SYMPOSIUM Q

Nucleation Phenomena–Mechanisms, Dynamics, and Structure

April 13 - 15, 2004

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* Invited paper

8:30 AM *Q1.1

Homogeneous Nucleation. Joseph L Katz, [1]Chemical and
Biomolecular Engineering, Johns Hopkins University, Baltimore,
Maryland; [2]Materials 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 gases
will be reviewed. This review will include a discussion of experimental
results, and a comparison to theories. If time permits, some ideas on
what limits our understanding will be discussed.

9:00 AM *Q1.2

Nucleation and Growth of Colloidal Crystals. D. A. Weitz[1], Urs
Gasser[2], R. Christianson[1], A. Schofield[3] and P. N. Pusey[3]; [1]Dept. of
Physics & DEAS, Harvard University, Cambridge, Massachusetts;
[2]Dept. of Physics, University of Konstanz, Konstanz, Germany;
[3]Dept. of Physics and Astronomy, University of Edinburgh,
Edinburghu, 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 nature 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, which helps account for the very
rough surface morphology of the crystallites. We identify the size of
the critical nuclei, and can probe the crystalline structure of these
nuclei. We are also 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.

9:30 AM Q1.3

**Fluctuation Theory for the Equilibrium Size Distribution of
Nuclei.** Lin Zhuo 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 $z(R) = const. * exp[-\Delta\Phi(R)/kT]$ where Φ is a 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
$z(R)$ has not been rigorously dealt with, nor is there general
agreement on the form of $\Delta\Phi$, which has been variously identified with
the change in the Gibbs free energy, the Helmholtz free energy, or the
grand potential. We address this problem using statistical mechanics,
employing fluctuation theory to derive the relative probability of
forming an embryo cluster within a metastable phase. Regardless of
the nucleation process and the associated constraints, we show that
the relation for $z(R)$ is valid provided Φ is the availability.

9:45 AM Q1.4

Crystallization behavior in binary alkali halides. John Kieffer,
James Palko 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 even at 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 the 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.

10:30 AM *Q1.5

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 hydrogen bond network rearrangement and its
observation (highly nonlinear flash photolysis technique), (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 scales (about
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 involved in
HBNR of water, the inherent structure analysis and various analyses
were performed One of the methods, which may detect these
intermittent collective motions, is a higher nonlinear flash photolysis
experiment (2-dimensional 5th-order nonlinear response function),
since this method deals with the phase space dynamics of a system.
We have succeeded to reproduce the spectrum of this response
function for CS2 and water, which is found to be in very good
agreement with the experiment recently. Upon cooling, water freezes
into ice. This process is a most familiar phase-transition, occurring in
many places in nature, but has never been successfully simulated by a
computer simulation. Water molecules possess strong directionality of
hydrogen bonds (HB) and form a disordered three-dimensional HB
network (HBN). Since the global potential energy surface of HBN
rearrangement is rugged and complex, water is much harder to freeze
than simple liquids. Molecular dynamics simulations succeeded to
reproduce water freezing but only for very special cases, such as in
confined spaces, where the number of possible disordered HB network
structures is limited, and thus a pathway from a liquid state to a
crystalline structure can be rather easily found. In a full
three-dimensional pure water case, possible configurations are much
more diverse, but water finds pathways to a unique state with a
crystalline structure. This appears to closely resemble the
protein-folding problem, where a unique native structure is obtained
from numerous denaturated states and no successful simulation exists
for the folding of large proteins. We report the first successful
simulation for the pure water freezing process, which gives a
molecular level picture of, particularly, how an initial nucleus is
created and grows. References S. Saito and I. Ohmine., J. Chem.
Phys. 119, 9073-9087 (2003);, Phys. Rev. Lett. 88, 207401-1 (2002);
M. Matsumoto, S. Saito, and I. Ohmine, Nature, 416, 409 (2002).
(Movie of Water Freezing Process is available at web-site
http://www.chem.nagoya-u.ac.jp/ og/freezing/).

11:00 AM *Q1.6

**Isothermal Nucleation Rates in Supersonic Nozzles and the
Properties of Small Water Clusters.** Barbara Wyslouzil[1,2], Yoo
Jeong Kim[2], Gerald Wilemski[3], Judith Woelk[4] and Reinhard Strey[4];
[1]Chemical Engineering, Ohio State University, Columbus, Ohio;
[2]Chemical Engineering, Worcester Polytechnic Institute, Worcester,
Massachusetts; [3]Physics, University of Missouri - Rolla, Rolla,
Missouri; [4]Physical Chemistry, University of Cologne, Cologne,
Germany.

Particle formation in supersonic flows occurs in many natural and
industrial processes. As part of our ongoing studies of condensation in
supersonic flows we have developed techniques to extract quantitative
nucleation rates from supersonic nozzle experiments. To summarize,
we use conventional pressure trace measurements to define the
characteristic time, temperature and supersaturation that correspond
to the maximum nucleation rates. We then use small angle neutron
scattering experiments to determine the number concentration of the
aerosol that formed during the nucleation burst. After correcting for
the continued expansion of the gas between the nucleation zone and
the viewing volume, the experimental nucleation rate J is simply
equal to the aerosol number density divided by the characteristic
time. By using different nozzle designs, we measure nucleation rates
ranging from $10^{14} < J / cm^{-3}s^{-1} < 10^{17}$. Finally, we apply the first
and second nucleation theorems to the data and directly estimate the
number of molecules in the critical cluster $n*$ and the excess internal
energy $Ex(n*)$, respectively. The agreement between these values and
the classical values predicted assuming the critical cluster is a
compact spherical object are really quite good even though under our
conditions $n*$ is less than 10.

