Surface Science
Room 328 - Session SS2-TuM
Nucleation and Growth

Moderator: J.F. Wendelken, Oak Ridge National Laboratory

8:20am **SS2-TuM1 The Dynamics of Crystallite Shape Transformations**, ***J.E. Reutt-Robey***, *D.B. Dougherty,* University of Maryland **INVITED**

At the nanoscale, the shape of a crystallite is remarkably sensitive to the local chemical potential. While much is known about equilibrium crystal shapes (ECS), the mechanism and rate by which a crystallite morphology evolves in response to abrupt changes in temperature and gaseous environments are largely unknown. Using variable temperature STM as our experimental probe, we have investigated the reshaping dynamics of submicron lead crystallites prepared in their near-ECS on Ru(OOO1). In the case of chemical (oxygen) adsorption, we observe a dramatic particle reshaping into a heavily faceted structure.@footnote 1@ We show that this reshaping is triggered by surface impurities, which are needed to nucleate lead oxide grains. Once nucleated, an oxide grain grows laterally on the crystallite surface in an apparent autocatalytic process. Although nucleation is temperature insensitive, subsequent oxide grain growth rates depend on temperature, presumably due to limiting lead mobility at our temperature of investigation. These results are consistent with independent measurements of step fluctuation kinetics. We show how temperature reduction leads to a "flattening" of supported neat crystallites through a monolayer-by-monolayer peeling mechanism.@footnote 2@ From the step peeling kinetics, and simulations with continuum models, we find that the kinetics of monolayer peeling is limited by multi-layer relaxations. Atomistically, these relaxations represent limited mass transfer across the curved facet boundary. Within the thermal window of our measurements, we show that particle reshaping is not reversible and discuss the limiting nucleation barriers.@footnote 3@ @FootnoteText@ @footnote 1@K. Thurmer, E. Williams, and J.E. Reutt-Robey, Science 297, 33-35 (2002). @footnote 2@K. Thurmer, J.E. Reutt-Robey, E.D. Williams, M. Uwaha, A. Edmundts, H.P. Bonzel, Phys. Rev. Lett. 87 (2001) 186102. @footnote 3@K. Thurmer, J.E. Reutt-Robey, E.D. Williams, Surf. Sci., in press.

9:00am **SS2-TuM3 Fluctuations of Islands on Anisotropic Surfaces@footnote 1@**, ***F. Szalma***, *T.L. Einstein,* University of Maryland, College Park

We have performed kinetic Monte Carlo simulations to model the decay and edge-fluctuations of islands containing hundreds to thousands of atoms on (111) crystal surfaces. Investigating the dispersion of the Fourier modes@footnote 2@ of the fluctuations as a function of wavevector, we observe anomalous dispersion due to the geometrical fact that the equilibrium island shapes are anisotropic because of the intrinsic anisotropy of crystal surfaces. Contrary to results for the isotropic approximation,@footnote 3@ the Fourier modes are not eigenmodes of the system; however, they can be transformed into an eigensystem, which provides a means to determine the anisotropic line tension of the island. In recent experiments observing how small crystallite droplets approach their equilibrium state, these fluctuations are intimately related to their decay,@footnote 4@ and the line tension is a factor in determining their ultimate shape. Finally, comparison of theoretical and experimental configurations allows gauging of the suitability of the calculated energies used in the simulations. @FootnoteText@ @footnote 1@Work at UM supported by NSF Grants MRSEC DMR 00-80008 and EEC-0085604. FS also supported by OTKA D32835, Hungary.@footnote 2@S.V. Khare et al., Surf. Sci. 522 (2003) 75.@footnote 3@S.V. Khare and T.L. Einstein, Phys. Rev. B 54 (1996) 11752.@footnote 4@T.J. Stasevich, F. Szalma, and T.L. Einstein, submitted to SS17.

