SYMPOSIUM Q

Nucleation Phenomena—Mechanisms, Dynamics, and Structure

April 13 - 15, 2004

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* Invited paper
Homogeneous Nucleation, Joseph L Katz, Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland; 2Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland.

This talk will begin with a description of Nucleation Processes: why they occur, the types of barriers that cause them, and a brief discussion of various types of nucleation, i.e., homogeneous, heterogeneous, boiling from active sites, crystal nucleation. The present state of knowledge on the nucleation of supersaturated states will then be reviewed. The review will include discussion of experimental results, and a comparison to theories. If time permits, some ideas on limits our understanding will be discussed.

Nucleation and Growth of Colloidal Crystals, D. A. Weitz, Urs Gasser, R. Christian, A. Schofield and P. N. Pusey, Department of Physics & DEAS, Harvard University, Cambridge, Massachusetts; 2Department of Physics, University of Konstanz, Konstanz, Germany; 3Department of Physics and Astronomy, University of Edinburgh, Edinburgh, United Kingdom.

We use confocal microscopy to study the nucleation and growth of colloidal crystals. The use of microscopy allows the evolving nuclei to be probed in real space, and allows us to determine the shape of the nuclei as they grow. We are able to determine the surface tension between the growing crystals and the supercooled melt surrounding them, and find a very low value for which helps account for the rough surface morphology of the crystals. We identify the size of the critical nuclei, and can probe the crystalline structure of these nuclei. We also are able to estimate the nucleation rate and the nature of the growth of the crystals. In addition, confocal microscopy can be used to study the evolution of binary alloy colloidal crystals formed with particles of two different sizes.

Fluctuation Theory for the Equilibrium Size Distribution of Nuclei, Lin Zhao and David T. Wu, Mechanical Engineering, Yale University, New Haven, Connecticut.

Classical nucleation theory (CNT) models the nucleation process by which clusters of a stable phase grow and shrink through attachment and detachment reactions with monomers of a metastable phase. Because there is no general theory for the detachment process, the nucleation rate is formulated in terms of the attachment rates and the so-called constrained equilibrium cluster distribution, which takes the form $z(R) = \text{const.} \times \exp(\Delta \Phi(R)/kT)$ where $\Phi$ is the free energy and $R$ is the size of a cluster. In spite of the central role of the constrained equilibrium distribution in CNT, the soundness of this expression for $z(R)$ is valid provided the nucleation process and the associated constraints, we show that the relation for $z(R)$ is valid provided $\Phi$ is the availability.

Crystallization behavior in binary alkali halides, John Keiffer, James Pallo and Vashist Vasanthakumar, Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

We studied the crystallization behavior in binary mixtures of NaCl and CsCl, using large-scale MD simulations. Starting from pure NaCl, which crystallizes readily at even quench rates typical for MD simulations, we increase the CsCl content allowing us to suppress crystallization and observe glass formation in quenched specimens. Precursors to nucleation phenomena can be identified by reversing the time evolution of the simulation. Structural and energetic analyses are applied to both thermalized systems and the inherent structures corresponding to the system relaxed to the local potential energy minimum. Models of the energy landscape and their relation to whether a system is more likely to crystallize or form a glass in this system are proposed.

Water Dynamics: fluctuation and dynamics of freezing, Iwao Ohmine, Chemistry Department, Nagoya University, Nagoya, Japan.

Various aspects of Water Dynamics will be discussed; (1) Fluctuation and relaxation in a hydrogel, we discuss the reactivity of water molecules due to the strong disordered hydrogen bond network around the hydrogel. (2) Mechanism of water freezing, etc. Liquid water is amorphous gel-like in a short time scale, while it exhibits diffusional motion as an ordinal liquid in a very longer time scale. In between these time scale (at few to tens pico-seconds), the hydrogen bond network rearrangement (HBNR) occurs intermittently and locally in space, involving local collective motions accompanied with large fluctuations. In order to identify these intermittent local collective molecular motions and to explore the nature of the global potential energy surface influenced by HBNR of water, the inherent structure analysis and various analyses were performed to explain this motion. (3) Nucleation-Growth Kinetics, Vitaly A. Shneidman, Physics, New Jersey Institute of Technology, Newark, New Jersey.

Nucleation and growth of a stable phase is the most typical pathway of a phase transformation. A large number of nucleation models, often of very different mathematical structure, were suggested in the past, reflecting the diversity of the possible nucleation mechanisms in specific physical systems. Understanding of the intricate interrelations between different models and one's ability to break down the...
description into a model-independent ("universal") and model-specific parts, allows a more reliable interpretation of experimental data and leads to a more comprehensive overall nucleation picture. The present review will focus on two large groups of models. The first includes several classical models, such as those introduced by Becker and Doering, Turnbull and Fisher, or Zeldovich and Frankel. These models can be described exactly only in case of steady-state nucleation, but due to a large value of the nucleation barrier they also can be described asymptotically in the more challenging time-dependent situations. Asymptotic results clearly exhibit distinct universal and model-dependent behaviors. The main examples include the isothermal or transient nucleation, nucleation during quench or heating, etc. Relevant experiments also will be discussed. The second group includes models of lattice type, such as the Ising model in a magnetic field. Various types of lattice symmetries and different spin-flip dynamics are discussed in literature. The remarkable feature of such models is the possibility of a "first principle" evaluation of the nucleation rate, as well as of the growth rate of individual nuclei and of the interface. This can be used to test more phenomenological approaches, such as the classical models of nucleation, or the Kolmogorov-Avrani model of growth and interaction of nuclei. At very low temperatures the nucleation rate, including such delicate issues as the pre-exponential (which exhibits unexpected modulations when the field is changed) can be obtained analytically. The structure of the results is very different from what one would expect in the Becker-Doering approach. At higher temperatures large scale Monte Carlo simulations can be used. The general classical framework which views nucleation as a one-dimensional random walk (with a smooth transition to deterministic growth above the critical size) is valid here, although an account for rather strong time-dependent effects is required in more the thermodynamics of nucleation, on the other hand, is distinctly non-classical.

SESSION Q2: Solutions and Multi-Component Systems

Chair: Nitash Balsara
Tuesday Afternoon, April 13, 2004
Room 3000 (Moscone West)

1:30 PM *Q2.1
Dense Liquid Precursor for the Nucleation of Polymers of Sickle Cell Hemoglobin, Volodyi Peter and Oleg Galkin; Chemical Engineering, University of Houston, Houston, Texas.