11:30 AM *Q1.7

**Model-Dependence and Universality in the
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, Turnbul and Fisher, or Zeldovich and Frenkel. 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 components. 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. Results can be used to test more phenomenological approaches, such as the classical models of nucleation, or the Kolmogorov-Avrami 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 most cases. The thermodynamics of nuclei formation, on the other hand, is distinctly non-classical.

SESSION Q2: Solutions and Multi-Component Systems
Chair: Nitash Balsara
Tuesday Afternoon, April 13, 2004
Room 3009 (Moscone West)

1:30 PM *Q2.1
Dense Liquid Precursor for the Nucleation of Polymers of Sickle Cell Anemia Hemoglobin. Vekilov 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 (Hb) S 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 polymers using optical differential interference contrast microscopy 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 an a-priory 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 superposition of a density and a structure fluctuations. This finding 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. Anatoly Kolomeisky[1], Peter Vekilov[2] and Weichun Pan[2]; [1]Chemistry, Rice University, Houston, Texas; [2]Chemical Engineering, University of Houston, Houston, Texas.

Protein crystallization is a very complex process that is not well understood. Recent 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 behavior. In addition, the dependence of protein crystal nucleation rates on flow is discussed.

2:30 PM *Q2.3
Nucleation of Globular Protein Crystals From Solution. James D. Gunton[1], Andrey Shiryayev[1], Daniel Pagan[1] and Maria Gracheva[2]; [1]Physics, Lehigh University, Bethlehem, Pennsylvania; [2]School of Mathematics, University of Minnesota, Minneapolis, Minnesota.

High quality crystals are requisite for the determination of the structure of globular proteins via x-ray diffraction. Since the function of proteins is related to their structure, considerable 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 arises from 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 greater 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 density functional computations. 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 segregation processes in solutions and crystallization processes in 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, Bruxelles, Belgium.

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.

4:30 PM *Q2.6
Novel Methods for the Study and Control of Nucleation of Organic Molecular Crystals. Allan S. Myerson, Office of the Provost, Illinois Institute of Technology, Chicago, Illinois.

The first step in the crystallization process in the 'birth' of the new phase is known as nucleation. The control and study of necleation processes is difficult and the impact of nucleation on the polymorphic form obtained is not well understood. Recent work in our laboratory has focused on novel methods for the study and control of nucleation. One of these methods is known as non-photochemical laser induced nucleation. In this method short pulses of a high intensity laser were shown to induce nucleation in supersaturated solutions of organic molecular materials. In addition, recent work has shown that the polarization of laser can control the polymorph obtained in the glycine-water system. This method also provides a method of positional nucleation control and can impact the nucleation induction time and crystal size. A second method employed in our lab is electrodynamic levitation of single solution droplets. This containerless method allows studey of homogeneous nucleation and nucleation induction time statistics. Data obtained is suggestive of a two step nucleation model which will be discussed.

SESSION Q3: Nucleation in Condensed Media
Chair: Zhen-Gang Wang
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 to the formation of nuclei are extremely rapid and have escaped 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 these systems 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 disagreement with all know 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.
Ramanan Krishnamoorti and Cynthia Mitchell; 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 as they 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 morphologies 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.

9:30 AM *Q3.3
Interface properties and bubble nucleation in compressible mixtures containing polymers: Self-consistent field theory, thermodynamic perturbation theory and computer simulation. Marcus Muller[1], Luis Gonzalez MacDowell[2,1], Peter Virnau[1] and Kurt Binder[1]; [1]Institut fuer Physik, WA331, Johannes Gutenberg Universitaet, Mainz, Germany; [2]Facultad de Ciencias Quimicas, Universidad Complutense, Madrid, Spain.

Using self-consistent field theory[1], thermodynamic perturbation theory[2], and computer simulation[3] we investigate the phase behavior of compressible polymer+solvent mixtures, properties of interfaces between coexisting phases and of bubbles that nucleate in response to a pressure change. We focus on a mixture of a super-critical solvent and a polymer that exhibits a phase diagram of type III in the classification of Konynenburg and Scott. Our results are compared to experimental data for a mixture of carbon dioxide and hexadecane [4]. Attention is paid to correlate the description of the phase diagram with the properties of interfaces and the nucleation barrier that needs to be overcome to form a bubble of critical size, necessary for the decay of the corresponding super-saturated metastable state. To describe the compressible mixture of carbon dioxide and hexadecane we use a coarse-grained bead spring model. In the self-consistent field theory we employ a crude phenomenological virial expansion to capture the qualitative behavior. This techniques allows us to explore the phase behavior and nucleation properties over a wide range of parameters. Using thermodynamic perturbation theory we obtain a rather accurate equation of state for our model system and calculate the binodals and (mean field) spinodals. In the Monte Carlo simulations we calculate the phase diagram and analyze the formation of bubbles for selected parameters. Comparing the results of all three techniques to experiments we can asses the validity of our model and whether discrepancies arise from our coarse-grained model or the techniques used to investigate it. At low pressure, the density of the volatile solvent is small and interface and nucleation properties are similar to a one-component fluid. At higher pressure, however, we find a a triple point at which the polymer coexists with a vapor of solvent and a mixed solvent-rich liquid. The vicinity of the triple point alters the interface and nucleation behavior: There is a thick wetting layer of the (metastable) solvent-rich liquid at the interface between polymer and vapor, and the solvent condenses into a solvent-rich liquid inside small bubbles. We explore the dependence of the nucleation barrier on temperature, pressure and molecular weight of the polymer and relate our findings to the binodal and spinodal of the bulk. The extent to which real materials can be modeled will also be examined. [1] M. Muller, L.G. MacDowell, P. Virnau, K. Binder, J. Chem. Phys. 2002, 117, 5480. [2] L.G. MacDowell, P. Virnau, M. Muller, K. Binder, J. Chem. Phys. 2002, 117, 6360. [3] P. Virnau, M. Muller, L.G. MacDowell, K. Binder, New J. Phys. 2003 (in press). [4] K. Binder, M. Muller, P. Virnau, L.G. MacDowell, Adv. Polym. Sci. (in press).

