Monday Afternoon, November 4, 2002

Surface Science
Room: C-110 - Session SS2-MoA

Nucleation & Growth of Metals on Oxides & Semiconductors
Moderator: D.Y. Petrovykh, Univ. of Maryland/Naval Research Lab

2:00pm **SS2-MoA1 The Effects of Copper on the Hydrogen-Passivation of Si(001)**, ***A.R. Laracuente***, *L.A. Baker*, *L.J. Whitman*, Naval Research Laboratory

Foreign adsorbates can alter the morphology of surfaces and often have a dramatic impact on film growth. Given that most semiconductor devices are fabricated in hydrogen-rich environments on silicon substrates, it is important to understand how adsorbates affect the surface morphology of H-terminated Si surfaces. Currently, we are studying how copper modifies the morphology of monohydride-terminated Si(001). In the experiments, clean Si(001) surfaces are first exposed to 0.3 monolayer of Cu and then passivated with atomic H under conditions that produce a monohydride surface. The samples are characterized at room temperature using scanning tunneling microscopy (STM) and Auger electron spectroscopy (AES). We find that the main effect of Cu pre-exposure is the formation of pits on the surface. The pits are about 3 nm x 3 nm in size and one atomic layer deep. It appears that Cu induces Si etching during the atomic H exposure. Furthermore, the "pitted" H-terminated surface is subsequently dosed with Cu to investigate the effects of the pits on the growth of Cu. We will present our STM and AES results, and an analysis of the pit size distribution.

2:20pm **SS2-MoA2 Competing Classical and Quantum Effects in Shape Relaxation of a Metallic Island**, ***H. Okamoto***, *D. Chen*, Rowland Institute for Science, *T. Yamada*, NASA Ames Research Center

Pb islands grown on a silicon substrate transform at room temperature from the initially flattop facet geometry into an unusual ring shape with a volume-preserving mass transport process catalysed by the tip electrical field of a scanning tunnelling microscope. The formation of such ring shape morphology results from the competing classical and quantum effects in the shape relaxation. The latter also leads to a sequential re-growth on alternating strips of the same facet defined by the underlying substrate steps, showing for the first time the dynamical impact of the quantum size effect on the stability of a nanostructure.

2:40pm **SS2-MoA3 Formation of Monodispersed Cobalt Nanoclusters on the Si_3N_4(0001)-4x4 Surface**, ***C.-L. Wu***, *T.-B. Chou*, *S. Gwo*, *W.-C. Lin*, National Tsing-Hua University, Taiwan, ROC, *M.-T. Lin*, National Taiwan University, Taiwan, ROC

A novel phenomenon of forming monodispersed Co nanoparticles at room temperature on a single-crystal Si_3N_4 dielectric thin film is presented. Results of very narrow size distributions with an average size of ~30 Co atoms have been obtained. We have found that cobalt clusters deposited on Si_3N_4 are stable with respect to cluster agglomeration/coalescence and thermal decomposition. Also, we have confirmed that the average size of Co clusters is independent of the deposition time and insensitive to the magnitude of the deposition flux. Therefore, their areal density can be controlled by the deposition time. The motivation for using a single-crystal Si_3N_4 support is two-fold. First, the dielectric support reduces chemical intermixing and electronic coupling (Si_3N_4 is an excellent diffusion barrier with a bandgap energy of 4-5 eV) between metal clusters and the substrate compared with situations using semiconductor or metal surfaces. Second, the defect-free Si_3N_4 surface provides us a unique opportunity to study the formation of metal clusters without the influence of surface defects. Consequently, quantum effect can play an important role in the size control.

3:00pm **SS2-MoA4 The 'Three-Dimensional' Schwoebel-Ehrlich Barrier in Ag Crystallite Growth on Si(111)**, *W.X. Tang*, *K.L. Man*, Hong Kong University of Science and Technology, *H. Huang*, Hong Kong Polytechnic University, ***M.S. Altman***, Hong Kong University of Science and Technology

Growth morphology will be affected, or even dictated, by kinetic limitations that may be present during growth. One such limitation, which has received a great deal of attention, occurs in growth at surfaces when there is a Schwoebel-Ehrlich (SE) diffusion energy barrier to atomic motion descending a monolayer height step. We present evidence of an analogous 'three-dimensional' (3D) SE energy barrier to atomic diffusion across the ridge that separates two facets on a three-dimensional crystal. The 3D SE barrier stems from the reduced coordination at the ridge. Differences of the adatom formation energies on adjacent facets cause the 3D SE barrier to be asymmetric. Kinetically limited growth shapes of Ag crystallites on the Si(111) surface have been studied with low energy electron microscopy (LEEM) and diffraction (LEED). These growth shapes are in agreement with expectations from the asymmetry of the 3D SE barriers. LEEM observations of the modification of growth shapes caused by codeposition of surfactants are also consistent with modification of the 3D SE barrier caused by surface passivation. The 3D SE barrier is expected to be relevant to diffusion in the presence of multilayer height steps on surfaces, and is therefore also important for the development of film texture.

