be immobile. This phenomenon results in islands affixed to the side walls of substrate surface features. Focus is limited to growth on small amplitude sinusoidal substrate features as studied in detail recently in a series of experiments by Zhong et al. [J. Appl. Phys. 93, 6258 (2003); Appl. Phys. Lett. 82, 445 (2003)]. Their experiments provide evidence of the novel metastability and also illustrate that both kinetics and energetics have a role in guiding the positioning of islands. Insight to the nature of these effects is obtained from kinetic simulations based on their experiments.

11:15 AM JJ1.7/KK1.7/U1.7

In-Situ Studies of Cu₂O Nano-Island Formation on Cu (001). Jeffrey A. Eastman, Paul H. Fuoss, Guangwen Zhou, Lynn E. Rehn, Peter M. Baldo, Loren J. Thompson and Dillon D. Fong; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

The early-stage oxidation behavior of the Cu (001) surface is being investigated at the Advanced Photon Source via in-situ x-ray diffraction techniques. Single crystal (001) Cu thin films grown on (001) SrTiO₃ substrates are oxidized to form crystallographically-aligned Cu₂O nano-islands on the Cu surface. By measuring oxide island growth kinetics as a function of oxygen partial pressure, the thermodynamic limit between oxide growth and reduction has been determined for several temperatures and film thicknesses. We find the Cu/Cu₂O phase boundary at much larger oxygen partial pressure than predicted by bulk phase equilibria, and also find that the temperature dependence of this phase boundary is smaller than expected. Large reversible changes in the oxide lattice parameter of up to 0.5% in response to controlled variations in oxygen partial pressure in the chamber are also observed, possibly indicating an unexpectedly large stoichiometric range in Cu₂O nano-islands compared with bulk Cu₂O. Significant differences are seen in the oxidation behavior of thin film and bulk single crystal samples, leading to the conclusion that substrate constraints are influencing behavior. The prospects for engineering these constraints to influence nanopattern formation will be discussed.

11:30 AM JJ1.8/KK1.8/U1.8

Orientation dependence behavior of self-assembled (In,Ga)As quantum structures on GaAs substrates. Shahram Seydmohamadi, Zhiming M. Wang, Hong Wen and Gregory J. Salamo; Physics, University of Arkansas, Fayetteville, Arkansas.

The orientation of the substrate can play an important role in the formation of (In,Ga)As quantum structures grown on GaAs. In particular, the unique surface morphology of a high index substrate allows the substrate to act as a template for the growth of self assembled quantum wires (QWRs) and quantum dots (QDs). In this work, the formation of self assembled (In,Ga)As quantum structures are discussed as a function of crystallographic orientation of the GaAs substrates. We report on the effect of the orientation of a GaAs substrate on the evolution of strained (In,Ga)As quantum structures, along one side of the stereographic triangle from (100) towards (111)A, including (100) and (N11)A surfaces, where N is equal to 7, 5, 4 and 3. The samples were grown by UHV molecular beam epitaxy (MBE) and characterized by atomic force microscopy (AFM) and scanning tunneling microscopy (STM). For the same coverage of (In,Ga)As, a transition from zero dimensional (In,Ga)As QDs to one dimensional QWRs is observed as a function of the orientation of the substrate moving from (100) toward (311)A along the stereographic map. While (In,Ga)As QDs form on GaAs (100) and (711)A surfaces, we observe QWRs formation on GaAs (311)A and (411)A surfaces. In between, GaAs (511)A is covered by elongated (In,Ga)As QDs. When taken together with the observation of QDs on the GaAs (100) and (711)A surfaces and QWRs on the GaAs (311)A and (411)A surfaces, the texture observed on the GaAs (511)A surface is interpreted as observing a transition taking place from quantum dots to quantum wires on the (511)A surface. The overview picture then, is that a continuous transition from QD to QWR takes place along the mentioned stereographic direction. We will present an explanation for the transition from QD to QWR behavior along the stereographic triangle based on the changing surface morphology of the substrates.

11:45 AM JJ1.9/KK1.9/U1.9

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 depth 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, in quantitative agreement with recent experimental observations.

SESSION JJ2/KK2/U2: Joint Session: Patterning and Steps on Surfaces
Chairs: Jim Evans and Vivek Shenoy
Monday Afternoon, November 29, 2004
Room 210 (Hynes)

1:30 PM *JJ2.1/KK2.1/U2.1

One-dimensional interfaces in Two-dimensional Materials Structures*. Ellen D. Williams^{1,2}, Daniel Dougherty², Chenggang Tao², Oleksander Bondarchuk^{1,2}, Theodore L. Einstein^{1,2}, Michael S. Fuhrer² and Philip J. Rous³; ¹MRSEC, University of Maryland, College Park, Maryland; ²Physics, University of Maryland, College Park, Maryland; ³Physics, University of Maryland Baltimore County, Baltimore, Maryland.

Steps, island edges and domain boundaries are one-dimensional interfaces that serve as the locus of material transport, and as interfacial barriers for electron transport. These interfaces fluctuate under thermal excitation, with length and time scales that can be observed directly using scanning probe imaging. Quantitative characterization of these fluctuations using the tools of statistical mechanics yields energetic and kinetic parameters that can be used to predict evolution of structure under external driving forces (e.g. temperature gradient, growth or sublimation, electromigration). In addition, as the size of the bounded structure decreases into the nanoscale, the stochastic aspects of the fluctuations themselves become a significant component of the material properties. Scanned probe measurement of fluctuations, correlation, autocorrelation, survival and persistence, will be presented for steps (on Ag, Pb and C₆₀/Ag) and domain boundaries (Pb/Si, Ag/Si and C₆₀/Ag). The meaning of system size in designing, evaluating and using these results will be explained. The impact of the one-dimensional structures on electron flow will also be presented. Direct measurements of step fluctuations in the presence of an electromigration current density of up to 10⁵ A/cm² will be shown and interpreted in terms of the limits on effective charge for mass displacement at the line boundary. Measurements of the noise and resistivity in electron transport will be shown and characterized in terms of structural fluctuations in a film near the percolation threshold. * Different aspects of this work have been supported respectively by the DOE-BES, NSF-NIRT and NSF-MRSEC

2:00 PM *JJ2.2/KK2.2/U2.2

A Model of Patterning Molecular Dipoles on Solid Surfaces. Zhigang Suo, Harvard University, Cambridge, Massachusetts.

Abstract Adsorbed on a solid surface, a molecule can migrate and carry an electric dipole moment. A nonuniform electric field can direct the motion of the molecule. A collection of the same molecules may aggregate into a monolayer island on the solid surface. Place such molecules on a dielectric substrate surface, beneath which an array of electrodes is buried. By varying the voltages of the electrodes individually, it is possible to program molecular patterning, direct an island to move in a desired trajectory, or merge several islands into a larger one. The dexterity may lead to new technologies, such as reconfigurable molecular patterning and programmable molecular cars. This paper develops a phase field model to simulate the molecular motion and patterning under the combined actions of dipole moments, intermolecular forces, entropy, and electrodes. Slides of this talk will be available at www.deas.harvard.edu/suo Z. Suo and W. Hong, PNAS 101, 7874 (2004). Y.F. Gao and Z. Suo, J. Appl. Phys. 93, 4276 (2003). W. Lu and Z. Suo, J. Mech. Phys. Solids, 49, 1937 (2001).