The primary pathogenic event of sickle cell anemia is the polymerization of the mutant hemoglobin (HbS) within the red blood cells, occurring when HbS is in deoxy state in the venous circulation. Polymerization is known to start with nucleation of individual polymer fibers, followed by growth and branching via secondary nucleation, yet the mechanisms of nucleation of the primary fibers have never been subjected to dedicated tests. We implement a technique for direct determination of rates and delay times of primary nucleation of HbS fibers, based on direct detection of emerging HbS polymer using differential interference contrast microscopy and laser photolysis after laser photolysis of CO-HbS. We show that: (i) nucleation throughout these determinations occurs homogeneously and not on foreign substrates, (ii) individual nucleation events are independent of each other; (ii) nucleation induction times agree with a semi-empirical prediction based on Zeldovich's theory; (iv) the critical nucleus contains 11 or 12 molecules. (v) the nucleation rates are of the order of 106 - 108 cm-3s-1; The nucleation rate values are comparable to those leading to erythrocyte sickling in vivo and suggest that the mechanisms deduced from in-vitro experiments might provide physiologically relevant insights. The nucleation rate values are 9-10 orders of magnitude higher than those known for protein crystals. We also provide evidence that the nucleation of the sickle cell hemoglobin polymers proceeds via a precursor that is likely a metastable droplet of a dense liquid phase, evidenced in such solutions [Galkin et al, PNAS 99, 8479 (2002)], i.e., the nucleation process can be viewed as a supercritical fluid phase transition, and a structure fluctuation theory suggests that tools employed to control the dynamics of phase behavior in protein and colloid solutions may be applicable to control the pathogenic polymerization of HbS.

2:00 PM *Q2.2
Nucleation of Ordered Solid Phases of Proteins via Unstable and Metastable High-Density States: Phenomenological Approach, Alexander Vekilov, Maria Gracheva, Gregoire Nicolis, CP 231, Campus Plaine, Universite Libre de Bruxelles, Belgium; 1Chemistry, Rice University, Houston, Texas; 2Chemical Engineering, University of Houston, Houston, Texas.

Protein crystallization is a very complex process that is not well understood. Nevertheless experiments and computer simulations indicate that the nucleation rate of protein crystal growth has a complex dependence on temperature and concentrations, which cannot be explained by classical nucleation theory. We present a simple phenomenological theory that takes into account the possibility of intermediate high-density unstable and metastable states during the protein crystallization process. The protein crystal nucleation is analyzed for different sets of parameters. Our calculations indicate that the nucleation rates can be significantly enhanced by this mechanism. Theoretical predictions are in a good agreement with observed experimental results on nucleation of ordered solid phases of proteins. The approach discussed allows to predict how to grow good crystals from solution.

2:30 PM *Q2.3
Nucleation of Globular Protein Crystals From Solution, James D. Gunton1, Andrey Shiryeyev1, Daniel Pagan1 and Maria Gracheva2; 1Physics, Lehigh University, Bethlehem, Pennsylvania; 2School of Mathematics, University of Minnesota, Minneapolis, Minnesota.

High quality crystals are required for the determination of the structure of globular proteins via x-ray diffraction. Since the function of proteins is related to their structure, careful attention has been given to understanding how to grow good crystals from solution. Nucleation is the critical initial step in crystallization from a supersaturated protein solution and is known to depend sensitively on the initial conditions of the solution. Therefore considerable theoretical effort has been given to understanding the choice of initial conditions that yield optimal nucleation rates for these self-assembling, nanoscale protein molecules. It has been shown that the optimal choice corresponds to preparing the system near the critical point of the metastable fluid-fluid coexistence curve of the solution. The latter describes coexisting protein poor and protein rich fluid phases. It is also known that this metastable coexistence region contains protein-protein interactions whose range of attractive interactions is short as compared to the size of the protein molecules. This is in contrast with the case of small molecules, such as argon, whose range of attractive interactions is large as compared to the size of the molecules and which have been studied in much more detail than globular protein molecules. For such small molecules, the fluid-fluid coexistence curve is stable, rather than metastable. Several relatively simple models have been proposed to describe the protein-protein interactions, including a modified Lennard-Jones model, a short-range attractive square well interaction model and a van der Waals density functional model. This talk will focus on recent results for the phase diagrams and nucleation free energy barriers for some of these models. In addition, the relevance of such models for certain diseases, including hereditary cataracts and sickle cell anemia, will be briefly discussed.

3:30 PM *Q2.4
Dynamics of first-order phase transitions in multi-component systems: A new theoretical approach, Juern W. P. Schmelzer, Department of Physics, University of Rostock, Rostock, Germany.

In the theoretical description of nucleation-growth processes, currently Gibbs' classical thermodynamic theory of heterogeneous systems is predominantly employed in the description of the properties of the clusters. However, Gibbs' approach does not make it possible to describe, in general, the properties of the critical clusters, determining the rate of nucleation, in a sufficiently correct way. Moreover, Gibbs' approach is restricted in its applicability to thermodynamic equilibrium states exclusively. For this reason, it cannot give a theoretically founded prescription for the determination of the possible states of the clusters of sub- and supercritical sizes in dependence on supersaturation and cluster size. In order to overcome these shortcomings, in recent years a generalization of Gibbs' classical approach has been developed and employed for the description of nucleation processes. This generalization of Gibbs' classical method leads, for a variety of quite different applications, to dependencies of the work of critical cluster formation on supersaturation, which are qualitatively and widely even quantitatively in agreement with theoretical predictions of density functional methods. The theoretical methods and results are summarized in the first part of the contribution. They are then extended to a description of growth processes of single clusters and ensembles of clusters. In order to fulfill this task a new method for the determination of the state parameters of the clusters in dependence on their sizes is developed and outlined. It turns out as the result of the analysis that a variety of thermodynamic and kinetic parameters, determining cluster growth, become cluster size dependent as well.

The results are illustrated here for a model system (regular solutions) and applied then to the interpretation of experimental results on nucleation processes in solutions of polydisperse phase-separating polymers and glassforming melts. It is shown that the approach discussed allows to resolve a variety of problems in the interpretation of experimental data on the kinetics of phase formation processes which could not be given a satisfactory explanation so far.

4:00 PM *Q2.5
Fluctuation and Kinetic Effects in Protein Crystallization, Gregoire Nicolis, CP 231, Campus Plaine, Universite Libre de Bruxelles, Belgium; 1Chemistry, Rice University, Houston, Texas; 2Chemical Engineering, University of Houston, Houston, Texas.
Free energy based state diagrams are widely used to obtain valuable information on nucleation barriers and the crystallization of protein solutions. In this presentation an extended approach is outlined, accounting for kinetic effects related to strongly nonequilibrium conditions and for fluctuation-induced transitions between states. In particular, the enhancement of nucleation rate by the presence of an intermediate fluid phase, the formation of spatial patterns in post-nucleation competitive growth processes and the role of anisotropy in the formation of critical nuclei are addressed.

SESSION Q3: Nucleation in Condensed Media

Wednesday Morning, April 14, 2004
Room 3009 (Moscone West)

8:30 AM *Q3.1 Searching for the Critical Nucleus in Phase Separating Polymer Blends, Nitash P Balsara, Department of Chemical Engineering, University of California, Berkeley, Berkeley, California.

A wide range of phase transitions such as boiling, crystallization, and liquid-liquid phase separation are initiated by nucleation. Nucleation begins with the formation of microscopic nuclei, which then grow as the phase transition proceeds. In most systems, the processes that lead from formation to the growth of the critical nucleus are free from experimental scrutiny. We have constructed a model system wherein the formation of critical nuclei can be observed directly. Our system is a blend of two high molecular weight homopolymers. The initial stage of liquid-liquid phase separation in this system was studied by time-resolved small angle neutron scattering. We find that the scattering profiles are time-independent for scattering vectors larger than a critical scattering vector. We demonstrate the relationship between the critical nucleus size (Rc) and the critical scattering vector. The dependence of Rc on quench depth is in qualitative agreement with all known theories of phase separation kinetics (nucleation and growth or spinodal decomposition). In particular we find that Rc decreases monotonically with quench depth in the vicinity of the spinodal and is finite at the spinodal. Our experiments suggest that the conventional meaning of the binodal (cloud point) and spinodal (point of change in phase separation mechanism) curves need reexamination.

