# SYMPOSIUM R

# Morphology and Dynamics of Crystal Surfaces in Molecular and Colloid Systems

April 16 – 20, 2001

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# TUTORIAL

## ST R: OBSERVATION, MONITORING AND MANIPULATION OF SINGLE MOLECULES ON SURFACES AND INTERFACES
Monday, April 16, 2001
1:30 p.m. - 5:00 p.m.
Salon 12/13 (Marriott)

This tutorial will cover the techniques that allow observations, monitoring and in some cases, manipulation of single molecules or virus and broadly used techniques for such purposes, hence it will be the prime focus of the two lectures. The instructors will provide an overview – with some hindsight onto the history and evolution – of the atomic force imaging, including the most recent advances in fast imaging in quantitative phase imaging and the insight that these novel methods provide. The second part of the tutorial will be dedicated to single molecule manipulation and construction of protein molecular arrays on surfaces. The attendee will obtain fundamental background on the method, combined with an understanding of its strengths and limitations, and the promising areas of applications.

**Instructors:**
**Dr. Kevin Kjoller**, Digital Instruments, Veeco Metrology
**Dr. Siu-Tung Yau**, The University of Albany, State University of New York

### SESSION R1: INTERACTIONS AND NUCLEATION: FUNDAMENTALS
Chair: Peter G. Vekilov
Tuesday Morning, April 17, 2001
Salon 13 (Marriott)

**8:30 AM *R1.1**
SIMULATING CRYSTAL NUCLEATION RATES. Daan Frenkel, Stefan Auer, FOM Institute for Atomic and Molecular Physics, Amsterdam, NETHERLANDS.

Classical Nucleation Theory dates back to the 1920's and has been the standard tool to predict and interpret experiments on (crystal) nucleation. It is now becoming possible to compute absolute nucleation rates directly by computer simulation, even when the actual rates are as low as one nucleus per cubic centimeter per month! However, simulations of crystal nucleation in colloidal suspensions yield rather large discrepancies with experiment. In my talk, I shall review what simulation tells us about the pathway for colloidal crystallization and I shall discuss some of the factors that may be responsible for the discrepancy between simulation and experiment.

**9:00 AM *R1.2**
NUCLEATION OF CRYSTALS STUDIED THROUGH DENSITY FUNCTIONAL THEORY. David W. Oxtoby, Dmitriy Chekmarev, Lasse Rasmussen, University of Chicago, James Franck Institute, Chicago, IL.

We describe recent theoretical work based on density functional methods of statistical mechanics to study crystallization in colloidal suspensions and in protein solutions. Our particular focus is on nucleation dynamics, and we show that such complex fluids can behave quite differently from small molecules in their crystallization behavior. We also explore the possibility of forming metastable crystals either through direct homogeneous nucleation or through crystallization on patterned substrates or in the presence of external trapping fields induced by lasers.

**9:30 AM R1.3**
MICROMOLDING CRYSTALS VIA A POLYMER-INDUCED LIQUID-PRECURSOR (PILP) PROCESS. Yi-Yeoun Kim, Sung-Hwan Yoon, Laurie Gower, University of Florida, Dept. of MS&E, Gainesville, FL.

Our prior work has shown that polypeptide additives that are simple mimics to the acidic proteins associated with biominerals can induce a liquid-phase precursor to calcium carbonate, which upon solidification, leads to an assortment of non-equilibrium crystal morphologies. Certain attributes of the synthetic PILP-formed crystals are similar to those found in biologically-controlled mineralizations, and our recent work with calcium oxalate and phosphate shows certain similarities to pathological biominerals (e.g. kidney stones); therefore, we have proposed that this novel crystallization mechanism could play a key role in the morphogenesis of biominerals. In the biologically-controlled minerals, a key feature is the ability of organisms to form crystals with elaborate non-equilibrium morphologies by growing the crystals within organic compartments (e.g. sea urchin spines); however, it remains a mystery as to why the crystals adopt the shape of the compartment rather than form the more energetically favorable, faceted crystal habit. We believe that the liquid-like aspects of the PILP phase may make it amenable to molding, which could provide a plausible explanation for the low-temperature formation of "molded" biomineral morphologies. To test this concept, we are currently trying to determine if this polymer-induced liquid-precursor (PILP) phase can be manipulated for morphological control, and our approach is to use the soft lithography techniques of micro-contact printing and micromoulding in capillaries for the patterning and shaping of solution grown crystals via the PILP process.

**10:15 AM *R1.4**
LIQUID-LIQUID PHASE BOUNDARY AND PROTEIN HOMOGENOUS NUCLEATION RATES. Oleg Galkin, Peter G.Vekilov, Department of Chemistry and Center of Microgravity and Material Research and Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL.

The capability to enhance or suppress the nucleation of protein crystals opens opportunities in various fundamental and applied areas, including protein crystallography, production of protein crystalline pharmaceuticals, protein separation, and treatment of protein condensation diseases. We investigate the mechanisms underlying the nucleation of crystals of the model protein lysozyme. For these experiments we developed a novel method which: (a) Accounts for intrinsically stochastic nature of nucleation by carrying out multiple trials under identical conditions. (b) Separates nucleation from the ensuing crystal growth by decreasing supersaturation after a preset time. (c) Eliminates heterogeneous nucleation by monitoring the time dependence of the number of nucleated crystals. The presence of a metastable liquid-liquid (L-L) phase boundary in the phase diagram of the protein solution has a profound effect on J: nucleation rate has maximum near L-L boundary. Our results show that at the binodal rather then spinodal (located far beneath the binodal) J is enhanced by factors of 6 to 20 because of significantly faster nucleation of the liquid droplets. In the region of liquid-liquid demixing below the binodal, the nucleation rate decreases again. The found correlation allows control of the nucleation rate of protein crystals by using additives that shift the L-L boundary. We found that glycerol and polyethylene glycol (PEG) (that do not specifically bind to proteins) shift this phase boundary and suppress or enhance the crystal nucleation rates by factors of 2 - 3, although no simple correlation exists between the action of PEG on the phase diagram and the nucleation kinetics. The control mechanism does not require changes in the protein concentration, the acidity and ionicity of the solution. The effects of the two additives on the phase diagram depend on their concentration and this provides for further tuning of nucleation rates.

**10:45 AM *R1.5**
NANOPARTICLE CRYSTAL NUCLEATION: THE ROLE OF INTERACTION FORCES. C.F. Zukoski, N. Dixit and A. Kulkarni, Department of Chemical Engineering, University of Illinois, Urbana, IL.

Nanoparticle solubility is controlled by short range interactions such that on increasing particle concentration, rarely are fluid/fluid phase separations observed. Instead, the fluid/solid phase transition occurs at higher temperatures (weaker attractions) than the fluid/fluid phase boundary. Crystal nucleation follows expected dependencies on supersaturation but the absolute rates of nucleation are much lower than are expected based on what is known about nucleation of small molecule crystals. Nanoparticles rarely have isotropic interactions. The extent of "patchiness" of the interactions can be characterized by measuring the strength of interactions characterizing the metastable critical point. In this paper we explore the role of anisotropic (aleotopic) interactions on nanoparticle particle crystal nucleation. We present studies of rates of nucleation in the presence and absence of long range attractions showing that, under some conditions, the long range attractions do not alter the energetics of the phase transition of the free energy of critical cluster nucleation but have a dramatic impact on the rate of crystal formation. These observations are discussed in terms of the role anisotropic interactions on rates of crystal formation.

**11:15 AM *R1.6**
PHYSICAL PRINCIPLES OF BIOLOGICAL SELF-ASSEMBLY AS SEEN IN THE POLYMERIZATION OF SICKLE HEMOGLOBIN. Frank A. Ferrone, Department of Physics, Drexel University, Philadelphia, PA.

Sickle hemoglobin differs from the usual hemoglobin A by a single surface mutation on two of four subunits that replaces a negatively charged glutamic acid by a hydrophobic valine. This replacement permits assembly of 14-stranded fibers when the hemoglobin carries no ligand ($O_2$ or CO). The assembly of these fibers proceeds by a

novel double nucleation process in which polymerization begins by disfavored aggregation of solution molecules (homogeneous nucleation). Once fibers form, their surfaces add a small amount of stability to aggregates and heterogeneous nucleation occurs. The heterogeneous process causes the initiating homogeneous event to become magnified by polymer proliferation, and consequently the appearance of polymers displays stochastic variation representative of the first passage time for the very first nucleus to form. We have used such distributions of onset times to characterize nucleation and thus have characterized nuclei as well as polymers over a wide range of conditions. This allows us to employ scaling to dissect the association energy into contact energy between polymers, and vibrational entropy due to motion of monomers within the polymers. We find the vibrational contributions to be very significant, and have identified at least three modified hemoglobins in which vibrational alterations are the cause of dramatic difference in assembly behavior.

**11:45 AM R1.7**
LONG-RANGE LIKE-CHARGE ATTRACTION IN CONFINED COLLOIDAL SYSTEMS. Zhan Chen, Rajiv K. Singh, MS&E Dept, University of Florida, Gainesville, FL.

One of the most intriguing and puzzling observation in particle science and technology has been the experimental observation of electrostatic attraction between like-charged surfaces in confined or concentrated colloidal systems. The widely accepted DLVO theory (Derjaguin-Landau-Verwey-Overbeek) on colloidal stability, which was developed more than 50 years ago, predicts only long-range repulsive forces in like-charged colloidal systems. The origin of the attractive forces has baffled researchers for more than two decades. Some controversial explanations such as volume change, volume exclusion, and multi-body interactions have been proposed, however in all cases the predictions are not always consistent will experimental observations. Here we hypothesize, for the first time, a new theory based on solution of Poisson-Boltzmann equation of like-charged double layer interactions which includes mass conservation of cations and anions, which is violated by the classical DLVO theory. The solutions show the existence of a long-range electrostatic attractive force in addition to the conventional DLVO repulsive force. The attractive force increase with the degree of confinement, lower ionic strength of the solution, and higher charge density of surfaces, which is in agreement with the experimental observations.

SESSION R2/O2: JOINT SESSION
EPITAXIAL GROWTH II
Chairs: Thomas W. Michely and Arthur F. Voter
Tuesday Afternoon, April 17, 2001
Salon 7 (Marriott)

**1:30 PM *R2.1/O2.1**
CONVECTIVE STEP-BUNCHING ON CRYSTAL SURFACES. Andrew Zangwill, School of Physics, Georgia Institute of Technology, Atlanta, GA; Navot Israeli, Daniel Kandel, and Michael Schatz.

Recent theoretical work predicts that uniform step-flow growth can be unstable to step-bunching during heteroepitaxial crystal growth. In this talk, I show that step-bunching of this kind can occur via a convective instability. The convective nature of the instability implies a time-evolution for the system (more common in hydrodynamics and plasma physics) that should allow experimenters to discriminate strain-induced bunching from other types of bunching. More significantly perhaps, convective bunching lends itself to external control in a manner that suggests a new approach to nanoscale morphological patterning of crystal surfaces.

**2:00 PM R2.2/O2.2**
THE DECOMPOSITION OF tBAA ON SILICON FOR COPPER CVD. Che-Chen Chang, Ing-Jye Huang, National Taiwan University, Department of Chemistry, Taipei, TAIWAN, ROC.

Parallel to the shrinkage of feature sizes to 0.18 mm and below in integrated circuit fabrication is the emergence of a class of complexes that may be employed as CVD precursors of copper. Among the copper precursors used, $\beta$-diketonate complexes exhibited a high sublimation rate and a low pyrolysis temperature. The present study explores the possibility of using the nonfluorinated t-butylacetato complex of Cu(II) as the precursor. The $\beta$-keto ester appears to alter the properties of the metal $\beta$-diketonate complex substantially, leading to an improvement on the precursor reactivity. Static secondary ion mass spectrometry studies on the adsorption and decomposition of the ligand, tert-butylacetylacetate (tBAA), on Si(100) show that at low doses, all tBAA molecules dissociate readily upon adsorption on the surface at substrate temperatures as low as -160°C. The dissociation may occur through tBAA bonding via the ester or the diketo oxygen to the surface. The bond scission occurring at the tBuO-CO bond yields isobutene and surface hydroxyl species. In addition, the OC-CCO bond scission induced by tBAA surface bonding mainly via its carboxylic keto oxygen affords acetaldehyde radical, whereas that via the aceto oxygen yields carbon dioxide and isopropenoxy species. Upon acquiring surface hydrogen, an enol-keto conversion takes place for isopropenoxy species to yield acetone, even at low substrate temperature of less than -126°. The aceto oxygen pathway dominates the cleavage of the OC-CCO bond over the carboxylic keto oxygen path. Possible tBAA decomposition mechanisms at high exposures are also discussed.

**2:15 PM R2.3/O2.3**
RATE-EQUATION APPROACH TO ISLAND CAPTURE-ZONES AND SIZE DISTRIBUTIONS IN SUBMONOLAYER GROWTH. Jacques G. Amar, Univ. of Toledo, Dept. of Physics & Astronomy, Toledo, OH; Mihail N. Popescu, Fereydoon Family, Emory Univ., Dept. of Physics, Atlanta, GA.