3:20pm **SS2-MoA5 Self-organization of Semimetal Bi on Si(111)**, ***T. Nagao***, Tohoku University, Japan, *T. Kogure*, University of Tokyo, Japan, *J.T. Sadowski*, Tohoku University, Japan, *T. Sekiguchi*, *S. Hasegawa*, University of Tokyo, Japan, *T. Sakurai*, Tohoku University, Japan

We have studied the self-organization of epitaxially grown semimetal bismuth on Si(111) surfaces by in situ reflection high-energy electron diffraction (RHEED), scanning tunneling microscopy (STM), and 4-probe conductivity measurement. On the 7x7 surface, up to around 4ML, the system grows in a S-K like manner: [102] oriented flat-top islands grow after completion of disordered wetting layer. Sharp height distribution of these flat-top islands peaked at 1.2nm was clarified in a wide growth temperature range (290-550 K) as well as wide deposition rate (0.1-2.0 ML/min), which indicates the significance of the electronic effect in the film growth. After the connection of the flat-top islands, the growth mode switches to a nearly perfect FvM growth, and the connected layer self-organizes into a single-crystal ultrathin film with Bi(001)-1x1 surface as evidenced by in situ RHEED and ex situ XTEM. Four-probe measurements showed the largest resistance drop at around 4 ML followed by another gradual drop around 4-10 ML and finally approached to a conductivity only several times lower than the bulk value, unusual value for such thin films. The initial drop was associated with the percolation of the flat-top islands. The following gradual drop was assigned to the reduction in the (surface and bulk) roughness scattering, due to self alignment in the crystal orientation via drastic interfacial glide and mass transport of the flat-top nanocrystals which are initially loosely bound on the disordered wetting layer. The origin of this new type of electronic growth and its self-organization into perfectly ordered ultrathin film will be discussed in detail.

3:40pm **SS2-MoA6 Controlling Island Size Distributions for Metals on Oxides: Cu and Ni Islands on TiO_2(110)-(1x2)**, *J. Zhou*, *B.T. Long*, ***D.A. Chen***, University of South Carolina

Metal islands deposited on oxide surfaces are frequently used as model systems for understanding heterogeneous catalysts. In order to investigate how the surface chemistry of the metal islands may change as a function of island size, it is first necessary to produce islands with narrow size distributions. In these studies, Cu and Ni have been vapor-deposited onto a partially reconstructed TiO_2(110)-(1x2) surface and characterized by STM under UHV conditions. The key to achieving a uniform island size distribution for Cu on TiO_2(110)-(1x2) is a low D/F ratio, where D is the diffusion rate for Cu on the surface and F is the Cu deposition or flux rate. When rate of deposition is high relative to diffusion, the incoming Cu atoms have a greater probability of encountering another Cu atom and forming a new island before they are able to diffuse across the surface and contribute to the growth of an existing island; in this case, small islands of uniform sizes are formed with high island densities. When the rate of diffusion is high relative to flux, the incoming Cu atoms are more likely to diffuse to an existing island before encountering other Cu atoms; in this case, Cu islands of varying sizes with lower island densities are formed. We have varied the D/F ratio by changing both the deposition rate and the temperature of the surface during deposition. In all cases, the lower D/F ratio yields a more uniform size distribution. Notably, the Cu islands grown on this partially reconstructed TiO_2(110)-(1x2) surface produce high island densities (~$5x10^{12}/cm^2$ at 2 ML) due to high defect densities on the titania surface itself. Larger islands Cu (~100 Å diameter) with uniform size distributions can be produced by deposition at room temperature followed by annealing at higher temperatures. Investigations of Ni island growth on the reconstructed titania surface are currently underway.