2:30 PM *JJ2.3/KK2.3/U2.3

The Quasicontinuum Monte Carlo method for simulating surface growth. Leonard M. Sander¹, Jason Devita¹ and Peter Smereka²; 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, the effect of Ehrlich-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 and detachment from the islands on 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

Continuum Theory of Interacting Steps on Crystal Surfaces in (2+1) Dimensions. Dionisio Margetis¹ and Robert V. Kohn²;

¹Mathematics, M.I.T., Cambridge, Massachusetts; ²Courant Institute of Mathematical Sciences, New York University, New York, New York.

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 diffusion of adatoms across terraces, and the attachment and detachment of atoms 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 chemical potential for a sufficiently wide class of step 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 partial 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

Formation of Ridges on Patterned Mesas and Their Role in Evolution of Step Arrays on Mesas. Kee-Chul Chang and Jack M. Blakely; Materials Science & Eng, Cornell University, Ithaca, New York.

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 few 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 due to evaporation, the widely 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 Nanofacets on Vicinal SiC(0001) Surfaces and Its Application to Heterogeneous Nanostructures. Satoru Tanaka, Kazunori Terada, Tomoyuki Miyamoto, Masahiro Fujii and Ikuo Suemune; RIES, Hokkaido Univ., Sapporo, Japan.

Surface nanostructures by taking advantages of self-ordering or self-organization have been attracted much attention in nanofabrication of semiconductor 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 vicinal surfaces. Technologically important substrates such as Si and GaAs have been studied, both for device applications and for understanding of basic surface physics. Silicon carbide is an important compound semiconductor, which possesses polymorphism and a variety of superior characteristics such as wide band-gap and significantly electronic properties. It is thus a promising

semiconductor for the next generation of high power and high frequency electronic devices. Initially, we have investigated step/terrace configurations appeared on vicinal SiC(0001) surfaces after high temperature H₂ annealing and found that self-ordered nanofacets, consisting of pairs of (0001) and (11-2n), were generated [1]. The origins of such periodic nanofacets 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 nanofacets 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 ordered nanofacet formation 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. Tanaka, I. Suemune, Phys. Rev. Lett. 91, 226107-1(2003) [2] V. I. Marchenko and A. Y. Parshin, Sov. Phys. JETP 52, 1 (1980).

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

The Controlled Self-Assembly of Nano-Structures by the Activated Stranski-Krastanow Transition Method. Cheng-hsin Chiu, Z. Huang and C. T. Poh; Department of Materials Science, National University of Singapore, Singapore, Singapore.

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. 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 patterns on a flat surface of the SK system 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 island locations, 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 rims, 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 nano-structures 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. Ashwin Ramasubramanian 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 Schwoebel barrier at step-edges. This method is used to model recent experimental studies of relaxation of a Cu(001) 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 line-tension 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 coupling between 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 Driven Surface Dynamics on Solids. Sanjay V. Khare^{1,2}, S. Kodambaka^{1,2}, W. Swiech^{2,1}, K. Ohmori^{1,2}, I. Petrov^{2,1} and J. E. Greene^{1,2}; 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 (1500-1700 K) nucleation and shape-preserving growth of spiral steps rotating at constant temperature-dependent angular velocities ($\omega(T)$) around cores of dislocations terminating on TiN(111) in the absence of applied external stress or net mass change. We measure ω as a function of spiral geometry, N₂ partial pressure, annealing time, and temperature.

We find that ω is independent of the local environment and ambient, and decreases linearly with time. From the temperature-dependent ω data, we obtain an activation barrier of 4.9 ± 0.3 eV for the growth of 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 dynamics 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. ¹S. Kodambaka, S.V. Khare, W. Swiech, K. Ohmori, I. Petrov, and J.E. Greene, *Nature* 429, 49 (2004).

SESSION JJ3: Poster Session: Modeling of Morphological Evolution in Solids and Films
Chair: Christine Orme
Monday Evening, November 29, 2004
8:00 PM
Exhibition Hall D (Hynes)

JJ3.1

Island Formation During Submonolayer Deposition for Large Critical Sizes: Efficient Geometry-Based Simulation Approach. Maozhi Li¹, Maria C. Bartelt² and James W. Evans¹;
¹Ames Laboratory, Iowa State University, Ames, Iowa; ²Lawrence Livermore National Laboratories, Livermore, California.

Island formation during deposition is of fundamental and technological interest. For small critical size, i (above which islands are stable), kinetic Monte Carlo (KMC) simulation of atomistic models is efficient. KMC studies reveal that the form of the island size distribution (ISD) differs from predictions of traditional mean-field rate equation treatments due to subtle correlations between island size and separation. For larger $i > 3$, KMC simulation becomes inefficient due to the high density of diffusing adatoms. Thus, there is a need for alternative multiscale approaches, avoiding atomistic simulation of terrace diffusion, which can accurately predict the ISD. These approaches could replace atomistic simulation of adatom diffusion and associated island nucleation and growth with a continuum BCF-type analysis, or with a geometry-based formulation based on depletion and capture zones surrounding islands. We have successfully implemented the latter to obtain and compare the ISD's for $i=3, 6$, and 15.

JJ3.2

Time-Dependent Fields On Rectangular Substrates: Modeling Anisotropic Diffusion And Growth. Pu Yang¹ and John A. Venables^{1,2}; 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)2x1) when anisotropic diffusion, and possibly also attachment, would be more appropriate. Here we explore a method of using the discrete FFT for solving the time-dependent diffusion equation for ad-particles. This method is tested against the known result of diffusion from a 2D point source, with periodic boundary conditions. The FFT method gives a perfect match to the analytical solution for multiple point sources arranged on a lattice, except near (initial) field discontinuities. We solve the time-dependent anisotropic diffusion field with rectangular block sinks to simulate the growth of a regular array of islands using analogous methods. Programs are coded in MatLab 6.5; the calculation is fast, and the evolving diffusion field can be seen visually in the form of MatLab movies.

JJ3.3

Mound Formation and Evolution during Ag/Ag(100) Homoepitaxy. Kyle Caspersen⁴, Anthony Layson³, Patricia Thiel² and Jim Evans²; ¹Iowa State University, Ames, Iowa; ²IPRT, Iowa State University, Ames, Iowa; ³Chemistry, Denison University, Granville, Ohio; ⁴Chemistry, UCLA, Los Angeles, California.

Early studies of metal(100) homoepitaxy for Fe and Cu revealed formation of mounds (multilayer stacks of 2D islands) with rapid slope selection. The mounding instability is due to the Ehrlich-Schwoebel (ES) barrier inhibiting downward transport of deposited atoms, and slope selection reflects their downward funneling at step edges. STM studies of Ag/Ag(100) homoepitaxy at 300K combined with realistic atomistic modeling reveal the expected initial smooth growth, but followed by a prolonged regime of steepening exceeding 1000ML (with unexpected rapid roughening and slow coarsening), before a late-stage regime of slope selection (with roughening and coarsening at the same rate). The steepening regime is compressed at lower temperature.

Analysis of late-stage mound coarsening dynamics reveals a highly cooperative fluctuation-dominated process with strong up-down symmetry breaking, features which contrast predictions of standard continuum modeling with the appropriate four-fold symmetry.