9:20am **SS2-TuM4 The Importance of Substrate Steps on the Ripening of 3D Particles: Ag and Cu on Ru(0001)**, ***W.L. Ling***, *T. Giessel, K. Thürmer, R.Q. Hwang, N.C. Bartelt, K.F. McCarty,* Sandia National Laboratories

Many hetero-epitaxial systems grow in the Stranski-Krastanov mode, in which material added to a wetting layer results in 3D islands. Once nucleated, and after growth has stopped, these 3D islands can minimize surface and interfacial free energy if they grow taller. However, there can be large free-energy barriers to this vertical growth because of the apparent necessity of nucleating new layers on top of these islands. In fact, Mullins and Rohrer have shown that it is unlikely that such nucleation would occur during ripening.@footnote 1@ In this work, we have studied the evolution of 3D islands of Ag and Cu on Ru(0001) using low-energy electron microscopy. We find that vertical growth does not occur at all during ripening when the Ag or Cu film does not overlay substrate steps. On stepped sufaces, on the other hand, we find vertical growth readily occurs. Using real-time observations, we find that the vertical growth occurs by an unexpected route that does not require nucleation. Islands, which adopt flat tops in an early stage of growth, gain a layer when they descend a monatomic Ru step. In this manner, they maintain the flat tops throughout ripening but grow taller as they migrate downhill on the substrate. We have investigated the vertical growth rate as a function of step spacing and island height. We find that thin islands shrink and tall islands grow, and the growth rate increases with the step density. @FootnoteText@@footnote 1@W.W. Mullins and G.S. Rohrer, J. Am. Ceram. Soc. 83, 214 (2000).

9:40am **SS2-TuM5 Geometry-Based Simulation Algorithm for Island Formation during Submonolayer Film Growth**, ***J.W. Evans,*** Iowa State University*; M.C. Bartelt,* Lawrence Livermore National Laboratory*; M. Li,* Iowa State University

A current challenge is to develop efficient new coarse-grained simulation strategies which reliably predict the morphology of growing films. We present a geometry-based simulation (GBS) algorithm which avoids explicit treatment of the terrace diffusion of adatoms and their aggregation with islands - a computationally expensive component of either atomistic KMC simulation or continuum formulations. GBS characterizes island growth in terms of capture zones (CZ's), and implements simple but realistic geometric rules to incorporate crucial spatial aspects of the island nucleation process, i.e., nucleation nearby CZ boundaries. This approach reliably predicts island size distributions and spatial correlations, and is especially efficient for highly reversible island formation.

10:00am **SS2-TuM6 Pyramidal Faceted Ni Nanocrystals on W(111)**, ***Q. Wu***, *J. Kolodziej, H. Wang, T.E. Madey,* Rutgers University

Nanoscale features formed by nucleation of ultrathin Ni films on W(111) are studied by means of ultrahigh vacuum-STM, soft X-ray photoemission spectroscopy (SXPS) using synchrotron radiation, LEED, and AES. Whereas a single monolayer (ML) of Ni covers planar W(111) uniformly, we find that multilayers of Ni (~5 ML) follow the Stranski-Krastanov growth mode, and form clusters and islands on the Ni-covered W(111). Upon heating to ~600K, Ni clusters are found to aggregate into nanoscale pyramidal facets, which coexist with planar regions of Ni-covered W(111). This type of faceting is different from the monolayer-induced faceting of W(111) seen for Pt, Pd, Ir, and Rh: a single ML of Ni does not cause faceting of W(111). Thermal stability of Ni films on W(211) and W(111) is studied by SXPS and AES, which indicates that alloy formation between Ni and W occurs at temperatures @>=@700K. Further annealing of faceted Ni nanocrystals also leads to Ostwald ripening. Reactivity of Ni nanoclusters with adsorbates (e.g. oxygen and thiophene) is also investigated. The nucleation and growth of nanocrystals are discussed in terms of overlayer strain due to lattice mismatch.