9:00 AM *Q3.2 Heterogeneous Nucleation of Block Copolymers, Hannahon Chang, Ching-Chung Wu, Department of Chemical Engineering, University of Houston, Houston, Texas.

Understanding the influence of additives in controlling the equilibrium phase behavior and the kinetics of morphology development in multi-phase polymers has far reaching consequences on the understanding of liquid-liquid phase behavior. An important class of multiphase polymeric materials is microphase separated block copolymers and it is able to serve as model systems to understand surfactants, lipid bilayers and biomimetic systems, and their increased technological role in specialized applications. In this work we examine the influence of nucleating (nanoparticle) agents on the kinetics of microphase separation in a lamellae forming nearly symmetrical polystyrene-polyisoprene (PS-PI) block copolymer. The nucleating agents employed are chemically similar and differ primarily in their geometric characteristics. We have studied the kinetics of domain growth by a combination of small angle x-ray and neutron scattering, depolarized light scattering, and melt state viscoelastic measurements near the order-disorder transition temperature. The temperature of the mesoscale domains and location of nanoparticles are examined by atomic force microscopy and transmission electron microscopy and provide a crucial link to the understanding of the kinetics of domain growth. These results are interpreted in the context of current theories of nucleation.

10:30 AM *Q3.4 Recent developments in non-photochemical laser-induced nucleation, Bruce Garcia1, Janice Aber2, Jelena Matic3 and Allan Myerson2; 1Chemical & Biological Sciences & Engineering, Polytechnic University, Brooklyn, New York; 2Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois.

About 7 years ago, we accidentally discovered that intense, nanosecond, near-infrared pulses could induce nucleation in supersaturated solutions. We used this photo-induced physical phenomenon to the electric-field induced alignment of solute molecules, aiding in the formation of a critical nucleus. Since then, we have observed non-photochemical laser-induced nucleation (NPLIN) with a variety of small organic molecules in water and alcohol, including aqueous glycinie, which crystallizes into two different polymorphs depending on the laser polarization state. This talk will focus on the latest developments concerning NPLIN, including wavelength dependence and the effect of static electric fields.

11:00 AM Q3.5 Nucleation and Growth of Crystals in Fused Silica and Silicon by Strongly Nonlinear Surface Acoustic Waves, Peter Hess, Alexey Lomonosov and Thomas Krämer, Physical Chemistry, University of Heidelberg, Heidelberg, Germany.

Nucleation and growth of crystals in solids is a long standing problem.
in fracture mechanics. In Griffith theory the existence of micro-cracks is assumed and only their growth is considered. Accordingly, most previous fracture mechanics results, e.g. in silicon crystals, have been performed by applying a constant force perpendicular to an artificial precrack. With laser-excited and detected nonlinear surface acoustic waves (SAWs) the intrinsic nucleation and fracture process can be studied with unprecedented spatial and temporal resolution. By using the technique for launching short elastic surface pulses acoustic Mach numbers or strains in the range of 0.01-0.001 can be reached. This is sufficient to nucleate cracks in many materials. Experiments were performed in isotropic fused silica: amorphous single-crystal silicon. The failure process starts at or near the surface where the largest particle displacements are located. The crack field generated at the surface was detected by scanning force microscopy (SFM). To analyze the evolution of cracks into the depth of the solid the focused ion beam (FIB) technique was employed. Results obtained for fused silica indicate that initial failure occurs perpendicular to the SAW propagation direction via tensile opening stresses (mode I fracture behavior). The transient stress field, acting as driving force, is in operation essentially during the duration of the ns-SAW pulse, nucleation, and the first phases of crack evolution can be studied with this novel impulsive SAW method.

11:15 AM Q3.6

Nucleation and Growth Kinetic of Quasicrystalline Phase in Amorphous Al62 Cu25.5 Fe12.5 Thin Films, Didier Rouxel*, Nathalie Bonasso* and Philippe Pigeat†; LPMIA, University of Nancy I, Vincennes, Lorraine, France. Thin films of Al62 Cu25.5 Fe12.5 i-phase were prepared by FIB technique. Results obtained for fused silica indicate that initial failure occurs perpendicular to the SAW propagation direction via tensile opening stresses (mode I fracture behavior). The transient stress field, acting as driving force, is in operation essentially during the duration of the ns-SAW pulse, nucleation, and the first phases of crack evolution can be studied with this novel impulsive SAW method.

SESSION Q4: Nucleation in Confined Spaces

Chair: James Warren

Wednesday Afternoon, April 14, 2004
Room 3009 (Moscone West)

1:30 PM Q4.1


All theoretical treatments of nucleation agree that there is a time lag, t0, in the process of freezing before a steady state in the nucleation rate is reached. Treatments differ, however, in their descriptions of what happens in the transient period leading up to the steady state. The most promising of these treatments, perhaps, in the order of their appearance, are those by Kashchiev, Wu, and Shneiderman. Kashchiev's treatment gives the most specific prediction of the three but has been criticized as being based on rather severe approximations. Comparisons will be made of the results of the three theoretical treatments, and these will be compared with the results of computer-intensive molecular dynamics simulations of the kinetics of freezing by Turner & Chushak, and Huang. It turns out that Kashchiev's 1969 treatment, with no adjustable parameters describing the behavior as a function of t/t0, accounts very well for the simulations, as do both Wu's and Shneiderman's, also, provided that their undetermined parameters are adjusted to fit the data.

2:00 PM Q4.2

Phase field theory of nucleation and polycrystalline solidification, Laszlo Granasyl, Tamas Pusztai†, Tamas Borzsonyi†, Research Institute for Solid State Physics & Optics, Budapest, Hungary; †Center for Theoretical and Computational Materials Sciences, National Institute of Standards and Technology, Gaithersburg, Maryland.

A phase field theory of crystal nucleation will be presented. We demonstrate that fixing the model parameters via interfacial information from molecular dynamics simulations, the height of the nucleation barrier can be predicted with a good accuracy for simple liquids. Relying on a model we proposed recently [L. Granasyl, T. Borzsonyi, T. Pusztai, Phys. Rev. Lett. 88, art. no. 206105 (2002)], we study the nucleation and growth of polycrystalline matter, and address the formation of complex polycrystalline growth morphologies such as 'dizzy' dendrites, spherulites, and fractallike aggregates. It will be shown that static and dynamic heterogeneities, i.e. particulate additives and orientational defects quenched into the solid, play analogous roles in determining the evolution of polycrystalline growth patterns. Finally, we introduce walks into the simulations, and explore particle-field interaction and heterogeneous nucleation in alloys.

2:30 PM Q4.3

Argon Nucleation in a Cryogenic Nucleation Pulse Chamber, R. Strey, R. Band, A. Fliederer and J. Woelk; Institut fuer Physikalische Chemie, Universitaet zu Koeln, Koeln, Germany.