JJ3.4

Continuum Approach to Self-Similarity and Scaling in Nanostructure Decay Below the Roughening Temperature. Dionisios Margetis¹, Michael J. Aziz² and Howard A. Stone²;
¹Mathematics, M.I.T., Cambridge, Massachusetts; ²Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

This work focuses on a continuum description of the morphological relaxation of axisymmetric crystal surfaces with a single facet below the roughening temperature by use of partial differential equations (PDEs). For kinetic processes limited by the diffusion of adatoms on terraces between steps and the attachment and detachment of atoms to and from steps, the slope profile F outside the facet is described via a nonlinear, fourth-order PDE that accounts for step line-tension energy g_1 and step-step repulsive interaction energy g_3 . The PDE is derived from the step-flow difference-differential equations, which describe the motion of individual steps, and, alternatively, via a continuum surface free energy. The facet evolution is treated as a free-boundary problem recognizing that there is a region of rapid variations of F , a boundary layer, near the facet. For long times, axisymmetric shapes and sufficiently small ratio of step-step interaction strength to line-tension energy, $g_3/g_1 < O(1)$, singular perturbation theory is applied to self-similar shapes close to the facet. For pure diffusion-limited kinetics, scaling laws with g_3/g_1 are derived for the boundary-layer width, maximum slope and facet radius; and a universal ODE for F is derived and solved uniquely via applying effective boundary conditions at the facet edge. For the case with pure attachment-detachment limited kinetics a different scaling with g_3/g_1 is found for the boundary-layer width. The scaling results are in excellent agreement with kinetic simulations.

JJ3.5

The Complexities of Thin Film Oxidation Under UHV Conditions and the TFOx Kinetic Monte Carlo Simulation of Copper (001) Thin Film Oxidation. Richard John McAfee^{1,2}, Xuetian Han² and Judith Yang²; ¹Brashear Division, L-3 Communications, Pittsburgh, Pennsylvania; ²Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Copper oxidation has taken on special significance since the development of semiconductor devices using copper as the interconnect material. UHV Transmission Electron Microscopy studies 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 reconstruction 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 of copper atoms along either the [100] or [010] directions. The crystal structure of the oxide Cu₂O 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 to the (001) substrate is cube-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 nano-rods 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 equation 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 these 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 (O₂), 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. Initially, simulation 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.

JJ3.6

Morphological Evolution during Competitive Etching and Oxidation of Vicinal Si(100) Surfaces. Marvin Argulla Albao^{2,1}, Da-Jiang Liu², Cheol Choi³, Mark Gordon² and Jim Evans²; ¹Department of Physics And Astronomy, Iowa State University, Ames, Iowa; ²Ames Laboratory -USDOE, Iowa State University, Ames, Iowa; ³Department of Chemistry, Kyungpook University, Taegu, South Korea.

Exposure of a vicinal Si(100) surface to oxygen at around 550-600C produces etching-mediated step recession, although occasional formation oxide islands produces pinning centers for the receding 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 each 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.

JJ3.7

A Multiscale Model of the Si LPCVD Process. Carlo Cavallotti, Maurizio Rondanini, Maurizio Masi and Sergio Carra[†]; politecnico di 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 recombinative 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 systematically investigated the dependence of the growth morphology from 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 probable through the KMC simulations, using quantum chemistry.

JJ3.8

First-Principles Study for Epitaxial Growth of Zinc-Blende CrAs on GaAs Substrates. Kiichiro 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/CrAs are reported to be grown by molecular beam epitaxy (MBE). Many researchers have been interested in this new material and possible superstructures, especially in their magnetic properties. But theoretical studies for the growth mechanisms of them are few. We investigate theoretically the 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 and the top several layers of the substrates are structurally relaxed for the each pattern. We compare these calculated results and discuss theoretically on the possibilities and experimental conditions for the MBE growth of some superstructures consisted of the zinc-blende CrAs and GaAs.

JJ3.9

Analytic Bond-Order Potentials for the Simulation of the Growth of Semiconductor Films. Ralf Drautz¹, Duc

Nguyen-Manh², Dewey A. Murdick³, Xiaowang Zhou³, Haydn N. G. Wadley³ and David G. Pettifor¹; ¹Department of Materials, University of Oxford, Oxford, United Kingdom; ²Culham Science Centre, UKAEA, Oxfordshire, United Kingdom; ³Department 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 graining the TB electronic structure in terms of moments of the local density of states. The resultant σ and π bond orders quantify the ubiquitous concept of single, double, triple and conjugate 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.

JJ3.10

Modeling of Time Evolution of the Microstructure of VO₂(B) Films Deposited on Glass by MOCVD. M.B. Sahana, G.

Anathakrishna and S.A. Shivashankar; Indian Institute of Science, Bangalore, Karnataka, India.

The thin films of VO₂(B), a metastable polymorph of vanadium dioxide, grown at 370°C for 90 minutes on glass substrates by metalorganic chemical vapor deposition (MOCVD), using vanadylacetylacetonate have an intriguing and unusual microstructure comprised of ordered entities 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 VO₂(B). The distinctive microstructure of these films prompted us to carry out an investigation of the morphological evolution of VO₂(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. The 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 sheds some of its material. 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 duration of deposition. Such an 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 VO₂(B) films on glass.

JJ3.11

Molecular dynamics study on the asymmetric intermixing behavior of Co-Al and Co-Cu multilayer. Sang-Pil Kim^{1,2},

Seung-Suck Yoo^{1,3}, Seung-Cheol Lee¹, Kwang-Ryeol Lee¹ and Yong-Chae Chung²; ¹Future Technology Research Division, Korea Institute of Science & Technology, Seoul, South Korea; ²Department of Ceramic Engineering, Hanyang University, Seoul, South Korea;

For the development of thin film multiplayer 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 system. These two systems were chosen due to their significantly different thermodynamic characteristics: Co-Al system has a stable intermetallic phase of CoAl B2 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 Evolution of a Single Notch on the Surface Caused by Surface Reaction. Honghui Yu, Mechanical Engineering, The City College of New York, The Graduate Center of CUNY, New York, New York.

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 surface notch under stress dependant 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 conditions, the time to nucleate a crack for a deep and sharp notch 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 Rayleigh Instability of Thin Wires with Strong Circumferential Surface Energy Anisotropy. Wanxi Kan and Harris Wong; Mech. Eng., LSU, Baton Rouge, Louisiana.

The morphological stability of thin wires is important in electronic materials processing. As a first step in understanding the stability, we study the linear stability of a freely-suspended thin wire with strong circumferential surface energy anisotropy. Wires of triangular and square cross-sectional shapes are considered. These shapes are formed by a recently developed delta-function model of facets, which can easily control the degree of anisotropy [1]. An infinitesimal disturbance in the form of a normal mode is applied and its stability is analyzed. Capillarity-driven surface diffusion is taken to dominate the mass transport. The stability of the wire depends on the equilibrium shape of the wire and on the longitudinal 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 but 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 YanMei 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 Ginzburg-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 reversible growth. When applied to nucleation and growth 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 mound structures consistent with 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? Alain Karma and Tomorr Haxhimali; Physics, Northeastern University, Boston, Massachusetts.

Solidification dendrites typically grow along $\langle 100 \rangle$ 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. These simulations retain the first two terms in a cubic harmonic expansion of the anisotropic solid-liquid interfacial free energy. This parametrization has recently been shown to be necessary to reproduce quantitatively the entire solid-liquid gamma plot using atomistic simulations. We find that the traditional assumption that dendrites grow along directions that coincide with maxima of the interfacial free energy is incorrect. For a two-parameter cubic harmonic expansion of the gamma plot, this criterion predicts that possible dendrite growth orientations are limited to the discrete set of $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ crystallographic directions. In contrast, we find that dendrites can also grow for a continuous range of orientation in simulations, which includes experimentally observed orientations close to $\langle 110 \rangle$ or $\langle 320 \rangle$. We find that these orientations coincide very roughly in three dimensions with maxima of the mean curvature of the crystal-melt equilibrium shape. In the more analytically tractable two-dimensional case, we show that the continuous range of dendrite orientation seen in the simulations is accurately predicted by solvability theory, when extended to growth shapes that are not symmetrical about the growth axis.