We present a quantitative rate-equation approach to irreversible submonolayer growth on a two-dimensional substrate. Our method explicitly takes into account the existence of a denuded ("capture") zone around every island, the fluctuations in the capture-zone areas, and the correlations between the size of an island and the corresponding average capture zone. The evolution of the capture-zone distributions is described by a set of Voronoi-area evolution equations which are coupled to the usual rate-equations for the island-densities through local rates of monomer capture. The combined set of equations leads to a fully self-consistent calculation of the size- and coverage-dependent capture numbers. The resulting predictions for the capture-zone and capture number distributions are in excellent agreement with experimental results and Monte Carlo simulations. The corresponding island-size distributions and their dependence on coverage and deposition rate are also accurately predicted.

**2:30 PM R2.4/O2.4**
THEORETICAL ANALYSIS OF THE GROWTH MODE FOR SILVER METALLIC FILMS ON MgO SUBSTRATES. David Fuks, Mater Eng Dept, BGU, Beer-Sheva, ISRAEL; Simon Dorfman, Dept Phys, Technion, Haifa, ISRAEL; Eugene A. Kotomin, MPI, Stuttgart, GERMANY; Yury F. Zhukovskii, Inst Sol St Phys, Univ of Latvia, Riga, LATVIA; A.M. Stoneham, Dept of Phys & Astr, Univ College, London, UNITED KINGDOM.

It is demonstrated how the growth mode of thin metallic films on insulating substrates could be theoretically predicted combining thermodynamic approach and ab initio calculations for low-coveraged ordered metal/insulator interfaces. Theory predicts conditions for monolayer growth via spinodal decomposition, or for metal cluster nucleation-and-growth mode. This is illustrated by calculations for a long-debated Ag film deposition on MgO substrate. Our ab initio calculations predict high mobility of adsorbed Ag atoms on MgO substrate even at low temperatures which stimulates greatly their aggregation.

**2:45 PM R2.5/O2.5**
THE EVOLUTION OF SURFACE MORPHOLOGY CAN BE DOMINATED BY BULK (NOT SURFACE) PROCESSES. N.C. Bartelt, J.A. Nobel, and K.F. McCarty, Sandia National Laboratories, Livermore, CA.

The processes that control evolution of surface morphology are almost always viewed as occurring in the topmost one or two surface layers. However, in the work reported here we show that the smoothing of the NiAl (110) surface is dominated by direct exchange of bulk defects (vacancies) at the surface steps, not by surface diffusion. This conclusion is reached by measuring the kinetics of island decay using low-energy electron microscopy. Remarkably, the decay rates are constant in time and totally independent of the local environment (e.g., the width of the immediately adjacent terraces or the size of nearby islands). Given this lack of evidence for any surface current between islands of different curvature, we deduce that surface diffusion is not important to the smoothing process. Instead, we unambiguously show that bulk vacancies are responsible for the smoothing by directly measuring the exchange between bulk vacancies and the surface when the sample temperature is changed. Surface steps advance when temperature is increased and recess when temperature is decreased. These changes result from the increase (decrease) in bulk vacancy concentration for a temperature increase (decrease). Remarkably, the size change accompanying a temperature change is always precisely proportional to the perimeter (step length) of the island. Thus, we conclude that the atoms at surface steps undergo direct exchange with bulk vacancies. Since the steps are interacting directly with the bulk, the surface dynamics are independent of the local environment (i.e., step density and curvature). This conclusion is contrary to (current) conventional wisdom. By sinusoidally varying temperature and measuring the phase shift of step motion as a function of frequency, we can also estimate bulk vacancy diffusion constants.

This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported by the Office of Basic Energy Sciences-Division of Materials Sciences.

## 3:30 PM *R2.6/O2.6
EXPLOITING EPITAXY FOR NOVEL MAGNETIC MATERIALS. Roy Clarke, Alejandra Lukaszew, Ctirad Uher, Vladimir Stoica, Yongning Sheng, University of Michigan, Ann Arbor, MI.

Ever since lode stones were first used for navigation nearly a thousand years ago, microstructure has played a key role in the science and application of magnetic materials. The ability to control magnetic properties through a material's microstructure, and now nanostructure, is central to all current magnetics technology from high density recording media to the development of super-strong permanent magnets. The advent of epitaxy as a practical method for producing high quality thin film materials has opened up many new possibilities for novel magnetic structures, extending the range of growth control down to almost the atomic level. This presentation will focus on the use of template epitaxy to achieve well-defined microstructures and nanostructures in magnetic thin films, in many cases leading to materials that have no counterpart in the bulk polycrystalline form. We illustrate the competing effects of magnetocrystalline anisotropy, epitaxial strain and shape anisotropy, drawing on our recent work in the growth of ultrathin cobalt films on Cu-buffered Si (100) wafers. An important feature of this work is the interplay between low-temperature deposition and mass transport kinetics stimulated by carefully controlled annealing processes.

## 4:00 PM R2.7/O2.7
VACANCIES AND SURFACE MORPHOLOGY DURING LOW TEMPERTAURE HOMOEPITAXY OF METALS. Cristian E. Botez, William C. Elliott, Paul F. Miceli, University of Missouri-Columbia, Department of Physics and Astronomy, Columbia, MO; Peter W. Stephens, State University of New York, Department of Physics, Stony Brook, NY.

X-ray scattering experiments on the homoepitaxial growth of Ag and Cu show that high vacancy concentrations can be acheived during low temperature deposition. A unique aspect of x-ray scattering is the ability to probe the subsurface structure and the surface morphology simultaneously. It is observed that the vacancies, which can attain concentrations on the order of 2% in Ag, extend throughout the thickness of the deposited film. Moreover, the vacancies are found to have a profound effect on the evolving surface morphology for certain surfaces. The effect of vacancies on the surface morphology will be discussed in terms of prior studies of kinetic roughening in these systems.

## 4:15 PM R2.8/O2.8
CLOSING THE GAP BETWEEN CRYSTAL-GROWTH EXPERIMENTS AND ATOMISTIC MODELS: TEMPERATURE ACCELERATED DYNAMICS SIMULATION OF Ag/Ag(100). F. Montalenti, S. Swaminarayan, M.R. Sorensen, T.C. Germann and A.F. Voter, Los Alamos National Laboratory, Los Alamos, NM.

We investigate the first stages of growth of $Ag/Ag(100)$ at low temperature. By using the temperature accelerated dynamics (TAD) method [1] we are able to extend the standard molecular dynamics time scales by $\sim 10$ orders of magnitude, so that experimental deposition fluxes are matched. Indeed, we deposit $4ML$ of $Ag$ for a total simulation time of $\sim 1$ minute. No $a\ priori$ information on the relevant diffusion mechanisms is needed. We show that activated events can play an important role in determining the growing-surface morphology even at temperatures as low as $40\,K$. Two different impinging-atoms momenta are considered: $0.25\,eV$ and $0.025\,eV$. We show that by lowering the momentum, the role of activated diffusion events becomes crucial in causing film smoothness.
[1] M.R. Sørensen and A.F. Voter, J. Chem. Phys. **112**, 9599 (2000).

## 4:30 PM R2.9/O2.9
STM INVESTIGATION OF ENERGETIC INSERTION DURING DIRECT ION DEPOSITION. J.M. Pomeroy[a], A. Couture[a], J. Jacobsen[b], B.H. Cooper[c], J.P Sethna[a], J.D. Brock[a]. [a]Cornell Center for Materials Research. [b]Currently with Haldor Topsoe A/S, DENMARK. [c]Deceased August 1999.

In a continuing effort to probe the effect of atomic insertions during hyperthermal ion deposition, thin copper films have been deposited on single crystal copper substrates and characterized using a UHV

Scanning Tunneling Microscope. At low temperatures, atomic insertions provide a net downhill current that offsets the roughening effect due to uphill "Schwoebel" currents leading to a net smoothing of the surface. Thin films have been grown at several different energies targeted to observe a crossover from insertion driven smoothing to adatom-vacancy dominated roughening. Copper thin films are deposited near 20 eV using a mass selected ion deposition system that allows precise control over the energy of constituent atoms. Experimental observations are compared with a sophisticated Kinetic Monte Carlo and Molecular Dynamics hybrid (KMC-MD) simulation.

## 4:45 PM R2.10/O2.10
STUDIES OF SURFACE PATTERN ON Si(100) SURFACE AFTER Cu AND Sn DEPOSITION. Qin Hu, Martin Zinke-Allmang, Ian V. Mitchell, University of Western Ontario, Department of Physics and Astronomy, London, Ontario, CANADA.

We report our studies on Si(100) samples with Cu and Sn deposited in an MBE system followed by annealing. Imaging the surface pattern with AFM and SEM shows that Cu-Sn non-uniform clusters were formed with their shape not sensitive to the order of metal deposition. Changing the relative amount of Cu and Sn a range of varying morphologies were observed. Pyramidal pits were found on the Si(100) surface with Cu-Sn clusters nucleating and growing from those pits. The direction of growth of the pyramidal pits and clusters is $< 100 >$. The late stage growth mechanism of the Cu-Sn clusters differs from that of pure Sn clusters, leading to the discussion of the growth of epitaxial structures.

SESSION R3: THERMODYNAMICS OF SURFACES
Chair: Margret Giesen
Wednesday Morning, April 18, 2001
Salon 13 (Marriott)

## 8:30 AM *R3.1
CONCEPTS IN THE STATISTICAL PHYSICS OF ONE AND TWO-DIMENSIONAL OBJECTS ON SURFACES AND THEIR APPLICATION TO EXPERIMENTS AT THE SOLID/VACUUM AND THE SOLID/LIQUID INTERFACE. Harald Ibach, Sascha Baier, Christoph Steimer, Margret Giesen, Research Center Juelich, IGV, Juelich, GERMANY.

In the last decade an impressive number of papers have dealt with the statistical physics of one and two dimensional objects. Applied to solid surfaces, these objects can be monoatomic steps, islands, or a particular crystal face. The investigations concern the mean equilibrium structure of objects, fluctuations in the space and time domain, and growth/decay phenomena. Using the concepts of statistical physics, novel methodologies have been developed which serve to analyze the equilibrium structure, fluctuations, and growth/decay to determine the energies of particular structural configurations on surfaces as well as activation energies for processes involving the transport of atoms on surfaces. The presentation intends to provide a tutorial review of earlier and the most recent work. Examples to be presented include the equilibrium fluctuations of steps on vicinal crystal faces, studies of island decay and the analysis of the equilibrium shape of islands and the fluctuations around the equilibrium shape. A special advantage of the statistical analysis is that it is easily applied also to the solid/liquid interface. Because of the limited temperature window available in studies of the solid/liquid interface the direct observation of individual atom transport processes is not possible there and the statictical analysis is the only method to obtain quantitaive information on atom transport. It will be demonstrated in a number of examples how the atom transport at the solid/liquid interface is affected by the type of electrolyte, the electrode potential and the temperature and how activation energies for particular transport processes can be determined.

## 9:00 AM *R3.2
DIFFUSION DYNAMICS AT SURFACES: ISLAND MOTION, STEP FLUCTUATION, AND THE ATOMIC SLIDE PUZZLE. Joost W.M. Frenken, Kamerlingh Onnes Laboratory, Leiden University, Leiden, THE NETHERLANDS.

Atomic mobility at surfaces is a key ingredient in many important processes, such as crystal growth and heterogeneous catalysis. This talk highlights the important role played in this game by the steps [1], which serve as natural sources and sinks for ad-atoms and surface vacancies. The fluctuations in step position can be responsible for the motion of an entire ad-atom or vacancy island. The two-dimensional, diffusive motion of individual surface vacancies can turn an otherwise static terrace into a gigantic 'atomic slide puzzle' [2].
[1] H.-C. Jeong, E.D. Williams, Surf.Sci.Rept. 34, 171 (1999).
[2] R. van Gastel, E. Somfai, W. van Saarloos, J.W.M. Frenken, Nature, in press.

**9:30 AM R3.3**
ADATOM DIFFUSION PARAMETERS AND DIMER BINDING ENERGIES FROM ISLAND DENSITIES? Thomas Michely, Winfried Langenkamp, Henri Hansen, Carsten Busse, I. Physikalisches Institut, RWTH Aachen, Aachen, GERMANY.

For homoepitaxial growth on Al(111) and Pt(111) saturated island number densities obtained by scanning tunneling microscopy are analyzed up to 0.3 of the respective melting temperature by means of rate equation nucleation theory. Two problems in obtaining useful information from these island number densities are discussed. First, they are extremely sensitive to trace amounts of adsorbed impurities. Impurity influenced number densities give rise to extremely low effective attempt frequencies for adatom diffusion in the nucleation theory analysis. However, island number densities measured under nominally clean conditions result in adatom diffusion parameters, which are in good agreement with field ion microscopy (FIM) results and ab initio calculations. Second, dimer binding energies determined from island number densities are self consistent within the framework of nucleation theory, but for the Pt-system they are in striking contradiction to dissociation energies obtained by FIM measurements.

