SYMPOSIUM M

Morphology and Dynamics of Crystal Surfaces in Complex Molecular Systems

April 23 – 27, 2000

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* Invited paper

TUTORIAL

ST M: EXPERIMENTAL METHODS FOR INVESTIGATING CRYSTAL-FLUID INTERFACES
Sunday, April 23, 2000
9:00 a.m. - 4:00 p.m.
Golden Gate A2 (Marriott)

Molecular assembly and dynamics at crystal surfaces in complex molecular systems is of central importance in fields as diverse as geochemistry, crystal growth, structural biology, corrosion science, pharmaceutical production, and food science. In all of these areas, understanding surface morphology and dynamics requires consideration of multiple chemical species, molecular anisotropy, and the interface between the fluid and solid phases. This tutorial focuses on *in situ* experimental methods that provide information about the molecular structure, surface morphology and dynamics of crystal surfaces in contact with fluids. The tutorial will be comprised of three lectures covering Surface X-ray Diffraction and Reflectivity, Optical Interferometry, and Atomic Force Microscopy. Each lecture will cover the basic experimental approach including methods of sample preparation and fluid cell design. Important technical issues such as control over fluid flow and temperature will be discussed, and examples of applications to both inorganic and organic systems will be presented. Following the lectures, there will be an opportunity for hands-on experience with *in situ* atomic force microscopy on crystal surfaces.

Instructors:
Peter G. Vekilov, University of Alabama-Huntsville
Paul Fenter, Argonne National Labroratory
Christine Orme, Lawrence Livermore National Laboratory

SESSION M1: INORGANIC SYSTEMS–SURFACE MORPHOLOGY AND STEP KINETICS
Chairs: Peter G. Vekilov and James J. De Yoreo
Monday Morning, April 24, 2000
Golden Gate C2 (Marriott)

8:30 AM M1.1
FROM THE SOLID-FLUID INTERFACIAL STRUCTURE TO GENUINE MORPHOLOGY OF CRYSTALS. X.Y. Liu , Department of Physics, National University of Singapore, SINGAPORE.

The prediction of morphology of crystals has absorbed attention for more than 3 centuries. The subject becomes increasingly interesting due to its relevancy for industries such as pharmaceuticals, foods, materials, biomineralisation, etc. The morphology of crystals, which is determined by the kinetics of crystals, has been investigated both extensively and intensively for the last several decades, from the aspect of crystal surface structure. The main approach adopted is along the line of the so-called PBC or Hartman-Perdok theory. [1-2] Although the research has significantly advanced our knowledge on the surface structure of crystals in the vacuum environment, the prediction of the growth morphology of crystals in many cases is still distant from the genuine growth morphology of crystals. This is due to the lack of consideration of the growth kinetics and the effect of the fluid phase. Recently, we have successfully developed a completely new approach for the prediction of genuine growth morphology of crystals based on the growth kinetics. [3-9] This approach takes into account the effects of both solid and fluid, and focuses mainly on the structure of solid-fluid interfaces of complicated molecular systems. In this contribution, I will present some latest developments along this direction. This will include:
- the concepts of interfacial effective growth units and the surface activity of growth units;
- the calculation of the solid-fluid interfacial structure of complex molecular systems using the self consistent field theories and the solid-fluid interfacial structural analysis;
- the calculation of the entropic barrier of surface integration;
- the kinetic relations between the relative growth rate of internal and external controlling factors and the principles for the prediction of genuine growth morphology of crystals.
To demonstrate the principles, the formalisms are applied to predict the growth morphology of n $C_{24}H_{50}$ and n-$C_{21}H_{44}$ crystals grown from iso-octane and n-hexane solutions, together with other organic crystals. The results are confronted with experiments. Finally, the future trend along this direction will also be highlighted.
References:
1. P. Bennema, in *Handbook on Cryst. Growth*, edited by D.T.J. Hurle (North-Holland, Amsterdam, 1993) p.477.
2. P. Hartman, in *Morphology of Crystals, Part A*, edited by I.

Sunagawa, (Terra Sci., Tokyo, 1987) p.271.
3. X.Y. Liu and P. Bennema. *Phys.Rev.* B49, 765 (1994).
4. X.Y. Liu, E.S Boek, W.J. Briels and P. Bennema, *Nature* 374, 342-345 (1995).
5. X.Y. Liu, *J. Chem. Phys.* 102, 1373-1384 (1995).
6. X.Y. Liu, E.S Boek, W.J. Briels and P. Bennema, *J. Chem. Phys.* 103, (1995).
7. X.Y. Liu and P. Bennema, in *Current Topics in Crystal Growth Research* 2, 451 (1995).
8. X.Y. Liu and P. Bennema, *Phys. Rev.* B53, 2314 (1996).
9. X.Y. Liu, *Phy. Rev.* B60, 2810 (1999).

8:45 AM M1.2
THE STRUCTURE OF LIQUID Sn ON Ge(111). M.F. Reedijk[1], J. Arsic[1], F.K. de Theije[1], M. McBride[2], K. Peters[3] and E. Vlieg[1]. [1]RIM Dept. of Solid State Chemistry, University of Nijmegen, THE NETHERLANDS, [2]Lawrence Livermore National Laboratory, CA, [3]Surface Diffraction Beamline ID03, ESRF, Grenoble, FRANCE.

Solid-liquid interfaces play an important role in crystal growth. It is conjectured that the atomic structure at the solid-liquid interface determines important properties such as the growth shape and velocity and the effects of impurities and surfactants. Therefore, an atomic-scale understanding of these interfaces is important. Both the solid and the liquid structure at the interface may deviate from the bulk structure. The liquid side of the interface is thought to show pre-ordering towards the crystalline state. It is difficult to obtain atomic information of these interfaces. Atomic force microscopy (AFM) and surface x-ray diffraction (SXRD) are suitable techniques, especially for the solid part. This has already been done for some systems (for example KDP/water [1]). For the investigation of the structure at the liquid side of the interface AFM is less useful, so here SXRD is an important tool. We have investigated the liquid side of two such interfaces: KDP/water and Sn on Ge(111). The first system is rather complicated. We have clear evidence for layering in the liquid, but a full analysis awaits further data. For this reason we have investigated thin liquid Sn layers on a Ge(111) surface. This is a suitable model system, because the bulk melting temperature of Sn is relatively low and the vapor pressure is small, therefore a wide range of temperatures can be investigated. Experiments have been done for coverages ranging from 0.6 to 1.3 monolayers and temperatures ranging from room temperature to 500°C. At a number of points in the phase diagram full data sets have been measured, including crystal truncation rods (CTR's), specular and inplane data. Also the diffuse scattering from the liquid is measured. Even in liquid form, the Sn layer shows ordering due to the underlying substrate. This is visible in the contribution to the scattered intensity from the substrate, and also in the modulation of the diffuse scattering (liquid ring). As a function of temperature, the Sn behaves more liquid-like and less solid-like. This appears to be a continuous transition. [1] S.A. de Vries et al, Phys. Rev. Lett. 80, 2229-2232 (1998).

9:00 AM *M1.3
FUTURE TRENDS AND THE LATEST DEVELOPMENTS IN MEASURING NUCLEATION AND GROWTH OF CRYSTALS. Katsuo Tsukamoto, Faculty of Science, Tohoku University, Sendai, JAPAN.

Measuring nucleation and growth rates precisely are fundamental for the understanding of crystallization processes. This has been performed by developing modern observation methods, such as rapid dynamic light scattering or real-time phase-shift interferometry (RPSI). The latter has been employed also to measure the concentration and temperature distribution around a crystal. Some examples from apatite, calcite and protein crystals will be given, where metastable phases, which are commonly amorphous state, are formed prior to the nucleation of stable crystalline phase. These amorphous phases behave either like a buffer to keep the solute concentration constant or like nucleation centers for the coming stable phase, which depends on the difference of the interfacial energy between the stable phase and the metastable one.

9:30 AM *M1.4
EXTRACTING FUNDAMENTAL PARAMETERS FROM SURFACE MICROMORPHOLOGY. A.A. Chernov, University Space Research Association, Huntsville, AL.

The < 001 > growth steps on the (010) orthorhombic lysozyme face prograting into the +a direction were observed by AFM to be straight along the c-axis containing one kink per more than 500 lattice spacings. The steps moving in the -a direction are curved, including kinks of the same sign. The step rates in the +a and -a directing are close one to another and about 7 times lower than the step rate in the c-direction. These findings support decisive role of 1D nucleation and kink propagation, i.e. the kink flow mode of growth for the -a step. They also suggest unequal kink rates along the +a and -a steps, despite apparently similar molecular structures of these kinks. The

lysozyme is one of the overwhelming majorities of lattices with several not equivalent molecules per unit cell for which classical Kossel model should be generalized. Reconstruction of the (010) terraces via the a-spacing doubling was observed. Partition function of species in ideal gas is applied to large protein molecules in solution with due respect to rotational and translational degrees of freedom. Kossel model is still employed. This approach, together with the analysis of 1D nucleation and growth rate allows estimating intermolecular binding energy to be about 2kcal/mol. The step and surface coverages by admolecules are estimated to be 0.05 and 0.001. The approach provides also protein solubility inversely proportional to the temperature cubed and conventional Boltzman exponent with tripled binding energy i.e. the dissolution heat. If the dissolution entropy exceeds 3 conventional exponential increase of solubility with rising temperature follows. If the dissolution entropy is below 3, retrograde solubility is expected. This difference comes from different contributions of entropy and energy. A.A. Chernov, L.N. Rashkovich, I.V. Yaminsky, N.V. Gvozdev, J. Phys. Condens. Matter 11 (1999) in print.

10:30 AM *M1.5
FLUCTUATIONS OF STEP POSITIONS AT KDP CRYSTAL FACES. Leonid Rashkovich, Oleg Shustin, Tamara Chernevich, Moscow State Univ, Dept of Physics, Moscow, RUSSIA.

The fundamental parameters of layer-wise crystal growth at micro-level are kinks density and diffusion coefficient of step, frequencies of building units attachments and detachments. Aiming to determine these parameters fluctuations of step segments were investigated using in-situ atomic force microscopy with nanometric resolution. Experiment was conducted close to the crystal-solution equilibrium point. Step velocity (during growth and dissolving) did not exceed 1 nm/s. - Crystal lattice at prism and bipyramid faces (and its defects like edge dislocations) was distinctively fixed. - The steps looked very fragmented. It was not possible to distinguish individual kinks and straight segments without kinks. Thus, kink density was very high. It is of a sharp contrast with the situation on steps of protein crystals, where more than 100 building units are located between separate kinks. - The whole step and its segments are intensively fluctuating. In the one-line scanning regime we registered dependencies of the shift of step segment coordinate on time. The shifts were distributed by Gaussian function. - It is shown that fluctuation shift of a step fragment is proportional to the root of the fourth (but not the second) power of time. - During growth fluctuations at prism face are lesser than during dissolving. Inclusion of aluminum ions also reduces step fluctuations at growth. It is in agreement with the hypothesis on reduction of fluctuations due to partial fixing of step fragment by stoppers, having its effect only during growth. Impurity stoppers are probably mobile, as the interval of supersaturations between growth and dissolving is very short, if only exists. Interpretation of experimental data is based on the idea of Brownian motion as well as on fluctuations of interrelated step elements.

11:00 AM M1.6
SOURCES OF DIFFERENCES IN THE KINETICS OF STEP MOTION DURING GROWTH OF CRYSTAL SURFACES FROM SOLUTIONS. Jim J. De Yoreo, Terry A. Land, Christine A. Orme, G. Steven Bales, Mary T. McBride, Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA; Hui H. Teng and Patricia M. Dove, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA.

Using force microscopy to image crystal surfaces during growth from solutions, we investigated the dependence of surface morphology and step speed on supersaturation in a variety of systems including simple ionic solids (KH_2PO_4, $CaCO_3$ and $CaHPO_4(H_2O)$), hydrogen bonded organic compounds (2,5-diketopiperazines), and Van der Waals bonded macromolecules (proteins and viruses). From the dependence of critical length and step speed on supersaturation, we determined step edge free energies and kinetic coefficients of elementary steps. The wide variety of molecular sizes and bonding allowed us to examine differences in the behavior of systems for which the step edge energy varies by three orders of magnitude and the kinetic coefficient varies by seven orders of magnitude. We find that the supersaturation at which two-dimensional nucleation occurs is well correlated with the magnitude of the step edge energy as expected from standard equilibrium thermodynamic models. We also find that there is a systematic trend in step kinetics with increasing complexity of growth units. From a simple physical model we argue that the variation in step kinetics can be understood by taking into the account the effect of molecular size, mass and kink density on attachment/detachment rates without assuming significant differences in activation energies for attachment, which appear to vary by less than 0.2 eV. Using a kinetic Monte Carlo approach, we explore the role of these factors on step kinetics when step edge and surface diffusion processes are included. We show that, for steps with low kink densities near

equilibrium, increasing kink density with increasing supersaturation gives a non-linear dependence of step speed on concentration as is often observed in protein systems. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

11:15 AM M1.7
SURFACE EVOLUTION DURING THE GROWTH OF BRUSHITE (CaHPO4.2H20). Ana I. Villacamp, Christine A. Orme, James J. De Yoreo, Lawrence Livermore National Laboratory, Livermore, CA.; George H. Nancollas, State University of New York, Buffalo, NY.

In situ atomic force microscopy has been used to investigate the step dynamics and surface morphology of the (010) face of brushite (CaHPO4. 2H2O) while growing from solution. We used crystals nucleated both in a gelled media (agarose) [1] and in aqueous solution [2] as starting substrates. A study was conducted with the latter controlling the relative supersaturation, in a range between 0.016 and 0.277. We determined that the growth mode in this range of supersaturations is by the addition of material to existing steps rather than by the nucleation of new islands. We have measured the critical length for step motion and the velocity of the steps in the various step directions. Brushite grows from dislocations in triangular spirals. The step velocities are anisotropic with one step direction ~5 times slower than the other two steps. As expected, as the supersaturation increases, the critical length becomes smaller leading to a higher step density, the step speed increase and the effect of impurity pinning on steps is less apparent. Surprisingly, the velocity of a step in a given facet direction depends on the type of corners the step has even when the steps are many microns long. 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. 1. Unpublished results, Ana.I. Villacampa, Juanma Garcia-Ruiz. 2. Kostas D. Daskalakis, George H. Nancollas in Mineral Scale Formation and Inhibition, pp.219-230, Plenum Press, New York, 1995.

11:30 AM *M1.8
EQUILIBRIUM AND NON-EQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS OF CRYSTAL GROWTH. W.J. Briels, University of Twente, Computational Chemistry Group, Enschede, THE NETHERLANDS.

Monte Carlo as well as molecular dynamics simulations of growth rates of rough surfaces have been performed since more then twenty years now. With one exception all of them make use of non-equilibrium simulations. Recently, on the basis of Onsager's regression hypothesis a method was presented to calculate growth rates from equilibrium simulations. Both methods will be presented, and their relative merits will be discussed. In the case of flat surfaces direct molecular dynamics simulations of growth rates are much more difficult. Only interface structures and diffusion have been studied. Statements concerning growth rates must be based on parametrs entering very approximate models. One such model will be presented which has been successfully applied to the calculation of the morphology of urea grown from aqueous solutions.