JJ3.16

Simulation of Dendritic Solidification With Moving Solids. Jorge A. Vieyra and Adam C. Powell; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Simulating dendritic solidification with solids carried by a moving fluid requires solving the coupled partial differential equations for each the mechanisms involved in that process: heat conduction, fluid flow, elastic solid behavior, fluid-structure interactions, with vector-valued Allen-Cahn phase-field to describe solidification. Toward this end, we propose a mixed-stress formulation to model fluid-structure interactions with a diffuse interface in the order parameter field. This formulation uses a function of the order parameter to combine viscous stress in the fluid with elastic stress in the solid, where the latter is a function of elastic shear strain which is an additional tensor field. The crystal growth rate is a function of crystal orientation which rotates according to local vorticity; shear strain also rotates due to vorticity. This formulation should be applicable to a variety of systems in materials science like semi-solid metal formation, dendrite breakage, ceramic crystal precipitation, and even polymer systems.

JJ3.17

Morphology and resistance evolution during single asperity contact. Ji Hee Kim^{1,2}, Pil-Ryung Cha³, David J. Srolovitz² and Jong-Kyu Yoon¹; ¹School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; ²Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; ³School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea.

Electrostatically 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 surface diffusion limited capillarity effects and 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 electric potential within the body 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 in an axis-symmetric geometry. In the earliest stages, 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 widening of the necks and a concomitant decrease in the contact resistance. At the same time, a smooth trench develops near the asperity on the anode side.

JJ3.18

Modeling the Stability of TiO₂ Nanoparticles in Acid and Base. Amanda S. Barnard^{1,3}, Peter Zapol^{1,2,3} and Larry A.

Curtiss^{2,3}; ¹Center for Nanoscale 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. We have used a thermodynamic model designed 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 phase transition. As input for the model, density functional 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 solution 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.

JJ3.19

Kinetics of Interface Impurity Segregation Including the Effect of Nucleation and Growth of Islands of Segregated Atoms. Edward Feldman¹ and Tetyana Melnik²; ¹Matematicas,

Universidad Popular Autonoma del Estado de Puebla, 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 enrichment levels and kinetics of the segregation process 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 Gorsky-Bragg-Williams modelling and the resulting Fowler isotherm 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 time dependence of the interface 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 islands-like structure. The ranges 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 interface are separated and their duration is evaluated. To 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 spatial resolution and higher elemental sensitivity will provide better possibilities for direct experimental observation of about mentioned phenomenon and for comparison with the results of theoretical modeling.

JJ3.20

On the Nucleation, Localization and Stabilization of Coarse Slip Bands. Chehung Wei¹ and John L. Bassani²; ¹Mechanical

Engineering, Tatung 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 nucleation of CSBs, and a post-bifurcation analysis (M-K analysis) is used to predict the evolution of localized deformation in terms of the growth of very small imperfections. A physically-based hardening model which captures a wide range of observed 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.

JJ3.21

Influence of Strain from an Embedded Particle on the Microstructural Evolution of a Thin-Film System.

Steve Policastro² and Nitin Singh²; 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 strongly the evolving microstructure in the thin film owing to 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."

JJ3.22

Nucleation and growth of drugs and other crystalline solids on self-assembled monolayers on gold. Branko Zugic, 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 and from solutions that contain SAMs functionalized with a variety of different organic groups. We are studying 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 types of functional groups; (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 Asta

Tuesday Morning, November 30, 2004

Room 201 (Hynes)

8:30 AM *JJ4.1

Anisotropic Free Energies of Crystal-melt Interfaces.

James Robert Morris¹, Ruslan Davidchack², Mikhail Mendelev³ and David J. Srolovitz³; ¹Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Department of

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. Whereas there have been large discrepancies 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 $1/r^n$. 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-AC05-00OR-22725 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 *JJ4.2

Molecular Dynamics Simulations of Solid-Liquid Interface Mobility in FCC and BCC Metals. Jeffrey J. Hoyt¹, Mark D.

Asta², Deyun Sun³ and A. Karma⁴; ¹Sandia National Laboratories, Albuquerque, New Mexico; ²Dept. of Materials Science & Engineering, Northwestern University, Evanston, Illinois; ³Physics Dept., East China Normal University, Shanghai, China; ⁴Physics dept., Northeastern University, Boston, Massachusetts.

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, μ , 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 μ and a pronounced asymmetry between solidification and melting rates is observed.

9:30 AM JJ4.3

Simple Density Functional for Face Centered Cubic Crystals.

Kuo-An Wu and Alain Karma; Physics, Northeastern University, Boston, Massachusetts.

We extend the density functional based phase field approach to describe fcc crystals. 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.

9:45 AM JJ4.4

Equilibrium Solid-Liquid Interfacial Properties in Lennard-Jones Alloys. Chandler Becker¹, Mark D. Asta¹, J.J.

Hoyt² and S.M. Foiles²; ¹Materials Science and Engineering, Northwestern University, Evanston, Illinois; ²Sandia National Labs, Albuquerque, New Mexico.

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 atomic-scale 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.

10:30 AM *JJ4.5

Nucleation and polycrystalline growth in phase field theory.

Laszlo Granasy¹, Tamas Pusztai¹, James A. Warren² and Jack F.

Douglas³; ¹Research Institute for Solid State Physics and Optics, Budapest, Hungary; ²Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, Maryland; ³Polymer 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 diffusional 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 JJ4.6

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 as a function of time is given by 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 JJ4.7

Growth Front Nucleation: A Mechanism for Polycrystalline Growth. James A. Warren¹, Laszlo Granasy², Tamas Pusztai² and

Jack Douglas¹; 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 mode 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 a growth forms, reexamine some older experiments, and examine prospects for models of this phenomenon in three dimensions.

11:30 AM JJ4.8

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, Berkeley, California.

The microstructural evolution of polycrystalline columnar materials was modelled 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 premelting 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 to 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).

11:45 AM JJ4.9

Crystallization and Surface Morphology of Copper Nanoparticles. Yoshiaki Kogure and Masao Doyama; Teikyo University of Science & Technology, Uenohara, Yamanashi-ken, Japan.

Surface morphology and internal atomistic 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 consisted of (111) crystal faces, which has lowest surface energy. 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 crystallize easily. The process of crystallization is investigated. The atomistic structure in the particles are visualized through the distribution of potential energy, radial distribution function and the local crystalline order. The state of the boundaries and the point defects are allocated. The thermal vibration of atoms are generated and fluctuation of surface morphology is investigated. The temperature is increased up to 1000 K, and the diffusion of surface atoms is observed.

SESSION JJ5: Electrochemical Systems; Microstructure
in Metals
Chair: Jeff Hoyt
Tuesday Afternoon, November 30, 2004
Room 201 (Hynes)

1:30 PM *JJ5.1

Phase-Field Model of Nanoporosity Formation during Dealloying. Alain Karma and Sebastian Gurevich; Physics, Northeastern University, Boston, Massachusetts.

Dealloying is the selective removal of an element from an alloy. This process commonly yields open nanoporous structures which are potentially useful for applications that make use of ultra-high area metal surfaces, such as biosensors. In contrast, such structures, are highly undesirable in the context of corrosion because of the altered mechanical behavior of the porous overlayer. 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 sharp-interface equations. This model couples a non-conserved order parameter distinguishing between alloy and electrolyte to 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.