**10:15 AM *R3.4**
TUNING THIN-FILM STRUCTURE: ATOMISTIC MODELS OF GROWTH AND RELAXATION. Maria Bartelt, Lawrence Livermore National Laboratory, Livermore, CA.

A large number of elementary atomic processes influence the structure of films grown out of equilibrium, and mediate their relaxation towards equilibrium. One goal of recent modeling has been to identify processes which are fairly general, rank their influence under experimentally relevant conditions, and assess their impact on desired structures. Two basic classes of processes have emerged: processes that specify the deposition dynamics often reflect surface symmetry and conditioning, and thermally activated processes responsible for long-range surface mass transport. The former are usually system-specific, but can dominate behavior. E.g., the structure of molecular crystals (proteins, viruses, etc.) grown from solution can depend strongly on molecular conformation and packing geometry on the surface. For thermally activated processes, effective barriers and prefactors can be estimated from analyses of deviations from the equilibrium structure, both in simulations of lattice-gas models and in experiment, and from ab initio calculations. Thus, e.g., barriers for terrace diffusion control the characteristic island spacing at low temperatures; diffusion along steps and around corners controls the non-equilibrium island shape and the average profile of multilayer mounds; barriers for downward diffusion at step edges induce multilayer film roughness, and modify the size and spatial distribution of islands nucleated near descending steps; relaxation of surface features reflects details of mass transport along or escape from step edges, and the operation of exotic (fast) pathways for downward mass transport. However, precise information on deposition dynamics and surface diffusion rates is but one aspect in predicting non-equilibrium structure. The form of the correlations that develop in the film, and in essence control behavior, can only be exactly captured in simulations studies. Recent application to real systems demonstrated the power (and limitations) of such studies, and prompted significant revisions of traditional mean-field expectations.
Work supported by the USDOE under contract No. W-7405-Eng-48.

**10:45 AM *R3.5**
NUCLEATION, GROWTH AND SELF-ASSEMBLY OF METALLIC NANOSTRUCTURES. Harald Brune, Inst of Experimental Physics, Swiss Federal Inst of Tech, Lausanne, SWITZERLAND.

After giving a general introduction to the kinetics of nucleation and growth in molecular beam epitaxy we will discuss several means for the self-assembly of metallic islands with well defined size and mutual distance. These nanostructures are created with the perspective to investigate size- and coordination effects, e.g., on magnetism or on the reactivity and selectivity in a catalytic reaction. One possible way to realize equidistant atoms, molecules, or islands is to use long-range interactions between adsorbates. We show the existence of such interactions between metal atoms adsorbed on the (111)-oriented transition metal surfaces. The interactions are mediated by screening in the surface state. The interaction energy oscillates with $\lambda_F/2$, it reaches up to 60 Å and decays as $1/r^2$. It can be used to arrange adatoms or islands into hexagonal superlattices with period $\lambda_F/2$ ($\lambda_{F,Cu(111)} = 30$ Å; $\lambda_{F,Au(111)} = 37$ Å; $\lambda_{F,Ag(111)} = 76$ Å). Nanostructure arrays can also be realized using kinetically controlled growth on dislocation networks serving as templates. Here the island spacing is given by the misfit of the two elements used to produce the dislocation- or moiré-lattice. Their size distribution is given by the statistics of deposition. It has a half width at half maximum of 12% at $0.10\sim$ML, which is competitive with state-of-the-art semiconductor quantum dots; this value goes down to 4% at $0.5\sim$ML.

**11:15 AM R3.6**
EFFECTS OF THERMAL FLUCTUATIONS ON THE STRUCTURE AND PROPERTIES OF CHIRAL SINGLE-CRYSTAL PT SURFACES. David S. Sholl, Timothy D. Power and Aravind Asthagiri, Dept. of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA.

Many high Miller index metal surfaces are decorated with periodic arrays of steps and kinks that make these surfaces chiral [1]. Several groups have demonstrated experimentally and theoretically that this chirality can lead to enantiospecific adsorption properties for chiral adsorbates on these surfaces. Although theoretical studies of chiral metal surfaces have focused on perfect Miller index surfaces, real surfaces deviate from these structures due to thermal fluctuations in the surface steps. We have developed a lattice gas model for Pt step edge roughening based on extensive Density Functional Theory calculations of Pt atom self-diffusion by P.J. Feibelman [2]. This lattice gas model allows us to simulate the dynamics of Pt surface steps on time-scales of hours at experimentally relevant temperatures. We have used these simulations to study the impact of step fluctuations on the chiral nature of chiral Pt surfaces. We will discuss the effect of step fluctuations on the enantiospecific adsorption properties of chiral hydrocarbons adsorbed on chiral Pt surfaces and the implications of step fluctuations for experimental measurements of surface chirality.
[1] C.F. McFadden et al., Langmuir, 12 (1996) 2483.
[2] P.J. Feibelman, Phys. Rev. B., 60 (1999) 4972.

**11:30 AM *R3.7**
THE USE OF INSTABILITIES IN EPITAXIAL GROWTH FOR LATERAL PATTERNING OF SURFACES. Hans-Joachim Ernst, CEA Saclay, DSM/Drecam/Srsim, Gif Sur Yvette, FRANCE.

Current lithography-based techniques generally do not provide sufficient spatial resolution for lateral patterning of surfaces at the nanometerscale. The use of intrinsic instabilities in growth processes is currently actively explored as a promising pathway to reach this goal. The origin of these instabilities is traced back to the presence of an excess energy barrier for adatom diffusion over steps, the Ehrlich-Schwoebel barrier. Structural patterns can be created either by spontaneous self-organization of the material deposited, or by guided growth on prestructured substrates. The deposition of Cu on singular and vicinal Cu surfaces illustrates this approach, using Helium Atom Beam Scattering (HAS), Scanning Tunneling Microscopy (STM) and Low Energy Electron Microscopy (LEEM) as structural probes. Surprisingly, the interaction of green laser light with these surfaces leads as well to atomic scale restructuring.

SESSION R4: INTERACTIONS AND NUCLEATION:
COMPLEX SYSTEMS
Chair: Charles F. Zukoski
Wednesday Afternoon, April 18, 2001
Salon 13 (Marriott)

**1:30 PM *R4.1**
NUCLEATION, GROWTH AND COARSENING OF COLLOIDAL AND DIBLOCK COPOLYMER CRYSTALS. Zhengdong Cheng, J.C. Ruiz, M. Megens, A.D. Hollingsworth, C. Harrison, W.B. Russel, R. Register and P.M. Chaikin, Dept. of Physics and Chemical Eng, Princeton Univ., Princeton, NJ.

We have been studying the evolution of patterns and order in a number of molecular and colloidal systems. In the case of diblock copolymer films which microphase separate into ordered hexagonal lattices or striped patterns (two dimensional smectics) we have used time lapse atomic force microscopy to study annealing as a function of time. We find that the correlation lengths are determined by the density of disclinations (essentially the distance between disclinations is the orientational correlation length). The dynamics of coarsening are surprisingly governed by the annihilation of quadrupole disclinations rather than simple pairs of opposite disclinations. In the case of colloidal samples, we have been using confocal microscopy to watch the dynamics of individual particles as well as to track the interface between liquid and solid phases. We observe mostly heterogeneous nucleation and growth, with volume fraction (undercooling) dependence consistent with diffusion limited growth based on the long time self diffusion in the liquid state.

**2:00 PM R4.2**
POLYMER TEMPLATES DESIGNED FOR THE PREDICTIVE CONTROL OF CRYSTAL NUCLEATION. Brigid R. Heywood, Susan J. Hill, School of Chemistry and Physics, Keele University, UNITED KINGDOM; W. James Feast, Joanna Megson, Department of Chemistry, University of Durham, UNITED KINGDOM.

It is well documented that the growth of crystals in aqueous solution can be regulated by the introduction of tailor-made additives into the growth medium. Such additives have historically included dopant metal ions, and polyelectrolyes of varying molecular weight and chemical functionality. More recently, it has been established that polymeric templates of specific molecular design can be used to control the nucleation of inorganic crystals. Indeed, systematic research has now established that specific structural features must be programmed into these templates if they are to control the crystallographic orientation and consequently the habit of the crystals which form. In this paper, recent work on the design of novel high fidelity, auto-assembling polymeric templates programmed to control the polymorphic form, crystallographic habit and end morphology of inorganic crystals will be reviewed. A range of polymer formats (e.g. single and mixed identity oligomers, one or two component motifs, molecular weight, chemical functionality) have been investigated as well as different modes of template presentation (i.e. degree of interfacial ordering, dynamics of assembly).

### 2:15 PM R4.3
BIO-INSPIRED ROUTES TO NOVEL POLYMER-BASED INORGANIC MATERIALS. B.R. Heywood, S Hill, G.P. Mitchell, K. Pitt, School of Chemistry & Physics, Keele University, Staffordshire, UNITED KINGDOM.

It is now well established that functionalised polymers will influence the growth of inorganic materials. However, a close examination of the literature reveals that in the majority of cases the action of the polymers has been to control polymorph selectivity, crystal morphology or particle size. Indeed, there are only a few reports which detail any evidence of a structural relationship between the crystals and the polymer phase and where such reports do exist the association of the polymers and the crystals is largely advantageous. The objective of the current study was to explore the design criteria for polymers which will function in a predictive manner to control nucleation and dictate the subsequent disposition of the crystallisation products to generate hierarchical inorganic/organic composites. In the initial stages of this project the focus has been upon the chemical identity of the polymers; the preferred design strategy is to use a scaffold polymer which can be subsequently decorated by the directed adsorption of active chemical moieties capable of directing crystal nucleation at specific loci. The activity of these novel polymers in crystallisation assays for calcium phosphate and calcium carbonate minerals will be discussed in this paper.

### 3:00 PM *R4.4
$B_2$ OR NOT $B_2$ ... ? Seth Fraden, Emmanuel Belamie, Joshua Bloustine, Tuhin Virmani, Complex Fluids Group, Department of Physics, Brandeis University, Waltham, MA.

We have measured the cloud point temperature (which signifies a liquid - liquid phase transition) in mixtures of the protein lysozyme and the polymer poly(ethylene) glycol (PEG) as a function of polymer concentration (0 - 200 mg/ml) and molecular weight (400 - 35,000). The solvent was 0.2M Sodium Phosphate, 0.5M Sodium Chloride, pH 6.2 and the protein concentration was 48 mg/ml lysozyme. Additionally we measured the second virial coefficient, $B_2$, with light scattering. Surprisingly, our two principle findings ran contrary to expectation. First, we anticipated that adding PEG would induce an effective attraction between the proteins. Instead, we found that $B_2$ of protein increased with added PEG, indicating that PEG introduces an effective repulsion between lysozyme. Second, we speculated that the protein/PEG mixture could be modeled as an effective one-component system. By this we mean that we could predict the phase behavior of the lysozyme/PEG mixture by modeling the suspension as being solely composed of protein that interacts with the effective potential determined by the PEG and experimentally characterized by the measured $B_2$. Theory predicts that there should be a correlation between $B_2$ and the cloud point (see for example, Haas and Drenth, J. Phys. Chem. B **102**, 4226 (1998)). However, we found that there was no correlation between $B_2$ and the cloud point because different cloud point temperatures were measured for the same value of $B_2$. In conclusion, we have shown that the depletion mechanism (Asakura and Oosawa, J. Polym. Sci. 33, {183} (1958)) is not applicable for PEG/lysozyme mixtures and that $B_2$ and the liquid - liquid phase transition are uncorrelated in these mixtures.

### 3:30 PM R4.5
A COMBINED EXPERIMENTAL & COMPUTATIONAL STUDY OF SOLVENT/CRYSTAL INTERACTIONS. A.L. Braybrook, B.R. Heywood, R.A. Jackson, P. Karatzas, Keele University, Staffs, UNITED KINGDOM.

Of the many strategies which exist for the production of crystals, crystallisation from aqueous media continues as one of the dominant methodologies. One of the questions which this raises is what effect does the solvent phase have upon the growth of the crystals and can

the solvent/crystal interactions be tailored to introduce a level of control over the morphology and habit of the resulting solids. In this study we have investigated the consequence of quantitatively varying the dielectric of the aqueous solvent by the controlled addition of an alternate polar solvent. Here we report the effect of sequentially doping a supersaturated solution of Copper acetate with propan-1-ol. Computational modelling of solvent effects upon the growth form of inorganic crystals has been employed to develop our understanding of the role of solvents in directing crystal growth as opposed to the specific effects of dopants and additives.

### 3:45 PM R4.6
UNDERSTANDING THE KINETICS OF PHASE STABILITY UNDER HYDROTHERMAL CONDITIONS IN PERIODIC SURFACTANT TEMPLATED SILICAS. Adam F. Gross, Van H. Le, and Bradley L. Kirsch, Sarah H. Tolbert, UCLA, Dept of Chemistry and Biochemistry, Los Angeles, CA.