SESSION M2: FLUID-MINERAL INTERFACES
Chairs: Bill Casey and C. Barry Carter
Monday Afternoon, April 24, 2000
Golden Gate C2 (Marriott)

1:30 PM *M2.1
PROBING THE LIQUID-SOLID INTERFACE WITH X-RAY SCATTERING TECHNIQUES. Paul Fenter, Argonne National Laboratory, Argonne IL.

A long-standing problem in studies of the solid-liquid interface has been to understand the evolution of surface charge and its associated impact upon the mineral-fluid interface at the molecular level. We approach this challenge by making use of the unique properties of the third generation synchrotron X-ray sources, such as the Advanced Photon Source (APS), that provide a new opportunity to directly probe the structure of the liquid-solid interface through in-situ measurements. Recent work has used X-ray scattering techniques to probe the mineral-fluid interface and to relate these measurements to the evolution of surface charge and the structure of the electrochemical double-layer (EDL). Two examples of these studies include investigations of: (1) the calcite (104)-water interface as a function of pH using x-ray reflectivity. These measurements test predictions that the evolution of surface charge is controlled by the specific adsorption of molecular species that change the molecular surface termination. (2) The association of mono- and divalent ions with the rutile (110) surface using X-ray standing waves. These measurements demonstrate a direct sensitivity to important aspects of the pH-dependent EDL structure in response to changes in the rutile surface charge. Together these studies provide some of the first direct

structural measurements of pH controlled adsorption and structure of the mineral-fluid interface.

2:00 PM *M2.2
ATOMISTIC SIMULATION OF THE STRUCTURE OF CARBONATE (10$\bar{1}$4) SURFACES UNDER WET AND DRY CONDITIONS. Kate Wright, Royal Institution of Great Britain, London, UNITED KINGDOM; Randall T. Cygan, Sandia National Laboratories, Albuquerque, NM; Ben Slater, Royal Institution of Great Britain, London, UNITED KINGDOM.

Atomistic simulation methods have been used to model the structure of the (10$\bar{1}$4) surfaces of calcite, dolomite and magnesite under wet and dry conditions. The potential parameters for the carbonate and water species contain shell terms to model the polarizability of the oxygen atoms. Our static calculations show that these surfaces undergo relaxation leading to the rotation and distortion of the carbonate group with associated movement of cations. The influence of water on the surface structure has been investigated for monolayer coverage, and by bathing the surface in a layer of water 6.5 $\mathring{A}$ in depth. The extent of carbonate group distortion is greater for the dry surfaces compared to the hydrated surfaces, and for the dry calcite relative to that for dry magnesite. We have also carried out molecular dynamics calculations in order to assess the effects of temperature on the model. In addition, both static and dynamic calculations have been performed to study the sorption of Mg and Ca on the cleavage surface for all three minerals.

2:30 PM M2.3
IN SITU X-RAY REFLECTIVITY AND ATOMIC FORCE MICROSCOPY STUDIES OF THE ORTHOCLASE-WATER INTERFACE. N.C. Sturchio, P. Fenter, H. Teng, Argonne National Lab, Argonne, IL; P. Geissbuhler, Univ of Washington, Dept of Physics, Seattle, WA; K.L. Nagy, Univ of Colorado, Dept of Geol Sci, Boulder, CO.

Feldspar minerals are abundant in the Earth's crust. The reaction of feldspars with aqueous solutions produces clay minerals and has a strong influence on the chemistry of natural waters. The dissolution of feldpars is incongruent under some conditions and the dissolution mechanism depends on both solution and feldspar compositions. An altered layer (<1 to >1000 nm thick) may form at the feldspar-water interface during dissolution. Structural and compositional characterization of this altered layer at the feldspar-water interface is critical for understanding mechanisms of feldspar dissolution and clay mineral formation. We have begun to apply in situ X-ray specular reflectivity and atomic force microscopy measurements to study structure and dissolution of the orthoclase (001)-water interface at ~25 C. These studies of gem-quality orthoclase indicate that the orthoclase (001) cleavage surface has minimal roughness and exposes a single cleavage plane. The X-ray data also show that (1) only one of two possible surface terminations is exposed, (2) dangling Si and Al bonds are terminated by a species consistent with 1 ML of hydroxyl groups, and (3) the outermost layer of K+ ions is absent. A complex relaxation profile affects the near-surface structure and propagates ~30 $\mathring{A}$ into the orthoclase. Results of extended dissolution experiments under a variety of conditions will also be presented.

3:15 PM *M2.4
SURFACE REACTIVITY AND MICROSTRUCTURE DEVELOPMENT IN NANOCRYSTALLINE AGGREGATES. Jillian F. Banfield[1] and R. Lee Penn[1,2], [1]Univ. of Wisconsin - Madison, Dept. of Geology and Geophysics, Madison, WI; [2]current address: Johns Hopkins Univ., Earth and Planetary Sciences, Baltimore, MD.

Solution chemistry plays an important role in the growth and dissolution of natural and synthetic materials. We have characterized both single crystal growth and growth by agglomeration as a function of solution chemistry via a series of laboratory experiments using titanium dioxide. Hydrothermally coarsened titanium dioxide nanocrystals (anatase and brookite polymorphs) were examined using high-resolution transmission electron microscopy and X-ray diffraction peak broadening analysis. Factors such as ionic strength, identity of surface reactive chemical species, surface microstructure, and the size and morphology of building block crystallites are predicted and observed to strongly impact the final form of coarsening materials. Addition of strongly adsorbing organic acids changed the growth morphology of single nanocrystals. Changes in single crystal morphology were measured as a variation in the average relative ratio of the [001] to the [101] dimensions of anatase crystallites, and an overall decrease from 1.8 (additive-free experiments) to a minimum of

1.1 (utilizing strongly adsorbing organic acids as additives) was observed. Changing solution pH using hydrochloric acid caused dramatic changes in growth via oriented attachment. In the most extreme case, chains of anatase crystallites, hundreds of nanometers long and constructed from at least eight primary anatase crystallites, were formed by attachment across {112} crystallographic faces. When crystallographic faces are atomically rough, defects, ranging from edge to screw dislocations, are incorporated at attachment boundaries. Because oriented attachment is constrained only in two dimensions, the formation of twins and intergrowths at coherent attachment boundaries is predicted to occur and observed to occur at {112} attachment boundaries.

3:45 PM M2.5
STEP STABILITY AND MOLECULAR TEXTURE OF SULFATE CRYSTAL SURFACES STUDIED WITH SCANNING PROBE MICROSCOPIES. H. Shindo, T. Watabe, A. Seo, S. Kondo, K. Shitagami and Y. Namai, Chuo Univ, Department of Applied Chemistry, Tokyo, JAPAN.

Depending on arrangements of tetrahedral sulfate ions, sulfate minerals give crystal faces having various structures. Some of them are atom-flat and suitable for studying with scanning probe methods in the atomic level. Motions of monatomic steps during dissolution in aqueous solutions were followed for $CaSO_4$, $SrSO_4$ and $BaSO_4$ crystals using atomic force microscopy(AFM). Stabilities of the steps were evaluated by the speeds of step retreat. In addition to charge neutrality, smooth alignment of positive and negative charges to minimize dipoles perpendicular to the step is a key factor for its stability. Motions of less stable steps were followed by slowing down the dissolution process by addition of the salts to the solution phase. The growth process on $SrSO_4$(001) was observed in the solution. Multi-nucleation was first observed. After completion of the first layer, however, well-controlled layer growth followed in near equilibrium condition. Some surfaces have asymmetric structures due to tilt of the sulfate ions. Such asymmetry can be detected with frictional force microscopy (FFM). Change in the tilt directions at monatomic steps gives a clear frictional contrast. The relation between the tilt and the frictional asymmetry was determined using results of etching experiments. Surface corrugation is also reflected in anisotropy in the total friction. FFM is a promising tool in studying molecular textures of surfaces.

4:00 PM *M2.6
THE KINETICS OF CALCITE GROWTH: RE-INTERPRETING CHEMICAL AFFINITY-BASED RATE LAWS THROUGH THE LENS OF DIRECT OBSERVATIONS OF SURFACE PROCESSES. Patricia M. Dove, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA; H. Henry Teng, Argonne National Laboratory, Argonne, IL; Jim J. De Yoreo, Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA.

Chemical affinity-based rate laws are used across geochemical and materials communities to quantify mineral/material corrosion and growth kinetics. However, these rate laws are typically founded in assumptions regarding reaction mechanism with little evidence for surface processes. Using in situ Atomic Force Microscopy (AFM), calcite growth experiments were conducted on (104) faces to determine (1) supersaturation(s) range where growth occurs only by spiral formation; (2) critical supersaturation for activation of a surface nucleation mechanism; (3) step flow rates and corresponding slopes of growth hillocks; (4) surface normal growth rates of single spirals; (5) dependence of overall growth rate, Rm, upon dislocation source structure. Observations of growth show that at lower supersaturations (sigma = 0-0.8), growth is initiated by surface imperfections including screw dislocations. Thus, crystal defect-originated growth, in particular, spiral growth, is the manifested mechanism. When sigma > 0.8, 2D nucleation becomes dominant. Measurements of Rm on single-sourced spiral hillocks indicate a superlinear dependence of Rm upon chemical affinity. AFM observations demonstrate that growth kinetics is dependent upon the structures of dislocation sources with the dominant growth mode occurring by hillock development initiated at complex sources. Derivations of surface process-based rate expressions show a complex dependence of rate on chemical affinity. This dependence is approximated by second order affinity-based rate laws only under the special conditions that (1) growth proceeds by development of single sourced spirals and (2) growth occurs at very near equilibrium conditions where spiral formation is the only operative mechanism. This suggests growth experiments that measure temporal changes in solution chemistry yield a composite rate from different hillock types. Hence, chemical affinity based rate laws do not generally give meaningful interpretations of growth mechanism. By combining direct observations with macroscopic methods that monitor temporal changes in solution chemistry, rate laws with greater predictive capabilities may be possible.

4:30 PM <u>M2.7</u>
SOLUTION GROWTH OF EPITAXIAL GARNET FILMS ON
SINGLE-CRYSTAL SUBSTRATES. <u>David B. Beach</u>, Andrew E.
Morrell, Catherine E. Vallet, Oak Ridge National Laboratory,
Chemical and Analytical Sciences Division, Oak Ridge, TN; Jonathan
S. Morrell, Ziling B. Xue, University of Tennessee, Department of
Chemistry, Knoxville, TN.

Solutions of mixed-metal methoxyethoxides in 2-methoxyethanol were
used to deposit epitaxial thin-films of yttrium gallium garnet (YGG)
and rare-earth doped yttrium aluminum garnet (RE:YAG) on single
crystals of (100) oriented yttrium aluminum garnet (YAG). The YGG
films were extensively characterized by X-ray diffraction and found to
have grown with a simple cube-on-cube epitaxy. The full-width at
half-maximum (fwhm) of an omega scan about the (800) reflection
was 0.69°, and the fwhm of a phi scan about the (642) was 0.83°,
indicating that the YGG films were of good quality. The RE:YAG
films were characterized by Rutherford Backscattering Spectroscopy
(RBS) and were found to also be epitaxial and to have doping levels
consistent with the RE dopant concentration in the solution used to
cast the film.
This work was supported by the Division of Materials Sciences, Office
of Science, U.S. Department of Energy and was performed at the Oak
Ridge National Laboratory under contract DE-AC05-96OR22464 with
the Lockheed Energy Research Corporation.

4:45 PM <u>M2.8</u>
CRYSTAL-LIQUID BOUNDARIES IN LIQUID-PHASE SINTERED
CERAMICS. <u>N. Ravishankar</u>, C. Barry Carter, Department of
Chemical Engineering and Materials Science, University of Minnesota,
Minneapolis, MN.

Liquid-Phase sintering is a common route for processing many of the
commercial ceramic materials. Most of the liquid-phase sintering
systems have an eutectic phase diagram with a small solubility in the
solid phase. Sintering is usually carried out at temperatures slightly
above the eutectic temperature. At this temperature, there is a
considerable amount of solid which dissolves in the liquid and also a
reprecipitation of the solid which takes place simultaneously. This
solution-reprecipitation at the solid-liquid boundaries leads to
densification. The driving force for solution-reprecipitation is provided
by a difference in composition between the composition of the solid
which dissolves in the liquid and the composition of the reprecipi-
tating solid. A difference in curvature between adjacent grains leads
to grain boundary migration. The present work deals with use of
single-crystals, bicrystals and tricrystals to study this phenomenon in
detail. The advantage with the use of this geometry is to obtain useful
information regarding the influence of crystallographic orientation on
the process. Sapphire crystals with anorthite as the liquid phase is
chosen as the model system. Bicrystals are produced by hot-pressing
glass-coated sapphire single crystal to another blank single crystal of
sapphire. Observations of grain boundary migration in the bicrystals
and tricrystals lead to many important conclusions regarding the
solution-reprecipitation processes and grain boundary migration that
occur in a polycrystalline material.

SESSION M3: GROWTH OF ORGANIC FILMS AND
SUPRAMOLECULAR SOLIDS
Chairs: Michael D. Ward and Christopher M. Yip
Tuesday Morning, April 25, 2000
Golden Gate C2 (Marriott)

8:30 AM <u>M3.1</u>
EPITAXIAL GROWTH OF MOLECULAR FILMS. <u>Daniel E. Hooks</u>,
Eric Codner, Michael D. Ward, Dept of Chemical Engineering and
Materials Science, University of Minnesota, Minneapolis, MN.

Epitaxial molecular films are emerging as promising components for
electronic devices, sensors, displays, and logic elements because their
optical and electronic properties can be systematically manipulated at
the molecular level. The properties of molecular films depend strongly
upon their structure and orientation with respect to the substrate
upon which they are deposited. Therefore, their design and synthesis
requires careful attention to the interface between the primary
molecular overlayer and the substrate. While the influence of epitaxial
interactions at the overlayer-substrate interface on film structure and
orientation has been firmly established for inorganic and elemental
systems, epitaxial principles for crystalline molecular films have only
recently emerged. Low-symmetry molecular overlayers are commonly
stabilized by a form of epitaxy referred to as coincidence, which can be
analyzed and even predicted by geometrical analysis of the interface.
The length scale of phase coherence is directly related to the potential
energy of the interface. The principles of coincident epitaxy will be
discussed in the context of molecular films with superconducting,
semiconducting, and light-emitting properties, with a comparison of
geometrical lattice modeling and potential energy calculations.

8:45 AM *<u>M3.2</u>
TWO-DIMENSIONALLY ORDERED THIN FILMS OF
PHTHALOCYANINE, PERYLENES AND QUINACRIDONE DYES.
<u>Neal R. Armstrong</u>, Department of Chemistry, University of Arizona,
Tucson, AZ.