2:00 PM JJ5.2

Phase Field Model of Electrochemistry for the Ti-Ca-Cl Ternary System. Wanida - Pongsaksawad and Adam Clayton Powell; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The mechanism of titanium product formation is investigated for use in the design of various alternatives to the Kroll process. A Cahn-Hilliard model of electrochemistry for the Ti-Ca-Cl ternary system with composition-dependent mobility is applied to study morphology evolution at the cathode. The formulation used in this model assumes rapid charge redistribution in the electrolyte and transport-limited electrochemical reactions. Two-dimensional simulation results of a liquid-liquid system with fluid flow are presented as a function of applied voltage, surface energy and viscosity, and as expected, the cathode interface is less stable under

high electric field, low surface energy, and high viscosity. In addition, three dimensional results without flow are presented to illustrate the tendency of dendrites to break up relative to the two-dimensional case without flow.

2:15 PM JJ5.3

Superfill in the Presence of Accelerating and Leveling Additives. Daniel Josell¹, Thomas P. Moffat¹ and Daniel Wheeler²; ¹Metallurgy Division, NIST, Gaithersburg, Maryland; ²IREAP, University of Maryland, College Park, Maryland.

We detail the impact of competitive adsorption of additives on the morphological 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 deposition in patterned features. The accelerating additive has previously been shown to be responsible for the bottom-up superfill process that is used to fabricate copper metallizations in integrated circuits; quantitative prediction of bottom-up feature filling with both Cu and Ag due to the impact of local area change on the coverage of adsorbed accelerator has previously been accomplished using the Curvature Enhanced Accelerator Coverage (CEAC) mechanism with kinetics acquired from studies with planar substrates. The leveling additive is capable of displacing the adsorbed accelerating additive and thus decelerating the local deposition rate. This work, the first to quantify the interplay between superfill and leveling, demonstrates how the CEAC mechanism can be extended to account for the leveling additive. A direct result of this work is quantitative explanation of the ability of leveling additive to decrease, or eliminate, the bump that otherwise forms over superfilled features, the formation of the bump previously explained by the CEAC mechanism with just the accelerating additive.

2:30 PM JJ5.4

FiPy - An Object-Oriented Tool for Phase Transformation Simulations Using Python. Jonathan E. Guyer, Daniel Wheeler and James A. Warren; Metallurgy Division, NIST, Gaithersburg, Maryland.

The solution of coupled sets of partial differential equations (PDEs) is ubiquitous in continuum models of phase transformations, such as in phase field or level set simulations. We will present an object-oriented PDE solver, written in the Python scripting language, based on a standard finite volume (FV) approach. Numerous PDE solvers exist using a variety of languages and numerical approaches. Many are proprietary, expensive and difficult to customize. They are generally not tailored to the specific needs of phase transformation modeling. As a result, materials scientists spend considerable resources repeatedly developing limited tools for specific problems. Because of the specialized knowledge required, these tools often do not take advantage of more advanced numerical techniques that would permit simulation of larger systems for longer times. Our approach, combining the FV method and Python, provides a tool that is extensible, powerful and freely available. The framework includes terms for transient diffusion, convection, and standard sources, enabling the solution of arbitrary combinations of coupled elliptic, hyperbolic and parabolic PDEs, including higher-order expressions such as Cahn-Hilliard. Program flow is entirely under user control, using the high-level Python scripting language. We will present the representation and results of current models, including phase field and level set treatments of electrochemical, polycrystalline, and dendritic phase transformations.

2:45 PM JJ5.5

Nonlinear theory and simulation of crystal growth: Suppression of the Mullins-Sekerka instability and Shape Control. Shuwang Li^{3,1}, John Lowengrub¹, Perry Leo³ and Vittorio Cristini^{2,1}; ¹mathematics, u.c. irvine, irvine, California; ²Biomedical Engineering, UC Irvine, Irvine, California; ³Aerospace Engineering and Mechanics, U. Minnesota, Minneapolis, Minnesota.

In this talk, we consider the quasi-steady evolution of growing crystals. A re-examination of this problem reveals that the Mullins-Sekerka instability may be suppressed by appropriately varying the undercooling (far-field temperature) in time. For example, in 3-D, by imposing the far-field temperature flux (rather than a temperature condition), we demonstrate that there exist critical conditions of flux at which self-similar or nearly self-similar nonlinear evolution occurs and the shape is dominated by a given mode leading to non-spherical, self-similarly growing crystals. We then examine the stability of these self-similar and in doing so completely characterize the nonlinear stability of all crystals grown under self-similar flux conditions. We present both 2D and 3D results. We use accurate boundary integral methods in which a novel time and space rescaling is implemented. This enables us to accurately simulate the long-time, nonlinear dynamics of evolving crystals. Our analysis and simulations reveal that self-similar shapes are stable to perturbations of the

critical flux for self-similar growth, in the sense that the symmetry of the crystal remains unchanged. This suggests that in experiments, small oscillations in the critical flux will not change the main features 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 stabilization leads to the existence of universal 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 actually 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.

3:30 PM *JJ5.6

Using Grain Morphology to Extract Anisotropic Grain Boundary Properties. David J. Srolovitz, Hao Zhang and Mikhail I. Mendeleev; Mechanical & Aerospace Eng., Princeton University, Princeton, New Jersey.

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 upon the anisotropy in grain boundary mobility, grain boundary free energy/stiffness, efficiency with which the boundary absorbs defects, . . . In this presentation, we discuss how we can use grain morphology to deduce the anisotropy of the quantity that describes how quickly a particular boundary migrates in capillarity-driven situations (i.e., the reduced mobility - the product of the grain boundary mobility and the grain boundary stiffness). We apply this method to extract the inclination dependence of the reduced grain boundary mobility at fixed misorientation from a molecular dynamics simulation of the migration of a boundary delimiting a cylindrical grain. 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.

4:00 PM JJ5.7

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 $\Sigma=11$ [110] asymmetrical tilt GBs with various inclination angles. Molecular statics and dynamics 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 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 JJ5.8

Grooving of a Grain Boundary by Evaporation-Condensation below the Roughening Transition. Howard Alvin Stone¹, Michael J. Aziz¹ and Dionisios Margetis²; ¹Engineering & Applied Sciences, Harvard University, Cambridge, Massachusetts; ²Department of Mathematics, MIT, Cambridge, Massachusetts.

The development of surface grooves at grain boundaries that intersect a planar surface is analyzed for the case that 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, so the resulting groove profile is 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 JJ5.9

Grain Boundary Grooving by Surface Diffusion with Strong Surface Energy Anisotropy. Tinghui Xin and Harris Wong; Mech. Eng., LSU, Baton Rouge, Louisiana.

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 grows following 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 JJ5.10

Stability of amorphous regions in crystalline matrices. Krisztian Kohary, Victor M. Burlakov and David Pettifor; Materials, Oxford University, Oxford, Oxfordshire, United Kingdom.

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 one. Using this approach we have studied the collapse of amorphous regions in thin crystalline films. We found that writing an amorphous spot is assisted by motion of low-energy facets, while its collapse is due to the mobility of the high-energy facets. The approach is easily transferable onto realistic network and non-network materials and can be applied to studying those 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.)

SESSION JJ6: Solution-Phase and Polymer Film Growth
Chair: George Gilmer
Tuesday Evening, November 30, 2004
Room 201 (Hynes)

8:00 PM *JJ6.1

Monte Carlo Simulations of KDP Crystal Growth. Luis A. Zepeda-Ruiz, George H. Gilmer and Maria Bartelt; Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, California.