10:20am **SS2-TuM7 Growth and Stability of Bi Films on Si(111) Studied by LEEM**, *G.E. Thayer,* IBM T.J. Watson Research Center*; J.T. Sadowski,* Tohoku University, Japan*;* ***R.M. Tromp***, IBM T.J. Watson Research Center

The structural and electronic properties of ultra-thin metal films on semiconductor surfaces have attracted much recent interest primarily due to the dominating dependence of novel device performance on metal contacts. Since contacts are interfaces, contact issues are real problems where surface science can provide insightful solutions. Understanding the factors governing heteroepitaxial growth, such as surface free energies and stress relaxation effects are important, and in situ electron microscopy can play a unique role in investigating the processes involved. Using low-energy electron microscopy (LEEM) we observed real-time growth of Bi on Si(111). With the surprisingly large lattice mismatch of 17% between bismuth and silicon, one might expect growth of Bi/Si(111) to be almost certainly dominated by strain, and therefore three dimensional. Up to about five monolayers, the Bi film grows with small grain (012) oriented islands on top of a uniform wetting layer. Above five monolayers, the crystal orientation dramatically flips from (012) to (111), from a four-fold symmetry to a three-fold symmetry, into a flat single crystal film (grains are approximately 100µm@super 2@ in size). The transition occurs very quickly with grains transitioning at a rate of 1µm@super2@s@super -1@. After the transition into a (111) oriented epitaxial film, the growth continues in a two-dimensional layer-by-layer mode of bi-layers. The thermodynamic stability of Bi/Si(111) films was also investigated by annealing the films to

temperatures of up to 150°C (melting temperature of Bi is 220°C), where dewetting becomes important, even prior to melting.

10:40am **SS2-TuM8 Nucleation Kinetics during Homoepitaxial Growth of TiN(001) by Reactive Magnetron Sputtering**, ***M.A. Wall***[1], *D.G. Cahill, I. Petrov,* University of Illinois at Urbana-Champaign; *D. Gall,* Rensselaer Polytechnic Institute; *J.E. Greene,* University of Illinois at Urbana-Champaign

Polycrystalline TiN is extensively used as a diffusion barrier in microelectronics, as a hard wear resistant coating on cutting tools, and as a corrosion and abrasion resistant layer on optical components. The performance of TiN in all these applications is dependant on the texture of the layer, which is in turn a function of the film growth parameters and nucleation kinetics. To gain an atomic-scale understanding of the processes which govern TiN nucleation, we grow epitaxial layers on TiN(001) via reactive magnetron sputtering in an ultra-high vacuum (UHV) system and employ in-situ scanning tunneling microscopy (STM) to investigate the dynamics. In addition, we perform density functional calculations in order to guide the interpretation of our experimental results. The characteristic island size R@sub c@ necessary to nucleate a new layer on a growing island is measured as a function of growth temperature T@sub s@ and nitrogen fraction f@sub N2@ in an Ar/N@sub 2@ mixture. By applying nucleation rate theory to temperature dependant R@sub c@ data obtained from layers grown with f@sub N2@ = 1, we extract a diffusion activation energy E@sub s@ = 1.4±0.1 eV for T@sub s@ @<=@ 865 °C where nucleation is diffusion limited. For T@sub s@ @>=@ 910 °C, nucleation becomes limited by the formation of unstable clusters, and we extract an adspecies formation energy E@sub f@ = 1.4±0.2 eV. When f@sub N2@ is reduced from 1 to 0.1, E@sub s@ = 1.1±0.2 eV which results in a factor of two increase in R@sub c@ at a given T@sub s@. The activation energy we calculate for Ti diffusion on TiN(001) is 0.4 eV, significantly smaller than E@sub s@ extracted from our experiment, indicating that Ti is not the dominant diffusing species. Based on calculated binding energies of TiN@sub x@ clusters, the dominant diffusing species is likely TiN@sub x@, with 1 @<=@ x @<=@ 3.