Thin films of strongly light absorbing and highly luminescent dyes,
such as the phthalocyanines, perylenes and quinacridones, can be
created either by vacuum deposition approaches (OMBE), or by new
self-assembly approaches in combination with LB/Schaefer method
deposition. This talk will review the current state-of-the-art in the
OMBE formation of such thin films, starting with the types of
ordering achievable in monolayers on single crystal surfaces.
Formation of ordered multilayers of these materials is strongly
dependent upon selection of molecular systems which possess layer
planes in their bulk structures. In all OMBE deposited films, however,
the quality of the final deposit is strongly dependent upon symmetry
and lattice match with the substrate. More coherent films have
recently been created with solution-processable phthalocyanines,
modified with side chains which direct self-assembly into rigid
columns and bilayer sheets, which then lend themselves to patterning
on surfaces, and highly anisotropic optical and electrical properties,
not easily achieved in vacuum-deposited materials.

9:15 AM <u>M3.3</u>
MOLECULAR STRUCTURE OF CONDENSED ORGANIC FILMS
STUDIED USING AFM. <u>Marat Gallyamov</u>, Igor Yaminsky, Moscow
State Univ, Physical and Chemical Depts, Moscow, RUSSIA;
Gennadiy Zhavnerko, Vladimir Agabekov, National Academy of
Science of Belarus, Inst of Chemistry of New Materials, Minsk,
BELARUS.

Langmuir monolayers of organic long-chain amphiphilic compounds
(acids, ketoamides) were transferred onto solid substrate surfaces of
using traditional Langmuir-Blodgett (LB) technique and a new
method based on horizontal precipitation (HP). It was shown that in
most cases the HP method is more preferable for creation of
monolayer coatings (whereas LB technique is more convenient for
multi-layer structures formation). The main advantage of HP
approach is that low film adhesion to a substrate is not a critical
obstacle of the transfer procedure. Generally the HP-created
monolayer films are more uniform and less-defective in comparison
with ones created by LB technique. In some cases it was possible to
create stable monolayer coating using HP-method only (for example:
organic acids films transferred on mica substrate without the presence
of counterions in subphase). Another advantage of HP approach is the
possibility of monolayer deposition "as is" without distortion of its
morphology during deposition. It opens new perspective in investi-
gation of monolayer behavior onto liquid/gas interface. AFM provides
unique information both about general structure of film on micron
level and about molecular packing (subnanometer level) in selected
region of film surface. The lattice crystallographic parameters are
measured on the basis of molecularly resolved images of the films. The
measurement error less than few percents was achieved due to
elimination of thermal drift, accurate calibration of piezoscanner,
minimization of hysteresis in experimental setup (we also paid
attention to minimization of probe destructive influence onto film
studied). The analysis of the measured lattice parameter is done using
the principle of close packing of carbohydrate chains while taking into
account the influence of the substrate and the specific features of
film-forming procedure.

9:30 AM <u>M3.4</u>
TEMPLATING IN POLYMORPHIC AND ORGANIC FILM
HETEREROSTRUCTURES GROWN BY ORGANIC MOLECULAR
BEAM DEPOSITION. <u>T.S. Jones</u>, S. Heutz, S.M. Bayliss, R. Cloots,
R.L. Middleton and G. Rumbles, Centre for Electronic Materials and
Devices and Department of Chemistry, Imprial College, London,
UNITED KINGDOM.

The growth of complex multilayer molecular thin film structures is a
crucial component in the formation of organic light emitting devices.
A key issue is the effect that the underlying film has on the properties
and morphology of the film growing in the next and subsequent
layers. In this work we assess these effects by considering multilayer
structures containing metal free phthalocyanine (H_2Pc) and/or
perylene 3,4,9,10-tetracarboxylicacid dianhydride (PTCDA) deposited
on glass substrates by organic molecular beam deposition. The
structure of the films has been characterised by powder X-ray
diffraction, whilst the surface morphology has been assessed using
both atomic force microscopy and optical interference microscopy. In
the case of double layers of different polymorphic forms (α, β_1 and
β_2) of H_2Pc, the morphology and structure of the second layer is
determined by the properties of the first layer, independent of the
growth conditions used to deposit the second layer. This suggests a
strong templating effect by the underlying polymorphic layer. For the

growth of $H_2Pc/PTCDA$ heterostructures, the first layer deposited is again shown to have a dramatic influence on the properties of the second layer. The crystal structure of the second layer reflects those of the first layer suggesting that structural templating occurs during the growth of heterostructures. The surface morphology of the second layer is also found to be affected by the first layer. The effect is particularly marked when PTCDA is grown on a β-phase H_2Pc film. The PTCDA appears strained and aggregates in large islands on the smooth H_2Pc film. Electronic absorption spectroscopy also shows that the electronic properties of the second layer may be influenced by the first layer. DFT calculations have been used to simulate the second layer absorption spectrum in order to define the structure and electronic properties of this templated phase.

10:15 AM M3.5
POLYMORPHISM IN PHTHALOCYANINE THIN FILMS: MECHANISM OF THE $\alpha \to \beta$ PHASE TRANSITION. S. Heutz, S.M. Bayliss, G. Rumbles and T.S. Jones, Centre for Electronic Materials and Devices and Department of Chemistry, Imperial College, London, UNITED KINGDOM.

Free base phthalocyanine films have been grown on glass substrates by organic molecular beam deposition and are shown to display different polymorphic forms depending on the growth conditions. The metastable α-phthalocyanine films grown at room temperature can be transformed to the stable β-form by in-situ annealing of the sample. The two phases have previously been identified, but no complete study of the mechanism and the transition states of the transformation has been carried out. We find that the $\alpha \to \beta$ transformation involves a number of transition states whose morphological, structural and spectroscopic properties can be identified using atomic force microscopy (AFM), optical interference microscopy, X-ray diffraction and electronic absorption spectroscopy. AFM results show that small spherical crystallites typical of the α-phase become elongated upon annealing. With increasing annealing time the β-phase nucleates at a finite number of sites across the sample leading to the formation of islands with an ill-defined shape. These islands grow into large, slender crystals oriented parallel to one another over large areas and the domains cover the entire surface of the sample. Quantitative analysis of the size distribution of the crystals and domains has been carried out as a function of annealing time. The β-crystals become more slender and merge, whilst the domain size saturates and the number density of the domains remains constant throughout the transformation. These results are consistent with a model in which the transformation occurs via discrete nucleations. The film thickness plays a crucial role. Below 66 nm the α-film sublimes before the transformation can occur. At intermediate thickness ($66 \to 190$ nm), competition between β crystallisation and α sublimation is observed and it is only for film thickness > 190 nm that complete transformation can be observed.

10:30 AM *M3.6
POLARITY: A TUNABLE PROPERTY OF MOLECULAR CRYSTALS. Juerg Hulliger, University of Berne, Department of Chemistry and Biochemistry, Berne, SWITZERLAND.

Basic principles are reviewed which provide new access to the synthesis of acentric molecular crystals along with an application to the design of intermolecular interactions and the crystallisation of polar molecular materials. Because of the process of crystal growth, the primary confinement for the alignment of dipolar molecules is given by a surface-nutrient interface and not by the bulk state as usually assumed for the prediction of crystal structures by computational methods. Subject to defined restrictions, spontaneous polarity formation in slowly growing crystals can be regarded as a simple isomerisation reaction with respect to up and down orientations of dipole moments in crystals. Following results of Monte Carlo simulations, performed for ad-layers on non-relaxing substrate layers, we conclude: (i) Although binding motifs (synthons) are important to induce 1D or 2D order into chains, ribbons and planes, lateral interactions between such structural elements enter polarity formation by a much higher weight factor. (ii) Particular lateral interactions favorising parallel alignment are not necessary to obtain polarity in some molecular crystals. Channel-type inclusion materials represent a solution to (ii). Experimental confirmation is provided by e.g. a large number of polar inclusion compounds of perhydrotriphenylene (PHTP). It is shown that in general a combination of van der Waals interactions for a 2D confinement (alignement of molecular frames) and one most non-bonding recognition motif (driving up and down orientation of dipoles) can optimise polarity formation in host-guest lattices. In essence, we review that in molecular crystals polarity is a tunable property, and that a supramolecular synthesis can produce a material and a property by parallel reactions. Scanning pyroelectric microscopy and phase sensitive second harmonic microscopy were used to demonstrate a bi-polar growth state.

11:00 AM M3.7
STUDYING THE GROWTH MECHANISM FOR SELF-ASSEMBLED MICROPOROUS CRYSTALS OF HETEROPOLYANIONS. Syed Ali Shah, Charles F. Zukoski, University of Illinois at Urbana-Champaign, Dept of Chemical Engineering, Urbana, IL.

Phosphotungstate anion (PTA) crystallization offers a unique opportunity to investigate nanoparticle, hierarchical self assembly. PTA anions are 1.2 nm diameter strong acid molecules important as industrial shape-selective catalysts for the conversion of methanol into paraffinic species. The shape selectivity arises from the crystallization of these particles into highly faceted, microporous crystals ($\sim$100 m^2/g). The conditions giving rise to microporous crystal formation are poorly understood but are key to understanding PTA catalytic potency. Electron diffraction patterns and scanning electron micrographs taken during the initial stages of ammonia PTA growth reveal the formation/nucleation of spherical nanoparticles (10-50 nm in diameter) with a body centered cubic microstructure. As the PTA assemblies grow, the electron diffraction patterns remain unchanged indicating that the crystal planes of the nanocrystallites within the aggregates are unidirectionally oriented. Surface area studies indicate that the final crystals are microporous with average pore sizes of 1.4-1.5 nm. An aggregative mechanism is hypothesized where 8-10 nm nanocrystals form and aggregate in an oriented manner to yield the final crystals. This growth mechanism will be critically evaluated.

11:15 AM M3.8
SCANNING FORCE MICROSCOPY STUDIES OF COMBINED CHEMICAL AND MECHANICAL STIMULATION ON INORGANIC SINGLE CRYSTAL SURFACES: NANOMETER WEAR AND TIP-CONTROLLED DEPOSITION. Rizal Hariadi, Steve Langford, Tom Dickinson, Washington State University, Dept. of Physics, Pullman, WA.

Manipulation, modification, and processing of materials often depends on combining stimuli (example: ion bombardment + heat), frequently exploiting synergisms. Here we examine the simultaneous application of mechanical and chemical stimuli leading to nanometer scale wear or deposition from solution. in several model carbonates and phosphates. These studies support and improve our understanding of how stress and confinement on short length scales can strongly influence kinetics of dissolution and redeposition. Our major tool is Scanning Force Microscopy (SFM), where we examine surface modification on the nanometer size scale by a tip which realistically represents a well characterized single abrasive particle or a single asperity. Crystal structure is shown to dominate the wear processes observed. We also present a newly discovered process–tribologically controlled redeposition –i.e., layer by layer crystal growth manipulated by the SFM tip which again is strongly crystallographic. Features as small as a few nm have been readily generated. Both wear and redeposition can be used to generate atomically flat surfaces.

11:30 AM *M3.9
STRUCTURE-FUNCTION RELATIONSHIP IN THE ANTIFREEZE ACTIVITY OF ENGINEERED ALANINE-LYSINE ANTIFREEZE POLYPEPTIDES. Andrzej Wierzbicki, Department of Chemistry, University of South Alabama, Mobile, AL.

Antifreeze proteins have been recently the subject of many structure-function relationship studies regarding their antifreeze activity. Many attempts have been made to elucidate this structure-function relationship by various amino acid substitutions, but to our knowledge there has been no successful first principles *de novo* design of a functional nonequilibrium antifreeze polypeptide that would bind to a designated ice plane along a specific direction in this plane.
We will discuss the results of an entirely *de novo*, structure-function inspired design of alanine/lysine rich antifreeze polypeptide. This 43 residue alanine/lysine based polypeptide exhibits characteristic nonequilibrium freezing point depression, typical for nonequilibrium antifreezes and binds to the designated (2-10) planes of ice along the [122] vector. The structural and thermodynamic properties of this polypeptide were determined using Circular Dichroism Spectroscopy and its nonequilibrium antifreeze characteristics were investigated using a novel ice etching method and Nanoliter Osmometry. Implications of our findings for the structure-function inspired design of polypeptide inhibitors of crystal growth will be also discussed.

SESSION M4: BIOGENIC AND BIOMIMETIC
SYSTEMS
Chairs: Patricia M. Dove and Neil Sturchio
Tuesday Afternoon, April 25, 2000
Golden Gate C2 (Marriott)

1:30 PM *M4.1
TEMPLATED CRYSTALLIZATION OF CALCITE ON PATTERNED SELF-ASSEMBLED MONOLAYERS.
Joanna Aizenberg, Lucent Technologies, Bell Labs, Murray Hill, NJ.

Modern technologies require innovative methods for controlled fabrication of crystalline materials with complex form. A range of strategies has been explored to regulate nucleation and growth of crystals based on molecular recognition at organic/inorganic interface. While these studies have shown the great potential of using supramolecular templates to govern crystallization, but it remains a challenge to control simultaneously the precise localization of particles, their nucleation density, size, morphology and crystallo-graphic orientation. This paper reports that by micropatterning self-assembled monolayers (SAMs) with rapidly and slowly nucleating regions of proper geometry and interfacial chemistry and by taking advantage of the induced mass transport, it is possible to achieve a remarkable level of control over all these parameters. We focus on crystallization of calcite ($CaCO_3$) on patterned SAMs of $HS(CH_2)_n X$ ($X = CO_2H$, CH_3, SO_3H, OH, PO_3H_2, $N(CH_3)_3Cl$) supported on Ag, Au and Pd, although the experimental conditions and the mechanisms discussed are applicable to the templated nucleation of a wide range of inorganic materials. Crystallization is confined to well-defined, spatially delineated sites and results in the formation of large-area, high-resolution inorganic replicas of the underlying organic patterns. The nucleation density may be controlled by varying the area and distribution of rapidly nucleating regions of SAMs, and fine-tuning of the crystallographic orientation of the forming crystals can be achieved by using different functional groups and metal substrates.

2:00 PM M4.2
LATTICE RESOLUTION IMAGING OF CALCIUM CARBONATE CRYSTAL SURFACES, AS MODULATED BY PROTEINS EXTRACTED FROM ABALONE NACRE. James B. Thompson, George T. Paloczi, Johannes H. Kindt, University of California, Dept of Physics, Santa Barbara, CA; Martina Michenfelder, University of California, Marine Science Institute, Santa Barbara, CA; Bettye L. Smith, University of California, Dept of Physics, Santa Barbara, CA; Galen D. Stucky, University of California, Dept of Chemistry, Santa Barbara, CA; Daniel E. Morse, University of California, Marine Science Institute, Santa Barbara, CA; Paul K. Hansma, University of California, Dept of Physics, Santa Barbara, CA.

Atomic force microscopy (AFM) was used to observe the interaction of soluble proteins extracted from abalone (Haliotis rufescens) nacre with growing calcite crystals. These interactions resulted in a morphological transition from calcite to aragonite growth. Individual proteins were seen to attach to calcite growth step edges and inhibit calcite growth. A second type of protein was seen to attach directly to the calcite (104) surface, and may have acted to nucleate aragonite growth. The transition from calcite to aragonite was observed on the molecular level. Thus, proteins extracted from nacre bind the calcite surface at specific sites that are related to their function.

2:15 PM M4.3
SELECTIVE BINDING OF CHIRAL AMINO ACIDS TO ATOMIC STEPS OF CALCITE. Christine Orme, Aleksandr Noy, Mary McBride, Jim De Yoreo, Lawrence Livermore National Laboratory, Livermore, CA.