Potassium dihydrogen phosphate (KDP) is widely known for its non-linear optical properties and its applications in laser technology. In the past few years, KDP has been widely studied due to its direct use on the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory where it is employed for optical switching and frequency conversion of the initial infrared light to ultraviolet light. In this presentation, we use Monte Carlo simulations to investigate the mechanisms of KDP growth. In particular, we present results for elementary/multiple step velocity as a function of supersaturation, s , along with the formation and evolution of macrosteps. The mechanism for the formation of macrosteps, several elementary steps in height, will be discussed. Additional simulations were carried out to investigate the effect of impurities during KDP growth. It was found that impurities induced a "dead-zone" (a regime of low supersaturation) where no growth occurred. All of our results are compared with theoretical models and recent experimental data.

8:30 PM *JJ6.2

The Role of Water Structuring for the Thermodynamics and Kinetics of Phase Transitions with Proteins. Peter Vekilov, Chemical Engineering, University of Houston, Houston, Texas.

The kinetic coefficients for protein crystallization are three to four orders of magnitude lower than those for small-molecule substances. Toward understanding the reasons underlying the slow growth of protein crystals, I first discuss experimental data indicating that the attachment of molecules to a crystal or cluster is not additionally slowed down by a long-life transition state, and can be viewed as an act of Brownian diffusion into the growth site. A peculiarity of the incorporation process is that diffusion has to overcome a barrier stemming from the repulsive intermediate-range interaction between

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/s, i.e. comparable to 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, 6277 (2000); *Proc. Natl. Acad. Sci. USA* 100, 792 (2003); *Phys. Rev. Lett.* 84, 1339 (2000); *Acta Crystallogr. D* 58, 1611 (2002); *Biophys. J.* 85, 3935 (2003); *Phys. Rev. Lett.* 90, 225503 (2003); *J. Am. Chem. Soc.* 125, 11684 (2003)

9:00 PM *JJ6.3

Surface freezing and the kinetics of the isotropic-smectic phase transition. Zvonimir Dogic, 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 wetted 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 JJ6.4

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 interests in vacuum deposited polymer thin films because they have become more technically important for microelectronic 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 weight. Besides 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 overhang configuration, which will block the space it covered from the access of other incoming monomers. Here we have constructed a simple 1+1 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 are qualitatively consistent with some existing experimental results. Acknowledgement: Work supported by NSF.

9:45 PM JJ6.5

Abstract Withdrawn

SESSION JJ7: Epitaxial Thin Film Growth: Strain Effects and Instabilities
Chair: Xiangrong Wang
Wednesday Morning, December 1, 2004
Room 201 (Hynes)

8:30 AM JJ7.1

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 examining 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 JJ7.2

Atomistic Modeling and Experimental Observations of Simultaneous Plastic and Elastic Relaxation in 3D-dislocated Ge Islands on Si(001). Anna Marzegalli¹, Francesco Montalenti¹, Armando Rastelli³, Hans von Kaenel² and Leo Miglio¹; ¹INFM and L-NESS, Dipartimento di Scienza dei Materiali, University of Milano-Bicocca, Milano, Italy; ²INFM and L-NESS, Dipartimento di Fisica, Politecnico di Milano, Polo Regionale di Como, Como, Italy; ³Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany.

Atomistic simulations based on Tersoff potentials are used to investigate strain relaxations in dislocated Ge islands on Si(001). Detailed information about elastic energy and strain fields, as produced by the simultaneous elastic and plastic relaxation are obtained. Intriguing features closely related to experimental observations appear. In particular, our theoretical calculations provide an explanation for STM and AFM images showing asymmetric dome-shaped island growth along the [110] direction, triggered by dislocation nucleation in the so-called "cyclic growth" phenomenon [1,2].

9:00 AM *JJ7.3

First-Principles Studies of Growth and Structural Properties of Surfaces. Kalman Varga^{1,2}, Ligen Wang³, Sokrates Pantelides^{4,2} and Zhenyu Zhang^{2,1}; ¹Department of Physics, University of Tennessee Knoxville, Knoxville, Tennessee; ²Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Department of Physics, University of Nebraska, Lincoln, Nebraska; ⁴Department of Physics, Vanderbilt University, Nashville, 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 studies on Ge film growth on Si(100) as a prime example for a system where realistic atomistic 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 proper inclusion of the Ge dimer buckling and the (2xN) superstructure on the Ge toplayer. 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 (2xN) 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 JJ7.4

Atomistic Simulation of Stress Evolution in the Early Stages of Volmer-Weber Growth. Chun-Wei Pao^{1,2}, Mikhail I. Mendeleev^{1,2} and David J. Srolovitz^{1,2}; ¹Princeton Institute for the 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 static-relaxation/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

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

9:45 AM JJ7.5

Contrasting Growth Modes of Mn on Ge(100) and Ge(111) Surfaces: Subsurface Segregation versus Intermixing.

Wenguang Zhu^{1,2}, Hanno Weitering^{3,1}, Enge Wang², Efthimios

Kaxiras⁴ and Zhenyu Zhang^{1,3,4}; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²International Center for Quantum Structures 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 "subsurfactant 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 *JJ7.6

Ab Initio Modeling 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-immiscible 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 electron-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 disilicide nanowires on Si(100) will be shown.

11:00 AM JJ7.7

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 symmetry surfaces exhibit a multitude of interesting 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 theoretical arguments, we address experimentally observed transitions between two types of rippled states on (110) surfaces. We discuss several intermediary interface states intervening, via consecutive transitions, between the two rippled states. One of them is the Rhomboidal Pyramid State, theoretically anticipated by L. Golubovic, A. Levandovsky, and D. Moldovan [Phys. Rev. Lett. 89, 266104 (2002)] and subsequently seen, by de Mongeot and coworkers, in the epitaxial erosion of Cu(110) and Rh(110) surfaces. In addition, we find a number of interesting intermediary states having structural properties somewhere between those of rippled and pyramidal states. Prominent among them are the Rectangular Rippled states of long roof like objects (huts), that represent the long times form of the

interfacial state recently revealed in the epitaxial growth on Al(110) surface. Also, we predict the existence of striking interfacial structures that, unusually, carry persistent surface currents of ad-atoms. These here called Buckled Rippled interface states are far-from-equilibrium relatives of the Abrikosov vortex state in type-II superconductors. By using the bridging of length scales theoretical arguments, here we argue that the experimentally seen Cold Rippled state is, in fact, our Buckled Rippled state.

11:15 AM JJ7.8

Numerical Simulation of Facet Formation and Coarsening Modeled by a Geometric Evolution Law.

Frank Hausser and Axel Voigt; Crystal growth group, caesar, Bonn, Germany.

We consider surface modulations in crystal growth and study the formation of facets. Thereby the dynamics is assumed to be essentially interface-controlled and driven by a strongly anisotropic surface energy together with a constant jump of the chemical potential at the interface and modeled by a geometric evolution equation, which leads to facets and corners in the corresponding Wulff-shape. This interface evolution law, which has been derived from a curvature dependent interfacial energy by Gurtin and Jabbour, is solved numerically for a 1-dimensional interface using parametric finite elements. The numerical results indicate two basic stages for the formation of facets and corners. First a rather periodic structure of hills and valleys is formed, being in agreement with the most unstable wave length of the linearized dynamics. At the second stage three distinct morphologies emerge, depending on the growth rate of the surface: faceting and coarsening occurs, periodic patterns emerge, or the surface becomes rough. We investigate the dependence of the three regimes on the parameters in the evolution law.

11:30 AM JJ7.9

Coarsening Dynamics of Faceted Crystal Surfaces: The Annealing-to-Growth Transition.

Stephen J. Watson, ESAM, Northwestern University, Evanston, Illinois.