Real time X-ray diffraction is used to examine the kinetics of phase transformations in periodic silica/surfactant composites. The structures of these surfactant templated silicas are controlled by the interplay between surfactant packing, charge density matching at the inorganic/organic interface, and the rigidity of the inorganic network. Understanding this interplay is important for the controlled production of periodic mesoporous silicas, which are formed by removing the surfactant from the inorganic/organic composite phase. In these experiments, we use hydrothermal conditions to drive a transformation from a hexagonal honeycomb nanoscale architecture to a layered lamellar phase of the composite material. Controlled variable pH is used to modify the framework rigidity and inorganic charge density through selective silica chemistry; the effect of these chemical changes on the composite phase stability is then monitored through in-situ small angle X-ray diffraction. The results of kinetic modeling indicate that the transformation pathways available in these composites are a strong function of the framework rigidity, with stable intermediate phases occurring when silica flexibility is increased. The effect of framework rigidity on composite metastability is determined by measuring activation energies for this rearrangement process. In-situ condensation of the silica framework is shown to dramatically increase the barrier for rearrangement. Finally, a detailed examination of the observed phases allows us to separate the role of surfactant volume and surfactant curvature in driving these structural rearrangements. The overall result is a fairly complete picture of how atomic scale inorganic chemistry and molecular level organic packing interplay in a dynamic way to control nanometer scale periodicity in surfactant templated silicas.

### 4:00 PM *R4.7
TWO-AND-THREE DIMENSIONAL DNA-DRIVEN ASSEMBLY OF COLLOIDAL MATERIALS. Chad A. Mirkin, Northwestern University, Evanston, IL.

DNA is arguably the most powerful, yet underutilized, synthon available to the materials chemist. In this presentation, methods for forming two and three-dimensional crystalline arrays of nanoparticles from DNA will be described. Specifically, the ability to control the placement and orientation of nanoparticles with respect to one another within the context of both surface architectures and extended polymers will be described. The structure, properties, and applications of these novel materials will be presented.

SESSION R5: POSTER SESSION
Chairs: Peter G. Vekilov and Joanna Aizenberg
Wednesday Evening, April 18, 2001
8:00 PM
Salon 1-7 (Marriott)

### R5.1
A COMPARSION ZnO AND Zn(OH, S) NANO-PARTICLE THIN FILMS PREPARED BY COLLOIDAL AND NON-COLLOIDAL ROUTES. Sophie Gledhill, John Hutchison, Dept of Matls Sci, Oxford Univ, UNITED KINGDOM; Peter Dobson, Christian Kaufmann, Dept of Engr Sci, Oxford Univ, UNITED KINGDOM; Sven Neve, Hahn-Meitner Inst, Berlin, GERMANY.

ZnO and Zn(OH, S) nano-particle thin films were prepared by two routes based on ultrasonic spray pyrolysis. The first route involves spraying a colloidal suspension of either ZnO or Zn(OH, S) to form films of the respective colloids. The second route uses aqueous solutions for spray pyrolysis; zinc nitrate for ZnO film growth, and zinc acetate and thiourea for Zn(OH, S) film growth. The suspension of ZnO colloid was prepared from zinc nitrate and borane-di-methylamine complex. The Zn(OH, S) colloidal suspension was prepared from zinc acetate, thiourea, ammonia and hydrazine. The colloidal particles were analysed, by deposition on C-coated Cu grids,

using HREM (JEOL 4000). Remarkably regular hexagonally shaped colloidal crystals in a size range of 100-200nm as well as dispersed colloids of size 4-10nm were observed. By varying solution concentration, dispersion and preparation techniques it was possible to control the extent of colloid agglomeration and crystallisation. UV-visible spectroscopy was used to determine the colloid formation and growth. The solutions were then dispersed using an ultrasonic nebulizer, which formed aerosol droplets of $\approx 3\mu m$ in size. The droplets were then passed through a chamber under a controlled heated flow of nitrogen gas and impinged a substrate held at a range of temperatures between $100°C$ and $300°C$. The resulting films were inspected under the HREM and SEM (Hitachi S520) to determine the grain size and homogeneity of coverage. The deposited films were not only highly sensitive to the solutions used but also the parameters imposed by the deposition kit (such as carrier gas flow rate and temperature). The dependence of the colloidal growth conditions is discussed and the potential for using films consisting of these nanoparticles for photovoltaic applications is assessed.

## R5.2
SURFACE MORPHOLOGY, SELF-ASSEMBLED CUBIC STRUCTURE, AND GROWTH BEHAVIOR OF MICELLE-TEMPLATED MESOPOROUS SILICA THIN FILMS PREPARED BY SPIN-COATING. <u>Chi Won Ahn</u>, Joong Keun Park, Korea Advanced Institute of Science and Technology, Department of MS&E, Taejon, KOREA; Mahn Won Kim, Korea Advanced Institute of Science and Technology, Department of Physics, Taejon, KOREA.

A structure-controlled mesoporous thin film has attracted many interests because of its various applications in membranes, chemical sensors, and electronic and photonic devices. In this work, triblock copolymers (PEO-PPO-PEO) with a high HLB (hydrophile lyophile balance) number (> 20) have been used as a structure-directing agent. They made a micellar cubic structure in a solution. Tetraethoxysilane (TEOS) is used as a precursor of silica. We made a uniform thin film by a spinning technique. The thickness of thin films was controlled from 10 nm to 500nm by variation of micelle concentration in the solution. The Internal structure and surface morphology of the thickness-controlled thin film was investigated by atomic force microscope (AFM), transmission electron microscope (TEM), X-ray reflectivity, and ellipsometry techniques. From the surface morphology and thickness data, we can presume the growth mechanism of the micellar cubic structure in thin films. We will discuss about the influence of the micelle concentration on the growth behavior of thin films.

## R5.3
Abstract Withdrawn.

## R5.4
X-RAY SPECULAR BACKDIFFRACTION FROM THIN CRYSTALLINE LAYER DEPOSITED ON THE CRYSTALLINE SUBSTRATE. Petros H. Bezirganyan (Jr.), State Engineering Univ of Armenia, Dept of Computer Science, Yerevan, REPUBLIC OF ARMENIA; Hakob P. Bezirganyan, <u>Siranoush E. Bezirganyan</u>, Yerevan State Univ, Faculty of Physics, Yerevan, REPUBLIC OF ARMENIA; Hayk H. Bezirganyan (Jr.), Yerevan State Univ, Faculty of Applied Mathematics, Yerevan, REPUBLIC OF ARMENIA.

The X-ray investigations of the structure and morphology of thin films deposited on crystalline substrate, as well as the investigations of the interface between thin films and substrate or of the other ordered assemblies are very important e.g. in the areas of semiconductor growth and epitaxy (particularly for the characterisation of interface quality and non-destructive control during the growth process), and are of great interest, both in basic research and in materials science. The traditional methods of process control are not effective if the thickness of investigated structure is several nanometers. In general the sensitivity of growth process control can be improved by using the Grazing-Angle Incidence X-ray Diffraction (GIXD) technique. The Grazing-Angle Incidence X-ray Backdiffraction (GIXB) is considered e.g. in [1, 2], and is more sensitive to lattice spacing period and radiation wavelength than conventional GIXD technique. We consider in this paper theoretically the GIXB from the thin layer ordered only in one direction and deposited on the substrate, which is ordered in the same direction with the same value of the spacing period, but have a shift in the space phase. We assume that the ordered direction is parallel to vacuum-layer plane boundary (entrance surface). GIXB is considered to be dependent on the value of the phase shift between the space periods, as well as of the Bragg angle.
[1]. A.P. Bezirganyan, P.A. Bezirganyan, Phys. Stat. Sol. (a), 105, 345 (1988).
[2]. A.P. Bezirganyan, Phys. Stat. Sol. (a), 109, 101 (1988).

## R5.5
MORPHOLOGY OF PATTERNED InP AND GaP SURFACES PREPARED BY SPONTANEOUS ANISOTROPIC CHEMICAL ETCHING. Elena V. Basiuk, <u>Jose-Manuel Saniger-Blesa</u>, Jose-Guadalupe Baouelos, Centro de Instrumentos, Universidad Nacional Autonoma de Mexico, Mexico-City, MEXICO; Jaqueline Caoetas Ortega, Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Mexico-City, MEXICO.

One of the most important parameters in semiconductor technology is the one which describes disorders and defects of the crystal. Selective chemical etching is a widely used method to examine crystal disorders, defects, dislocations, etc. Anisotropic etching phenomenon is used for the preparation of textured surfaces in the technology of semiconductor photoelectric and optical devices, such as solar cells, diffraction gratings, and laser diodes. The use of InP and GaP-based materials is expected to appear more advantageous for the above purposes, and the development of anisotropic etching techniques is now of particular interest. V-groove shaped and mesa-shaped substrates are a subject of intensive research in creating new semiconductor structures overgrowth to design and manufacture novel magnetic-field sensors. In the present paper we report on a spontaneous anisotropic etching of InP(100), InP(111) and GaP(100) surfaces in acidic etchants giving rise to different surface microreliefs (asterisk- and parquet-like, grooves, etc.) without the use of masking, photochemical and photoelectrochemical techniques. Morphology of the microrelief surfaces, as studied by SEM and AFM, and the etching kinetics is discussed. Estimation of the activation energy demonstrates that the etching with microrelief formation occurs in the kinetic region. The most interesting InP microrelief is the one two-dimensional groove-shaped, which might be suitable to produce antireflection surfaces for solar cells. The conditions have been optimized to form this microrelief with a given period within 1.8-3.7 mkm. Morphology of different textured GaP surfaces is also discussed.

## R5.6
PECULIARITIES OF POSITRON ANNIHILATION WITH ELECTRONS IN THE VICINITY OF NANOVOIDS IN AMORPHOUS AND CRYSTALLINE TRIGLYCERIDES. Ivan S. Gulyi, <u>Tamara A. Rashevskaya</u>, Ukrainian State Univ of Food Technologies, Kiev, Ukraine; Mikhail M. Nishchenko, Stanislaw P. Likhtorovich, Kiev, UKRAINE.

The presence of nanovoids in the structure of fatty-acid triglycerides was confirmed by means of the positron annihilation spectroscopy. The nanovoids are formed between closely packed hydrocarbon moieties of fatty acids at the boundaries of monomolecular layers. The lengths of such quasi-onedimensional nanovoids are constrained by the terminating methyl groups and their mean radius depends on transverse distances between the molecules and the lattice type. The nanovoids radius varies in the course of the crystalline lattice ordering and during the structural relaxation of an amorphous phase. The influence of these processes on the probability of positronium annihilation within nanovoids and their radii was studied in case of high melting triglycerides. Triglyceride samples were prepared using fractional crystallization of the milkfat solution in acetone at $20°C$ (1st fraction) and $13°C$ (2nd fraction). Positron annihilation with electrons in the vicinity of nanovoids is shown to occur from bound electron-positron state (positronium atom, Ps) and probability S of this process is linearly decreasing with increasing nanovoid radius, r. r varies in the ranges of 0.25 - 0.53 nm and 0.20 - 0.36 nm for the 1st and for the 2nd fraction, respectively. Extrapolation of direct line S = f(r) to the intercept with abscissa provides the critical radius, R, of the nanovoid to the interior of which an electron can tunnel with subsequent formation of Ps. R is equal to $0.81 \pm 0.02$ nm for the 1st fraction and $0.66 \pm 0.02$ nm for the 2nd one. Amorphization does not affect the value of R but leads to the decrease in the slope dS/dr by 17% on average. It means that electron binding to the atoms in triglyceride molecules packed in amorphous structure is stronger compared to that in the crystalline state. On the basis of these results, the electron work function for the interior surface of nanovoid is suggested to be lower in crystalline triglycerides compared with amorphous ones.

## R5.7
SURFACE CHARACTERIZATION OF CHOLESTEROL MONOHYDRATE CRYSTALS BY CHEMICAL FORCE MICROSCOPY. <u>Richard S. Abendan</u>, Jennifer A. Swift, Georgetown University, Department of Chemistry, Washington, DC.

Knowledge of the molecular level structure of crystal surfaces is an important factor in understanding the growth processes of crystalline organic materials. The composition and distribution of functional groups on the terminal (001) surface of cholesterol monohydrate single crystals has been investigated with atomic force microscopy (AFM). Using AFM techniques, we have investigated the surface structure under a variety of solution conditions using both conventional tips and tips chemically modified with self-assembled monolayers. By exploiting variations in the measured adhesive and frictional forces

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between the functionalized tip and surface, the molecular composition of the surface can be elucidated.

## R5.8
MODELING PREDICTIONS OF THE MORPHOLOGY OF ZINC OXIDE IN AQUEOUS SALT SOLUTIONS. Nelson S. Bell, R. Cygan and J. Voigt, Sandia National Laboratories, Albuquerque, NM.

Soft solution processing to form novel material structures requires an understanding of the growth forms of individual crystals. In this study, molecular dynamics calculations were performed to predict the equilibrium habit of zinc oxide crystals. Calculations were performed simulating aqueous and salt environments to correlate with experimental forms produced under a variety of synthesis conditions. Surface interactions are examined regarding synthesis salts and specific adsorbates. This investigation contributes to understanding the mechanism of forming nanostructured zinc oxide films.
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-ACO4-94AL85000.