10:30 AM *Q3.4
Recent developments in non-photochemical laser-induced nucleation. Bruce Garetz[1], Janice Aber[1], Jelena Matic[1] and Allan Myerson[2]; [1]Chemical & Biological Sciences & Engineering, Polytechnic University, Brooklyn, New York; [2]Chemical 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 of urea in water. We attributed this photophysical 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 glycine, 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 Cracks in Fused Silica and Silicon by Strongly Nonlinear Surface Acoustic Waves. Peter Hess, Alexey Lomonosov and Tamas Lucza; Physical Chemistry, University of Heidelberg, Heidelberg, Germany.

Nucleation and growth of cracks 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 experiments, 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 without precrack. By using the absorption-layer method 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 and anisotropic 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 analize 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). Due to the dynamic interaction with the propagating SAW pulse during the limited time of growth the cracks bend forward at the surface and in the bulk into the direction of surface pulse propagation. In anisotropic silicon, on the other hand, the weakest cleavage planes dominate crack evolution after impulsive nucleation. For a SAW pulse propagating in the <112> direction on the Si(111) plane cracks were observed in the <110> direction at the surface by SFM. They extend into the bulk along the {11-1} cleavage plane, at least to a depth of several micrometers, independent of propagation along the [-1-12] or the [11-2] direction. Besides crack initiation by a tensile opening stress the SFM pictures reveal also contributions from shear sliding effects in silicon (mode II fracture behavior). Since 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[1], Nathalie Bonasso[2] and Philippe Pigeat[1]; [1]LPMIA, University of Nancy I, Vandoeuvre, Lorraine, France; [2]LERMPS, Tech. Univ. of Belfort-Montbeliard, Montbeliard, Franche-Comt, France.

Nucleation and growth kinetic were studied in amorphous thin films of Al, Cu and Fe, of the stoechiometric composition of the quasicrystalline icosahedral phase Al62 Cu25.5 Fe12.5 (i-phase). Depending on the temperature, nucleation of cubic beta phase or icosahedral phase occurs. From this study, we deduce a nucleation density of the icosahedral phase as a function of temperature. To obtain i-AlCuFe very thin films with sufficient quality to study their physico-chemical properties, simultaneous deposition of the three elements is performed under UHV. In order to describe, understand and optimise the crystallisation paths, 100nm thick deposits have been made on amorphous carbon coated TEM grids. The growth of icosahedral phase in a mixture of Al62, Cu25.5 and Fe12.5 (in at. percent) is then directly studied in situ by TEM during different annealing protocols. Several TEM grids were overlaid during the same deposition. Each grid was heated up to different temperature plateaus in the range of 300K to 873K and observed in real time by TEM. Four stages have been observed. Up to plateaus at 673K (observed during 70 hours) the mixture remains amorphous. For plateaus in the range 673K - 723K, nucleation and growth of beta-phase in remnant amorphous mixture is observed. Only for plateaus performed at temperature above 723K, we observe after the previous primary crystallisation the nucleation and growth of i-phase, around beta-phase and in the remaining amorphous matrix enriched in aluminium. Thus, a study as a function of time at 673K allowed the kinetic growth of the beta-phase to be established. The same study above 723K allowed the kinetic law of the growth of icosahedral particles to be described and extract the value of the activation energy of the reaction. These icosahedral particles seem to nucleate at the beta-particles / amorphous phase interface. At the end of the growth of isolated i-particles it is observed a second order discontinuity due to the superimposed coalescence kinetic of the reaction between neighbouring crystallites. At this moment, the whole film is transformed in quasicrystalline phase. This duration recorded versus the temperature allow us to plot the Temperature Time Transformation (TTT) curve for quasi crystallization in the mixture Al62, Cu25.5 and Fe12.5. From the radius of the i-particles for each annealing temperature just before their coalescence we deduce a nucleation density at the origin of the reaction (in the range 2.1019 - 7.1019 m-3). This density increases with temperature as Arrhenius-type equation with activation energy equal to 29.4 kJ mol-1.K-1, values in accordance to the activation energy for diffusion previously determined during the growth of i-particles.

11:30 AM *Q3.7
Controlled Nucleation in Metastable Phases: A New Route to Micropatterned Single Crystals. Joanna Aizenberg, Bell Labs/Lucent, Murray Hill, New Jersey.

Micropatterning of single crystals for technological applications is a complex, multistep process. Nature provides alternative fabrication strategies, when crystals with exquisite micro-ornamentation directly develop within pre-organized frameworks. Borrowing from the biomineralization principles, we have developed a new crystallization strategy for the synthesis of micro- and nanopatterned oriented calcite crystals: utilization of amorphous-to-crystalline transitions using specially designed structural templates with integrated nucleation sites. In our approach, the chosen 3D templates serve several functions: induce the formation of a metastable amorphous film with the predetermined micropattern, define the location and crystallographic orientation of the calcite nucleus, relax the tensile stress in the deposited film, and provide discharge sites for excess water and possibly other impurities during the crystallization process. This strategy allowed us to directly fabricate large (1 mm) single crystals of calcite with sub-micron patterns and controlled crystallographic orientations. We believe that the proposed mechanisms are of general importance in materials chemistry.