The morphology and coarsening dynamics of a micro-faceted crystal surface annealed in contact with its melt is known to change dramatically if, in addition, the crystal is subject to net growth. We present a theoretical study of this annealing-to-growth transition by considering representative thermal annealing (A) and net-growth (G) continuum models. In each case, our theory provides a complete characterization of the morphology and coarsening dynamics in terms of an associated Piecewise-Affine Dynamic Surface (PADS). The distinctive coarsening laws $\mathcal{L} \sim t^n$ for the increase in time, t , of the characteristic facet size \mathcal{L} , follow directly from the scaling properties of the associated PADS. Large scale numerical simulations of the coarsening dynamics of each PADS will also be presented, which reveal both dynamic scaling of a variety of surface statistics as well as surprising correlation effects.

11:45 AM JJ7.10

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(number of facets) instead of O(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 benefits of the method are 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.

1:30 PM *JJ8.1**Post-Deposition Dynamics of Epitaxial Two-dimensional Nanostructures on Metal(100) Surfaces.** Da-Jiang Liu¹ and J.W. Evans²; ¹Ames Laboratory (USDOE), Iowa State University, Ames, Iowa; ²Ames Laboratory (USDOE) and Department of Mathematics, Iowa State University, Ames, Iowa.

Since functional devices invariably involve structures that are out-of-equilibrium, back-to-equilibrium dynamics is an important aspect for understanding and control of nanostructures on surfaces. Here we focus on the post-deposition dynamics of two-dimensional structures formed during epitaxial growth of Cu(100) and Ag(100) thin films. Among the processes studied are: diffusion, sintering, and shape relaxation. Atomistic and continuum modeling have been used effectively to describe dynamics on various length and time scales. More importantly, by combining the two approaches, we reveal the applicability of conventional continuum models (and by extension, conventional scaling rules) for different situations. We find that for non-nucleation-mediated processes, the continuum model (especially after incorporating anisotropy) applies to surprisingly small length scales, while significant deviation are found for nucleation-mediated processes. Interestingly, the same process, e.g., sintering, can belong to both categories depending on the geometry of the structure. Additionally, some details of atomistic processes, such as kink rounding barrier, also have effects.

2:00 PM JJ8.2**First Principles Calculations of Pd Cluster Diffusion on TiO₂ (110).** John C. Hamilton¹, Lani Sanders², A. K. Datye³ and B. S.Swartzentruber²; ¹Sandia National Laboratory, Livermore, California; ²Sandia National Laboratory, Albuquerque, 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 diffusion 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 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 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 certain size of about 50 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.

2:15 PM JJ8.3

Chemical-Reaction-Limited Kinetics in Adsorbate-Enhanced Surface Self-Diffusion. W. L. Ling, N. C. Bartelt, K. Pohl, J. de la Figuera, R. Q. Hwang and K. F. McCarty; Materials Physics, Sandia National Labs, Livermore, California.

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 in general about the underlying atomic mechanisms of this enhancement. One proposal is that adsorbates react with the substrate to form mobile species. For example, calculations show that Cu₃S₃ clusters, compared to Cu adatoms, have a much lower 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 mechanism of surface mass transport that takes into consideration the rate at which adsorbates and adatoms react on the terrace to form a mobile adspecies. This terrace-reaction-limited kinetics is fundamentally different from the well-known diffusion-limited and attachment/detachment-limited kinetics. By solving coupled diffusion equations with appropriate boundary conditions, we show that our model gives three different regimes of surface mass transport. We compare the model predictions to experimental observations by low-energy electron microscopy of transport on the Cu(111) surface with controlled amount of S. Just as in the model, three regimes are observed: first, the clean Cu limit, when Cu monomers dominate the surface transport; then the intermediate regime at low S coverage or temperature, when the clusters are becoming important but surface mass transport is limited by the terrace reaction rate; and finally for high enough S coverage or temperature, when the Cu₃S₃ clusters dominate the surface transport with kinetics similar to the Cu monomer transport. [1] P.J. Feibelman, Phys. Rev. Lett. 85, 606 (2000). SNL is a Lockheed Martin Company, operated for US DOE under contract DE-AC04-94AL85000.

2:30 PM *JJ8.4

Cluster Diffusion and Coalescence on Metal Surfaces: Applications of a Self-Teaching Kinetic Monte-Carlo Method. Talat Shahnaz Rahman, Physics, Kansas State University, Manhattan, Kansas.

The Kinetic Monte Carlo (KMC) method has become an important tool for examination of phenomena like surface diffusion and thin film growth because of its ability to carry out simulations for length and time scales that are relevant to experiments. But the method has limited predictive power because of its reliance on predetermined atomic events and their energetics as input. We have developed a novel method, within the lattice gas model in which we combine standard KMC with automatic generation of a table of microscopic events, facilitated by a pattern recognition scheme. Each time the system encounters a new configuration, the KMC algorithm initiates a procedure for saddle point search around a given energy minimum using a "spherical repulsion" method. Nontrivial paths are thus selected and the fully characterized transition path is permanently recorded in a database for future usage. The system automatically generates all possible single and multiple atom processes that it needs for a sustained simulation. Results will be presented for the diffusion and coalescence of adatom and vacancy cluster islands on Cu(111) and compared with those obtained from standard KMC simulations with a fixed data base of atomic events. While simulations reveal the presence of a number of multiple atom processes, it will be shown that for adatom cluster diffusion their importance decreases with increasing cluster size and decreasing surface temperature. Subtle differences in the evolution of the morphology of the two types of monoatomic steps of Cu(111) will also be discussed in the light of their relative stability. (Work done in collaboration with O. Trushin, A. Kara, C. Ghosh and A. Karim and supported in part by NSF grant EEC-0085604 and a CRDF grant).

3:30 PM *JJ8.5

Modeling and Simulation for Dynamics of a Step Edge. Russel Caflisch, UCLA, Los Angeles, California.

This talk describes a model for the dynamics of a step edge and numerical simulation of the model. The model includes attachment and detachment at the edge, diffusion along the edge, attachment at kinks and creation and merger of kinks. The numerical simulation is performed in the context of a level set method for simulation of epitaxial growth. The model is partially validated by comparison to results from kinetic Monte Carlo simulations.

4:00 PM JJ8.6

Phase-field modeling of step motion: An investigation of step bunching and meandering. John Lowengrub¹, ZhengZheng Hu¹, Steven Wise^{1,3} and Axel Voigt²; ¹mathematics, u.c. irvine, irvine, California; ²Research Center Caesar, Bonn, Germany; ³Biomedical Engineering, UC Irvine, irvine, California.

Thin film growth by molecular beam epitaxy (MBE) generally produces defect-free, high quality single crystal materials that have a wide range of applications. Microscopic processes include deposition of atoms, atom adsorption and desorption, adatom diffusion, island

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 atomic steps that provide 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, discontinuous adatom densities across steps and a model for the Ehrlich-Schwoebel barrier. We use 2nd order accurate finite difference fully implicit discretizations and solve the nonlinear equations at the implicit time level using an efficient nonlinear multigrid method. An advantage of this approach is that it is very efficient and there is at most a first order time step constraint (time step less than a constant times the space step). We then use the phase-field model to examine the morphological stability of step trains. In particular, we characterize the step bunching and meandering instabilities in two-dimensions.

4:15 PM JJ8.7

Continuum Description of Step Motion by Lagrangian Coordinates. Dionisios Margetis and Rodolfo R. Rosales; Mathematics, M.I.T., Cambridge, Massachusetts.

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 diffusion 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 non-dimensional parameters. 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 drastically 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) kinetics 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.

4:30 PM JJ8.8

From Atomistic to Continuum Descriptions of Morphological Evolution. Christoph Haselwandter and Dimitri Vvedensky; The Blackett Laboratory, Imperial College, London, United Kingdom.