## R5.9
EPITAXIAL GROWTH OF CHOLESTEROL CRYSTALS ON MINERAL SUBSTRATES. M. Crina Frincu, Jennifer A. Swift, Georgetown University, Department of Chemistry, Washington, DC.

Epitaxial relationships between the surfaces of inorganic and bio-organic crystals can be an important factor in crystal nucleation and growth processes in a variety of biological environments. The deposition of cholesterol monohydrate crystals in vivo is an undesirable crystallization process that leads to a variety of human diseases including the formation of gallstones. A modeling algorithm that deals with simple geometric lattice matching (EpiCalc) has been used to identify mineral surfaces that may serve as epitaxial substrates for the nucleation and growth of cholesterol monohydrate crystals. Experimentally, cholesterol crystal growth has been monitored in vitro through model nucleation studies and by in situ Atomic Force Microscopy. Elucidation of these epitaxial factors may help in our general understanding of pathogenic crystallization events.

## R5.10
CRYSTAL NUCLEATION AND GROWTH IN GEL MEDIA. Rositza I. Petrova, Jennifer A. Swift, Georgetown University, Department of Chemistry, Washington, DC.

Developing a molecular-scale understanding of crystal nucleation and growth processes is of fundamental importance for materials ranging from metals to small molecules to macromolecules. While gel matrices have been successfully used as a growth medium for many inorganic and macromolecular crystals for many years, little is known about the molecular-level interactions between the crystal and gel during the crystallization process. We are currently attempting to elucidate the specific physico-chemical role(s) of the gel during crystal nucleation and growth. Our preliminary systematic studies of simple enantiomorphous salt ($NaClO_3$ and $NaBrO_3$) growth in different chiral hydrogel environments have generated novel data related to nucleation rates, morphology and long-range ordering in crystalline solids grown under such conditions.

## R5.11
SURFACE STRUCTURES OF WET AND DRY Fe-OXIDE AND Fe-HYDROXIDE. Huifang Xu, TEM Laboratory, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM.

Surface structure and chemistry of Fe-oxides and Fe-hydroxides take important roles in regulating trace metals in groundwater and interactions between minerals and bacteria in groundwater. The structure and chemistry of the surfaces may be different in dry and aqueous environments. Surfaces of alpha-$Fe_2O_3$ and beta-FeOOH colloids (nanocrystals) were investigated by using high-resolution TEM and associated techniques. The surface of dry alpha-$Fe_2O_3$ (annealed at high temperature) is basically same as its bulk structure. However, the surface of the alpha-$Fe_2O_3$ in aqueous solution displays a layer of amorphous coating. It is inferred that the coating layer (with thickness of 2 to 3nm) is amorphous Fe(III)-hydroxide. Therefore, sorption of metal ions on the alpha-$Fe_2O_3$ in aqueous environment is controlled by the amorphous coating layer, not crystalline $Fe_2O_3$. Plutonium sorbed on the $Fe_2O_3$ is incorporated into the amorphous Fe-hydroxide layer. However, plutonium "sorbed" on surface of amorphous silica is in the form of nanocrystals of Pu-(hydr)oxide on surface. The surface of beta-FeOOH is a poor crystalline layer. The crystallinity of the layer is between crystalline beta-FeOOH and amorphous Fe-hydroxide. The thickness of the layer is corresponding to the thickness of a Fe-O(OH) octahedral layer.

## R5.12
MELTING OF A QUASI-TWO-DIMENSIONAL METALLIC SYSTEM. Dmitriy S. Chekmarev, David W. Oxtoby, Stuart A. Rice, The James Franck Inst, The Univ of Chicago, Chicago, IL.

We analyze the melting of a quasi-two-dimensional metallic system using the results of a series of Monte Carlo simulations of an array of $Pb$ atoms. The system was chosen to model the melting behavior observed for the monolayer of $Pb$ that segregates in the liquid-vapor interface of a dilute $Pb$ in $Ga$ alloy [PNAS **96**, 13009 (1999)]. Our calculations employed a realistic pair interaction potential between lead pseudoatoms, one that is known to describe accurately the properties of the three-dimensional metal near the melting point. Our results reveal that in the quasi-two-dimensional $Pb$ system melting is a two-stage process which proceeds through formation of a stable intermediate hexatic phase, in agreement with the prediction of the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory. Both the solid-to-hexatic and the hexatic-to-liquid transitions are found to be first order in our simulations.

SESSION R6: PATTERN FORMATION
Chair: James J. De Yoreo
Thursday Morning, April 19, 2001
Salon 13 (Marriott)

**8:30 AM \*R6.1**
ROLE OF LENGTH SCALES IN PATTERN FORMATION DURING CRYSTAL GROWTH. Robert F. Sekerka, Zhiqiang Bi, Carnegie Mellon University, Physics and Mathematics, Pittsburgh, PA.

Crystal growth morphologies are the result of phenomena that take place on many length scales. These scales range from the atomic scale (Angstoms) through the mesoscopic scale (nanometers through micrometers) to the macroscale (millimeters and larger). An understanding of facetting, crystal habits, cellular growth and dendritic growth involves integration of information from all of these length scales, but current theory is unable to incorporate all of these scales simultaneously in a tractable manner. The classical approach has been to use information of the atomic scale to help to achieve a phenomenological understanding on the mesoscopic scale, examples being the concepts of interfacial free energies (surface tension) and kinetic laws that relate local crystal growth rates to local departures from thermodynamic equilibrium. These mesoscopic phenomena then provide boundary conditions for the solution of transport equations that must be solved on the macroscale. This classical approach has been quite successful, and has led, for example, to the theory of morphological stability. A more recent approach to incorporate phenomena on the mesoscopic and macroscopic length scales is phase field theory, according to which an auxiliary variable, the phase field (an order parameter) is introduced. The phase field varies continuously but varies rapidly in the vicinity of diffuse interfaces, which replace the sharp interfaces of the classical approach. By means of an entropy functional, which depends on the gradients of the phase field in addition to its value, the dynamical equations incorporate automatically the boundary conditions on the mesoscopic scale. Solving these "stiff" dynamical equations numerically, however, presents significant computational challenges. Recent results of cellular growth morphologies obtained by solving the phase field model will be presented and discussed.

**9:00 AM R6.2**
A NEW DELTA-FUNCTION MODEL OF FACETS. Tinghui Xin, Harris Wong, Louisiana State Univ, Dept of Mechanical Engineering, Baton Rouge, LA.

Facet formation and evolution are important in many processes, such as crystal growth, solidification, and grain growth during annealing. Current models of facets usually choose a particular form of anisotropic surface energy and then compute the interfacial profile. This approach works fine if the surface energy anisotropy is weak and the interfacial profile is smooth. However, when the anisotropy increases, the surface profile starts to intercept itself. This non-uniqueness makes it difficult to model strong anisotropy in interfacial evolution. We have developed a new scalar model of facets that eliminates the non-uniqueness of interfacial profile. Planar facets and sharp corners can be easily handled by the new model. In addition, it can be incorporated directly into different theories of interfacial evolution. The new model also allows a simple proof of Wulff's theorem. In this talk, we will present the new model and discuss its applications.

**9:15 AM R6.3**
INVESTIGATION OF (2x1) $SrTiO_3(001)$ SURFACE RE-CONSTRUCTION USING ELECTRON DIFFRACTION.

<u>Natasha Erdman</u>, Laurence D. Marks, Institute for Environmental Catalysis, Department of MS&E, Northwestern University, Evanston, IL.

Mixed metal oxides with a perovskite structure $ABO_3$ (where A is a group I or II cation and B is a transition metal) play an important role in photocatalysis [1] and epitaxial growth of superconducting thin films [2] and have been a focus of many theoretical and experimental studies. The structure of $SrTiO_3$ can be described as a close-packed lattice of oxygen with Ti in octahedral interstitial sites and 12-fold coordinated Sr. If one considers an ideal bulk-terminated (001) surface, two configurations are possible: (a) Ti and O termination with a ratio of 1:2 (essentially $TiO_2$ stoichiometry); or (b) Sr and O termination with a ratio of 1:1 (essentially SrO). However, considering the fact that under various conditions (atmosphere, pressure and temperature) transition metal (e.g. Ti) oxides can exhibit different valences and coordination numbers, the picture becomes rather complicated. In this paper we present the results obtained using electron diffraction and Direct Methods in order to solve (2x1) $SrTiO_3$ (001) surface structure. The (2x1) $SrTiO_3$ surface reconstruction was obtained by annealing the sample at 950-1050C with a constant flow of oxygen. Off zone-axis electron diffraction patterns and bright-field images were obtained using the UHV-H9000 Hitachi transmission electron microscope operated at 300kV. A plausible solution in terms of the scattering potential map was obtained using Direct Methods for both p2mg and pm symmetries. Scattering potential maps obtained through the diffraction intensity data suggest that a possible solution to the (2x1) surface reconstruction might be the formation of a $TiO_2$ phase on the surface of $SrTiO_3$ (001) through a crystallographic shearing mechanism. Similar mechanism has been suggested previously [3,4], however the exact nature of the surface formation (i.e. what is the exact displacement of the atoms from their bulk positions, whether some desorption/adsorption of oxygen occurs) is still to be determined.

References:
1. J.G. Mavroides, J.A. Kafalas, and D.F. Kolesar, Appl. Phys. Lett. 28 (1976) 241.
2. P. Chaudhari, R.H. Koch, R.B. Laibowitz, T.R. McGuire, and R.J. Gambino, Phys. Rev. Lett. 58 (1987) 2687.
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4. K. Szot, W. Speier, Phys. Rev. B. 60 (1999) 5909.

### 9:30 AM <u>R6.4</u>
ANOMALOUS GROWTH OF POLAR ORGANIC MATERIALS - A Re-APPRAISAL. <u>John N. Sherwood</u>, University of Strathclyde, Department of Pure and Applied Chemistry, Glasgow, Scotland, UNITED KINGDOM.

Acentric organic crystals which comprise polar molecules show a considerable anisotropy of growth which leads to the characteristic polar morphology of these materials. Basically this asymmetry results from the difference in growth rates of the crystal faces which lie normal or are angled to the polar axis. This effect reaches its extreme in highly polar materials which show zero growth in one polar direction and rapid unstable growth in the other. As the supersaturation is decreased in an attempt to improve the perfection of the latter, the crystal also ceases to grow in this direction although some other faces continue to develop. Similarly, increases in supersaturation to encourage the former to grow, results in the nucleation of 180°; twins on this surface which then grow away rapidly. This characteristic behaviour is usually ascribed to the absorption of solvent molecules on the polar surfaces. Recent studies show that the same behaviour results when the materials are grown from the vapour phase. Thus the anomalous growth which gives rise to the polar morphology is a consequence of the structural properties of the solid and the interface rather than the result of impurity/solvent inhibition of growth. Structural analysis confirms this relationship and suggests that the controlling factor is the surface free energy as defined by the charged nature of the exposed surfaces. The basic observations which led us to these conclusions will be described together with the results of structural and theoretical modelling studies of the surfaces.

### 10:15 AM <u>*R6.5</u>
COMPLEX PATTERN FORMATION IN SIMPLE DENDRITIC SYSTEMS. <u>M.E. Glicksman</u>, A.O. Lupulescu, J.E. Frei and C. Giummarra, Rensselaer Polytechnic Institute, MS&E Department, Troy, NY; M.B. Koss, College of the Holy Cross, Department of Physics, Worcester, MA; J.C. LaCombe, University of Nevada, Mackay School of Mines, Reno, NV.

Dendritic growth is a fundamental pattern-forming phenomenon occurring in crystallization. Dendrites are the ubiquitous mode of crystal growth in freezing alloys, because they exhibit morphologies most suited to heat and mass transfer at mesoscopic scales. Dendritic patterns develop at the smallest microstructural scales of interest in alloy ingots and castings. Dendritic growth in pure materials provides one of the simplest non-trivial examples of non-linear pattern formation. Specifically, dendritic growth in a pure melt at constant pressure evolves under a single control parameter: viz., the supercooling. The key results from a series of microgravity space flights, called the Isothermal Dendritic Growth Experiment (IDGE), will be discussed. Specifically, the scaling laws for dendritic pattern formation in ultra-pure succinonitrile (SCN) and pivalic acid (PVA) were found to follow relationships derived from theories of diffusion transport and morphological stability. Transport theory provides a definitive prediction between the growth Peclet number (the steady-state product of dendritic growth speed and tip radius scaled to the diffusivity) and the dimensionless supercooling (thermal supercooling scaled to the characteristic temperature of the material). The IDGE uniquely proved that diffusion transport theory predicted the correct relationship. Arguments based on morphological stability suggest independently that a key scaling law for steady-state dendritic growth is the product of the growth speed and the square of the crystal radius remains a constant, independent of the supercooling. IDGE data were used to test this prediction, and demonstrate its robustness. Finally, during the last flight of the IDGE, experimental evidence based on video data suggested that characteristic frequencies, or limit cycles, might account for the observed growth dynamics. These data and their interpretation will be presented.