Proteins regulate macroscopic morphology of inorganic crystals found in biological systems. Molluscan proteins which regulate calcium carbonate growth are rich in acidic amino acids such as aspartic acid and glutamic acid. In this study we investigate the interaction of calcite atomic steps with aspartic acid. The {104} cleavage plane of calcite was imaged using an AFM under conditions of both growth and dissolution. Only the acute steps are affected while the obtuse steps remain unperturbed. We find that the D and L forms of aspartic acid break the crystal symmetry by selectively binding to different faces that are related by a glide plane and consequently, hillocks grown in the presence of D and L aspartic acid are related by mirror symmetry. SEM images of nucleated crystals grown in the presence of these amino acids also confirm these changes and show the macroscopic effect of the modification of the atomic step directions. During calcite dissolution the addition of aspartic acid changes the etch pit shape from the rhombohedral symmetry associated with pure calcite to a trapezoidal shape. None of the new facets coincide with any of the original stable calcite step directions. Three of the new step directions are the same for both D and L aspartic acid, but one of the steps is consistent with the development of a face from the {1$\bar{1}$0} family. D and L enantiomers form faces related by a glide symmetry. 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

2:30 PM *M4.4
ANTIBODIES SPECIFIC TO CRYSTAL SURFACES.

STEREOCHEMICAL RECOGNITION, EFFECTS ON CRYSTAL GROWTH AND MORPHOLOGY. Merav Geva, David Izhaky, Naama Kessler, Reinat Nevo, Daniele Perl-Treves, Lia Addadi, Dept. of Structural Biology, Weizmann Institute of Science, Rehovot, ISRAEL.

The interactions between proteins and crystal surfaces can range from totally non-specific physical adsorption of the macromolecule on the surface to the most highly specific complementarity. These interactions may result in acceleration of crystal formation or in inhibition of crystal growth, depending on the state and nature of the protein and on the stage of the crystallization. Among proteins, antibodies are the tool that nature evolved to recognize foreign invaders. Recognition occurs through complementarity of their binding sites with the surface of the invader. When introduced into an organism, crystals do not expose to the environment the whole chemical entity of their component molecules but rather appear as highly structured repetitive macromolecular substrates. An antibody that recognizes a crystal face could thus bear in its binding site a structured imprint of a number of molecular moieties exposed on the crystal surface. Monoclonal antibodies (Mabs) were produced from mice injected with crystals of cholesterol monohydrate and 1,4-dinitrobenzene (DNB). A number of these Mabs were selected for study, amongst which two are specific to one cholesterol and one DNB crystal face, respectively. Analysis of the derived sequences of the variable regions of these monoclonal antibodies, combined with molecular modeling of their structures, suggests a close correlation with the structure of the recognized crystal surface. The antibody-crystal surface complementarity is manifested in selective binding, changes in crystal morphology and crystal nucleation. The antibody that recognizes one face of cholesterol crystals, selectively interacts also with monolayers of cholesterol and ent-cholesterol, but not of epicholesterol. These experiments open the way to an analysis of the stereochemical recognition of antibodies at organized surfaces.

3:30 PM *M4.5
BIOGENIC INSPIRATION FOR THE CONTROLLED NUCLEATION AND GROWTH OF INORGANIC MATERIALS. Brigid R. Heywood, Susan Hill, Kate Pitt, Paul Tibble, Staurt Williams, Crystal Science Group, School of Chemistry and Physics, Keele University, Keele, Staffs, UNITED KINGDOM.

The development of effective protocols for the control of crystal structure, size and morphology attracts considerable interest given the requirement for particles of modal size and shape in many areas of particle processing and the importance of crystallochemical selectivity in determining the exploitable properties of crystalline solids. In biological systems there are numerous examples of advanced crystal engineering in which materials are deposited in a highly controlled manner to produce crystal phases that are unique with respect to their structure, habit, and uniformity of size. A review of biomineralisation will show that while a complex array of strategies have evolved for regulating crystal growth, one feature is common to the biological paradigm. Specific and selective interactions between supramolecular organic structures and the nascent inorganic solids play a fundamental role in controlling the deposition of the biominerals, and ordering the assembly of these units into hierarchical structures. In order to gain a better understanding of the molecular recognition events which direct information exchange at the organic-inorganic interface, a bio-inspired crystal chemical approach has been adopted. For this work organised organic assemblies (e.g. surfactant aggregates, peptide mimics, glycomers, H-bonded polymers, dendrimers) of precise molecular design (head group identity, packing conformation, primary sequence etc.) are being assayed for their effectiveness in controlling the formation of crystals. It is evident from these studies that the chemical organisation of the polymeric microenvironment operates at the molecular level to control certain aspects of the nucleation, growth and stabilisation of inorganic particles. By systematically changing the molecular motif of the organic template we have established that the size, crystallographic orientation, growth and assembly of the mineral phase can be tailored to function. These results have relevance not only to our understanding of biomineralisation but also suggest a multiplicity of exploitable opportunities for the engineering of crystals.

4:00 PM *M4.6
ARCHITECTURE AND FUNCTION OF FRACTURE-RESISTANT, BIOLOGICAL MATERIALS. Paul K. Hansma, Ille Geheschuber, Bettye Smith-Maddux, Mario Viani, James Thompson, Johannes Kindt, Department of Physics, University of California, Santa Barbara, CA; Daniel Morse, Department of Biology and Marine Biotechnology, University of California, Santa Barbara, CA; Galen Stucky, Department of Chemistry and Materials, University of California, Santa Barbara, CA.

A new generation of Atomic Force Microscopes, AFMs, has the potential to revolutionize our understanding of the properties of biomaterials. Preliminary data on the proteins involved in abalone

and coccolith growth suggests that smaller proteins are used for controlling crystal phase, while larger, modular ones are involved as structural elements. For example, the protein recently named lustrin acts as a very high technology glue to hold together the mineral tablets in abalone shells. A similar, modular protein appears to be used by diatoms to attach themselves to surfaces. These modular proteins provide effective energy absorption and appear to be the real key to understanding the impressive fracture resistance of many biological composite materials.

4:30 PM M4.7
AMELOGENIN PROTEINS MODULATE CRYSTAL HABIT OF OCTACALCIUM PHOSPHATE AND HYDROXYAPATITE CRYSTALS IN *IN − VITRO* MODEL SYSTEMS.
Janet Moradian-Oldak, Hai Bo Wen, Alan G. Fincham, Center for Craniofacial Molecular Biology, Univ South California, School of Dentistry, CA; Mayumi Iijima, Asahi Univ, School of Dentistry, Gifu, JAPAN.

Recent studies have indicated that amelogenin nanospheres, the principle protein component of developing tooth enamel may play critical roles during the initiation and growth of enamel crystallites by providing the dynamic structural framework (or network) within which the crystals grow. This study was undertaken to investigate interactions of amelogenin with octacalcium phosphate (OCP) and apatite. Apatite crystals were grown from a supersaturated calcifying solution on a bioactive glass in the absence (SCS) and the presence of amelogenin (SCS_{rM179}). OCP crystals were grown; (a) in a 10% gelatin gel containing 0-2% amelogenin where the crystals were formed in a double-diffusion chamber, and (b) in a 10% pure amelogenin gel, where crystal growth takes place in between a cation-selective and a dialysis membrane. Amelogenin promoted the formation of bundles of lengthwise apatite crystals which were oriented parallel to each other when grown on (SCS_{rM179}). It was found that individual apatite crystals within those bundles adopted an elongated, curved shape. The stronger 002 preferential orientation of the crystals formed by (SCS_{rM179}) indicated this elongation to be parallel to the c-axis. OCP crystals formed in 10% gelatin gel containing 1-2% amelogenin were longer (3-5 times larger in aspect ratio) than the OCP crystals formed in 10% gelatin without amelogenin. A profound effect was that found in the cation selective membrane system when 10% amelogenin affected the growth morphology in a specific manner. Affected crystals had a length to width ratio twice larger than that of control crystals while the width to thickness ratio was about 1/12 of that of the control crystals. The data presented here suggest that amelogenin nanospheres modulate the growth morphology of apatite and OCP crystals and indicate a significant functional roles for amelogenin proteins during the *in vivo* oriented growth of enamel crystallites.

4:45 PM M4.8
INVESTIGATING THE FACTORS EFFECTING PATHOGENIC CRYSTALLIZATION EVENTS. Jennifer A. Swift, Mary Hoffa, Richard Sharpe, Georgetown University, Department of Chemistry, Washington, DC.

The development of gallstones, kidney stones, atherosclerotic and brain plaques, and various joint diseases are all examples of pathogenic crystallization processes. In vivo isolation and identification of the agent(s) responsible for controlling such undesirable crystallization processes can be difficult, given the inherent complexity of native biological systems. We are currently investigating the molecular scale nucleation and growth processes of known components of crystalline pathogens by using in situ Atomic Force Microscopy and simplified model crystalline systems. By elucidating the effect of various parameters such as crystal surface structure and defects, crystal growth mechanisms and potential epitaxial relationships with other crystalline species, we hope to ultimately gain insight into how to prevent such crystallization processes from occurring.

SESSION M5/H5: JOINT SESSION:
GROWTH AND MORPHOLOGY AT THE OXIDE
SOLUTION INTERFACE
Chairs: Elias Vlieg and Karl Sieradzki
Wednesday Morning, April 26, 2000
Golden Gate C2/C3 (Marriott)

8:30 AM *M5.1/H5.1
INTERPRETATION OF MODEL CAPACITANCES IN TERMS OF THE STRUCTURE OF THE ELECTRIC DOUBLE-LAYER AT THE OXIDE-WATER INTERFACE. Dimitri A. Sverjensky, Johns Hopkins Univ., Dept. Earth and Planetary Sciences, Baltimore, MD.

Systematic analysis of surface charge as a function of pH and ionic strength for a wide range of metal oxides and 1:1 electrolytes in water has resulted in a set of internally-consistent model capacitances (C1) referring to the inner layer of the triple-layer model (TLM). The values of C1 show systematic trends with electrolyte cation radius that can be interpreted using electrostatic theory. The TLM assumes that a layer of electrolyte cations lies at an unspecified distance (b) from the 0-plane. It is hypothesized here that the distance b is determined by two layers which may interpenetrate: a layer of water molecules and the layer of electrolyte cations. It follows that the TLM capacitances can be regressed in terms of the cation radius yielding an interfacial dielectric constant equal to 37 and values of b characteristic of different solids. On rutile, anatase, magnetite and manganese dioxide, b is equal to 1.9A plus the crystallographic radius of the electrolyte cation: for the series Li, Na, and Cs, C1 decreases because b is equal to 2.6, 2.9 and 3.6A, respectively. On these solids, the alkali cations appear to be dehydrated and very close to the 0-plane, possibly forming inner-sphere complexes. In contrast, on hematite, b is equal to 2.1A plus the radius of the hydrated electrolyte cation. Consequently, for the series Li, Na, and Cs, C1 increases because b is equal to 4.6, 4.0 and 3.8A, respectively. Similar considerations apply to goethite, silica and alumina, where Li and Na also appear to be hydrated, possibly forming outer-sphere complexes.

9:00 AM M5.2/H5.2
EVOLUTION OF CORROSION PROCESS ON METALLIC THIN FILM MEDIA. Andrei V. Mijiritskii, Frans C. Voogt, Dik O. Boerma, Groningen University, NVSF, Materials Science Centre, Groningen, THE NETHERLANDS.

Understanding the oxidation mechanism for multi-layered metal films is of high importance for preventing metal-based storage media from failure due to corrosion. In this work, the oxidation of epitaxial Ag/Fe and Ni/Fe bi-layers was studied by x-ray photoelectron spectroscopy (XPS), Rutherford back-scattering spectroscopy (RBS), nuclear reaction analysis (NRA), x-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and conversion electron Mössbauer spectroscopy (CEMS). The epitaxial Ag/Fe and Ni/Fe bi-layers were grown on MgO(100) by molecular beam epitaxy (MBE) or laser ablation deposition (LAD) and subsequently subjected to *in situ* or *ex situ* oxidation in O_2 at elevated ($200−300°C$) temperatures. Different O_2 pressures were applied in the range from 1×10^{-6} mbar to 100 mbar. In both Ag/Fe and Ni/Fe cases the oxidation of Fe was found to initiate through the structural defects present in the Ag or Ni overlayers. The defects consist of domain boundaries and pin-holes formed due to lattice mismatch. The further development of the Fe-oxide growth was found to depend on the overlayer material. Models explaining the observed large difference in oxidation behaviour of the two types of bi-layers are proposed. The dependence of the oxide growth on the O_2 pressure is also discussed.

9:15 AM M5.3/H5.3
EPITAXIAL ELECTRODEPOSITION. Julie K. Barton, Eric W. Bohannan, Run Liu, Mark G. Shumsky, Alexey A. Vertegel and Jay A. Switzer, Univ of Missouri-Rolla, Dept of Chemistry and Graduate Center for Materials Research, Rolla, MO.

The traditional synthetic routes to epitaxial films involve deposition from the gas phase. Epitaxy usually requires similar structures for the film and the substrate, as well as a good match of their lattice parameters. Recently, we reported electrodeposition of epitaxial δ-Bi_2O_3 [1], Cu_2O [2] and PbS [3] on single crystal Au substrates. Here, we extend this work to other oxide materials, including ZnO, Tl_2O_3 and α-PbO_2. These systems are characterized by either very high lattice mismatch (158% in the case of Tl_2O_3), or different lattice symmetry (hexagonal ZnO and orthorhombic α-PbO_2 on cubic Au). Epitaxy is achieved by forming coincidence lattices, in which the structure of the film is rotated with respect to the substrate. We also show the possibility of electrodepositing epitaxial semiconductor heterojunctions, such as Cu_2O/PbS(100) on single crystal Au(100). 1. J.A. Switzer, M.G. Shumsky and E.W. Bohannan, Science 284, 293 (1999). 2. E.W. Bohannan, M.G. Shumsky and J.A. Switzer, Chem. Mater. 11, 2289 (1999). 3. A.A. Vertegel, M.G. Shumsky and J.A. Switzer, Angew. Chem. Intl. Ed., in press.

9:30 AM M5.4/H5.4
MODELING THE COUPLED EFFECTS OF INTERFACIAL AND BULK PHENOMENA DURING SOLUTION CRYSTAL GROWTH. Yong-Il Kwon, Bhushan Vartak and Jeffrey J. Derby, Department of Chemical Engineering and Materials Science, Army HPC Research Center, and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, MN.

Solution crystal growth processes are governed by complex interactions of bulk transport phenomena, surface diffusion, and crystal growth kinetics. Of critical practical importance is the stable growth of discrete facets of large crystals at fast rates. However,

crystal quality is often compromised during fast solution growth by a host of morphological flaws including macrosteps, step bunches, and inclusions. These instabilities arise from the complex interplay between transport and kinetic factors. We present a novel model for the growth of a vicinal facet from solution, which couples surface phenomena and bulk effects. The surface kinetic model, based on the theory of Burton, Cabrera, and Frank (BCF), rigorously accounts for the interactions of discrete growth steps through surface diffusion fields, adsorption and desorption events, ledge growth kinetics with Schwoebel effects, and convective transport due to step motion. This model is self-consistently coupled with a bulk transport model which describes bulk diffusion to terraces, direct bulk diffusion to growth steps, and bulk convective transport due to step motion and applied flow fields. No analytical approximations are made, rather the simultaneous governing equations are solved numerically by an efficient, moving-boundary finite element method. The coupled transport-kinetic model is applied to elucidate mechanisms responsible for step growth dynamics which occur during solution crystal growth. Effects of solution hydrodynamics, different bulk and surface diffusivities and incorporation rates, and the rate of generation of growth steps on the stability of a step train will be discussed.