SESSION Q4: Nucleation in Confined Spaces
Chair: James Warren
Wednesday Afternoon, April 14, 2004
Room 3009 (Moscone West)

1:30 PM *Q4.1
Nucleation Kinetics: Theoretical Inferences vs. Computer Simulations. L. S. Bartell, Chemistry, University of Michigan, Ann Arbor, Michigan.

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 Shneidman. 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 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 Shneidman'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 Granasy[1], Tamas Pusztai[1], Tamas Borzsonyi[1] and James A Warren[2]; [1]Research Institute for Solid State Physics & Optics, Budapest, Hungary; [2]Center for Theoretical and Computational Materials Science, 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 nucleation barrier can be predicted with a good accuracy for simple liquids. Relying on a model we proposed recently [L. Granasy, 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 walls into the simulations, and explore particle-front interaction and heterogeneous nucleation in alloys.

2:30 PM *Q4.3
Argon Nucleation in a Cryogenic Nucleation Pulse Chamber. R. Strey, K. Iland, A. Fladerer and J. Woelk; Institut fuer Physikalische Chemie, Universitaet zu Koeln, Koeln, Germany.

Recent careful nucleation rate measurements on 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 poorly known for practically relevant vapors like water, 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

chamber operating at temperatures of 80 K and below. In this chamber argon-helium mixtures are adiabatically expanded and nucleation is induced. 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^{20} and 10^{10} too low within our experimental window $40 < T/K < 60$. 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. Ehud 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 by non-birefringent lipidic cubic phases - the in cubo crystallization. The crystal structure of the light-induced proton pump bacteriorhodopsin (bR), grown from a monoolein lipidic cubic phase, was solved at atomic resolution, revealing the first high resolution structure 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 sensory rhodopsin II, 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 Macroscopic Model vs Experimental Results. Anthony Saugey[1], Jean-Louis Barrat[2] and Lyderic Bocquet[2]; [1]MSGMGC, Ecole Centrale Lyon, ECULLY, France; [2]LPMCN, Claude Bernard University, LYON, France.

We present experimental and theoretical results on intrusion-extrusion cycles of water in hydrophobic mesoporous materials, characterized by independent cylindrical pores. Experimental characterisations indicate two different mechanisms for intrusion and extrusion. Intrusion takes place at thermodynamic equilibrium whereas extrusion occurs via a nucleation process. A macroscopic model is developed, taking into account two possible shapes of the critical nuclei. Inclusion of line tension effects gives good agreement with the experimentally observed values of nucleation barriers. Negative line tension values are found and confirmed by monte carlo and umbrella sampling simulations on a lattice-gas model.

4:15 PM Q4.6
Investigation of noble gas cluster formation in amorphous carbon matrix. Francisco Chagas Marques, Paulo Fernando Barbieri, Myriano Henriques de Oliveira and Rodrigo Gribel Lacerda; IFGW/DFA, 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 carbon as high-pressure cell for trapping nobles 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 strained 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 (intrinsic 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
Crystallization of Proteins in a Nanoliter Microfluidic System. Rustem F Ismagilov, Bo Zheng and L Spencer Roach; Chemistry, The University of Chicago, Chicago, Illinois.

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.; Roach L. 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 aqueous 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 minituarization 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
Direct Modeling of Solid-State Nucleation Phenomena using Feature-Activated Molecular Dynamics. Manish Prasad and Talid Sinno; University of Pennsylvania, Philadelphia, Pennsylvania.

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 without mechanistic assumptions, dilute concentrations of the nucleating species, coupled with relatively slow diffusion rates make this task computationally challenging. In this talk a hybrid molecular dynamics approach is presented in which only regions around defects are simulated with MD ("active" regions), while regions far away are assumed to be perfect ("static" regions). The static regions provide boundary conditions for the active regions. A unique feature of this method is that the interfaces between the active and static regions are dynamic, governed by systematic "activation" and "de-activation" of atomic thermal excitation (activity) in response to defect feature migration, aggregation, and dissolution. The method is demonstrated using the phenomenon of vacancy aggregation in two systems: silicon and copper. In both cases, a crystal lattice containing about $10\hat{5}$-$10\hat{6}$ atoms is used to follow the trajectory of a large number of vacancies and their clusters. It is shown that the computational time per MD step is independent, for a given number of defects, of the actual system size, making it suitable for modeling of dilute systems. Furthermore, as nucleation and growth of vacancy clusters proceed, the total number of active atoms decreases, increasing the overall simulation speed up to an order of magnitude for the systems considered. The predictions are verified against traditional MD simulations and the nucleation mechanism quantitatively interpreted with a continuum mean-field model.

SESSION Q5: Poster Session
Wednesday Evening, April 14, 2004
8:00 PM
Salons 8-9 (Marriott)

Q5.1
Generation of atto-liter protein droplets at predetermined locations through liquid-liquid phase separation. Mrinal Shah, Oleg Galkin and Peter G Vekilov; Department of Chemical Engineering, University of Houston, Houston, Texas.