Stochastic differential equations for the fluctuations of atomistic models of epitaxial growth are derived from their master equations. Coarse-graining transformations of the equivalent Langevin equations produce continuum equations that embody the behavior of these models at intermediate length and time scales. This provides the basis for a multiscale approach to epitaxial systems in that fluctuations associated with atomistic processes are explicitly incorporated into the coarse-grained morphological evolution of the growing surface. We apply our analysis to several standard models of growth and address several issues raised by recent kinetic Monte Carlo simulations.

4:45 PM JJ8.9

A New Monte Carlo Model for Simulations of Surface Dynamics. Ramana 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 can be quite varied depending on their neighborhood. In a conventional 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 choice of the energetics. 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 (the Gibbs-Thomson relation). It is shown the excess free energy of the island edge due to curvature is accommodated by a combination of changes in the adatom and vacancy densities.

SESSION JJ9: Thin Film Deposition Studies

Chair: Da-Jiang Liu

Thursday Morning, December 2, 2004

Room 201 (Hynes)

8:30 AM JJ9.1

Island Growth in the Presence of Anisotropic Diffusion with Long Atomic Jumps. P. Alex Greaney¹ and Daryl C. Chrzan^{2,1};

¹Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California; ²Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, California.

Kinetic Monte Carlo (KMC) simulations have been conducted to study the influence of a recently predicted surface crowding (Phys. Rev. Lett., Vol. 90, (2003), 156102) on the nucleation and growth of islands during the early stages of thin film epitaxy. Comparisons are made between island populations grown in the presence of the same anisotropic macroscopic diffusion tensor but with differing microscopic diffusion mechanisms. In one instance only anisotropic nearest neighbour hopping is permitted, and in other simulations nearest neighbour hopping is isotropic but long atomic jumps are permitted in one direction. The densities of stable islands are compared with the predictions of a mean field set of rate equations. It is found that long atomic jumps reduce the efficiency with which monomers search the bare substrate and subsequently increase the density of stable islands. The long atomic jumps also change the concentration of monomers around growing islands, and suppresses a kinetic morphological instability in which islands become elongated. This work is supported by the National Science Foundation, under grant EEC-0085569, and computational resources were provided by Lawrence Berkeley National Laboratory.

8:45 AM JJ9.2

Diffusion in Potential Fields: Time-Dependent Capture on Radial and Rectangular Substrates. John A. Venables^{1,2} and Pu

Yang¹; ¹Physics and Astronomy, Arizona State University, Tempe, Arizona; ²Physics and Astronomy, University of Sussex, Brighton, United Kingdom.

In rate equation models of nucleation and growth on surfaces, and 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 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 context of growth on Si(001), are ongoing, and the latest results will be presented. 1. S. Ovesson, Phys. Rev. Lett. 88, 116102 (2002) 2. J.A. Venables and H. Brune, Phys. Rev. B66, 195404 (2002) 3. R. Grima and T.J. Newman, Phys. Rev. E (in press)

9:00 AM JJ9.3

Quasicontinuum Monte-Carlo Simulation of Surface Growth.

Jason P. DeVita¹, Leonard M. Sander¹ and Peter Smereka²; ¹Physics, University of Michigan, Ann Arbor, Michigan; ²Mathematics, 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 JJ9.4

Kinetic Monte Carlo Simulations of the Development of Various Cu₂O Island Morphologies during Oxidation of Cu (100) Thin Films. Xuetian Han, Richard J. McAfee and Judith C. Yang; Materials Science and Engineering, University of Pittsburgh,

Pittsburgh, Pennsylvania.

Surface oxidation processes play critical roles in environmental stability, high temperature corrosion, electrochemistry and catalysis. Thin oxide films, formed by direct reaction between metal surfaces and gaseous O₂, are also widely used as sensors, dielectrics, and corrosion inhibitors. Because of its importance, much work has been done to investigate this process using many different techniques, yet fundamental understanding of the initial oxidation kinetics, from the oxide nucleation to coalescence, is still surprisingly not well understood. We have extensive experimental results of the nano-oxidation process of Cu(100) thin films via in situ ultra-high vacuum transmission electron microscopy (UHV-TEM) at various temperatures and oxidation pressures. The initial oxidation kinetics bear a striking resemblance to heteroepitaxy, where oxygen surface diffusion is the primary mechanism of Cu₂O island nucleation and growth. Yet, theoretical analysis is necessary for deeper understanding of these nano-scale processes and island morphology variation under different oxidation conditions. To meet this objective, a 2-D thin film oxidation (TFOx) model based on kinetic Monte Carlo has been developed. This model explicitly considers elementary steps including adsorption, O₂ dissociation, surface diffusion, aggregation and desorption. By adjusting several main input parameters (deposition rate, sticking probabilities, lifetime, etc), which represent various temperature and oxidation pressure, the kinetic simulation resembles the experimental observations on the nucleation and growth behavior. 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 interfaces between the oxide and the substrate is reduced changing the energy balance associated with 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 gradients characterizing the net effect on 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 JJ9.5

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. The layer coverage and the ratio of average island volume to average island size values are reported for the initial stages of island growth from submonolayer thicknesses up to a few monolayers. Our results show that, at small deposition angles and at limited or no surface diffusion included, the average growth rate of islands 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 JJ9.6

Evolution of the Shape of Patterned GaAs Surfaces During Epitaxial Growth. Anders Ballestad¹, R. Kumaran¹, Bayo Lau¹, J. H. Schmid¹, 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 regrowth on patterned surfaces, including in particular an amplitude overshoot [2]. We have investigated the morphology changes that occur during MBE growth of semiconductor films with a range of surface slopes, using a combination of in-situ optical monitoring, ex-situ structural characterization and theoretical modeling. From observations of the topography of films grown on random and lithographically textured GaAs (100) 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 funneling 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 single crystal surfaces during vapor deposition that includes the 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 regrowth on patterned GaAs surfaces as a function of layer thickness and growth temperature for surface slopes up to 50%. The model is highly non-linear for large surface slopes, consistent with experiment. 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, $\delta_t h = \nu \nabla^2 h - \lambda \nabla^2 (\nabla h)^2$, in which the coefficients can be expressed in terms of microscopic physical parameters and are flux dependent, as observed experimentally. Experimental results will be presented on surface shapes as a function of growth rate and pitch of the substrate surface pattern (200 nm - 3 microns). 1. A. Ballestad, *et al.*, PRL 86, 2377 (2001); PRB 65, 205302 (2002) 2. Shah *et al.*, APL 83, 4330 (2003); H.-C. Kan *et al.*, 92, 146101 (2004) 3. A. Ballestad, *et al.*, cond-mat/0404341.

10:30 AM JJ9.7

Molecular Dynamics Simulation of Low- and High-Temperature Molecular Beam Epitaxy and GaAs(001) Surface Phase Reconstruction. Dewey A. Murrick¹, Xiaowang

Zhou¹, Haydn N. G. Wadley¹, Ralf Drautz² and David G. Pettifor²; ¹Department of Materials Science & Engineering, University of Virginia, Charlottesville, Virginia; ²Department 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 a classical MD environment will be briefly outlined. 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 under contract No. GG10551-119199, Carey Schwartz and Julie Christodoulou program managers.

10:45 AM JJ9.8

The Effect of Hydrogen Passivation Surface and Particle Size Ratio on Silicon Nanoparticles Coalescence. Takumi Hawa^{1,2} and Michael R. Zachariah^{1,2}; 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 significant 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 Kohen-Tully-Stillinger empirical interatomic 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 forming 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 JJ9.9

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 Ehrlich-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).