Recent careful nucleation rate measurements on a variety of systems (e.g., water, alcohols, oils) provide clear evidence of a weaker temperature dependence than predicted by classical nucleation theory (CNT). Latest theoretical developments like e.g. density functional theory (DFT) rely on the exactness of intermolecular potentials which are not widely known for practically relevant vapor pressure, but well-known for noble gases. Therefore we took up the challenge to provide experimental nucleation rate data for argon in order to close the gap between theory and experiment. We built a nucleation pulse

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chamber operating at temperatures of $80 \text{ K}$ and below. In this chamber argon-helium mixtures are adiabatically expanded and nucleation is induced using noble gases. The number density $N$ of nucleated droplets is detected by constant-angle light scattering so that in principle nucleation rates can be obtained. Unfortunately, the growth of argon droplets is (yet) found to be too fast to decouple nucleation and growth. However, the experiments already performed allow us to present onsets of nucleation of argon and set a narrow margin for the nucleation rates. We find CNT to predict nucleation rates being factors between $10^2$ and $10^4$ too low within our experimental window 40 $< T/\text{K} < 60$. Also for argon the experimental temperature dependence is weaker than that of CNT. Interestingly, DFT accounts for about 5 orders of magnitude and slightly corrects the temperature dependence.

3:30 PM Q4.4

**Nucleation and growth of membrane protein crystals from ordered lipidic cubic matrices.** Emad M. Landau, Physiology and Biophysics, The University of Texas Medical Branch, Galveston, Texas.

We have developed a novel concept for the crystallization of membrane proteins using highly viscous, optically transparent and non-birefringent lipidic cubic phases - the in cubo crystallization. The crystal structure of the light-induced proton pump bacteriorhodopsin (bR), grown from a monoein lipidic cubic phase, was solved at atomic resolution, confirming the trinucleotide repeat structure of the first two intermediates of the photocycle of bR, illustrating the early rearrangements that occur upon photoexcitation. Recent crystallization of other membrane proteins from lipidic cubic phases, including rhodopsin, a photosynthetic reaction center, and the Nicotinic acetylcholine receptor illustrate the generality of the in cubo crystallization methodology. The molecular events that lead to nucleation and crystal growth in cubo will be discussed.

4:00 PM Q4.5

**Liquid-Vapor Equilibrium and Nucleation in Cylindrical Pores:** A Monte Carlo Model vs Experimental Results. Anthony Saugy1, Jean-Louis Barrat2 and Lyderic Bocquet1.

We present experimental and theoretical results on intrusion-extrusion cycles of water in hydrophobic mesoporous materials, characterized by independent cylindrical pores. Experimental characterizations indicate two different mechanisms for intrusion and extrusion. Intrusion takes place at temperatures exceeding the thinning temperature of a biological membrane. In parallel, we have demonstrated that BR molecules packed in 3D crystals undergo a light-induced photocycle that is very similar to that of BR in the native purple membrane. This finding was followed by the determination of the high-resolution structures of the first two intermediates of the photocycle of BR, illustrating the early rearrangements that occur upon photoexcitation. Recent crystallization of other membrane proteins from lipidic cubic phases, including rhodopsin, a photosynthetic reaction center, and the Nicotinic acetylcholine receptor illustrate the generality of the in cubo crystallization methodology. The molecular events that lead to nucleation and crystal growth in cubo will be discussed.

4:15 PM Q4.6

**Investigation of noble gas cluster formation in amorphous carbon matrix.** Francisco Chagas Marques, Paulo Fernando Barbiere, Myranno Henrique de Oliveira and Rodrigo Griebel Lacerda, IFGW/DFPA, UNICAMP, Campinas, SP, Brazil.

Hard amorphous carbon films usually present very high stress, which hinders most technological applications. Nevertheless, this high stress can be useful for some scientific investigation. In this work we use amorphous carbons as trapping-nucleus gas cell for trapping noble gases under high pressure. This approach enables us to investigate the effects of the internal pressure on the implanted noble gases atoms subjected to the highly stressed environment of the carbon matrix. This is an interesting approach to study noble gases under high pressure, because of the facility for handling the samples, which is a problem when using the conventional diamond anvil cells. Using the above approach we studied the local environment of noble gases atoms implanted into an amorphous carbon (a-C) matrix. Thin a-C films were prepared by ion-beam-assisted deposition (IBAD) using noble gases. Photoemission spectroscopy (XPS/UPS), Electron Energy Loss Spectroscopy (EELS), and Raman scattering indicate that the material is composed of compressed and dense sp2 network (90% by EELS). By intentionally changing the a-C deposition conditions we were able to trap noble gas atoms under different internal pressure (intracase stress) ranging from 1 GPa up to 10 GPa. Extended x-ray absorption fine spectroscopy (EXAFS) was performed to investigate the interatomic distance of the implanted noble gases as a function of the intrinsic stress of the carbon matrix. The analysis of XANES (x-ray near edge spectroscopy) and EXAFS indicate that clustering of noble gas is induced by high pressure.

4:30 PM Q4.7


This presentation will describe a microfluidic system for protein crystallization using nanoliter volumes of solutions. This system is based on the one recently reported in Zheng B., Rostem F. S., Ismagilov R. F.; "Screening of Protein Crystallization Conditions on a Microfluidic Chip Using Nanoliter-Size Droplets", J. Am. Chem. Soc. 2003 125 (37):11170-11171. Crystallization is conducted in nanoliter noble gas droplets surrounded by a water-immiscible oil. Hundreds of these droplets with controlled composition can be set up in minutes under computer control, essentially covering the entire phase space of crystallization for a given set of reagents. This system is used to investigate scaling of homogeneous and heterogeneous nucleation upon miniaturization of the crystallization volume. In addition, methods of control of nucleation and growth on small spatial scales will be presented. These methods, in combination with technological developments, have the potential to facilitate reliable production of high-quality protein crystals for structural studies.

4:45 PM Q4.8


We present a novel hybrid molecular dynamics (MD) scheme, suitable for efficient modeling of defect and impurity nucleation and growth in solid-state systems such as crystalline semiconductors and the metallic alloys. While molecular dynamics simulation offers a direct probe of nucleation kinetics and cluster morphology that is very similar to that of bR in the native purple membrane. This finding was followed by the determination of the high-resolution structures of the first two intermediates of the photocycle of bR, illustrating the early rearrangements that occur upon photoexcitation. Recent crystallization of other membrane proteins from lipidic cubic phases, including rhodopsin, a photosynthetic reaction center, and the Nicotinic acetylcholine receptor illustrate the generality of the in cubo crystallization methodology. The molecular events that lead to nucleation and crystal growth in cubo will be discussed.
energy barrier delays the generation of a new phase, or, at deep quenches, an unstable state. We investigate the structure and dynamics of the system emerging upon crossing the metastability/instability boundary. We use lysozyme, a model protein for which the phase diagram is established. We show that the evolution of the structure factor during nucleation is similar to that during melting and recrystallization. We also show that the metastability boundary is delineated upon crossing the metastability boundary, in agreement with predictions of non-mean-field theories. More importantly, these results show that the spinodal is not defined by a sharp line in the phase diagram but rather by an ill-defined region in the high-pressure phase diagram. These results also show that the generation of a predetermined number of droplets of a chosen size can be reproducibly accomplished at low undercoolings in the nucleation regime. However, the nucleation of these droplets occurs at random locations, while the nucleation of droplets over electrodes. Towards such refinement of the droplet generation technique, we show that the generation of droplets of the dense amorphous phase is initiated by a peak in the dielectric constant and recrystallization, leading to the formation of a new phase. We show that the application of an external field. Tzu-Ling Li and YewChung Sermon Wu; Material Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

Q5.2 Nucleation Problems in Location Control of Crystal Grains in Excimer Laser Crystallization of Silicon Thin Films.