Atto- and femto- liter droplets of protein solution containing of the order of 1000 protein molecules are of interest for emerging bio-sensor, bio-fuel cell, and other technologies. Since existing methods cannot produce protein arrays of such sizes, we propose to utilize the separation of the protein solution into two liquid phases that can be controlled through the solution temperature. The structures emerging after liquid-liquid (L-L) phase separation and the dynamics of the process are studied as characteristics of a fundamental biological phenomenon and a method of organization of the intracellular space, as well as a precursor for the formation of protein solid phases that underlie several diseases: sickle cell anemia, eye cataract, Parkinson's, Alzheimers's, Huntington's, etc. Quenching a homogeneous solution of off-critical composition below the phase boundary of its coexistence with another phase may yield either a metastable state, where a free

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energy barrier delays the generation of a new phase, or, at deep quenches, an unstable state. We investigate the structure and dynamics of the new phase 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 spinodal decomposition and reveals no peculiarity predicted 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 area below the binodal curve. 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 envisioned applications will likely require deposition of the droplets over electrodes. Towards such refinement of the droplet generation technique, we show that the generation of droplets of the dense protein phase can be induced over micrometer-size electrodes by applying a moderate potential of 1 V. The electric field acts to increase the counterion concentration above the electrodes, facilitating L-L phase separation. The droplets land on the electrodes pulled by combined gravity and electric forces. We show that the application of such low voltage does not alter the configuration, structure or activity of the lysozyme molecule.

Q5.2
Nucleation Problems in Location Control of Crystal Grains in Excimer Laser Crystallization of Silicon Thin films.
Hideya Kumomi and Masahiro Okuda; Leading Edge Technology HQ, Canon Inc., Atsugi, Kanagawa, Japan.

A method is proposed[1] for controlling the location of crystal grains in polycrystalline silicon (Si) thin films formed by excimer pulsed-laser crystallization of amorphous Si thin films, which is a rapid melting and quenching process within several tens to hundreds nanosecond. 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 cools down below the melting temperature and 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 sites. While the method basically relies on the survival of the seed crystals 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 sites is limited 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 model[2] for the grain impingement 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[3] 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 emphasize the necessity of developing and adopting a theoretical approach to the athermal nucleation for understanding the melting and recrystallization in the method for the grain-location control. [1] H. Kumomi, Appl. Phys. Lett. **83**, 434 (2003). [2] J. P. Leonard and J. S. Im, Appl. Phys. Lett. **78**, 3454 (2001). [3] J. S. Im, V. V. Gupta, and M. A. Crowder, Appl. Phys. Lett. **72**, 662 (1998).

Q5.3
Crystal growth mechanism of hen egg lysozyme under external field.
Tzu-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.

Q5.4
Structure and dynamics within monolayer p-phenylene oligomer films on graphite.
Edward James Kintzel and Kenneth W. Herwig; Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The two-dimensional structures within monolayer films of the aromatic molecules p-terphenyl (p-3P), p-quaterphenyl (p-4P), and p-sexiphenyl (p-6P)adsorbed onto the basal plane of graphite have been investigated by neutron scattering. Structural measurements were carried out at sample/substrate temperatures ranging from 22-370 K. Preliminary analysis of the two-dimensional diffraction peaks for these films indicates that the molecules are oriented with their long-axis parallel to the substrate surface. An investigation into the dynamics reveals molecular length playing an integral role in the melting temperature of these films. A phase change, as indicated by an abrupt change in the quasielastic scattering occurs at approximately 250-275 K for p-3P and 300-325 K for p-4P. Up to approximately 370 K, no change was observed in the character of the dynamics for p-6P.

Q5.5
Pyrochlore-perovskite phase transition in hydrothermally derived lead titanate starting from amorphous titania.
Zhiyuan Ye, Elliott B. Slamovich and Alexander H. King; School of Materials Engineering, Purdue University, West Lafayette, Indiana.

Nanocrystalline lead titanate was synthesized by reacting amorphous titanium oxide in aqueous solutions of potassium hydroxide and lead acetate at 200 °C. X-ray diffraction (XRD) and TEM studies suggest that the initial KOH concentration influenced the nucleation and growth behavior of the lead titanate nanoparticles. Lead titanate powders were processed in aqueous solutions containing 0.10 M lead acetate, with varying Pb:Ti ratio and varying concentrations of KOH. Lead titanate processed in 0.01 M KOH and 0.10 M KOH first formed snowball-like pyrochlore nanoparticles. Further hydrothermal treatment transformed the pyrochlore phase to perovskite without significantly changing the particle morphology. This suggests that the phase transformation occurs via local diffusion. Increasing lead to titanium ratio in the initial solution accelerated the pyrochlore phase formation and the pyrochlore-perovskite phase transformation. For powders processed in 1.0M KOH, the perovskite and pyrochlore phase formed simultaneously. Then the remaining pyrochlore phase transformed to perovskite. The directly formed perovskite and perovskite transformed from pyrochlore exhibited very different morphologies. Higher KOH concentration suppressed the pyrochlore formation.

Q5.6
A Study of Long-Time Crystallization Kinetics for Hard Spheres in a Reduced-Gravity Environment.
Wesley M. Kopacka[1], William B. Russel[1] and Paul M. Chaikin[2];

[1]Chemical Engineering, Princeton University, Princeton, New Jersey; [2]Physics, Princeton University, Princeton, New Jersey.

The crystallization of colloidal suspensions has been a well-studied phenomenon over the past few decades. Recent investigations in micro-gravity have shown behavior not typical of suspensions studied under normal gravity such as dendritic growth and crystallization in the glassy regime. A new high-density colloidal suspension has been developed using sterically stabilized PMMA-PHSA particles in a three-component index- and density-matching solvent mixture of cis/trans-decalin, tetralin, and tetrachloroethylene. Using a combination of light scattering techniques and utilizing the phase behavior of colloidal systems to characterize the particles, the model system has been developed to minimize sedimentation and charge effects. Without the effects of sedimentation, these suspensions can be studied over larger periods of time, allowing for more in-depth, quantitative analysis of crystal nucleation, growth, and aging. Characterization results and preliminary measurements on a crystallizing sample will be discussed in hopes to help bridge the gap between theory and experiment.

Q5.7
Structure-Morphological Changes of IVa, Va Thin Metal Films on Oxidized Silicon Surface.
Natalya M Sushkova, Inst. of Phys. Chemistry, Moscow, Russian Federation.