### 10:45 AM <u>R6.6</u>
Abstract Withdrawn.

### 11:00 AM <u>R6.7</u>
PHASE-FIELD SIMULATIONS OF NON-ISOTHERMAL BINARY ALLOY SOLIDIFICATION. <u>Irina Loginova</u>, Gustav Amberg, KTH, Dept of Mechanics, Stockholm, SWEDEN; John Ågren, KTH, Dept of MS&E, Stockholm, SWEDEN.

A phase-field method for two-dimensional simulations of binary alloy solidification is studied. Phase-field equations that involve both temperature and solute redistribution are formulated. The equations are solved using FEM with triangular elements on unstructured meshes, which are adapted to the solution. Dendritic growth into supersaturated melt is simulated for two temperature regimes: (a) the temperature is prescribed on the boundary of the computational domain and (b) the heat is extracted through the domain boundary at a constant rate. In the former regime the solute redistribution is compared with the one given by an isothermal model. In the latter case the influence of the size of the computational domain and of the heat extraction rate on dendritic structure is investigated. It is shown that at high cooling rate the supersaturation is replaced by thermal undercooling, as the driving force for growth.

### 11:15 AM <u>R6.8</u>
INTERFACE ENERGY ANISOTROPY IN Al-4.0 wt% Cu ALLOY. <u>Shan Liu</u>, Ralph E. Napolitano, Rohit K. Trivedi, Ames Laboratory-USDOE, Iowa State University, Ames, IA.

The anisotropy in interface properties plays a crucial role in pattern formation and microstructure selection. Specifically, the interface energy anisotropy dictates the dendrite growth direction and tip morphology and determines the length scales of cellular and dendritic microstructures in solidification process. An experimental technique was developed to measure the anisotropy in the solid/liquid interface energy from the equilibrium shape of fine liquid droplets entrained in the solid. The anisotropy value was obtained from the two-dimensional shape of the cross-section of the sample in the (001) plane of the solid. A four-fold symmetry of the droplet cross-section was clearly observed and the anisotropy parameter was found to be ~1%.

### 11:30 AM <u>*R6.9</u>
MULTIPHASES AND INTERFACES IN THE 3-D ASSEMBLY OF PERIODIC STRUCTURES. <u>Galen Stucky</u>, Jennifer Cha, Peter Albius-Henning, Ryan Hayward, Karen Frindell, Larken Euliss, Brad Chmelka, Univ of California, Dept of Chemistry, Matls Dept and Dept of Chemical Engr, Santa Barbara, CA.

The use of kinetic control, competing non-equilibria and equilibria phenomena, multiphase media and the dynamics of assembly that takes place at organic/inorganic interfaces are powerful tools for the synthesis of 3-d hierarchically structured composite materials that have patterned structural and physical properties from the nanometer to the micron scale. Domain separation can be defined by hydrophobic/ hydrophilic, polar/nonpolar, and even by electrolyte concentration. Multiphase media combined with block copolymers, block polypeptides or protein molecules provide a very useful synthetic approach to the direct, single system synthesis of systems with multi-scale structural and functional properties. This talk will describe some of our recent efforts in this area.

SESSION R7: STRUCTURE AND MORPHOLOGY
Chair: Robert F. Sekerka
Thursday Afternoon, April 19, 2001
Salon 12/13 (Marriott)

**1:30 PM *R7.1**
PHYSICAL MICROSTRUCTURE OF NANOSCALE BACTERIAL
MAGNETITES. Molly R. McCartney, ASU, Center for Solid State
Science, Tempe, AZ; Peter R. Buseck, ASU, Depts of Geology and
Chemistry/Biochemistry, Tempe, AZ; Richard B. Frankel, Cal Poly
State Univ, Dept of Physics, San Luis Obispo, CA.

Magnetite crystals in magnetotactic bacteria are typically organized
in chains and have specific crystal morphologies within each cell type.
In some bacterial strains, the crystals are cuboctahedra, whereas in
other bacterial strains the crystals are elongated along a [111] axis
parallel to the chain direction (1).The elongated magnetite crystals
are typically ca. 40 to 100 nm long, within the permanent,
single-magnetic-domain size range. Here we report on studies of the
micromagnetic structure and crystal morphology of magnetosome
magnetite crystals in magnetotactic bacteria by off-axis electron
holography (EH) (2), high-resolution transmission electron microscopy
(HRTEM), and electron diffraction (ED). Idealized habits of bacterial
magnetite can be inferred from HRTEM and ED. In strains with
elongated crystals, the idealized habits consist of combinations of
{100}, {111} and {110} forms, with pseudo-hexagonal prisms of six
elongated (110) faces, (111) face caps, and smaller corner faces. This
morphology is consistent with the electronic contribution to the EH
phase deviations in [110] and [112] zones perpendicular to the [111]
elongation axis, which show a (110) face (flat top) perpendicular to
the beam, and an intersection between adjacent (110) faces (tent-top)
perpendicular to the beam, respectively (3) . Thus EH can be used to
confirm the morphology of nanoscale bacterial magnetites derived
from two-dimensional projections.
RBF and PRB wish to acknowledge support from the National
Science Foundation.
1. B. Devouard et al. (1998). American Mineralogist 83: 1387-1399.
2. R.E. Dunin-Borkowski et al. (1998). Science 282: 1868-1870.
3. M.R. McCartney et al. (2000). Acta Miner-Petr. Szeged 41B, 53-54.

**2:00 PM R7.2**
Abstract Withdrawn.

**2:15 PM *R7.3**
THE SOLID-LIQUID INTERFACE STRUCTURE OF GROWING
CRYSTALS. Elias Vlieg, Dept of Solid State Chemistry, University of
Nijmegen, THE NETHERLANDS.

In order to understand the growth mechanism of a crystal in detail,
one needs to know the atomic/molecular-scale structure at the
interface of the crystal with its mother phase. Two main experimental
techniques are available to obtain such knowledge: scanning-probe
microscopy (such as STM and AFM) and X-ray diffraction (using
synchrotron radiation). In this contribution our X-ray diffraction
results will be emphasised. In general both sides of the interface are
interesting, since they both may differ from the bulk phase. At the
crystalline side relaxations and reconstructions may occur as well as
adsorption of additives, while the liquid phase is expected to show
pre-ordering owing to the presence of the ordered crystal. All these
effects are important for a fundamental understanding of the growth
and the resulting morphology of crystals. Two types of systems will
be discussed. One is the ionic crystals KDP and ADP. We have found
similarities as well as differences in the surface structure of these
isomorphous crystals. Layering has been observed in the liquid in
direct contact with the crystal. Determining the structure of the
liquid near the interface is quite difficult for the KDP and ADP
systems, because the solution contains many components. For this
reason we have also investigated liquid Pb and Sn layers on Ge(111)
crystals as model solid-liquid interfaces. We find that the metal layers
are quasi-liquid, and show both solid-like and liquid-like behaviour.
As a function of temperature, the metal films behave more liquid and
less solid-like.

**3:15 PM *R7.4**
MONTE CARLO SIMULATION OF KDP CRYSTAL GROWTH
MORPHOLOGIES. J. Iwan D. Alexander, Department of Mechanical
and Aerospace Engineering, Case Western Reserve University,
Cleveland, OH; Kok Ngai Loo, Genometrix Incorporated, The
Woodlands, TX.

This paper outlines the application of a Monte Carlo model to
simulate the growth of Potassium Dihydrogen Phosphate (KDP). The
model is based on a simplified description of the crystal's tetragonal
structure. A structural model based on connected nets in KDP
crystals is developed and applied to their growth. Three types of
connected nets were identified: (010), (011) and a hydrogen bond or
h-bond "pseudo-net". These were used to formulate sticking and

surface diffusion probabilities for attachment to (010) surfaces based
on the nearest and next-nearest neighbor occupation condition of
surface sites. Similarly the (011) nets were used to formulate the
sticking and surface diffusion probability for the (011) pyramidal
growth surfaces. Finally, the h-bond "pseudo net" was used to modify
the probabilities for the (011) growth model to provide additional
anisotropy to the sticking and surface diffusion probability. The main
morphological feature observed on small length scales in AFM images
and on larger (micron) length scales in AFM and interferometric
microscopy images, is that growth hillocks tend be triangular and
possess three "faces" with distinctly different slopes. Through
systematic variation of the model parameters, the relationships
between these slopes and the prevailing supersaturations were
established. The linear relations obtained from the simulations agree
with trends observed in experiments. From these relationships, the
surface free energy was calculated and compares well with
experimentally obtained values. While it was found that the
structural model (TM3) proposed for growth on the (011) face
described the observed hillock shapes quite well, the hillock
orientation was incorrect. An extension of the model to account for
activated surface diffusion jumps was found to lead to the observed
hillock orientation. The approach developed shows that models based
on non-cubic lattices that can be used to investigate the details of
lattice structure effects on crystal growth morphologies.

**3:45 PM R7.5**
DIFFERENTIAL PHASE-SHIFTING INTERFEROMETRY FOR
STUDIES OF STEP PATTERN EVOLUTION DURING SOLUTION
GROWTH. N.A. Booth[1,3], P.G. Vekilov[1,2] and A.A. Chernov[3].
[1]Center for Microgravity and Materials Research, University of
Alabama in Huntsville, Huntsville, AL. [2]Department of Chemistry,
University of Alabama in Huntsville, Huntsville, AL. [3]Universities
Space Research Association, Marshal Space Flight Center, Huntsville,
AL.

For in-situ studies of the formation and evolution of step patterns in
solution growth, we have assembled an experimental setup based on
Michelson interferometry with the growing crystal surface as one of
the reflective surfaces. The crystallization part of the device allows
optical monitoring of a face of a crystal growing at temperature stable
within 0.05 degrees Celsius in a developed solution flow of controlled
direction and speed. The reference arm of the interferometer contains
a liquid-crystal element that allows controlled shifts of the phase of
the interferograms. We employ an image processing algorithm which
combines five images with a pi/2 phase difference between each pair of
images. The images are transferred to a computer by a camera
capable of capturing 60 frames per second. The device allows data
collection data regarding growth over a relatively large area
(approximately 4 sq. mm) in situ and in real time during growth. The
estimated dept resolution of the phase shifting interferometry is about
50 Angstrom. The lateral resolution, depending on the zoom ratio,
varies between 0.3 and 5 micrometers. The crystal chosen as a model
in this work is potassium dihydrogen phosphate (KDP). This optically
non-linear material is widely used in frequency doubling applications
and there have been a number of studies of the kinetics of KDP
crystallization that can serve as a benchmark for our investigations.
We present quantitative results on the onset, initial stages and
development of instabilities in moving step trains on vicinal crystal
surfaces at varying supersaturation, flow rate, and flow direction.
Comparisons with theory allow tests of the mechanism of step
bunching that have been put forth by theory.

**4:00 PM R7.6**
EFFECT OF IMPURITIES ON THE KINETICS OF STEPS ON
THE {101} AND {100} FACES OF KDP. Ana I. Villacampa, Terry
A. Land and James J. De Yoreo, Dept. of Chemistry and Materials
Science, Lawrence Livermore National Laboratory, Livermore, CA.

Our approach consits in studying the interaction between impurity
stoppers($Fe^{3+}$ and $Al^{3+}$) with a moving step in KDP crystal growth
by direct observation with AFM on the prismatic {100} and pyramidal
{101} faces. The growth experiments in situ are performed with a
extremely sensitive control of the supersaturation, following the step
motion and morphology as the supersaturation is changed. Compared
with the results (Land et al.) observed with $Fe^{3+}$ in the {100} face,
significant differences were noted in the shape and in the height of the
steps performing experiments with 500, 1000 and 1500 ppb of $Al^{3+}$.
The appearance of supersteps (macrosteps formed by thousands of
steps) in the presence of $Al^{3+}$ has been observed. Also the dead zone
is different that in the presence of $Fe^{3+}$. We have followed the
behaviour of steps on the {101} face and we correlate the density of
pinning sites with the interaction of impurity stoppers in the face.
Terry A. Land, Tracie L. Martin, Sergey Potapenko, G. Tayhas
Palmore, James J. De Yoreo, Nature, vol 399, pp. 442-445, (1999).
This work was performed under the auspices of the U.S. Department
of Energy at Lawrence Livermore National Laboratory under contract
number W-7405-ENG-48.

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**4:15 PM R7.7**
MORPHOLOGICAL AND DYNAMICAL CHANGES DURING
INTERACTION OF SILICON WITH GOLD, ALUMINUM SILVER
AND COPPER. Boris Bokhonov, Mikhail Korchagin, Institute of
Solid State Chemistry, Siberian Branch, Russian Academy of Sciences,
Novosibirsk, RUSSIA.