This work was supported in part by the National Science Foundation. Support was also provided by the Minnesota Supercomputer Institute and the U.S. Army, Army Research Laboratory, Army HPC Research Center. No official endorsement should be inferred.

10:15 AM *M5.5/H5.5
THE CRYSTAL-SOLUTION INTERFACE. Leslie Leiserowitz, Meir Lahav, Dept. of Materials and Interfaces, The Weizmann Institute of Science, Rehovot, ISRAEL.

Nucleation, growth, habit and composition of solution-grown molecular crystals are strongly affected by the nature of the solvent and the presence of molecular additives in the solution. This influence is primarily a result of interaction between the "foreign" molecules and the crystal faces. The structural nature of such interactions was, and still is, generally deduced from a knowledge of the crystal structure and from macroscopic properties, such as the morphology and symmetry of the resulting crystal.

Recently, molecular dynamics simulations and experimental methods such as atomic force microscopy, nonlinear optical spectroscopy, neutron and X-ray reflectivity, and grazing incidence X-ray diffraction (GIXD), have been applied to probe the structure of the crystal-fluid interface at the subnanometer scale. GIXD has matured on studies of metal and semiconductors surfaces and used for interfacial systems such as thin molecular films on water. The technique has begun to be applied to characterize the surfaces of minerals and the molecular crystal-solution interface.

The interplay between crystal nucleation, growth, morphology, twinning and the crystal-liquid interface shall be addressed where techniques such as GIXD have been applied to help elucidate the structure of the solid solution interface.

10:45 AM M5.6/H5.6
THE ACIDIC AND REDUCTIVE DISSOLUTION OF γ-MnOOH DURING THE SORPTION AND OXIDATION OF CR(III). Robert Weaver, Michael Hochella, Jr., Virginia Polytechnic Institute, Dept. of Geological Sciences, Blacksburg, VA.

The interaction of $Cr(III)_{aq}$ with Mn-oxide surfaces is complex, characterized by the simultaneous reductive dissolution of the Mn-oxide surface and oxidation of Cr(III) to the more toxic Cr(VI) species. Our experimental approach to understanding these reactions has been 3-fold: 1) to directly observe these surface reactions using fluid-cell AFM, 2) to identify and quantify the reaction products using XPS, and 3) to measure the aqueous concentrations of Cr_T, Cr(III) and Mn(II) using ICP and colorimetric analysis. Our in situ fluid-cell AFM observations show the growth of Cr microprecipitates and the dissolution of the manganite (110) and (100) surfaces to be spatially heterogeneous. Because of this heterogeneity, it is difficult to measure the rate of Cr-bearing microprecipitate growth or manganite dissolution. However, with exposure to a pH 4.5, 100μM Cr(III) solution for one hour, we have observed simultaneous growth and dissolution at the mineral-water interface. The Cr-microprecipitates cover existing hillocks to a thickness of up to approximately 2nm and do not appear to nucleate with preference along step edges. Observations of surfaces reacted for up to 30 hours show these precipitates to undergo continued growth or dissolution. SEM images of these reacted surfaces have revealed highly eroded, kinked steps in some areas. However, immediately adjacent step edges may appear undisturbed. These AFM and SEM observations suggest that the solution conditions are locally more aggressive at certain topographic or structural sites. XPS results from cleaved surfaces and powders reacted under conditions analogous to the AFM experiments show a progressive increase in Cr with time up to 8 hours, then remaining constant suggesting surface saturation. The oxidation states of the Cr and surface Mn, as determined from multiplet splitting, remain

throughout the experiment as Cr(III) and Mn(III), respectively. Ongoing experiments are focused on measurement of Mn(II) and Cr(VI) concentrations produced as a function of time and initial [Cr(III)].

11:00 AM M5.7/H5.7
MISORIENTED ATTACHMENT: PREFERENTIAL DISSOLUTION IN HETEROGENITE (CoOOH). R. Lee Penn, Department of Earth and Planetary Sciences; Alan T. Stone, Department of Geography and Environmental Engineering; David R. Veblen, Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD.

High Resolution Transmission Electron Microscopy (HRTEM) results show a strong crystal-chemical and defect dependence on the mode of dissolution of synthetic heterogenite (CoOOH) particles. As-synthesized heterogenite particles are micron-size plates (aspect ratio $\sim1/30$) constructed of crystallographically oriented $\sim$3-nm primary particles or are single $\sim$21-nm unattached heterogenite platelets (aspect ratio $\sim1/7$). Reductive dissolution; using 10 μM to 2 mM hydroquinone, acetate buffer (pH $\sim$4.6), and 0.4 mM total Co as heterogenite particles; was examined in order to evaluate morphology evolution as a function of reductant concentration. Two end-member modes of dissolution were observed: 1) non-specific dissolution of macroparticles and 2) preferential dissolution along misoriented boundaries. In the case of non-specific dissolution, average macro-crystal size and morphology is not altered as building block crystals are consumed. The result is web-like particles with similar breadth and shape as undissolved particles. Preferential dissolution involves the formation of channels or holes along boundaries of angular misorientation. Such boundaries involve only a few degrees of tilt, but dissolution occurs almost exclusively at such sites. Energy Filtered TEM thickness maps show that the thickness of surrounding material is not significantly different from that of undissolved particles. For comparison, unattached $\sim$21-nm heterogenite particles underwent partial reductive dissolution using hydroquinone, and HRTEM results show dissolution primarily at the {101} and {102}, or edge, crystal faces and no significant dissolution at the (001), or basal, crystal faces. This suggests that the reactive surface area is dominated by edge faces and that basal faces are essentially non-reactive under these conditions. Finally, natural heterogenite from Goodsprings, Nevada shows morphology and microstructure similar to that of the synthetic heterogenite macroparticles.

11:15 AM M5.8/H5.8
HALOGEN CORROSION OF TiO$_2$: A FIRST-PRINCIPLES STUDY. Andrew A. Quong, Babak Sadigh, C.M. Schaldach and W.D. Wilson, Lawrence Livermore National Laboratory, Livermore, CA.

The corrosion of Ti shows an unusual dependence on which halogen anion is in solution. Cl, Br, and I are expected to have increasing pitting potentials, yet it observed that Br has a significantly lower pitting potential. In order to get a clearer understanding of the surface chemisty that governs this reaction, we have performed first-principles density functional calculations of the interaction of these anions on a TiO$_2$ surface. We consider the adsorption of these anions at different surface sites and address the role of surface defects. The influence of the electrochemical double layer is also considered.

11:30 AM *M5.9/H5.9
TOTAL ENERGY CALCULATIONS OF IRON AND ALUMINUM OXYHYDROXIDE BULK PHASES AND SURFACES. James R. Rustad and Kevin M. Rosso, Pacific Northwest Natl Lab, Richland, WA.

The intrinsic stabilities of the oxyhydroxide polymorphs constitute an important set of controls on the structures of hydroxide/oxyhydroxide precipitates on mineral surfaces. For example, as CrOOH grows on magnetite through chromate reduction, the fact that CrOOH has only been characterized in the heterogenite and manganite structures would suggest that other possible structures, such as the diaspore/goethite structure may not be exhibited by CrOOH. On the other hand, it is possible that the structures are more a function of kinetics than of intrinsic lattice stability, with intrinsic equilibrium structural preferences playing only a minor role in which type of structure forms. To shed some light on this issue, plane-wave pseudopotential methods are used to investigate the structures and total energies of AlOOH and FeOOH in the five canonical oxyhydroxide structures: diaspore (goethite), boehmite (lepidocrocite), akaganeite, guyanaite, and grimaldiite. The local density approximation was used in conjunction with ultrasoft pseudopotentials in full optimizations of both AlOOH and FeOOH in each of these structures. Structures are in reasonably good agreement with experiment, with lattice parameters and bond lengths within 3 percent of the experimental ones. Neither AlOOH nor FeOOH have been identified in the grimaldiite or guyanaite structures, however we find that total energies for AlOOH and FeOOH in these structures are comparable to or lower than the total energies of the commonly observed polymorphs. The near equality of

the total energies of each of the different polymorphs suggests that kinetic factors are more important in determining the structure of these polymorphs than intrinsic stabilities.

1:30 PM *M6.1/H6.1
FUNDAMENTAL ASPECTS OF ALLOY DISSOLUTION.
K. Sieradzki, Dept. of Mechanical and Aerospace Engineering, Arizona State Univ., Tempe, AZ.

Conventionally, the critical potential marks the onset of bulk dealloying and the development of a bi-continuous solid/void microstructure. The current density below the critical potential is only weakly dependant on potential and the physical processes responsible for this passive-like behavior are poorly understood. We will present experimental data connecting the surface morphology evolution to the current density in each of these regions, and discuss analytical models that have been developed to describe this complex behavior.

2:00 PM *M6.2/H6.2
3D PATTERN FORMATION AND POROSITY IN BINARY ALLOY CORROSION. Jonah Erlebacher, Michael J. Aziz, Harvard University, DEAS, Cambridge, MA; Karl Sieradzki, ASU, Tempe, AZ.

Electrochemical dissolution of the less noble component of a binary alloy has long been known to result in extended three-dimensional nanoporous structures of the more noble species. We used a kinetic Monte Carlo model to examine the microscopic origin of such pore formation. We have found that a model that incorporates only (1) diffusion of all species and (2) dissolution of the less noble species exhibits the entire range of current/voltage behavior seen in real experiments. In particular, the model is quantitatively compared to dissolution data of Ag-Au alloys.

2:30 PM *M6.3/H6.3
DEALLOYING OF LOW INDEX Au_3Cu AND Cu_3Au SINGLE CRYSTALS: AN IN-SITU STM STUDY. Gerald A. Eckstein, Andrea S. Dakkouri, Hermann Kaiser, University of Erlangen-Nuremberg, Department of Corrosion Science and Surface Technology (LKO), Erlangen, GERMANY; Martin Stratmann, Max Planck-Institute of Iron Research, Dusseldorf, GERMANY.

Alloys are of great technological importance because their properties can be tailored by changing the chemical composition. Detailed information about the surface properties of alloys is essential for a deeper understanding of complex interfacial reactions in fields like selective corrosion and heterogenous catalysis. At present a detailed understanding of the selective corrosion of binary alloys is still lacking. We present a detailed study of UHV experiments, classical electrochemical results and in-situ STM investigations on low index Au_3Cu and Cu_3Au single crystals. The results were used to evaluate the mechanism of selective copper dissolution and formation of the Au-rich protective layer in the low current ($E<E_c$) potential region during anodic polarization of Au_xCu_y alloys.
The stability of binary alloys in aqueous environments depends on the alloy composition at the surface, their surface preparation and the electrolyte. For this reason the single crystals were prepared under UHV conditions and characterized by LEED, UHV-STM and surface X-ray diffraction (SXRD). These surface studies revealed new structural models for the topmost surface region and represent an ideal starting point for electrochemical and in-situ EC-STM studies on defined surfaces. Electrochemical studies in sulfate media by cyclic voltammetry and current-time transients enabled us to get a deeper understanding on different electrochemical behavior of low index single crystals. The Au_3Cu and Cu_3Au surfaces showed different critical regimes dependent on the netplanes. Kinetic data have been obtained which describe the early stages of dealloying. In comparison to sulfate media, chloride caused a decrease in E_c which is also dependent on the netplanes.
In situ EC-STM was used to study the nature of surface morphology during dealloying of Au_3Cu and Cu_3Au at potentials below the critical potentials. The electrochemical behaviour was correlated with alteration of surface morphology observed by in situ EC-STM. The results demonstrate also the necessity of careful electrode preparation under UHV conditions to get reproducible data.

3:30 PM *M6.4/H6.4
IN-SITU STUDIES OF THE ATOMIC-SCALE DYNAMICS OF COPPER DISSOLUTION. Olaf Magnussen, Universität Ulm, Abteilung Oberflächenchemie and Katalyse, Ulm, GERMANY.

The anodic dissolution of a bare metal surface is one of the most basic processes in electrolytic corrosion, however, a detailed picture of the underlying microscopic mechanisms and dynamics is only emerging. The kinetics of metal dissolution are determined by the removal of atoms at atomic kinks in the steps on the crystal surface. We demonstrate here that the local rate of these atomic-scale processes, which can not be obtained from electrochemical measurements due to the generally unknown kink density, can be measured directly using methods based on in-situ scanning tunneling microscopy. As an example the anodic dissolution of Cu single crystals in acidic electrolytes was investigated, with particular emphasis on Cu(100) in HCl solution. The latter system is especially well suited for these studies, since the Cu surface is covered in the dissolution regime by an ordered c(2x2) Cl adlayer, which induces a pronounced facetting of the steps. This results in straight {001}-oriented steps with a very low density of structurally well defined kinks, facilitating the separation of individual kinks. Various approaches for the study of the fast dynamic processes at individual kinks by in-situ STM are discussed. First we show that the motion of kinks along the step, which by far exceeds the temporal resolution of conventional scanning probe microscopes, can be directly observed by a novel high-speed electrochemical STM, recently developed in our group. Atomic resolution studies by this instrument with acquisition rates of up to 30 images per second confirm that local dissolution as well as the reverse local growth processes proceed via subsequent removal/addition of atoms at kink sites starting at the corners of the terraces. Better suited for quantitative studies is a second type of experiments, where STM scan lines are alternately recorded at two positions along the step, which allows to measure the propagation time of kinks between these positions. From a statistical analysis and a simple random-walk model detailed data on the kink dynamics can be obtained. Both methods indicate high local rates and pronounced local dissolution/ redeposition fluctuations at the individual kinks even at the onset of Cu dissolution with average kink propagation and reaction rates in the range of 10^3 and 10^5 atoms s^{-1}, respectively. In addition, they reveal a second, unexpected collective process, where not one but two rows of the elementary cells are removed.

4:00 PM M6.5/H6.5
COMPUTER MODELING OF CORROSION PROCESSES. MOLECULAR DYNAMICS AND HARTREE-FOCK CALCULATIONS. R.I. Eglitis, Institute of Materials Research and Engineering, Singapore, SINGAPORE; M.R. Philpott, Institute of Materials Research and Engineering and Departments of Chemistry and Material Science, National University of Singapore, SINGAPORE; S.V. Izvekov, Institute of Materials Research and Engineering, Singapore, SINGAPORE.

It is extremely important to understand the fundamental mechanisms involved in corrosion and find ways for its inhibition. The dissolution of metal is an important step in corrosion. Taking into account that the predictive power of first principles quantum electronic structure calculations due to increased speed of computers and recent developments of a new and powerful computational methods that allow one to model aspects of corrosion processes we have explored features of the potential energy surface (PES) of a metal atom (ion) leaving a hydrated metal surface using quantum electronic structure calculations for a model that retains the key physics of the dissolution process. In separate calculations aspects of dissolution/deposition dynamics are followed using ab initio molecular dynamics. Scenarios for dissolution include adatom detaching from kink, step or terrace site. Comparisons between (001) and (111) are described as well as for atom in the (001) surface plane.