Nucleation problems in location control of crystal grains in excimer laser crystallization of amorphous Si thin films, which is a rapid melting and quenching process within several tens to hundreds nanoseconds. The method enables one to grow uniformly-sized large grains at artificial sites. The artificial site is a small portion where many nanometer-sized crystallites are embedded in the amorphous matrix of the starting thin film. A part of the embedded crystallites survive the melting and serve as a seed crystal in the following recrystallization. The seed crystal at the site starts to grow immediately after the molten matrix begins to cool below the melting temperature. The growth rate now continues to grow beyond the site, while the surrounding molten region goes into supercooling. When the supercooling becomes substantially large after some period, crystallites randomly nucleate from the molten phase at a high rate. Some of the random crystallites which are nearest to the site, finally impinge upon the large crystal grain that has already grown from the seed crystal. The location of the large crystal grains is thus controlled at the site. While the method basically relies on the survival of the seed crystallites at the artificial site, there are many nucleation problems involved. The most essential is the random nucleation of crystallites from the supercooled molten Si in the final recrystallization. The size of the large grains grown at the site is determined by the time when the random nucleation of the crystallites occurs. For estimating how the grain size is determined, we conducted numerical simulation based on time-dependent Ginzburg-Landau equation and heat equation, employing stochastic models for the grain growth and classical isothermal nucleation theory. The simulation predicts the reduction of the cooling rate enhances the grain size, which is qualitatively in agreement of the experimental evidence. However, the size distribution calculated by the simulation is far broader than the experimental result. This could be due to the flaw in the model employing the classical isothermal nucleation theory, since the nucleation is essentially an athermal process under a condition far from the equilibrium. It is also noted that the solid-phase nucleation of crystallites occurring before the melting, which is athermal as well, is another essential problem. In this paper, we discuss these nucleation problems presenting the simulation and experimental results, and discussing the need for developing and adopting a theoretical approach to the athermal nucleation for understanding the melting and recrystallization in the method for the grain-location control.

Q5.3 Crystal growth mechanism of hen egg lysozyme under external fields. Tsu-Ling Li and YewChung Sermon Wu; Material Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

Crystal growth mechanism of hen egg lysozyme under various electric fields is discussed. Electrolyte with different shapes will induce different fields that effect the crystallization driving force and the morphology of crystals. In this study, atomic force microscopy was used to investigate the kinetics of the growth mechanism.
2) Further layer development continuous in two ways: during the course of further enhancement of thickness of metal oxide layer (from 0.7nm to 1.4nm) at high condition free on the form of 3D islands and simultaneously there develops roughness of silicon oxide mixed in areas of pure silicon. 3) Redistribution of oxide layers greater than 1.4nm thicknesses on silicon surface leads to formation of tightly packed-evaporated nonmonolayer regions. The metal oxide will change in morphology of metal oxide films being strictly accompanied by changes in their compositions. The effectiveness of topochemical reaction of silicon oxide by metals with high affinity to oxygen and development of 3D monatomic oxide nanoparticles depends on their chemical activity and rises in the row V-Nb-Ti, but also depends of their atomic weight and increases in V-Nb rank. For the purpose of many development of 3D nanostructures the metal oxides were formed by multi-step deposition of Ti, V and Nb on silicon substrates as well.

Q5.8 Metamorphosis of InP self-organized islands and the two-dimensional ordered distribution influenced by mismatched GaInP/GaAs epitaxial layers. Hao Wang, Changjun Liao, Guanzhan Fan and Songhao Liu, School for Information and Optoelectronic Science and Engineering, South China Normal U., Guangzhou, China.

The self-organized InP islands, which were grown on the different GaInP epitaxial layers, were utilized to find the influence of the stress between the epitaxial layers and the islands. The shape of the islands were elongated because of the increasing stress. This phenomenon has been analyzed and simulated to show that the shape optimization and stability of the islands can be achieved by minimizing the total energy. For the self-organized islands at the surface of epitaxial layers were analyzed by scaling theories to show a periodical distribution. Some kind of epitaxial layers, for example, the mismatched GaInP on the GaAs(100) tilt to (111) 15, can improve the periodicity of the island distribution.

Q5.9 A Phase-Field Model for Step Bunching Instabilities and Step Meandering Instabilities due to Elastic Interactions between Steps. Dong-Hye Yeon1, Pil-Ryung Cha1, Jin-Young Kim1 and Jong-Kyu Yoon2; 1School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; 2Princeton Materials Institute, Princeton University, Princeton, New Jersey.

There is an increasing need for an understanding the mechanism of the nanostructural self-organization on solid surfaces because of its wide range of applications. Long-range elastic strain interactions among the steps and the extra step line energy are the important factors, and many theoretical approaches have been reported to explain the energetics and kinetics of the steps by the interplay of the elastic strain energy and the step line energy. During the growth of islands, the shape of the islands on the vicinal surface and their motions can be explained by the behavior of the adatoms such as absorption, diffusion, desorption and incorporation into steps. At the steps, there exists surface forces originated from various factors, such as interfacial lateral strain, stress, the total number of visits to lattice sites and the number of visits to step-edges (the so-called Ehrlich-Schwoebel barrier). The correct theory for irreversible nucleation on top of a continuous island is used to interpret STM results on Cu/Cu(111) [1]. The time-dependent solution to the 2D diffusion field is demonstrated using an FFT-based method that allows for both nucleation and subsequent growth on an anisotropic (rectangular) lattice. Our latest simulations have to be tested against model-oriented experiments.

A Study of Precipitation Kinetics: Experiments and Simulations. Steven Van Petegem1, Kelly Verheyen2, Paolo Politi3, Claudio Castellano3, Paul Scherrer Institute, Villigen PSI, Switzerland; 2SCK/CEN, Mol, Belgium; 3Charles University, Prague, Czech Republic.

The composition of nano-precipitates and the identification of defect clusters in irradiated steels is still an issue with many open questions. Nowadays multi-scale computer modelling is a new tool that can help solving these questions. But to justify this approach the computer simulations have to be tested against model-oriented experiments. Therefore advanced experimental tools are needed that can characterize both qualitative and quantitative the small defects present in the model materials. Here we present the results on a Fe-Cu model alloy with variable Cu content. The nucleation and growth kinetics of nano-precipitates in this system have been simulated using kinetic Monte Carlo. We have used Small-Angle Neutron Scattering (SANS) and Positron Annihilation Spectroscopy (PAS) in combination with positron calculations to study nano-precipitates during aging, starting from the very early stages of precipitation. More specific, Positron Annihilation Lifetime Spectroscopy (PALS) is used to identify free volume defects and Coincidence Doppler Broadening of Annihilation Radiation (CDBAR) is used to detect the nano-precipitates. Positron calculations on modelled nano-precipitates show that PAS can detect precipitates as small as 0.5 nm and exhibits saturation behavior at about 1 nm. SANS on the other hand is sensitive for precipitates with a diameter larger than 1-2 nm. This makes the two techniques appropriate, complementary tools to investigate nano-precipitates over a wide size range.