The in situ electron microscopic investigations of the formation of
eutectic alloys in the systems: amorphous Si / particle Au (Al, Ag,
Cu) showed that the formation of eutectics is preceded by metal
diffusion into amorphous silicon with the formation of metastable
amorphous metal silicide. Supersaturation and decomposition of the
metastable amorphous metal silicide leads to the evolution of
polycrystal silicon. For the systems crystalline (100)Si / particle Au
(Ag, Cu), an oriented formation of the liquid eutectic alloy is
observed. The reaction front formed during heating between liquid
eutectic alloy and single-crystal silicon had a strict orientation
relationship to the crystallographic axes of single crystal (100)Si. The
direction of front movement was strictly coincident with the directions
of the type [100]Si. The growth of the eutectic melt during the
annealing of the system crystalline (100)Si / particle Al takes place
isotropically. The crystallization of liquid eutectic alloy leads to
topotaxial evolution of gold (copper or silver) silicide islands at the
interface: crystal eutectics-single crystal silicon when, and the
formation of dislocation net near the interface.

**4:30 PM *R7.8**
IN-SITU MASS DIFFUSIVITY TECHNIQUE. R. Michael Banish,
Lyle B. Jalbert, Center for Microgravity and Materials Research,
University of Alabama-Huntsville, Huntsville AL; J. Iwan D.
Alexander, Department of Mechanical and Aerospace Engineering,
Case Western Reserve University, Cleveland, OH.

We have developed a technique for the measurement of diffusivities in
liquids over a wide temperature range. A radiotracer, initially located
at one end of the cylindrical diffusion sample, is used as the diffusant.
The sample is positioned in a concentric isothermal radiation shield
with collimation bores located at defined positions along its axis. The
intensity of the radiation emitted through the collimators is measured
vs. time with solid state detectors and associated energy
discrimination electronics. Diffusivities are calculated from the signal
difference between pairs of collimation bores. Self-diffusivities
obtained with In/In114m in space and on Earth illustrate the high
precision obtainable with this technique. The In/In114m space data
were close to the ground results, however, the data scatter was much
less. By employing a tracer that emits photons of different energy, and
thus, different self-absorption, transport in the bulk of the sample can
be distinguished from that in the proximity of the wall. No difference
was found. Because of the mathematical algorithm used in this
technique the diffusivity at several temperatures can be measured
utilizing a single sample. In support of this work 2-D numerical
modeling of the effect of various blockages on the concentration profile
and the resulting apparent diffusivity were conducted. For the
methodology that we use very little effect was seen except in the case
of extreme blockages. These results have been experimentally verified
(using the above two measurement location methodology) with
In/In114m diffusion studies. The resulting diffusivity of samples run
with blockages of greater than 50% between the radiotracer and host
sections and "voids" of greater than 10% were essentially the same as
normally run samples. Terrestrial results for other liquid metals will
be presented.

SESSION R8: CONTROL OF THE NANOSCALE
Chair: Joanna Aizenberg
Friday Morning, April 20, 2001
Salon 12/13 (Marriott)

**8:30 AM *R8.1**
NANOSCALE ELECTROCHEMISTRY. Rolf Schuster, Viola
Kirchner, Laurent Cagnon, Gerhard Ertl, Fritz-Haber-Institut der
Max-Planck-Gesellschaft, Berlin, GERMANY; Philippe Allongue,
Physique des Liquides et Electrochimie, Paris, FRANCE.

Small structures of nanometer dimensions are mostly fabricated by
lithographic methods or by metal deposition under UHV conditions.
Recently also electrochemical methods became very promising,
because the number of steps involved in the fabrication might be
significantly reduced. However, the application of electrochemical
methods is usually hampered by the long range charging of the double
layer and the consequently weak spatial confinement of the reactions.
Recent methods to circumvent these constraints are reviewed. These
range from the controlled nucleation and growth of nm clusters up to
the electrochemical micromachining with submicrometer resolution.
Particular emphasis is put on the use of ultra-short voltage pulses of
only nanosecond duration to localize the consequent electrochemical

reactions. This method enables the direct three-dimensional
micromachining of materials like Cu, Co, stainless steel and Si with
sub-micrometer resolution.

**9:00 AM *R8.2**
PLACEMENT, CONTROL, AND ISOLATION OF MOLECULES
VIA DIRECTED ASSEMBLY. P.S. Weiss, Department of Chemistry,
The Pennsylvania State University, University Park, PA.

We manipulate and measure the properties of single, isolated
molecules and of bundles of molecules, selectively placed into
monolayer films. The structure of these films is determined by
controlling the defect type and density in the films in order to tune
their properties. We then process the films to insert single molecules,
to insert bundles of molecules, or to graft new molecular terraces onto
existing domains by using these defects to advantage. The inserted
molecules can function as molecular switches or serve as the anchor
points for polymerization. We also prepare films with well defined
interfaces between separated components so that insertion, deposition,
or reaction can be directed to these molecularly sharp boundaries. We
connect our scanning tunneling microscopy measurements to electron
transfer phenomena that are ubiquitous in such areas as biochemistry
and electrochemistry by separating the transconductance into
components arising from transport through the molecule vs. the
tunneling gap outside the film. We show how these components can be
measured independently. We switch the conductance states of
measured numbers of molecular switches using the electric field
applied by the scanning tunneling microscope. We demonstrate how
proximity can affect electronic structure, potentially limiting ultimate
device densities or providing new opportunities for coupling and
tuning devices or components.

**9:30 AM R8.3**
Abstract Withdrawn.

**10:15 AM *R8.4**
FORMATION AND MANIPULATION OF PROTEIN
STRUCTURES ON THE NANOSCALE. S.-T. Yau, A. Kaloyeros, J.
Castracane, University at Albany-SUNY, Albany Institute for
Materials, Albany, NY; B. Thomas, Marshall Space Flight Center,
University Space Research Association, Huntsville, AL; S. Weinkauf,
Technical University Munich, Department of Chemistry, Munich,
GERMANY; P. Vekilov, University of Alabama in Huntsville,
Department of Chemistry and Center for Microgravity and Materials
Research, Huntsville AL.

The attainability of nanoscale biomolecular architecture is becoming a
relevant issue in biotechnology. Structures composed of a small
number of biomolecules either in their natural environment or under
ambient conditions can be used in many applications. Various forms
of structures of a biomolecule under different conditions have to be
studied before architectural design and construction can be carried
out. In this talk, we present atomic force microscopy (AFM) studies
on the formation of nanoscale protein structures formed on solid
surfaces. AFM imaging was performed both in buffer solutions
(in-situ) and under ambient condition to observe the self-assembled
structures of several proteins. The observed structures include
two-dimensional (2D) crystals, one-dimensional (1D) chains, and
supramolecular clusters. Our in-situ imaging of three-dimensional
(3D) protein crystals allowed the first time visualization of the
evolution of single point defects. Two kinds of manipulation of the
protein structures have been performed using the AFM tip as a
mechanical tool. The AFM tip was used to cleave 2D structures into
fragments. The results suggest the mechanism of the formation of the
structures. When the cleaving action was applied to individual point
defects of a growing 3D crystal, it was found that defects could be
eliminated so that that regular lattice was restored. Also, the tip was
used to engrave a solid surface to generated patterns. Protein
molecules were selectively deposited into the patterns. The result
shows the feasibility of protein architecture on the nanoscale.

**10:45 AM R8.5**
NANOSTRUCTURING OF VICINAL Ag SURFACES INDUCED BY
CHEMISORPTION OF A LARGE ORGANIC MOLECULE: PTCDA
ON Ag(775) AND Ag(976). Stefan Schmitt, Eberhard Umbach, Univ
of Wuerzburg, Dept of Experimental Physics II, Wuerzburg,
GERMANY; Moritz Sokolowski, Univ of Bonn, Dept of Physical
Chemistry, Bonn, GERMANY.

PTCDA is a relatively large (0.9nm x 1.4nm), planar organic molecule
which can form large, highly ordered domains with commensurate
superstructures on noble metal surfaces. We have investigated the
interaction of PTCDA with stepped Ag(111) surfaces, namely a
nominally (775) and a (976)-oriented surface. The experiments were
performed using LEED and STM under UHV-conditions, as well as
AFM under ambient conditions. The two vicinal surfaces have equal
terrace widths (about one molecule wide), but different step

directions. In both cases PTCDA prefers adsorption at step sites. For submonolayer coverages the PTCDA molecules create Ag facets stabilized by densely-packed PTCDA superstructures between large step-depleted (111) (uncovered) terraces. PTCDA deposition on the Ag(775) surface at low temperatures and subsequent annealing create several facet types differing in slope and azimuthal orientation. Together with the step depleted (111) terraces some of them form a nearly perfect stripe pattern with a structural width of some tens of nanometers. AFM measurements reveal a hill-and-valley structure on a micrometer scale varying the local orientation of the substrate by several degrees. This roughness appears to be an irreversible effect after several sample preparation and cleaning cycles. The stripe-pattered domains depend on the local surface orientation; several distinct orientations are clearly preferred. For increasing sample temperature the different facets are successively removed. We find that the thermally most stable facet requires a local azimuthal misorientation of the surface of about 40 degrees, which corresponds to the (976) orientation. Indeed, on this particular surface only one facet dominates and creates a uniform stripe-pattern with a structural width of about 100 nm. We will present experimental results demonstrating a new self organization method for the preparation of well-ordered nanostructures including a discussion of the microscopic mechanism.

**11:00 AM <u>R8.6</u>**
Abstract Withdrawn.


SESSION R9: CRYSTAL-SOLUTION INTERFACES
Chair: Alexander J. Malkin
Friday Morning, April 20, 2001
Salon 12/13 (Marriott)

**11:15 AM <u>*R9.1</u>**
DYNAMICS, MORPHOLOGY AND ATOMIC STRUCTURES OF COPPER/ELECTROLYTE INTERFACES - AN IN-SITU STM STUDY. <u>Peter Broekmann</u>, Michael Wilms, Alexander Spaenig, Mihai Anastasescu, Britta Obliers, Wojciech Lisowski, Klaus Wandelt, Institute of Physical Chemistry, Bonn, GERMANY.

The phenomenon of specific anion adsorption on copper electrode surfaces has been investigated by use of high resolution in-situ STM and cyclic voltammetry. Specifically adsorbed anions are well known to strongly influence the properties of electrode surfaces. In many cases specifically adsorbed anions induce a drastic change not only of the atomic structures but also of the surface morphology and the surface dynamics. Strongly adsorbing anions like halogenides stabilize a new equilibrium shape of the electrode surface. In this scenario copper steps are preferentially aligned parallel to the close packed adsorbate rows rather than parallel to the main symmetry axes of the copper substrate. These reorganization processes are driven by the tendency to minimize the interface free energy in the presence of electrosorbed ions. To realize such a massive reorganization of the surface morphology a massive mass transport of electrode material is required. These structuring processes become possible because of an anion driven enhancement of the surface mobility. An alternative route to minimize the interface free energy is an anion induced reconstruction of the topmost substrate layer as known from the sulfate covered Cu(111) electrode surface. By means of selective imaging using certain combinations of tunneling parameters it is possible to image not only the adsorbate but also the underlying reconstructed substrate. These kinds of spectroscopic like STM experiments allow further insight concerning the absolute adsorption sites of these anions.

**11:45 AM <u>R9.2</u>**
NONLINEAR DYNAMICS OF GROWTH STEPS IN THE MIXED KINETICS-BULK TRANSPORT REGIME. <u>Peter G. Vekilov</u>, Siu-Tung Yau, Hong Lin, Olga Gliko, Department of Chemistry and Center for Microgravity and Materials Research, University of Alabama in Huntsville, Huntsville, AL.

Using atomic force microscopy and optical interferometry techniques during crystallization of the proteins ferritin, apoferritin, lysozyme, thaumatin and hemoglobin C, we found that that the local growth rates and step velocities and densities are not steady but fluctuate by several times their average values, even under steady external conditions. The step density variations indicate that these fluctuations occur through the formation and decay of step bunches. Based on scaling arguments and numerical simulations, we argue that the fluctuations are the response of the coupled (bulk) transport and kinetics (of interacting steps on the interface) to finite amplitude perturbations. In search of means to reduce and eliminate his unsteady behavior that may be detrimental to the crystals quality, we accelerated the bulk transport towards the interface by forced solution flow. We found that this results in lower fluctuation amplitudes. AFM

results on step bunching for ferritin and apoferritin indicate that the response of these transport-controlled systems to faster or slower bulk transport is opposite to that of lysozyme. We found that step bunching and kinetics fluctuations are suppressed if the relative weight of transport in the overall process control is higher. Our observations with all studied proteins indicate that the step bunching dynamics is controlled by the kinetic Peclet number, i.e., the relative weight of bulk transport and interface kinetics in the growth process. This number can be modified by either forced solution flow or suppression of buoyancy-driven convection, through growth under reduced gravity or in viscous media. Hence, our model provides a rationale for the choice of specific transport conditions to minimize unwanted instabilities [Chem. Rev. 100 (2000) 2061].