Composition and morphological nonuniformity of rfsputtering deposited Ti, V and Nb layers (thicknesses in range from monolayer to 2.0nm) on oxidized (100)Si surface were examined by XPS *insitu*, SEM, EPMA and TEM. There are at least three stages of the interaction of metals of high affinity to oxygen with silicon oxide: 1)At the initial stage Ti, V and Nb atoms reduce surface of silicon oxide and cover it by monolayer of metal oxides (TiO_2, Nb_2O_3 or V_2O_5).

2)Further layer development continuous in two ways: during the course of farther enhance of thickness of metal oxide layer (from 0.7nm to 1.4nm) its growth conditions realize in the form of 3D islands and simultaneously there develops roughness of silicon oxide mixed with areas of pure silicon. 3)Re-distribution of oxide layers greater than 1.4nm thicknesses on silicon surface leads to formation of tightly packed hexagonal nonuniform films of metal oxides. All changes in morphology of metal oxide films are strictly accompanied by changes in their compositions. The effectiveness of topochemical reaction of reduction of silicon oxide by metals with high affinity to oxygen and development of 3D metal 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 more 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, Guanghan Fan and Songhao Liu; School for Information and Optoelectronic Science and Engineering, South China Normal U., Guang Zhou, China.

The self-organized InP islands, which were grown on the different GaInP epitaxial lyers ,were uitilized to find the influence of the stress between the epitaxial layers and the islands. The shapes 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. And 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-Hee Yeon[1], Pil-Ryung Cha[2], Jin-you Kim[1] and Jong-Kyu Yoon[1]; [1]School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; [2]Princeton 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 singular crystal surfaces, there exist many steps on the vicinal surface and their motions can be explained by the behavior of the adatoms such as absorption, diffusion, desorption and incorperation into steps. At the steps, there exists surface forces originated from various factors, such as applied lattice strain, surface stress, the epitaxial strain, and so forth. The elastic interactions generated by surface forces, influence the motions of the steps and affect remarkably adatom diffusion and self-organization of the surface. Much research has been performed to analyze the effects of elastic interaction between the steps on the dynamics of steps. However, these approaches include the moving boundary problems where the position of the steps and the edges of islands should be tracked every time. A phase field model can be an alternative method to overcome this difficulty and to reflect the kinetics of the steps appropriately. In this study, a phase field model is presented, which considers both elastic interaction between the steps by surface forces and the adatom diffusion phenomena on the crystal surface. The present model is based on the Ginzburg-Landau approach on phase transition and reduces to the Gibbs-Thompson equation at step edge. In addition, the elastic field, which is generated by the surface force, is calculated using elastic surface Green function under the assumption that the atomic displacement field would decay exponentially from the surface. Using the resulting atomic displacement, the elastic interactions between the surface steps, such as monopole-monopole interactions, monopole-dipole interaction and dipole-dipole interactions, are incorporated into the model. Through phase field model, step bunching instabilities and step meandering instabilities are investigated. Step bunching instabilities and step meandering instabilities at both linear and nonlinear regime are presented in the case that elastic interactions exist. The presented instabilities are simulated and investigated using phase field model. And the kinetics of islands growth on vicinal surfaces is presented. It is analyzed that the elastic interactions retard the coarsening of islands and the self-organized structure in elastically anisotropic case is simulated.

Q5.10

A Study of Precipitation Kinetics: Experiments and Simulations.
Steven Van Petegem[1], Kelly Verheyen[2], Jan Kuriplach[3], Lorenzo Malerba[2] and Almazouzi Abderrahim[2]; [1]Spallation Neutron Source Division, Paul Scherrer Institute, Villigen PSI, Switzerland; [2]SCK/CEN, Mol, Belgium; [3]Charles 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 behaviour 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 Venables, [1]Physics and Astronomy, Arizona State University, Tempe, Arizona; [2]Physics 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 numbers 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 Politi[1] and Claudio Castellano[2]; [1]IFAC-CNR, Sesto Fiorentino, Italy; [2]Dipartimento 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 submonolayer 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; 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.
Xiaoda Xu[1], Michael Cortie[1] and Mike Stevens[2]; [1]Institute for Nanoscale Technology, University of Technology, Sydney, Sydney, New

South Wales, Australia; [2]CMF, University of Technology, Sydney, 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 exploited. Nevertheless, the uniform film texture and 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 related to the interplay between the rates 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 ostensibly influenced the results because the glass surface composition and surface tension change accordingly. The glass was pretreated with 1:1 sulfuric acid (H2SO4), 98% H2SO4 and buffered fluoric acid (HF). 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 MOCVD thin films of SrTiO3 and (Ba,Sr)TiO3 on Pt and SiO2 surfaces. Stephan Regnery[1,3], Peter Ehrhart[1], Krzysztof Szot[1], Yong Ding[2], Jiaquing He[2] and Chun-Lin Jia[2]; [1]IFF/EKM - Forschungszentrum Juelich, Juelich, Germany; [2]IFF/IMF - Forschungszentrum Juelich, Juelich, Germany; [3]Aixtron AG, Aachen, Germany.