4:15 PM M6.6/H6.6
Transferred to M5.3/H5.3

SESSION M7: POSTER SESSION:
MORPHOLOGY AND DYNAMICS OF CRYSTAL
SURFACES IN COMPLEX MOLECULAR SYSTEMS
Chair: Jeffrey J. Derby
Wednesday Evening, April 26, 2000
8:00 PM
Salon 1-7 (Marriott)

M7.1
FORMATION OF A CELLULAR CRYSTAL SUB-MICRO-STRUCTURE IN BUTTER WITH ADMIXTURES.
Tamara A. Rashevskaya, Ukrainian State University of Food Technologies, Kiev, UKRAINE.

The ecological situation of the last decades has aroused a profound interest of all countries in manufacture of products with admixtures of natural raw materials. We have developed new types of butter with

admixtures of vegetable raw materials possessing an extremely plastic consistency. The influence of red-beet cryopowder admixtures (obtained by sublimation drying) on formation of the sub- microstructure of the milk fat phase has been studied by the electron microscopy method. A cellular crystal structure was found to be formed in the butter on the fat globules surface as well as in the interglobule sphere. The size of cells is around 100 nm. The mechanism of the structure formation has also been studied. In the processes of the milk fat phase crystallization water-soluble beet components play the role of admixtures enriching the boundary layer of the fat component crystallization interface. It conduces to morphological changes of fat and water phase separation surface which has clearly been fixed on the electron microscopic photographs. Knobs with the average diameter of around 60 nm are the initial stage of the cellular structures formation of which the cellular structure is formed thereafter. Interaction of the fat and water phases in the processes of the structure formation has been found. The knobs are formed of the most high-melting fat glycerides and are surrounded by concentric rings of ultradisperse water particles with the size of 3 to 12 nm. During the milk-fat hardening process the most low-melting glycerides along with moisture are rejected by the moving crystallization interface to the cells boundaries. The ultradisperse water particles tend to occupy a stable thermodynamic position and are arranged on vertices and faces of four-, five- or six-angle fat crystals with octahedral, decahedral and icosahedral forms. The plastic consistency of the butter is explained by the cellular sub-microstructure formation.

M7.2
EFFECT OF ADDITIVES ON THE CRYSTALLISATION OF SOME BIOMOLECULES: CYSTINE, CALCIUM OXALATES, CALCIUM PHOSPHATES. S. Narayana Kalkura, G.R. Sivakumar, E.K. Girija, N. Meenakshi Sundaram, P. Ramasamy of Crystal Growth Center, Anna University, Chennai, INDIA.

Cystine is a dibasic sulfur containing amino acid present in the body. Cystine was crystallised using solution and gel methods. Crystals of single, twinned, bunched hexagonal,cubic, rectangular and bipyramidal morphologies have been obtained. Effect of Ca, Fe and Iodine were studied on the crystallization of Cystine. Hollow rectangular crystals of cystine were obtained for Ca doping where as Fe produced fibers of cystine. Calcium oxalate is the major inorganic component of urinary calculi. Effect of cadmium, lead, and zinc on crystallization of Calcium oxalate was studied. Cadmium and lead increased the primary agglomeration where as Zn increased the secondary agglomeration. Zn also modified the morphology of Calcium oxalate crystals. The studies on nucleation and growth of dicalcium phosphates have received considerable attention as a precursor and a source of calcium and phosphate ionic species involving biomineralisation. Effect of Cd and Zn was studied on the crystallization of dicalcium phosphate (DCP) and dicalcium phosphate dihydrate (DCPD). Presence of cadmium produced bending in the crystals of DCP whereas zinc enchanced the primary agglomeration of DCPD crystals. The modified crystals have been studied by SEM, XRD, and ICPAES analyses and the results will be discussed in detail.

M7.3
SURFACE INVESTIGATIONS OF AMINO ACID BINDING ON CALCITE. Mary T. McBride, Christine A. Orme, Aleksandr Noy, Jim J. De Yoreo, Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA.

In previous work using in-situ AFM and SEM we investigated interactions between calcite crystal surfaces and aspartic acid. We observed that calcite crystals, grown in the presence of D-(right-handed) and L-(left-handed) aspartic acid became elongated in the (001) directions and expressed an unequal mixture of {hk0} facets. These results indicate that: 1) aspartic acid adsorbs to the surface, 2) the adsorption is stereospecific, involving the stereotopic carbon atom and at least one other atom, and 3) that binding does not inhibit step growth but reduces step edge free energy (in a manner similar to the behavior of surfactants). Here we present the results of our molecular dynamics/molecular mechanics studies on the interactions of D and L-aspartic acid on a number of calcite faces and we discuss our findings in the context of several proposed adsorbate binding models. We have used external reflection-absorption FTIR to investigate the dynamics of the solid/solution interface of a calcite/aspartiic acid system. Assuming that the calcite surface is a termination of the bulk crystal, the observed shifts in vibrational bands in the FTIR spectra are related to restructuring of the organic film. The FTIR results will also be discussed in the context of proposed adsorbate binding models. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

M7.4
ANOMALOUS GROWTH OF CALCIUM CARBONATE INDUCED WITH SILICATE IONS. Hiroaki Imai, Tomohiro Terada, Satoshi Yamabi, Naotatsu Shikazono and Hiroshi Hirashima, Keio Univ, Dept of Applied Chemistry, Yokohama, JAPAN.

Investigation of the effects of additives on the growth of calcium carbonate is important for clarifying the mechanism of biomineralization. In this work, we studied morphological evolution of calcium carbonate grown in silica colloid. The growth behavior of calcium carbonate was found to be drastically influenced with variation of pH of silica colloid. Although normal rhombohedral crystals of calcite were formed at neutral pH, roughening of the surface and formation of spicular morphology of the crystals were observed with increasing pH. Finally, a sheaf-of-wheat morphology was produced above pH 10. Since silicon was detected on the surface of the carbonate crystals, the morphological changes are ascribed to selective adsorption of silicate ions on the surface. Influence of the silicate ions on the surface roughening and the anomalous growth of calcite is discussed.

M7.5
INTERSTITIAL ATOMS DIFFUSION IN THE BULK AND AT THE SURFACE OF CRYSTAL. SURFACE SEGREGATION. Dmitry V. Schur, Mykhaylo M. Baklanov, Evgen Horungyi, Institute of Hydrogen and Solar Energy, Kiev, UKRAINE; Sveltana Yu. Zaginaichenko, Institute for Problems of Materials Science of NAS, Kiev, UKRAINE; Zinaida A. Matysina, Dnepropetrovsk State University, Dnepropetrovsk, UKRAINE; Iryna B. Plisak, Lviv State Ivan Franko University, Lviv, UKRAINE.

Theoretical investigation of diffusion, distribution and thermally activated redistribution of impurity interstitial atoms C (hydrogen, carbon) about the volume and surface both of crystalline films and massive crystals AB have been realized. These crystals have b.c.c, lattice and various types of free facets. The dependence of hydrogen and carbon filling of the surface and volume interstitial sites upon the films temperature and composition have been studied.
The change of thermodynamic parameters, as temperature T and pressure P, leads to the redistribution of C atoms in the system. The thermally activated processes of C atoms redistribution along the volumetric and surface film interstices in AB alloy are being investigated.
The formulae for the equilibrium concentrations of interstitial atoms C and the rate or time of relaxation of interstitial atoms redistribution in dependence on the a, b concentrations of A, B alloy components, on the long range order n in the A, B atoms distribution at the sites of crystal lattice, on the temperature T, on interaction energies v_{AH}, v_{BH} of atomic pairs AH, BH have been determined. It has been found the formula for critical pressure P*, which stimulate the surface segregation of the C atoms.
Theoretical calculations have been compared with experimental data concerning the surface enrichment by hydrogen of the Pd-H, Ti-H alloys and these alloys with impurity of Ag, Au, In, Mo, Co, Pt and for graphitization of Fe-C, Co-C, Ni-C alloys and Fe-C alloy with the addition of Cr, V, Co, Ni, Ti metals. The agreement of theory and experimental data has been satisfactory.

M7.6
THE MOLECULAR STRUCTURE OF INTERFACE IN THE CRYSTAL-MELT SYSTEM. THE CRYSTAL SURFACE ROUGHNESS. Zinaida A. Matysian, Dnepropetrovsk State University, Dnepropetrovsk, UKRAINE; Volodymyr Belsky, Institute of Chemical Physics of Metals, Kiev, UKRAINE; Liliya M. Gerych, Kherson Industrial Institute, Kherson, UKRAINE; Dmitry V. Schur, Mykola Baklanov, Institute of Hydrogen and Solar Energy, Kiev, UKRAINE; Svetlana Yu. Zaginaichenko, Institute for Problems of Materials Science of NAS, Kiev, UKRAINE; Yevgen Z. Kurtyak, Ivano-Frankivsk State Technical University of Oil and Gas, Ivano-Frankivsk, UKRAINE.

The surface of crystal may be flat lattice plane or it may have specific defects, and so be rough. For some external planes with sites, the crystal surface may have a complex stepline structure depending on the type of lattice and the indices of this plane.
Our work deals with the results of theoretical analysis of the crystal-melt interface. The (100) face of the rhombohedral crystal lattice characteristic for the metals of the bismuth group is examined. The crystal is assumed to be in equilibrium with the melt. The existence of an interphase transition zone between the crystal and the melt is supposed. It is assumed that atomic density and position of the atoms in the liquid phase near the boundary are the same as in the crystal. The energy of the boundary between crystal and melt is calculated in the quasi-chemical approximation taking into consideration the correlation in the substitution of lattice sites by atoms and the atomic interaction anisotropy.
Such interfacial characteristics as the free energy Φ and atomic roughness S are discussed. The Φ and S values are determined for various values of the interaction energies V_{jk}, v_{jk} (j,k =s,l) between s,l atoms belonging to the solid and liquid phase. V_{jk}, v_{jk} (j,k =s,l)

are the energies of strong and weak bonds, respectively. The calculated results for dependence of the change in free energy Φ on the 'solid' atoms concentration for cases with accounting for correlation and anisotropy and without accounting for the latter are presented. The molecular roughness S of the interface is determined. The effect of correlation and anisotropy on the crystal surface roughness is ascertained. The comparison of the theoretical calculation with experimental data for bismuth permitted one to obtain some information about the atomic interaction in solid, liquid and different phases.

M7.7
INFLUENCE OF EXTERNAL TEMPERATURE FIELD ON FORMATION OF EUTECTICS PATTERN. <u>Alex Gusikov</u>, Institute of Solid State Physics, Academy of Sciences of Russia, Moscow District, Chernogolovka, RUSSIA.

We consider a model of directed crystallization. We write the boundary value problem to a curvilinear coordinate frame attached to the interface. The theory of perturbations is formulated for small perturbations of temperature and component concentration without introduction of additional parameters. We study stability of the interface of a binary alloy for various values of the component concentration and give a conclusion of analytical expression for period of eutectic pattern. The obtained expressions for period of beam eutectic pattern in essence differ from expressions of the theory of the Hunt and Jackson. According to the theory of the Hunt and Jackson the period depends on a diffusivity parameters of the phase diagram, surface tension and velocity of transition of interface. The expression, obtained by us, does not contain any of these parameters except for the interface velocity. Principled difference of these expressions is that expression of the theory of the Hunt includes parameters of a diffusion problem, and obtained here expression includes parameters of the heat conduction equation. But it is correctly only in the event that the values of the segregation coefficient k differ from equilibrium. The calculations show, that the value k = 1 is boundary between stable and unstable range of the system [A. Gus'kov Formation of periodic structure under crystallization of eutectics. Electronic Journal Investigated in Russia, 28, 1999 http://zhurnal.mipt.rssi.ru/articles/1999/028e.pdf]. Here we expand model of this paper. We include equation of external temperature field in the system and find dispersion equation of such model. We consider an influence this temperature field on stability of the system. Calculations demonstrate that external temperature field remove value k = 1 from boundary between stable and unstable range. We find also period of eutectics pattern in the case consideriong of external temperature field. This work supported by the Russian Foundation for Basic Research, Grant N 97-02-16845.

M7.8
INFLUENCE OF {0112} FACE ON GROWTH SURFACE ON THE IMPURITY DISTRIBUTION IN PERIODICALLY POLED $LiNbO_3$:Nd:Mg SINGLE CRYSTAL. <u>Tatyana Chaplina</u>, Inessa Naumova, Nina Evlanova, Stanislav Blokhin, Sergey Lavrishchev, Tamara Chernevich, Oleg Shustin, Moscow State Univ, Dept of Physics, Moscow, RUSSIA.

Bulk periodically poled lithium niobate single crystal is a promising material for nonlinear optical devices using quasi-phase-matching. $LiNbO_3$:Nd:Mg single crystal was grown by the Czochralski method along the normal to the {0112} close-packed face. Periodic temperature oscillations on the crystal-melt interface arising during the crystal growth in asymmetric temperature field, it leads to modulations of instantaneous growth rate. Growth surface fixed of impurities and correspondingly of domain walls were studied by the method of X-ray microanalysis , the selective chemical etching, interface method and the atomic force microscope. In the central part of the crystal the growth surface coincides with the face, it was atomically smooth and characterized by the tangential (layer-by-layer) growth mechanism (facet growth). Growth surface of periphery region was atomically rough and characterized by normal growth mechanism (nonfacet growth). Different growth mechanisms of facet and nonfacet regions give different pictures of impurity distribution. Periodic oscillations of Nd and Mg impurity concentration were in antiphase; this situation was caused by different effective distribution coefficients. The effect of the face reveals itself in the increasing neodymium concentration and in the creation of smooth domain boundaries. Impurity capture coefficient K depends on crystal growth rate on facet growth region in the most degree than on periphery region. Accordingly the theory (V.V. Voronkov, 1975) the dependence K (V) must valid only for facet growth. We observed this dependence on nonfacet region also. This fact requires the additional consideration.

M7.9
MEASUREMENT OF ORGANIC MATTER COATING THICKNESS ON MINERAL SURFACES BY SMALL-ANGLE X-RAY SCATTERING METHOD DEVELOPMENT. <u>Chao Shang</u>, James A.

Rice, South Dakota State Univ, Dept of Chemistry & Biochemistry, Brookings, SD; J.S. Lin, Oak Ridge National Laboratory, Solid-State Division, Oak Ridge, TN.

Humin is the dominant fraction of soil and sediment organic matter. It forms by the interaction of organic matter with soil clay minerals. Physically, it can be conceptualized as a composite material consisting of an organic layer coating mineral surfaces. Currently, the nature of the organic-mineral interface is unknown. Small-angle x-ray scattering (SAXS) is a technique which is useful for studying the surface physical properties of particles with a dimension from a few to thousands angstrom. In this work, the organic coating thickness of a system consisting of montmorillonite as a mineral phase and a cationic surfactant (alkyltrimethylammonium bromide) as a sorbed organic phase is used as a model of humin. The scattering intensity of a montmorillonite system with concentration ranging form 0.5 to 3.4 weight % was measured to calculate the surface parameters of the clay. The adsorption of the surfactant on montmorillonite, and the dispersion and scattering properties of the organic-clay complexes were studied. In this presentation, we will report the preliminary results on the exploration of SAXS to measure the thickness of organic matter coatings on this model organo-mineral complexes.