11:00am **SS2-TuM9 Pt Adsorption on Chiral SrTiO@sub3@ Surfaces**, ***A. Asthagiri***, *D.S. Sholl,* Carnegie Mellon University

The existence of intrinsically chiral surfaces provides many opportunities related to the catalytic chemistry and separation of chiral molecules. A key difficulty in realizing the potential of this approach has been the production of surfaces with reasonable surface area. We describe results that underpin efforts to epitaxially deposit ultra-thin films of metal on metal oxide substrates. The success of these efforts requires careful control of the film morphology of the underlying substrate and knowledge of the growth modes of metal on these surfaces. To this end, we have performed extensive plane wave Density Functional Theory (DFT) calculations to describe the bonding of Pt on a variety of SrTiO@sub3@ surfaces. These calculations include both terminations of all three low Miller index surfaces, (100), (110), and (111), and two representative stepped surfaces, (620) and (622). Our results show that epitaxial growth of Pt on the substrates can be expected, and that step flow growth should be feasible for the stepped substrates. Our results provide quantitative insight into the experimental observations made by our collaborators for these systems, including the existence of inversion domains for Pt films on SrTiO@sub3@(111). We will discuss the implications of our calculations for the practical growth of chiral metal films on SrTiO@sub3@ substrates.

11:20am **SS2-TuM10 High-Temperature Low Energy Electron Microscopy Studies of Spiral Dislocation Dynamics on TiN(111) Terraces**, ***S. Kodambaka***, *S.V. Khare, W. Swiech, K. Ohmori, I. Petrov, J.E. Greene,* University of Illinois at Urbana-Champaign

We have grown epitaxial TiN(111) layers by reactive evaporation onto Al@sub 2@O@sub 3@(0002) substrates and used in situ high-temperature low-energy electron microscopy to study surface morphological evolution on large (> 4 µm) atomically-smooth TiN(111) terraces during annealing at temperatures T@sub a@ in the range 1500 and 1750 K (T@sub a@ = 0.47-0.55T@sub m@, where T@sub m@ is the melting point in K). At each annealing temperature, we observe rotation of screw dislocation segments lying in the surface slip plane around the immobilized segment of the dislocation lying out of the slip plane resulting in a spiral with steps oriented along . Step heights are proportional to the number of revolutions in the slip plane. We find that the total length of the dislocation line increases with annealing time as the spirals undergo a shape-preserving anti-clockwise motion with a constant angular velocity. From the temperature-dependent angular velocity measurements, we determine an activation barrier of 5.0±0.2 eV, with a prefactor of 10@super 14+/-0.5@ s@super -1@, for spiral rotation. Studies of this process, a single-ended Frank-Read source, provide insight into understanding dislocation multiplication mechanisms occurring in highly refractory, technologically important transition-metal nitride layers.

11:40am **SS2-TuM11 Conversion from Nanowire to Epilayer: Epitaxial Growth of Bi on Si(114)-2x1**, *S. Cho,* ***J.M. Seo***, Chonbuk National University, Korea

The Bismuth (Bi) adsorption on the reconstructed Si(114)-2x1 has been studied using STM under UHV. Among 1-D features of Si(114)-2x1, such as Tetramer, Dimer and Restatom rows parallel to [-110] direction, Bi atoms preferentially adsorbed on the Tetramer rows and formed 1-D wires whose separation is 1.6 nm. The periodic structure in the Bi wire along [-110] has been converted to 3a (a=0.38 nm) from 2a of clean Si(114). The Bi wire of the second layer adsorbs between the Bi wires of the first layer, and shifts by 1.5a along the row. The Bi wires of subsequent layers also adsorb between the previously formed Bi wires in the same fashion. Such epitaxial growth continues unless the defects like substrate vacancies interfere. The packing unit is a Bi-dimer and the hexagonal packing has been confirmed by the hexagonal pattern of the facet near the ledge. It has been concluded that the reasons for 2-D epitaxial growth of Bi on Si(114) are the followings; the first, the existence of preferential adsorption site on Si(114), and the second, the adjustable lattice-matching between the Bi-dimer row and the substrate along as well as perpendicular to the wire.

[1] **Morton S. Traum Award Finalist**

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