(Ba0.70Sr0.30)TiO3 and STO, are grown by MOCVD on SiOx/Si(100) and Pt/TiO2/SiO2/Si substrates. The first nucleation steps are investigated by SPM and XPS. For deposition on metallic Pt the local electrical conductivity, 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 565C 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 base 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, 565C, randomly oriented grains (typical in-plane size 10-20nm) with a high density of twins, whereas (100)-oriented defect free grains of only slightly increased size were observed at 655C. For SrTiO3 a similar (100) texture was observed and 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 rusponi, nicolas Weiss, Tristan Cren, 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 leading to s = 2.5±0.2 atoms. Upon reaching the dimer diffusion onset, the dimers join to form tetramers, and some of them reach the trimers to form pentamers (s = 4.8±0.3 atoms). This step-wise increase continues for Co/Pt(111) until sizes as large as 10 atoms. The cluster diffusion energies are sufficiently far apart for each cluster size such that the jumps in mean size occur well separated in annealing temperature, approximately every 40 K. A similar behaviour is also observed for Pt/Pt(111). Our method should generally be applicable for adsorbates with large cohesive energies where clusters diffuse before they start to dissociate. The second part of the talk will be focused on the nucleation of Co/Pt(111). For this system it is known that some of the Co atoms get incorporated into

the first atomic plane of the substrate upon deposition at 300 K [1]. Thereby they respond to the tensile stress of the Pt(111) surface and lead to its reconstruction. The presence or absence of intermixing and the 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]. The behavior of Co/Pt(111) can be ascribed to diffusion in the presence of the first reconstruction nuclei. [1] E. Lundgren, B. Stanka, W. Koprolin, M. Schmid, and P. Varga, Surf. Sci. 423, 357 (1999). [2] J. A. Meyer and R. J. Behm, Surf. Sci. 322, L275 (1995).

11:00 AM Q6.6
Dislocations and dislocation forests: 2ML Cu/Ru(0001). Farid El Gabaly[1], Kevin F. McCarty[2] and Juan de la Figuera[1]; [1]Dpt. de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Madrid, Madrid, Spain; [2]Sandia 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 know in detail and which allows a study of dislocation interaction with well defined dislocation forests through measurements of domain evolution 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 with a well defined geometry. 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 moving within a single rotational domain, while they slow when crossing the threading dislocations at the edges of the rotational domains. Atomistic simulations based on semiempiric potentials will provide further insight into the experimental observations. This 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 Li[1,2], Darin Leonhardt[1,2], Ying-Bing Jiang[3], Huifang Xu[3], Steven R J Brueck[2], Stephen Hersee[2] and Sang M. Han[1,2]; [1]Chemical & Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; [2]Center for High Technology Materials and Department of Electrical and Computer Engineering, University of New Mexico, Albuquerque, New Mexico; [3]Earth 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 a 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 microscope images of the resulting Ge-Si interface reveal that the heterojunction is atomically abrupt with no observable dislocations. Only stacking faults exist above the oxide layer, but terminate within 80 nm from the interface.

11:30 AM Q6.8
Interface Distributions in Systems of Coarsening Crystals.
Tomoko Sano and Gregory Rohrer; Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

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 more complex and growth and shrinkage may be limited by the surface attachment/detachment rate, the motion of ledges, 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 $SrTiO_3$ and $BaTiO_3$ 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 at different annealing times. Findings show that grains in both the $SrTiO_3$ and $BaTiO_3$ systems are faceted. The average crystal shape of $SrTiO_3$ in the eutectic liquid at 1500°C is dominated by {100} facets and is therefore similar to the equilibrium crystal shape of $SrTiO_3$ 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 McGraw[1] and David T Wu[2]; [1]Environmental Sciences, Brookhaven National Laboratory, Upton, New York; [2]Mechanical 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 an analytical 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 balance, we address this shortcoming and derive kinetic extensions of the nucleation theorem that gives the derivative of 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 fluxes in composition space.

SESSION Q7: Nucleation on Surfaces II
Chair: John Venables
Thursday Afternoon, April 15, 2004
Room 3009 (Moscone West)

1:30 PM *Q7.1
Self-organized growth of cobalt nanostructure on Au(111) vicinal nano-patterned substrates : two-dimensional long-range order and atomic processes. Sylvie Rousset[1], G Baudot[1], S Rohart[1], V Repain[1], Y Girard[1], H Bulou[2], C Goyhenex[2] and L Proville[3]; [1]CNRS UMR 75-88, GPS, Paris, France; [2]CNRS UMR 75-04, IPCMS, Strasbourg, France; [3]CEA, SRMP, Saclay, France.

Self-organization phenomena allow to organize regular nanostructures over macroscopic areas with a high spatial density [1]. However, intrinsic defects such as step edges hamper the long-range ordered arrays of nanostructures since steps are often the main defect killing the nano-patterned surface coherence. Steps can also favor large cluster growth which hinders the uniformity of nanostructure sizes. Since macroscopic averaging methods are still commonly used for measuring physical properties of the nanostructures, these defects represent major drawbacks. In order to overcome these difficulties, a novel approach based on strain-relief vicinal patterned substrates is demonstrated for two-dimensional (2D) self-ordered growth. Unprecedented 2D long range ordered growth of uniform cobalt nanostructures has been achieved using Au(788) or Au(11,12,12)

vicinal surfaces which are spontaneously patterned in two dimensions at a nanometer scale with a macroscopic coherence length. Performing the cobalt growth on a substrate cooled down to 130 K allows a high degree of nanostructure uniformity [2]. In order to understand the atomic processes responsible for the large plateau of temperature (60K-300K) where such an ordered growth occurs, we have performed extensive variable temperature STM experiments. The atomistic mechanisms leading to the many nano-dots array are elucidated by comparing statistical analysis of in-situ VT-STM images with a multi scaled numerical simulation combining both Molecular Dynamics (MD) for the quantitative determination of the activation energies for the atomic motion and the Kinetic Monte Carlo (KMC) method for the simulations of the mesoscopic time evolution of the Co submonolayer. Eventually such a high quality of both long-range and local ordered cobalt growth opens up the possibility of making measurements of physical properties of such nanostructures by macroscopic integration techniques. [1] H. Brune et al., Nature 394, 451 (1998). [2] V. Repain et al., Europhys. Lett. 58, 730 (2002).