SESSION Q6: Nucleation on Surfaces I
Chair: Harald Brune
Thursday, Morning, April 15, 2004
Room 3009 (Moscone West)

8:30 AM Q6.1 Effects of Repulsive Interactions on Nucleation and Growth on Surfaces. John A. Venables1, Physics and Astronomy, Arizona State University, Tempe, Arizona; 2Physics and Astronomy, University of Sussex, Brighton, United Kingdom.

Nucleation and growth on surfaces has been extensively studied using rate and rate-diffusion equation models, and the diffusion limit has often been applied to predict nucleation densities and other mean-field quantities. Recent experiments and calculations have shown that weak repulsive interactions between adsorbate atoms may shift nucleation kinetics towards the attachment-limited case at low temperatures. The transient nucleation regime is more important in the latter case, due to a combination of delayed nucleation and reduced capture. A time-dependent interpolation scheme between attachment- and diffusion-limited capture number has been proposed, and used to interpret STM results on Cu/Cu(111) [1]. The time-dependent solution to the 2D diffusion field is demonstrated using an FFT-based method that allows for both nucleation and subsequent growth on an anisotropic (rectangular) lattice. Our latest models and computations are presented. 1. J.A. Venables and H. Brune, Phys. Rev. B66, 195404 (2002)

9:00 AM Q6.2 Theory of second layer nucleation in epitaxial growth. Paolo Politi1 and Claudio Castellano2; 1IAC-CNR, Sesto Fiorentino, Italy; 2Dipartimento di Fisica, Universita' di Roma La Sapienza, Roma, Italy.

According to standard mean field theories, the rate of dimer formation during epitaxial growth is proportional to the square of the adatom density. This recipe for nucleation is used for studying adatom layer as well as second layer nucleation and for implementing nucleation in growth models where adatoms are treated through a continuous model. The mean field recipe is generally wrong. The physical reason of such breakdown may be traced back to simple properties of random walks, but more precisely, to the difference between the total number of visits to lattice sites and the number of visits to distinct sites. As a consequence of that, mean field overestimates the rate of dimer formation by a factor which increases exponentially with the additional barrier at step-edges (the so called Ehrlich-Schwoebel barrier). The correct theory for irreversible nucleation on top of a terrace is reported and discussed.

9:30 AM Q6.3 Nucleation and growth of gold nanoparticle coatings on glass. Xiaodin Xu, Michael Cortie3 and Mike Stevens1; 1Institute for NanoScale Technology, University of Technology, Sydney, Sydney, New
South Wales, Australia; 2CMF, University of Technology, Sydney, New South Wales, Australia.

The technology of nanoscale gold films deposited onto glass by vacuum sputtering is well known in solar glazing. However, aqueous deposition of gold for this purpose appears to be rarely, if ever, commercially practiced. Nevertheless, the high reflectance of the film makes it pleasant. Neutral color of coatings of gold nanoparticles suggest their use in this application. The results of this research shows that the optical transmission or reflection spectra obtained from such coatings was directly influenced by the interplay of nucleation and growth of the particles, the manner in which they aggregate, and the nature of the prior treatment of the glass surface. Samples with a similar surface coverage of gold nanoparticles may exhibit quite different transmission spectra, depending on the morphology of the coating. Different pretreatment schemes for the glass also essentially influenced the results because the glass surface composition and surface tension change accordingly. The glass was pretreated with 1:1 sulfuric acid (H2SO4) and buffered HF (H2SO4 and buffered fluorine or NF). For the glass pretreated with buffered HF, there was higher sodium content and lower contact angle compared with glass surface treated with H2SO4. The gold subsequently deposited onto the former glass also indicated a different transmission spectrum. The texture of gold nano coatings on glass pretreated with buffered HF was also more uniform than that of glass pretreated with sulfuric acid. Further study also found the glass pretreated with sulfuric acid tended to form the gold nano coating with dual peaks at around 540 nm and 700 nm, while the surface pretreated with buffered HF tended to form the gold nano coatings with a single broad peak at around the 700 nm. These trends were modeled using classic heterogeneous nucleation and growth theory.

9:45 AM Q6.4

Nucleation and Growth of MOVC thin films of Si2O3 and (Ba, Sr)TiO3 on Pt and SiO2 surfaces. Stephan Bogner1,2,3, Peter Ehbart1, Krzysztof Szot1, Yong Ding2, Jiaquing He2, Chun-Lin Jin2, 1IFF/EKM - Forschungszentrum Juelich, Juelich, Germany; 2IFF/IMF - Forschungszentrum Juelich, Juelich, Germany; 3Aixtron AG, Aachen, Germany.

Ba(0.70Sr0.30)TiO3 and STO, are grown by MOCVD on SiOx/Si(100) and Pt/TiO2/SiO2/Si substrates. The first nucleation steps are investigated by XPS and XRD. For deposition on metallic Pt the local electronic density of states measured in contact mode of the SPM, directly reveals the nuclei of the insulator. There are major differences due to the deposition temperature whereas the Ba/Sr ratio has minor effects on the nucleation. At a deposition temperature of 950°C we observe a quasi homogeneous nucleation all over the Pt grains, which have a typical diameter of about 100nm whereas at higher temperatures the nucleation is mainly observed at the platinum grain boundaries. The difference to the nucleation on SiOx will be discussed on the basis of high resolution AFM images and on differences in the chemistry of the nuclei, composition and chemical state of the residing metals, as determined by XPS. The further film growth and the microstructural evolution is investigated by HRTEM images in cross section and plane view and by XRD. For BST on Pt we observed at low deposition temperatures, 550°C, randomly oriented grains (typical in-plane size 10-20nm) with a high density of twins, whereas (100)-oriented defect free grains are observed at annealing above 750°C. These results are in agreement with the high resolution XPS images taken in cross section and plane view and by XRD. For BST on Pt we observed at low deposition temperatures, 550°C, randomly oriented grains (typical in-plane size 10-20nm) with a high density of twins, whereas (100)-oriented defect free grains are observed at annealing above 650°C. This agrees with the texture of the grain boundaries observed by XRD. The in-plane grain size was increased. The difference of the texture to observations with other deposition techniques will be discussed.

10:30 AM Q6.5

Coarsening in presence of cluster diffusion and nucleation with insertion, stefano rasponi, nicolas Weiss, tristan cran, philipp buluschek and harald brune; IPN, EPFL, Lausanne, Switzerland.