4:00pm **SS2-MoA7 Surface Nanostructuring to Control Size and Composition of Individual Oxide Supported Nanoparticles**, ***A. Kolmakov***, University of California, Santa Barbara, *D.W. Goodman*, Texas A&M University

A key to the technological utilization of oxide supported metal nanoparticles as an active element in gas sensing devices and catalysts is an atomic level understanding of their role in the chemical reaction. The chemical and physical properties of nanoparticles dispersed on oxide surfaces exhibit a marked dependency on their size, shape, composition and electronic interaction with the support. To explore this avenue a umber of methods of producing and delivery of size selected clusters from the gas or liquid phase to the oxide surfaces have been developed during the last decade. Alternatively, recent achievements in single molecule and clusters spectroscopy with NSOM and SPM and TEM proved the feasibility of so called individual approach where instead of probing the ensemble of size selected particles, imaging and spectroscopy of the individual oxide supported nanoparticles with different sizes and composition is performed and compared during the single experiment. Using Ag, Au and alloy clusters supported on TiO_2 (110) as a model system, we demonstrate several experimental schemes for studying individual supported metal clusters using oxide surface nanostructuring in conjunction with SPM. Namely, on slightly reduced TiO_2 we create laterally confined and precisely located areas with controllably modulated defect densities by exploiting a "tip shadowing" technique to synthesize a nanostructured mask. Since the diffusion length of the adsorbate atoms and eventually the cluster nucleation density are strongly mediated by surface defect densities in these areas, a well-defined and controllable variety of cluster sizes is accessible for imaging and spectroscopy within the field of view of the SPM. A similar procedure is applied for tuning the doping level of individual, metal particles. The spectroscopic and morphological changes of the individual clusters were probed in situ while exposuring the sample to elevated pressure of reactive gases.

4:20pm **SS2-MoA8 Nucleation and Sintering Kinetics of Pd on** a-**Al_2O_3(0001)**, ***S.L. Tait, Jr.***, *L.T. Ngo, Q. Yu, S.C. Fain, Jr., C.T. Campbell*, University of Washington

Low-temperature methane combustion for applications in electric generator turbines is catalyzed by Pd nanoparticles to minimize NO_x pollution. The reaction depends on the dissociation of methane molecules on the Pd surface. Nanoscale Pd particles contain coordinatively unsaturated Pd atoms, making them more active for the dissociation of CH_4. We have studied the growth of Pd nanoparticles on the α-Al_2O_3(0001) surface. The alumina single crystal was cleaned by annealing in air and in vacuum. The cleanliness and structure of the surface were verified by XPS and LEED. Experiments were conducted on the unreconstructed 1x1 and the reconstructed $\sqrt{31}$x$\sqrt{31}$ R±8.9° surfaces. Wide terraces were observed on the surface with non-contact atomic force microscopy (NC-AFM). Sub-monolayer doses of Pd were deposited by vapor deposition. NC-AFM was used to observe the growth of Pd nanoparticles upon annealing. These measurements provide information about the Pd particle size, number density and morphology. The Pd showed a tendency to cluster at step edges. To measure Pd particle sintering kinetics and size effects thereon, temperature-programmed ion scattering spectroscopy was used to monitor the fraction of the surface covered by Pd particles continuously as the surface was heated at 1 K/s. The number density of the Pd particles was measured before and after heating using NC-AFM. Curiously, large regions of the surface were found to be void of clusters even at step edges. A mechanism involving the various elementary steps in atom and cluster migration is being developed to model the kinetics of sintering with physically reasonable parameters. Work supported by DOE-OBES Office of Chemical Sciences and the M. J. Murdock Charitable Trust. LTN supported by the IGERT Nanotechnology Fellowship.

4:40pm **SS2-MoA9 The Domain Boundary Barrier on Intermixed SbGe(001)**, *M. Li*, ***E.I. Altman***, Yale University

The nucleation and growth of epitaxial Ge structures on the intermixed SbGe(001) surface below the Sb segregation temperature was studied using scanning tunneling microscopy (STM). The drastic changes in the density, shape and size of the epitaxial structures as a function of Sb concentration in the Ge(001) substrate reveal the favored nucleation of Ge ad-dimers on Ge instead of Sb. The lack of Ge epitaxial structures on Sb suggests the enhanced surface diffusion on Sb-passivated surface. The Ge epitaxial structures always situate in the proximity of domain boundary between mainly bean-shaped Sb dimer domains and Ge dimer domains in the substrate. A one-directional repulsive potential barrier at the Sb-Ge domain boundary is proposed that inhibits the diffusion of Ge dimers from Ge domains to Sb domains and thus the nucleation of epitaxial structure is confined to Ge domains.

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