M7.10
MORPHOLOGY TRANSITIONS AND DYNAMICS OF CRYSTAL SURFACES OF Si_3n_4 GROWN FROM COMPLEX SILICATE LIQUIDS. <u>Lingling Wang</u>, T-Y. Tien, Dept of Materials Science & Engineering, University of Michigan, Ann Arbor, MI; I-Wei Chen, Dept of Materials Science & Engineering, University of Pennsylvania, Philadelphia, PA.

Silicon nitride is one of the most important covalent ceramics for structural applications. The development of a rod-like morphology is essential for its superior properties and has been intensely studied for 30 years. Recently, using growth conditions with dilute crystal concentrations, we have discovered a novel shape transition in this system. In particular, the end of the elongated rod is found to have a concave morphology, similar to those seen in eutectic growth by Jackson and Hunt but for an entirely different physical origin. This shape transition is size and velocity dependent, and its onset can be further tuned by adjusting the magnitude of the driving force, the chemistry of the additives, and the starting powders. The simplified problem with cylindrical symmetry has been analytically modeled by solving the coupled transport equations on the crystal surfaces and in the liquid, and the more complete solution considering the hexagonal rod geometry has been obtained numerically. The interface structures that underly the dynamics of growth anisotropy have also been elucidated using high resolution transmission electron microscopy. The generality of these observations and their implications to crystal growth in other complex molecular systems will be discussed.

M7.11
EXPERIMENTAL STUDIES OF CRYSTALLIZATION KINETICS IN POROUS MEDIA. <u>Leonid Bronfenbrener</u> and Eli Korin, Ben-Gurion Univ of the Negev, Dept of Chemical Engineering, Beer-Sheva, ISRAEL.

Experimental and theoretical studies on crystallization processes in porous media (for example fine-grained soils) show that the front of macroscopic ice formation lags significantly behind the incipient freezing boundary. This finding points to the existence of an intensive phase transition region, or kinetic zone, in which migration and crystallization of water take place simultaneously. Theoretical analysis of this process requires thermodynamic and kinetic data on the system, which are specific to each of the frozen soil and have to be determined experimentally. In this work, an experimental system for determination of the thermodynamic and kinetic data was designed and built. Experimental measurements were carried out for two different types of soil: sitly clay (fined-grained soil) and sand. The results showed that the kinetic data can be expressed in a simple form, in which the overall crystallization rate is directly proportional to the first-order of the deriving force with a constant coefficient 1/t (where t is the characteristic time of the system). The deriving force in this expression is defined as the diference between the existing and the equilibrium unfrozen water content in the soil. Application of the experemental results to theoretical analysis of crystallization processes in porous media is presented and discussed.

M7.12
PREPARATION OF CdTe NANOWIRE ARRAYS USING A NONAQUEOUS ELECTRODEPOSITION PRECESS IN POROUS ANODIC ALUMINUM OXIDE TEMPLATE. Dongsheng Xu, Institute of Physical Chemistry, Peking University, Beijing, PR CHINA; Dapeng Chen, Department of Material Science & Engineering, Yunnan Polytechnic University, Kunming, PR CHINA; Xuesong Shi, Institute of Physical Chemistry, Peking University, Beijing, PR CHINA; <u>Guolin Guo</u>, Institute of Physical Chemistry,

Peking University, Beijing, PR CHINA; Linlin Gui, Institute of Physical Chemistry, Peking University, Beijing, PR CHINA; Youqi Tang, Institute of Physical Chemistry, Peking University, Beijing, PR CHINA.

In the past few years, one-dimensional nanostructural materials, such as nanotubes and nanowires, have attracted much attention both because of their importance in fundamental and the wide-range potential applications in nano devices. Many experimental approaches to fabricate nanowires have been reported, utilizing a variety of nano-fabrication techniques, and crystal growth methods including arc discharge, laser ablation, catalytic CVD growth and template synthesis, etc. In this field, it is still a challenge to synthesis an aligned and well-distributed nanowire arrays as well as highly crystallized structure. In this paper, we have successfully prepared the orient CdTe nanowire arrays by dc electrodeposition in porous anodic aluminum oxide template from an ethylene glycol solution of 1M $CdCl_2$ containing 0.01M $TeCl_4$ and 0.3M KI. The nanostructure and morphology as well as the atomic composition characterization of these nanowires are carried out by SEM, TEM, EDAX and XRD techniques.

SESSION M8: MACROMOLECULES
Chairs: Alex J. Malkin and Christine A. Orme
Thursday Morning, April 27, 2000
Golden Gate C2 (Marriott)

8:30 AM M8.1
THE NUCLEATION AND CRYSTALLIZATION OF HARD SPHERE COLLOIDS. Frank B. van Swol, Sandia National Laboratories, Catalytic and Porous Materials Dept. and The University of New Mexico, Department of Chemical and Nuclear Engineering, Albuquerque, NM.

The crystallization of hard sphere colloids constitutes one of the simplest examples of self-assembly in complex systems. Hard sphere colloids can often be viewed as a prototype for more complex suspensions (e.g. protein solutions). Specific issues of recent interest include the phase diagram, the stacking order of the equilibrium crystal, the effects of size ratios and more generally polydispersity, nucleation and growth, and the role of gravity. We report on recent lengthy molecular dynamics simulations of nucleating and crystallizing hard sphere models. The simulations address the effects of the overall starting density on nucleation and the rate of growth. Our simulations provide an explanation for the puzzling results of recent space shuttle experiments of crystallizing colloidal suspensions. These experiments reported finding more random hcp crystals than on Earth were typically found. We also present a test of homogeneous nucleation theory by analyzing the coexistence properties of stable crystal nuclei in the canonical ensemble. Homogeneous nucleation theory is used to derive an accurate value for the crystal fluid interfacial tension. These particular simulation results are compared to the experimental results reported in recent years by van Megen and co-workers.

8:45 AM M8.2
THERMODYNAMICS OF THE MACROMOLECULAR PHYSISORPTION AT THE SOLID-LIQUID INTERFACE. Paolo Samorí, Humboldt University Berlin, Department of Physics, Berlin, GERMANY; Klaus Müllen, MPI for Polymer Research, Mainz, GERMANY; Jürgen P. Rabe, Humboldt University Berlin, Department of Physics, Berlin, GERMANY.

Molecular self-assembly, namely the spontaneous well-defined association of molecules, is the basis of many successful strategies to produce nano- and meso-scopic-structures that adopt thermodynamic minima. The generation of complex, multicomponent three dimensional structures involve intramolecular, as well as inter-molecular and interfacial interactions. Besides, the possibility to understand and control the processability in thin films through self-assembly is crucial for their technological applications in the field of molecular recognition and molecular electronics. We describe here STM work which monitors the self-assembly of soluble alkylated oligomeric and polymeric para-phenyleneethynylenes in monolayers at the solution-HOPG interface. Phenyleneethynylene trimers pack in an epitaxial 2D polycrystalline structure. The molecular dynamics at the interface exhibits Ostwald ripening, which is driven by a minimization of the line energies. A high resolution imaging enabled us to bestow information into the kinetics of this process and to draw some conclusions on thermodynamic and kinetic contributions to this grain coarsening. The corresponding polydisperse system was visualized with molecular resolution. The macromolecules exhibit a nematic-like molecular order at the interface with HOPG. Single rods are aligned along preferential orientations according to the symmetry of graphite. The true molecular lengths were evaluated quantitatively from STM

images. It revealed a macromolecular fractionation occurring at the interface between the organic solution and the solid substrate. Being the macromolecular physisorption governed by a competition between entropic and enthalpic gains, for stiff polymers, the adsorption of the longest chains which are sufficiently straight is favored. Comparing this result with the one obtained with Monte Carlo simulations of the macromolecular physisorption of rigid rods on HOPG, it is possible to gain deeper insights into this phenomenon and to discern the enthalpic and entropic contribution leading to this fractionation. This result paves the way towards the use of self-assembly at surfaces to filter a polymeric solution.

9:00 AM *M8.3
REAL TIME IN-SITU MONITORING OF MOLECULAR PROCESSES DURING GROWTH OF PROTEIN CRYSTALS. S.-T. Yau, Bill R. Thomas, Dimiter N. Petsev and Peter G. Vekilov, Center for Microgravity and Materials Research and Department of Chemistry, University of Alabama-Huntsville, Huntsville, AL.

Using the atomic force microscope (AFM) in-situ during the crystallization of the proteins ferritin and apoferritin, we studied the processes of crystal growth at the molecular level. We show that the density of the incorporation sites (kinks) on growth steps propagating on the surface (i) is the same as at equilibrium, and (ii) does not depend on the macrosopic step orientation since during growth the steps consist of segments along the dense crystallographic directions. Observation (i) allows evaluation of the bond energy between molecules in the crystal. Furthermore, we determine the frequency of attachment of molecules at the kinks and show that step motion is fully described by this frequency and the kink density. We show that impurity molecules adsorb on the surface of a growing crystal at concentrations two-three orders of magnitude higher than in the solution bulk. We identify the impurity molecules as ferritin dimers and determine their shape as two connected spheres. We monitor impurity dimer incorporation by the growing crystal layer and show that the trapped dimers initiate series of point defects that cause lattice strain. Thus, unlike in semiconductors, the defects therefore are nonequilibrial. The point defects replicate in subsequent layers due to the elastic strain. The strain may be resolved by a plastic deformations giving rise to mosaicity in the crystal. We demonstrate that using single-molecule manipulation with the AFM tip the defects can be healed to restore the regular lattice.

10:00 AM *M8.4
THE DEFECT STRUCTURE AND GROWTH KINETICS OF STMV CRYSTALS. Yurii Kuznetsov, Alexander Malkin, Alexander McPherson, University of California, Irvine, Department of Molecular Biology & Biochemistry, Irvine, CA.

To grow good diffracting macromolecular crystals is a long-standing problem. Incorporation of macromolecular impurities into growing crystal and the presence of point and linear defects have always been considered to be the most important factors influencing the diffraction properties of macromolecular crystals. Using AFM we are studying the defect structure and growth kinetics of two crystal forms, orthorhombic and cubic, of satellite tobacco mosaic virus. Grown at the same growth conditions, orthorhombic crystals produce X-ray diffraction data to at least 1.8 A resolution while cubic crystals to about 4.0 A. In the orthorhombic crystal form each virus particle has eight neighbors, four of which are within the crystal surface. The crystals have a high density of point defects. They are very stable and do not dissolve even in water. Growth steps propagate through the fence of point defects even at micromolar concentrations of the precipitant. In the cubic crystal form each virus particle has 12 neighbors. These crystals dissolve at virus concentrations less than the equilibrium concentration, the value of which depends on the precipitant concentration. Cubic crystals have a very low point defect density; however, once they become larger, screw dislocations and cracks appear. Screw dislocations have extended cores the size of which depends on Burgers vector. Growth steps can not propagate between two dislocations by incorporation of virus particles into the step edge when the distance between dislocations is less than 3 microns. In that case growth steps propagate by formation of protuberances on step edges. Some structural features that influence diffraction properties of macromolecular crystals will be discussed.

10:30 AM *M8.5
INVESTIGATING PROTEIN-PROTEIN INTERACTIONS IN THE SOLID-STATE: STUDIES OF INSULIN SELF-ASSEMBLY. Christopher M. Yip, Institute of Biomaterials and Biomedical Engineering; Depts. of Chemical Engineering and Applied Chemistry, and Biochemistry, University of Toronto, Toronto, Ontario, CANADA.

Controlling how molecules associate, both in solution and ultimately into well-defined supramolecular assemblies, therefore represents a powerful means of designing materials with tailored physical, and in the case of pharmaceutical compounds, therapeutic characteristics.

For biomolecules, their amino acid sequence and molecular conformation, both in solution and the solid-state, play a critical role in defining their self-association characteristics. Recent developments in scanning probe microscopy (SPM) have proven ideal for probing such assembly mechanisms and studying protein-protein interactions. Our investigations of biomolecular self-assembly have focused on the therapeutically important hormone insulin. Stored in the pancreas as a hexameric complex, the active form of insulin is the monomer and thus the design of new insulin-based therapies for the treatment of diabetes has focused primarily on manipulating the insulin hexamer-monomer dissociation pathway. Since diabetes therapies rely on both soluble and crystalline forms of insulin, it is essential to consider insulin self-assembly into the solid state, especially in the design of extended time-action therapies. Our in situ SPM studies provided detailed insights into the dynamics of insulin crystal growth, real-space determination of local insulin packing motifs, and direct measurement of insulin-insulin binding forces. Combined with molecular modelling, our studies reveal how subtle changes in amino acid sequence and surface hydrophobicity can dramatically affect local interfacial structure and influence biomolecular assembly.

11:00 AM *M8.6
THE ROLE OF MACROMOLECULAR X-RAY CRYSTALLO-GRAPHY IN MODERN BIOTECHNOLOGY. Alexander McPherson, Dept of Molecular Biology and Biochemistry, University of California, Irvine, CA.

The current revolution in molecular biology and biochemistry has been driven by two salient technologies, recombinant DNA procedures, and precise determination of the molecular structures by X-ray diffraction. In a sense, the former provides biotechnology with a synthesis capability for proteins and nucleic acids that was previously lacking, while the latter supplies the analytical capability also previously absent. The use of recombinant DNA technology has matured over the past two decades and has now reached the point where it has assumed a place of routine, assured application. This is not yet true of X-ray diffraction of macromolecules, which is still an actively developing field. The reason that X-ray analysis has lagged, in spite of an earlier start, is that one specific component of the X-ray crystallographic process has remained somewhat intractable. That is the growth of macromolecular crystals suitable for application of the X-ray diffraction technique. As a consequence, protein, virus, and nucleic acid crystal growth has taken on great importance to molecular biology, and to biotechnology. If the problems associated with macromolecular crystal growth can be overcome, it will unloose a resurgence of progress in the development of new uses for proteins in medicine, agriculture, and industrial chemistry. Problems in macromolecular crystal growth are now being addressed with a wide variety of physical, chemical, and even genetic methods, and some of these will be described in this presentation. In addition, some attention will also be devoted to the role of X-ray crystallography and crystal growth in particular in the context of the new initiative by the National Institutes of Health to determine the detailed atomic structures of all of the gene products, proteins, produced by the human genome.

SESSION M9: INORGANIC SYSTEMS
II–IMPURITIES AND DEFECTS
Chairs: Alex A. Chernov and Katsuo Tsukamoto
Thursday Afternoon, April 27, 2000
Golden Gate C2 (Marriott)

1:30 PM M9.1
STEP BUNCHING NEARBY A COMPLEX DISLOCATION SOURCE. Sergey Potapenko, Livermore, CA.

We consider a step generation by a complex dislocation source when a period of spiral revolution is about of time of impurity adsorption. In this case step velocity depends on the life time of the terrace. Such system can have several steady rotations corresponding to different surface concentration. When the source is complex, nonequilibrium adsorption can lead to a step bunching, and the source will be generating a macrostep. Conditions of this instability was obtained based on a model of nonequilibrium adsorption.