We present a new method to create small 2D islands through coarsening via cluster diffusion. The cluster diffusion barrier often is a monotonic function of cluster size. Therefore increasing temperatures switch on diffusion for one cluster size after the other. This leads to a staircase in mean island size s as a function of annealing temperature. Starting with monomers, produced by statistical growth, one gets a jump to dimers and trimers at the onset temperature of monomer diffusion rates and an abruptness of the interface play an important role for magnetic properties. Our nucleation studies revealed conventional on-surface diffusion and nucleation up to 180K. After this temperature the island density continues to decrease, but with a smaller slope in its Arrhenius representation. This behavior is different from the one anticipated for systems with exchange, where the island density increases with increasing temperature after the onset of exchange [2]. Furthermore, we observe a dependence of the rate of nucleation on the presence of the first reconstruction nuclei. [1] E. Lundgren, B. Stanka, W. Kopolin, M. Schmid, and P. Varga, Surf. Sci. 432, 357 (1999). [2] J. A. Meyer and R. J. Behm, Surf. Sci. 322, L375 (1995).

11:00 AM Q6.6

Dislocations and dislocation forests: 2ML Cu/Ru(0001), Farid El Gabaly1, Kevin F. McCarty2 and Juan de la Figuera1; 1Dep. of Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Madrid, Madrid, Spain; 2Sandia National Laboratories, Livermore, California.

The interaction of a single dislocation with a dislocation forest is a basic problem in plasticity and dislocation behavior. The problem is quite difficult to analyze both theoretically and experimentally. We report a thin film system where the dislocation structure is known in detail and which allows a study of dislocation interaction with well defined dislocation forests through X-ray measurements in real time. The system studied, 2ML Cu/Ru(0001), presents three equivalent rotational domains formed by parallel Shockley dislocations at the Cu/Ru interface. Threading dislocations emerge only at the boundaries between rotational domains. Twin-like domains are also present with Shockley partial dislocations between the two Cu layers. We present a low Energy Electron Microscope study of the evolution of both types of domains. It will be shown that at temperatures where the rotational domains do not change much, the twin-like domains evolve rapidly in a very specific way: the Shockley partial dislocations that bound the twin-like domains move very fast when nucleating an additional twin-like domain, while they slow when crossing the threading dislocations at the edges of the rotational domains. Atomic simulations based on semiempirical potentials will provide further insight into this complex behavior. The work was supported by the Comunidad Autonoma de Madrid through project No. 07N/0041/2002, and by the USDOE, Office of Basic Energy Sciences, Division of Materials Sciences. J. de la F. gratefully acknowledges a Ramon y Cajal contract from the Spanish Ministry of Science and Technology.

11:15 AM Q6.7

Molecular Beam Epitaxy of Threading-Dislocation-Free Ge on Si through Vias of SiO2, Nanotemplate and by Self-Directed “Touchdown” of Nanoscale Seed Pads, Qiming Li1,2,3, Darin Leonhardt1,2, Ying-Bing Jiang3, Hufang Xu1, Steven R J Brocke1, Stephen Hersce1 and James R Mail1; 1Chemical and Materials Engineering, University of New Mexico, Albuquerque, New Mexico; 2Center for High Technology Materials and Department of Electrical and Computer Engineering, University of New Mexico, Albuquerque, New Mexico; 3Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico.

We demonstrate that Ge can be selectively grown on Si through openings in a SiO2 nanotemplate by solid source molecular beam epitaxy. The selectivity relies on the thermal instability of GeO and SiO near 650°C. Ge islands grow in the template windows and coalesce on top of the template, forming an epitaxial lateral overgrowth (ELO) layer. Cross-sectional transmission electron microscopy images show that the Ge seeds and the ELO layer are free of threading dislocations. Only stacking faults are generated but terminate within 70 nm of the Ge-Si interface, while twins along [111] planes are observed in the ELO layer. The threading-dislocation-free Ge seeds and ELO layer are attributed to epitaxial necking, as well as Ge-Si intermixing at the interface. We also demonstrate that high quality Ge can be grown on Si by self-directed “touchdown” of nanoscale (~8 nm) Ge pads through a thin layer of SiO2 during molecular beam epitaxy. The oxide layer is chemically produced on Si(100) and Si(111) in a H2O2/H2SO4 solution. When the oxidized Si substrate at 620°C is exposed to Ge molecular beam, the thermal instability of GeO creates relatively uniform-size nanoscale windows in the oxide layer. Ge selectively grows in the windows and coalesces to form an epitaxial lateral overgrowth (ELO) layer. The thickness of the ELO layer arbitrarily exceeds the critical thickness. Transmission electron microscopy images of the resulting Ge-Si interface reveal that the hetereojunction is atomically abrupt with no observable dislocations. Only stacking faults exist above the oxide layer, but terminate within 80 nm from the interface.
The driving force for coarsening is provided by the excess interfacial free energy. In the case where the interfaces are isotropic, crystals are expected to grow and shrink in spherical shapes at a rate limited by diffusion and predicted by classical coarsening theory. However, when the interface energy of the coarsening phase is anisotropic, the driving forces are modified and growth and shrinkage may be limited by the surface attachment/detachment rate, the motion of ledge, or the nucleation of new layers. To understand how interface anisotropy affects coarsening, we have measured the distribution of crystal sizes and shapes as a function of time for SrTiO₃ and BaTiO₃ coarsening in a titania rich eutectic liquid at 1500°C and 1345°C, respectively. A stereological analysis of crystal shapes measured by AFM and orientation data measured by OIM provides an average crystal shape for each material and ante datum are presented. Findings show that grains in both the SrTiO₃ and BaTiO₃ systems are faceted. The average crystal shape of SrTiO₃ in the eutectic liquid at 1500°C is dominated by (100) facets and is therefore similar to the equilibrium crystal shape of SrTiO₃ in air at 1400°C. The average crystal shape in the eutectic liquid is apparently independent of size. Furthermore, the observed grain size distributions are not constant with time and are not consistent with the classical coarsening models. The influence of the singular bounding surfaces on the coarsening mechanism will be discussed.

11:45 AM Q6.9
Kinetic Extensions of the Nucleation Theorem. Robert McGraw¹ and David T Wu². ¹Environmental Sciences, Brookhaven National Laboratory, Upton, New York; ²Mechanical Engineering, Yale University, New Haven, Connecticut.

The so-called nucleation theorem is a thermodynamic relation that gives the derivative of the height of the nucleation barrier \( W^* \) with respect to the supersaturation \( S \) or the temperature \( T \). In addition to aiding in the interpretation of experiments, the nucleation theorem has been used as a theoretical tool and guide for introducing a molecular basis to phenomenological nucleation theories. An obvious limitation of the theorem, however, is that \( W^* \) is not a directly observable quantity. Using the law of mass action and detailed molecular distribution of reciprocal equilibrium cluster growth rates, we introduce an approximate analytic function for the nucleation theorem that gives the observable nucleation rate \( J \) with respect to \( S \) or \( T \). For single component systems, we show that the first and higher-order derivatives of \( J \) with respect to \( S \) can be interpreted in terms of the cumulants of a molecular distribution of reciprocal equilibrium cluster growth rates, while the derivative of \( \ln(J/J(CNT)) \) with respect to \( T \), where \( J(CNT) \) is the rate from classical nucleation theory, is obtained as a distribution over differences in cluster energy and interpreted using molecular and phenomenological cluster models. For multicomponent systems, we show that the derivative of the nucleation rate with respect to \( S \) can be expressed as an average over the distribution of local fluctuations in composition space.
clusters over regular and faulted sites, which are immobilized by addition of an adatom. Using field ion microscopy data as an input for a modified rate equation approach allows to quantitatively reproduce the experiments. Predictions for the dependence of the fault nucleation probability on fault energy and cluster mobility are derived by the rate equation approach. The atomic mechanisms of self-healing of the faulted surface phase are identified. Self-healing takes place upon encounter of regular and faulted islands by an assimilation process. Contributions of Carsten Busse, Celia Polop, Andreas Lammenschop, Michael Mueller and Kirsten Albe to this work are acknowledged.