2:00 PM Q7.2
Void Nucleation and Cluster Ejection during Short-Pulse Laser Ablation: Large-Scale Molecular Dynamics Simulations. George H Gilmer, Mike D Shirk, Alexander M Rubenchik, Ray P Mariella, Luis Zepeda-Ruiz, Sherry L Baker and Babak Sadigh; Lawrence Livermore National Laboratory, Livermore, California.

Metal ablation is simulated using molecular dynamics techniques. The interaction of femtosecond laser radiation with electrons in the metal target, and subsequent energy transfer between the electrons and the metal atoms during the first picosecond are modeled using a one-dimensional continuum code. The output from the continuum simulation provides initial conditions for the molecular dynamics simulation, which is used to follow the process for several hundred picoseconds. The deposition of the laser energy into a thin layer creates a highly non-equilibrium state of matter, resulting in a variety of surface morphologies. These simulations provide a detailed picture showing the melting of the near-surface regions and the nucleation of voids in the melt as a rarefaction wave moves through. Void growth and coalescence results in the ejection of small particles and micron-sized droplets of liquid metal. The ejection of a liquid layer, approximately 10nm in thickness, is observed in a small range of energy densities just above the threshold for ablation. Detailed information on the ejected particle size distributions and temperature and pressure throughout the target are obtained, and information on the effect of initial target temperature and other conditions will be discussed. The morphology of the ablated surface is crucial to precise micro-machining applications, and the model results are consistent with experiments. Some implications of the results for pulsed laser deposition of thin films will be discussed, based on molecular dynamics and Monte Carlo modeling of the ejecta on various substrates. Movies of the molecular dynamics models will illustrate void nucleation, the resulting ablation of clusters and liquid droplets, and deposition onto a substrate. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

2:15 PM Q7.3
Probing the Influence of Impurities on the Nucleation and Growth of ZnO Quantum Dots using Electronic Absorption Spectroscopy. Daniel R. Gamelin and Dana A. Schwartz; Chemistry, University of Washington, Seattle, Washington.

Impurities may substantially influence crystal nucleation and growth in ways that are often difficult to observe directly. We will present some recent results in the use of electronic absorption spectroscopy as an in-situ probe of transition-metal impurities (dopants) introduced into homogeneous solution preparations of ZnO nanocrystals. Our studies reveal that even very chemically compatible dopants will inhibit both nucleation and growth quite strongly. We will present spectroscopic evidence for the existence of different compositions in the critical nuclei than in the fully developed nanocrystals, and the dependence of these compositions on synthetic parameters.

2:30 PM *Q7.4
Stacking faults in homoepitaxial growth.
Thomas Werner Michely, I. Physikalisches Institut, RWTH Aachen, Aachen, Germany.

Stacking fault formation during growth far from equilibrium may occur on fcc(111) surfaces, which supply regular and faulted adsorption sites. In homoepitaxy on Ir(111) stacking fault islands are readily identified with scanning tunneling microscopy by their distinct island shape. Based on the analysis of the temperature and flux dependence of the fault island nucleation probability an atomistic model for it is developed: The distribution of large metastable fault islands represents the Boltzmann distribution of those small mobile

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 Lammerschop, Michael Mueller and Karsten Albe to this work are acknowledged.

3:30 PM Q7.5
Geometry-Based Simulation (GBS) of Island Nucleation and Growth During Submonolayer Deposition. Maozhi Li[1], Maria Bartelt[2] and James Evans[1]; [1]Ames Laboratory, Iowa State University, Ames, Iowa; [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 [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 [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 spatial aspects of the island nucleation process (i.e., nucleation nearby CZ boundaries). GBS reliably predicts island size and spatial distributions, and is expecially efficient for highly reversible island formation. [1] M. C. Bartelt and J. W. Evans, Phys. Rev. B 54 (1996) 17359R. [2] M. Li, M. C. Bartelt, and J. W. Evans, Phys. Rev. B 68 (2003) 121401R.

3:45 PM Q7.6
Molecular Dynamics and First-Principles Calculations of Defect Precursors Formation in N doped Silicon. Abdennaceur Karoui, Faouzia Sahtout Karoui and George A. Rozgonyi; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

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 vacancies. This explains the dominance of SiO2 precipitation over large void formation. It appeared also from our calculations that N2 can also attract self-interstitial silicon thereby reducing A-defects in N-FZ Si, as reported experimentally. Table I: Formation energies of N-pairs and N-O complexes as calculated from DFT-LDA on 64 Si atoms supercells. ... N2 VN2 V2N2 N2O VN2O V2N2O (eV) -4.1 2.0 -5.2 -0.8 0.08 -0.64 Table II: Binding energies of V and O with N-pair, VN2 and V2N2 calculated using molecular dynamics. (eV) N2 VN2 V2N2 . O -2.8 0.8 -2.4 . V -0.2 -7.3 -0.3 . I -0.65

4:00 PM Q7.7
Spherulitic Nucleation of Yttrium-Aluminum Garnet. Randall Hay and Emmanuel Boakye; USAF, WPAFB, Ohio.

Nucleation of the equilibrium phase from sol-gel materials is a black box. Typically nucleation is site-saturated and spherulitic, and nucleation frequency is 1 nuclei 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 1000C 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. Rb 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 catalytsts. 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 [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. [1] J.B. Hannon, M. Copel, M.C. Reuter, R.M. Tromp, The Frustrated Alloying of Ge on Ultra-Flat Si(001), 50th AVS Symposium, SS3-MoM, 2003.