1:45 PM M9.2
EFFECTS OF NITROGEN IMPURITIES ON THE CVD GROWTH OF DIAMOND: STEP BUNCHING IN THEORY AND EXPERI-MENT. Femke de Theije, John Schermer and Willem van Enckevort, Research Institute for Materials, University of Nijmegen, Nijmegen, THE NETHERLANDS.

The step flow dynamics during homoepitaxial diamond deposition on vicinal {001} diamond surfaces in the presence of nitrogen impurities in the gas phase is investigated by experiments as well as by computer simulations. The adsorption of impurities on the diamond surfaces leads to step bunching, whereby complex two-dimensional patterns are formed. A mesoscopic Monte Carlo model is used to study this effect, whereby line tensions, anisotropy in step propagation, roughness of steps and impurity strength are introduced on a physical basis. The similarity between experimental results and the step configurations resulting from simulations is remarkable. Furthermore, the coexistence of both step bunching and an increased growth rate upon nitrogen addition is explained by the fact that nitrogen on the surface has a different effect on the diamond growth than sub-surface nitrogen. This study gives a demonstration of a fruitful co-operation between computer simulations and real world experiments, which leads to a better understanding of the physical processes occurring during crystal growth.

2:00 PM *M9.3
LIFE NEAR THE DEAD ZONE: RECOVERY OF SURFACES FROM IMPURITY POISONING DURING CRYSTAL GROWTH. T.A. Land, T.L. Martin, S. Potapenko, J.J. De Yoreo, Dept. of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA.

In-situ AFM has been used to investigate growth near the dead zone on the (100) face KDP. Models based on the classic theory of Cabrera and Vermilyea explain behavior near the dead zone in terms of impurity pinning of elementary step motion. Despite the general level of acceptance of this 40 year-old theory, a number of commonly investigated systems exhibit behavior not predicted by the models. Until now, no clear microscopic picture of impurity-step interactions existed. AFM shows that initially, in a nominally pure solution, the surface consists of a highly mobile combination of straight elementary steps and step bunches moving at constant speed. The addition of Fe3+ impurities has a dramatic effect on step motion and morphology resulting in both the elementary steps and the macrosteps becoming distorted and nearly immobile. This regime is known as the dead zone. Images show that the surface consists of an intertwined array of highly convoluted macrosteps and elementary steps that exhibit the classic appearance of impurity pinning. As the supersaturation is increased, surprisingly, we found that the macrosteps resumed growing first moving freely through a field of immobile elementary steps. These images show that, contrary to the assumptions of the classic impurity pinning models, resurrection out of the dead zone is not a result of elementary steps breaking through the fence of impurities, but rather, it occurs by the motion of macrosteps alone. This important observation explains the difference between what has been observed experimentally and what is expected from the Cabrera-Vermilyea-type models. We present a simple physical model that includes macrosteps and relates characteristics of growth near the dead zone to the time scale for impurity adsorption. Work was performed under the auspices of the DOE by LLNL under contract W-7405-ENG-48.

2:30 PM M9.4
INTERACTION OF MOVING STEPS AND CRYSTAL DEFECTS ON SPINEL SURFACES. Svetlana V. Yanina, Department of Chemistry, University of Minnesota, Minneapolis, MN; C. Barry Carter, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Many technologically important applications of ceramic materials, such as their use as catalysts, in information storage systems, etc., depend on effective utilization of certain structural and mechanical properties of their surfaces. In order to better understand surface properties, processes that take place at ceramic surfaces, such as step dynamics, need to be examined. Complex oxides, such as ferrites and transition-metal-based spinels, are widely used in industry. The objective of the present project is to study surface dynamics of the prototypical spinel, $MgAl_2O_4$, and to investigate high-temperature interactions between moving surface steps and lattice defects, such as dislocations, which are present in a crystal. This work is based on Scanning Probe Microscopy (SPM) observations of spinel surfaces which were heat-treated at high temperatures (1200-1900°C). The formation of evaporation patterns at the sites of terminating dislocations and the relationship between these patterns and regular surface steps, were studied. Steps on the (100) surface have a complex structure and may move across the surface as single entities or in step pairs (double steps). Both single and double steps align preferentially along $< 011 >$ directions. Evaporation patterns which form at dislocation-termination sites on the (100) surface have been examined in detail. The mechanism of formation of these patterns is proposed to be the development of spiral pairs (double spirals) which move in a coordinated manner. These findings are in contrast to observations of (111) spinel surface where both regular surface facets and evaporation patterns from dislocation sites consisted of double steps of uniform height. The nature of these steps will be discussed. Research supported by the U. S. Department of Energy under Grant No DE-FG02-92ER45465.

3:15 PM M9.5

RESOLVING THE CONTROL OF MAGNESIUM ON CALCITE GROWTH: THERMODYNAMIC AND KINETIC CONSEQUENCES OF IMPURITY INCORPORATION FOR BIOMINERAL FORMATION. Kevin J. Davis, Patricia M. Dove, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA; Jim J. De Yoreo, Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA.

The role of Mg^{2+} as an impurity in $CaCO_3$ is the focus of intense research due to the ubiquitous occurrence of natural magnesian calcites in biogeochemical environments through biomineralization. An understanding of the macroscopic processes that govern $Ca(Mg)CO_3$ biomineral formation requires characterization of the molecular-scale thermodynamic and kinetic controls on crystallization. Contact mode fluid-cell Atomic Force Microscopy (AFM) was used to determine the effect of Mg^{2+} on calcite growth kinetics in a flow-through environment. The parameters fundamental to calcite mineralization, step velocity and terrace width, were measured through in situ observations of individual growth spirals, as a function of supersaturation and Mg^{2+} impurity levels. Introduction of magnesium at the lowest concentration levels to the growth solutions caused monomolecular step velocities to increase along both the (+) and (-) directions. As magnesium concentration was further increased, step velocities along both directions began to decline while step edges became visibly roughened. These decreases in (+) and (-) step migration velocities were linearly dependent upon magnesium and were coincident with observations of increasing terrace widths. At higher $[Mg^{2+}]$, hillock morphology was significantly altered by modifying kink site activity and preferentially interacting with (-) vicinal faces, eventually expressing new step directions. The magnesium concentration required to halt growth shifted to higher values with increasing supersaturation of growth solutions. The dependence of step velocity on magnesium concentration is consistent with crystal growth impurity models for inhibition by incorporation, and is comparable to the behavior expected from bulk dissolution enthalpies for similar magnesian calcites. Contributions of impurity effects to the Gibbs factor and step-edge energy were assessed. This study is the first to document the microscopic role of magnesium in mediating calcite growth kinetics and to directly determine the mechanism of inhibition. Finally, we relate macroscopic thermodynamic measurements to molecular-scale growth processes.

3:30 PM M9.6

NOVEL STUDIES OF ROUGHENING OF THE PRISM PLANE OF ICE. Ann-Marie Williamson, Alex Lips, Unilever Research Colworth, Sharnbrook, UNITED KINGDOM.

Crystal growth kinetics and morphology depend on an interface parameter, the step free energy. This parameter is difficult to determine directly, but can be accessed indirectly from kinetic roughening studies, which probe the nature of the crystal surface. However, studies of roughening of the ice prism/melt interface have proved difficult experimentally, and estimates for the thermodynamic roughening temperature, TR, remain uncertain. We have successfully introduced a new methodology for the study of roughening of dilute crystal ensembles undergoing isothermal recrystallisation, which can be applied generally to study either crystal/melt interfaces, or crystal/solution interfaces for multi-component mixtures. We apply this methodology to study roughening of the prism plane of ice, and employ fructose as a convenient solute for controlling the dissolution temperature of ice. We adopt a two-fold approach: (i) Determination of the onset of faceting with curvature driving force, (ii) The direct study of the dependence of crystal faceting with temperature. We look for the onset of faceting of the prism plane of ice by following changes in growth morphologies of crystals oriented with their basal planes normal to the observation direction. Fourier analysis is used to quantify changes to crystal morphology, which are correlated with the curvature chemical potential of the ensemble. The two methods yield, for the first time, pragmatic estimates for the thermodynamic roughening temperature, TR, of the prism plane of ice in sugar solution, in the range $-8°C$ to $-12°C$. A preliminary investigation has been undertaken of conformity of the observed transition with an infinite order Kosterlitz Thouless process. If this applied, TR would be higher, but can not be accurately defined by the present data set.

3:45 PM M9.7

DIFFUSION CONTROLLED GROWTH OF ETCHPITS ON KDP CRYSTALS WITH POROUS SOL-GEL COATINGS. E.K. Wheeler, P.K. Whitman, T.A. Land, C. Thorsness, J.J. De Yoreo, J. McWhirter*, M. Hester and R. Aboud, Lawrence Livermore National Laboratory, Livermore, CA. *Union College, Schenectady, NY.

While the etching of crystal surfaces has been studied extensively both in liquid and vacuum environments, device applications often call for use of optical coatings which can be expected to drastically change the transport properties at the surface. Fusion laser systems often use potassium dihydrogen phosphate (KDP) crystals with porous antireflective coatings for harmonic frequency conversion. Recently, we discovered that, after exposure to ambient humidity, these crystal surfaces develop etchpits beneath the sol-gel coatings. Unlike typical etchpits on bare surfaces which occur preferentially at dislocations with a geometry determined by the step kinetics, these etchpits are homogeneously distributed with a density and average size governed by the relative humidity. Furthermore, the etchpits are self-similar in shape and possess facets corresponding to low-energy planes of KDP. We present results from optical microscopy, light scattering, NSOM and AFM that support the following model for etchpit formation in this system. Water absorbed into the porous sol-gel coating contacts the crystal surface causing etchpit nucleation at high undersaturation. The plume of KDP rising from an etchpit slowly diffuses laterally, dropping the undersaturation and shutting off nucleation in the surrounding area. Because surface diffusion is rapid compared to diffusion through the sol-gel, the etchpits continually undergo coarsening and equilibration to maintain a low-energy geometry and generate an average spacing. Growth continues until the reservoir of water in the sol-gel is saturated with KDP. The critical difference between etching on bare and coated surfaces is that the ratio of bulk to surface diffusivity is reversed so that the evolution of the etchpit population is determined by transport rather than surface kinetics. We show that the bulk diffusivity is reduced from $\sim 10^{-5}$ to $< 10^{-12} cm^2/s$ by application of the sol-gel coating, while estimates of the surface diffusivity from island coarsening on bare surfaces is $\sim 10^{-9} cm^2/s$. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

4:00 PM *M9.8

OPTICAL PROBES OF CRYSTAL GROWTH MECHANISMS: INTRASECTORAL ZONING. Richard W. Gurney, Miki Kurimoto, J. Anand Subramony, Loyd D. Bastin, Bart Kahr, University of Washington, Seattle, WA.

Impurities present in crystallizing solutions may become segregated within regions of the resulting crystals that correspond to specific slopes of growth hillocks. When the impurities are dyes or luminophores, chemical zoning of this sort results in distinct patterns of light or color that serve to identify growth active surface structures and crystal growth mechanisms. Moreover, the optical probes, most often oriented within the host crystals, reveal the specificity of non-covalent interactions between molecules and anisotropic hillocks. These examples of intrasectoral zoning during mixed crystal growth are illustrated for three substances, potassium dihydrogen phosphate, potassium sulfate, and alpha-lactose monohydrate, grown in the presence of an azo dye, a luminescent benzene derivative, and a luminescent protein, respectively. Our interpretations of crystal growth mechanisms are based on the results of optical spectroscopies, as well as interference contrast and scanning probe microscopies.

4:30 PM M9.9

GROWTH OF THE {101} FACE OF KDP CRYSTALS AT THE PRESENCE OF DYE CHICAGO SKY BLUE. Olga Gliko, Leonid Rashkovich, Moscow State Univ, Dept of Physics, Moscow, RUSSIA.

It has shown in [1], that the impurity Chicago Sky Blue stains strongly in light-blue color growth sectors of a pyramidal face and does not enter at all into growth sectors of a prism, whereas it is known, that the most of other impurities are absorbed mainly by prismatic faces. Qualitative observation [2] have shown, that the dye is captured by a crystal only at rather low temperatures and the capture is the stronger as the higher is the dye's concentration in a solution and higher is a supersaturation (s). In order to compare the effect of impurity on the movement of growth layers on pyramidal and prismatic faces, the influence of dye on the step velocity (v) and morphology of a surface were investigated by use of in situ interference technique. Experiments were carried out in the kinetic regime at 35-37 degrees Celsius. The dye effects the growth of the {101} face only when its concentration exceeds 1ppm (on a dissolved salt basis) and results in macrosteps formation on the most flat slopes of dislocation hills. The dependence v(s) being almost linear in a pure solution changes in a specific manner at the presence of dye. At the greater impurity concentration on the surface new rapidly varying sources of growth do appear, the macrosteps occur everywhere and dislocation hills disappear.The obtained results are interpreted from the point of a large mobility of adsorbed dye's particles those are effectively captured by growth layers and weakly retard their movement. [1]. J.A. Subramony, S.-H. Jang, B. Kahr, Ferroelectrics, 191 (1997) 293 [2]. N. Zaitseva, L. Carman, I. Smolsky, R. Torres, M. Yan, J. Crystal Growth, 204 (1999) 512

4:45 PM M9.10

THE X-RAY TOPOGRAPHIC MEASUREMENTS OF THE INHOMOGENEITY OF KDP FAMILY CRYSTALS.
Alexey E.Voloshin, Igor L. Smolsky, Shubnikov Inst of

Crystallography, Dept of Crystal Growth from Solutions, Moscow, RUSSIA; Natalia P. Zaitseva, Lawrence Livermore National Laboratory, Dept of Chemistry and Material Science, Livermore, CA.

Quantitative characterization of point-to-point lattice parameter changes in crystals is based on computer processing of plane wave X-ray topographs. This technique provides an observation of areas up to 10 cm^2, locality 3-10 μm and rather high sensitivity to crystal lattice distortions (Δd/d up to 10^{-7}-10^{-8}). This method is applied to the investigation of main kinds of inhomogeneity in rapidly grown KDP crystals: zonal, sectorial and vicinal sectorial ones. The influence of the following factors on crystal inhomogeneity was studied: surface orientation and morphology, temperature, growth speed and supersaturation. The main results are: 1) The most of strong kinds of inhomogeneity are sectoriality and vicinal sectoriality caused by difference in crystallographic orientation of steps. They provide inhomogeneity up to $5*10^{-5}$A. 2) In rapidly grown KDP crystals prism is much more uniform than pyramid. 3) Change of vicinal hillock slope provides the inhomogeneity compared with the level of vicinal sectoriality. 4) At high growth speed the difference in macrostep heights provides a significant inhomogeneity of approximately 30-40% of the vicinal sectoriality level. The macrostep is higher then the incorporated impurity content is more. 5) In KDP crystals the temperature alteration provides lattice parameter variations on the level of 10^{-6} A/degree. So the temperature instability during the growth doesn't affect significantly the crystal inhomogeneity. 6) The supersaturation itself doesn't affect the crystal inhomogeneity directly. 7) Growth speed as well as the difference in step orientation is the main factor, which directly defines crystal inhomogeneity. This work was partially supported by University of California, USA (contract No B304321).