3:30 PM Q7.5
Geometry-Based Simulation (GBS) of Island Nucleation and Growth During Submonolayer Deposition. M. C. Bartelt\textsuperscript{2} and James Evans\textsuperscript{1}; \textsuperscript{1}Ames Laboratory, Iowa State University, Ames, Iowa; \textsuperscript{2}Lawrence Livermore National Laboratories, Livermore, California.

Traditional mean-field rate equation formulations fail to describe island nucleation and growth during submonolayer deposition. This is due to the neglect of subtle correlations between island size and separation: larger islands have “much larger” capture zones (CZ’s) for deposited atoms \cite{1}. A current challenge is to develop coarse-grained simulation strategies which, like kinetic Monte Carlo simulation, avoid this shortcoming. Rather than the usual continuum PDE based approach, we develop a novel geometry-based simulation (GBS) strategy \cite{2} which completely avoids explicit (and often expensive) treatment of terrace diffusion. GBS determines island growth from CZ areas, and implements simple but realistic rules to incorporate key aspects of island nucleation process (i.e., nucleation near CZ boundaries). GBS reliably predicts island size and spatial distributions, and is especially efficient for highly reversible island formation. \cite{1,2} M. C. Bartelt and J. W. Evans, Phys. Rev. B 54 (1996) 17358R; \cite{2} M. Li, M. C. Bartelt, and J. W. Evans, Phys. Rev. B 68 (2003) 121401R.

3:45 PM Q7.6

The equilibrium atomic structure, energy of formation and stability of nitrogen-vacancy-oxygen complexes (N-V-O) involved in N doped silicon and oxynitride films have been calculated with Density Functional Theory (DFT). In addition, we used molecular dynamics to calculate the potential wells/barriers for vacancy and oxygen trapping/repulsion by these complexes. These calculations are essential for investigating the processes of nuclei formation in N doped silicon. Specifically, interaction of point defects with a number of pertinent chemical complexes was quantified by calculating the interaction potential gradient during point defect diffusion towards N-V-O complexes. The calculated energies of formation in the ground state are given in Table I. It appears that V2N2 when formed from VN2 is the most stable, followed by N2 (in split interstitial) and V2N2 formed from a divacancy absorbing a mobile N2. VN2 is less stable, but acts as an intermediary species for the formation of the more stable N2 and V2N2 complexes, which subsequently dominate the nucleation and growth of extended defects. Moreover, VN2 can only weakly couple to oxygen atoms, whereas it reconstructs into stable V2N2 by trapping a vacancy. Based on the stability character and the interaction potential between O or V and N2 or V2N2 (see Table II), these complexes act as preferential nucleation centers for oxygen precipitation more than as an effective trapping center for oxygen. Table II, compares the predictions of this model to recent observations by Hannon et al \cite{1} of a large scale self-coordinated process that equilibrates compositional imbalances in Ge/Si(001) heteroepitaxy. Our proposed general mechanism is another way mobility differences can lead to composition differences which could be exploited in nano-control of composition profiles. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract AC04-94AL85000. \cite{1} J.B. Hannon, M. Copel, M.C. Reuter, R.M. Tramp, The Frustrated Alloying of Ge on Ultra-Flat Si(001), 50th AVS Symposium, SS3-MoM, 2003.

4:00 PM Q7.7

Nucleation of the equilibrium phase from sol-gel materials is a black box. Typically nucleation is site-saturated and spherulitic, and nucleation frequency is a nuclear per cubic micron, so the smallest possible grain size is one micron. This grain size is too large for ceramic fibers, and many other structural and electronic ceramics as well. Typically a grain size less than one tenth of a micron is desired to form dense material, which means at least a 3 order of magnitude increase in the number of nuclei is necessary. Dopants that promote abundant nucleation of yttrium-aluminum garnet (YAG) were screened by a combinatorial method. The approach is based on a rapid TEM sample preparation and observation technique that uses a YAG precursor of Condea Disperal (transition-alumina) and yttrium nitrate to make thin films of YAG on nickel TEM grids. This allows large numbers of TEM samples to be rapidly prepared and observed. Heat-treatment for one hour at 1000°C was sufficient to nucleate YAG in the thin films. Small amounts of the precursor were doped with 1 mol\% of various oxide forming nitrates. Two dopants at 0.5 mol\% each were also tried, as well as several runs with four or more dopants. A total of 66 different dopant combinations were tried. YAG nuclei in the heat-treated thin films were counted from TEM micrographs. Nucleation frequency varied over two orders of magnitude. Many dopants reduced the number of nuclei by a significant amount. Nb or Li containing dopants caused local melting, sparse nucleation, and dendritic YAG growth that followed a wicking melt droplet. This structure may be useful for high surface area, high temperature catalysts. The most interesting structures were associated with dopants that were rejected by the growing YAG grains, but enriched in intergranular regions between these grains, preventing grain impingement.

4:15 PM Q7.8
Theory of Surface Diffusion Limited Surface Alloying During Growth. Roland Stumpf and Norm Bartelt; Sandia National Labs, Livermore, California.

It is often observed that deposited atoms directly exchange into the substrate to make a surface alloy during growth. An important question is how close the composition and structure of this alloy is to equilibrium under step flow conditions. In this talk we point out that the answer to this question depends crucially on how rapidly the atom exchanged out of the substrate diffuses relative to the deposited atom, the growth rate, and the farthest distance to a surface step. We show that slow diffusion of the exchanged atom can lead to large compositional variations across the surface. As an example of the possible importance of this idea we consider the much studied case of Ge deposition on Si(001). Our theoretical study analyzes the thermodynamics of the ground state of the SiGe surface alloy and the rates involved in surface diffusion and intermixing based on first-principles calculations. We find that diffusion and not intermixing barriers are rate limiting under typical experimental conditions. We discuss the role of ad-atoms, pure and mixed ad-dimers, and dimer vacancies in surface diffusion at 0, 1/2, and 1 ML Ge coverage. We find that most of the surface diffusion is ad-atom mediated, that Ge diffuses faster than Si, and that diffusion rates decrease with Ge coverage. The limited rate of Si diffusion from terrace to step above a certain Ge coverage creates a compositional imbalance between surface regions close to steps and far away from steps. The deposited Ge, with its larger mobility, can still reach the steps, leading to continued step flow growth without nucleation of new islands. We compare the predictions of this model to recent observations by Hannon et al \cite{1} of a large scale self-coordinated process that equilibrates compositional imbalances in Ge/Si(001) heteroepitaxy. Our proposed general mechanism is another way mobility differences can lead to composition differences which could be exploited in nano-control of composition profiles. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract AC04-94AL85000. \cite{1} J.B. Hannon, M. Copel, M.C. Reuter, R.M. Tramp, The Frustrated Alloying of Ge on Ultra-Flat Si(001), 50th AVS Symposium, SS3-MoM, 2003.