SESSION R10: BIOMINERALS AND ORGANICS
Chair: Brigid R. Heywood
Friday Afternoon, April 20, 2001
Salon 12/13 (Marriott)

**1:30 PM <u>*R10.1</u>**
INFLUENCE OF SURFACE SITES AND COMPLEXES ON METAL INCORPORATION INTO CALCITE. <u>Richard Reeder</u>, Evert Elzinga, SUNY Stony Brook, Dept of Geosciences, Stony Brook, NY.

Metal impurity incorporation at the (10.4) growth surface of calcite ($CaCO_3$) is strongly influenced by the availability and spatial distribution of structurally distinct surface sites. Reduced symmetry and constrained orientations of monolayer growth steps result in nonequivalent vicinal faces composing polygonized growth spirals over a wide range of growth conditions. Several studies have documented consistent trends of differential incorporation of both cation and anion impurities between nonequivalent vicinals, with subsequent formation of compositionally distinct vicinal subsectors. Explanations for the step-selective incorporation have focused on differences in the geometry among different kink sites. However, several exceptions to step-selective incorporation patterns on calcite (10.4) have been noted, including $Zn^{2+}$ and several tetrahedral metal-oxyanions. X-ray absorption fine-structure spectroscopy (XAFS) has been used to examine the local coordination of metal species sorbed at the calcite-water interface with the purpose of assessing its role in impurity incorporation. Zn K-edge XAFS spectra were collected for moist Zn-sorbed calcite pastes using fluorescence detection at the National Synchrotron Light Source, beamline X11A. Fitting results yield Zn-O distances and coordination numbers that are consistent with four oxygens, suggesting that $Zn^{2+}$ is sorbed on calcite as a tetrahedral surface complex. This contrasts with results for $Zn^{2+}$ incorporated into the calcite surface layers, where XAFS has shown octahedral coordination, characteristic of the host Ca, but with significant relaxation. Transition metals having a similar size as $Zn^{2+}$ (e.g., $Co^{2+}$) are expected to sorb as an octahedral complex. If that is the case, the $Zn^{2+}$ sorption complex may account for the anomalous incorporation behavior at calcite (10.4) surfaces. Parallel studies for metal oxyanions are underway. This finding implies that sorption preferences must also be considered, along with surface site geometry, as factors controlling impurity incorporation at mineral surfaces.

**2:00 PM <u>R10.2</u>**
MOLECULAR-SCALE MECHANISM FOR ALTERED CALCITE MORPHOLOGIES IN THE PRESENCE OF MAGNESIUM: IMPLICATIONS FOR IMPURITY MODIFICATION OF ANISOTROPIC MATERIALS. <u>Kevin Davis</u>, Patricia Dove, Virginia Polytechnic Institute and State University, Dept of Geological Sciences, Blacksburg, VA; James De Yoreo, Lawrence Livermore National Laboratory, Dept of Chemistry and Materials Science, Livermore, CA.

Magnesium is the principal modifier of calcite morphology in natural waters and is a key impurity in carbonate biominerals. However, a molecular-scale understanding of how magnesium determines calcite morphology has yet to be achieved due to a lack of microscopic observations. Here we use atomic force microscopy (AFM) to make molecular-scale observations of growth hillocks generated at dislocations on the cleavage surface of calcite. Growth of these polygonal hillocks generates two distinct pairs of crystallographically identical steps, denoted as 'acute' and 'obtuse', which differ in step-edge geometry and kink site structure due to differences in the orientation of the exposed carbonate groups. By monitoring the dynamics of these two different step-types in variable solution compositions, a plausible molecular-scale mechanism for altered calcite morphologies in the presence of magnesium was determined. In this study, we examined the effect of magnesium on calcite step-edge morphology. Magnesium was found to preferentially roughen the acute steps at all concentrations. With increasing magnesium concentration we observed a progressive rounding of the growth hillocks and

expression of new step directions due to a broadening of the acute/obtuse corners. Here we consider possible sources for these step-specific interactions. The smaller magnesium cations have previously been shown to preferentially incorporate into the more confined acute steps. Accordingly, it is possible that the new step directions are produced by stabilization of the acute/obtuse corners due to lattice mismatch at the boundary of the two different step-types. Increased expression of these new step directions should stabilize macroscopic facets that favor calcite morphologies that are elongated along the c-axis, which are known to occur in the presence of magnesium. This molecular-scale mechanism may explain certain macroscopic calcite morphologies observed in the presence of magnesium and may prove valuable in understanding the growth of other anisotropic materials.

### 2:15 PM R10.3
THE INFLUENCE OF PROTEIN MICROSTRUCTURE ON CALCIUM OXALATE MONOHYDRATE CRYSTALLIZATION.
Shouwu Guo, Michael D. Ward, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN; Jeffrey A Wesson, Department of Medicine, Nephrology Division, Medical College of Wisconsin and Department of Veterans Affairs Hospital, Milwaukee, WI.

Calcium oxalate monohydrate crystals are the principal component in kidney stones. The defense against stone formation is thought to be modification of calcium oxalate crystallization by proteins that are secreted into the urinary tract. These proteins are notably rich in acidic side chains, in particular aspartic acid and glutamic acid residues, which are thought to play a major role in protein crystal interactions. Previous experiments have shown that homopolymers of aspartic acid and glutamic acid cause dramatically different crystal morphologies during calcium oxalate crystallization. We have used real-time in situ atomic force microscopy to characterize the effects of these two model polypeptides on both growth and dissolution of calcium oxalate monohydrate (-101) surfaces by examination of the rates of pit formation (in dissolution, undersaturated aqueous media) and filling (in growth, supersaturated aqueous media) in a liquid cell. Each polypeptide inhibited both dissolution and growth at the crystal surface, with poly(aspartic acid) exhibiting an equivalent degree of inhibition at one-sixteenth the concentration of the glutamic acid polymer. Poly(aspartic acid), however, exhibited greater face-selectivity in growth and inhibition, selectively inhibiting growth and dissolution transverse to the fastest growing direction. The data suggest that poly(aspartic acid) binds preferentially to the (101) face during growth and dissolution.

### 3:00 PM *R10.4
AFM STUDIES OF VIRUS CRYSTALLIZATION.
Alexander J. Malkin and Alexander McPherson, Dept of Molecular Biology and Biochemistry, University of California, Irvine, CA.

In situ AFM revealed that growth of turnip yellow mosaic virus (TYMV) and cucumber mosaic virus (CMV) proceeded strictly by 2D nucleation. Capsomere structures of TYMV and CMV viruses were directly visualized. The molecular structure of the step edges were recorded and attachment rates of individual virions into the growth step were measured at different supersaturations. No detachment was observed even at equilibrium conditions. Step advancement proceeded through one-dimensional nucleation. Restructuring of the TYMV crystalline surface was observed. Studies of molecular dynamics on crystalline surfaces revealed adsorption of two types of virions and its aggregates on the crystalline surface. While one type of virion and their aggregates developed, as expected, into 2D nuclei, the other type of virion remained firmly attached to the crystalline surface with virtually no changes. This suggests that interactions of the latter type of virions with the underlying surface are probably non-crystallographic and can arise, for example, from minor modifications of their protein subunits. It was found that the (111) face of a CMV crystal is formed by domains. The domains are misoriented and often tilted, with a height differnce between them in the same growth layer in the range of 1-4 nm. Unit cell parameters within domains can differ as well. It was demonstrated that, due to weak interactions between growth layers all 2D nuclei which form on the (111) face are misoriented. Merging results in the formation of domains and a high degree of mosaicity. On the (100) face of CMV crystals, apparently weak interactions within the growth layer result in the formation of point defects upon consolidation of 2D nuclei. These observations could explain the poor diffraction properties of CMV crystals.

### 3:30 PM R10.5
HYDRODYNAMIC ATOMIC FORCE MICROSCOPY AND ITS APPLICATIONS TO CARBONATE MINERAL DISSOLUTION.
Steven R. Higgins, Lawrence H. Boram, Briana Greer, Carrick M. Eggleston, University of Wyoming, Department of Geology and Geophysics, Laramie, WY; Kevin G. Knauss, Lawrence Livermore National Laboratory, Geoscience and Environmental Technology Division, Livermore, CA; Barry A. Coles, Richard G. Compton, Oxford University, Physical and Theoretical Chemistry Laboratory, Oxford, UNITED KINGDOM.

One of the key problems that is difficult to address in many studies pertaining to dissolution and growth kinetics is the prediction of the near surface chemistry of the fluid phase. With very sluggish surface kinetics it is usually assumed that mass transport near the surface is not important. However, kinetic investigations by Scanning Probe Microscopy (SPM) necessarily require that the net flux at the surface is high enough for step motion to be observed over reasonable time scales. If the step kinetics are rapid enough to observe by SPM, then mass transport begins to be of concern with regard to its influence on the measured flux. Only recently has this problem been addressed quantitatively in SPM studies of heterogeneous kinetics by use of a precisely designed inlet jet(1). We will discuss this solution to the problem of controlled fluid transport in SPM fluid cells with special attention directed toward incorporation of the technology into the Hydrothermal Atomic Force Microscope(2). Our initial results for magnesium carbonate dissolution show that only under nearly stagnant fluid flow conditions does the problem of mass transport become important. However, results for calcium carbonate, whose heterogeneous rate constant for dissolution is 3-4 orders of magnitude higher than that of its magnesium counterpart, show that mass transport is non-negligible with regard to its contribution to the impedance under all but very high flow conditions. Heterogeneous rate constants for proposed macroscopic mechanisms will be examined in light of the corresponding SPM images.
References:
(1) Coles, B.A.; Compton, R.G.; Booth, J.; Hong, Q.; Sanders, G.H.W.J. Chem. Soc., Chem. Commun. 1997, 619-620.
(2) Higgins, S.R.; Eggleston, C.M.; Knauss, K.G.; Boro, C.O. Rev. Sci. Instrum. 1998, 69, 2994-2998.

### 3:45 PM R10.6
FORMATION OF A BURIED DENSITY GRATING ON THERMAL ERASURE OF AZOBENZENE POLYMER SURFACE GRATINGS.
Thomas M. Geue, Oliver Henneberg, Joerg Grenzer, Ullrich Pietsch, University of Potsdam, Institute of Physics, Potsdam, GERMANY; Almeria Natansohn, Queen's University, Department of Chemistry, Kingston, ON, CANADA; P. Rochon, Royal Military College, Department of Physics, Kingston, ON, CANADA.

The transformation of a lateral surface relief grating inscribed on a polymer film containing azobenzene moieties into a density grating of equal spacing buried under a smooth surface was found for the amorphous polymers poly(4-nitrophenyl)[4-[[2-(methacryloyloxy)-ethyl]ethylamino]phenyl]diazene

(pDR1M) and poly(2-chloro-4-nitrophenyl)[4-[[2-(acryloyloxy)-ethyl]ethylamino]phenyl]diazene (pDR13A) using a x-ray scattering experiment. We earlier reported [1] on a VIS diffraction experiment to follow the buried grating formation of pDR1M. Annealing the polymer samples, pre-inscribed with a surface grating, for several hours above the glass transition temperature creates a nearly sinusoidal lateral density difference up to about 10%. The new state is stable between room temperature and the decomposition temperature of the original polymer when the formation was performed under the influence of VIS light of 632 nm. Growth of ordered and/or liquid-crystalline aggregates is proposed as a most probable explanation for the process.
[1] U. Pietsch, Th. Geue, P. Rochon, A. Natansohn; MRS Spring Meeting 2000, EE3.9.

### 4:00 PM R10.7
URIC ACID CRYSTAL GROWTH MONITORED BY IN SITU ATOMIC FORCE MICROSCOPY. Ryan E. Sours, Jennifer A. Swift, Georgetown University, Department of Chemistry, Washington, DC.

Crystalline uric acid has been well established as one of the principle components of kidney stones and its sodium salt is responsible for gout, yet relatively little is known about the mechanism(s) of uric acid nucleation and growth at the molecular level. We have succeeded in growing polymorphic uric acid crystals by controlling solution pH, temperature, and supersaturation, and are currently investigating the molecular-level growth and dissolution of uric acid crystals in real time using in situ atomic force microscopy under various solution conditions. By monitoring the growth mechanism(s) on single crystal surfaces, we hope to gain a better fundamental understanding of the parameters affecting this important crystallization process.

### 4:15 PM R10.8
CONFORMATIONAL CHANGES OF ALPHA-HELICAL POLYPEPTIDES AT MINERAL INTERFACES. Michael J. Read, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA; Sandra L. Burkett, Dept of Chemistry, Amherst College, Amherst, MA.

The interface between the organic and inorganic components is a key determinant of biomineralization processes. The interactions between organic molecules such as proteins and peptides and inorganic building blocks give rise to the complex, ordered structures that are characteristic of biomineralized systems. An understanding of these interactions is critical for application to the bio-inspired synthesis of novel materials. In many of the systems studied previously, it is assumed that the arrangement of functional groups within the organic matrix is static during the mineralization process. The current investigation focuses on conformational changes that are induced in polypeptides at the interface with inorganic mineral substrates. Some of the ultimate goals of this approach include understanding interfacial interactions relevant to proteins in biomedical materials applications and exploiting this structural dynamism in the development of new synthetic composite materials.