Monday Afternoon, October 25, 1999

Surface Science Division
Room 606 - Session SS1+EM-MoA
Metals on Oxides

Moderator: U. Diebold, Tulane University

2:00pm **SS1+EM-MoA1 Nucleation and Growth of Copper Islands on TiO@sub2@(110): Evidence for Self-limited Island Sizes***, **D.A. Chen**,* University of South Carolina*; M.C. Bartelt, R.Q. Hwang, K.F. McCarty,* Sandia National Laboratories

Metal-oxide interfaces play an important role in a variety of technological applications, including those involving the design of electronic devices, sensors and heterogeneous catalysts. In order to develop a fundamental understanding of these metal-oxide interfaces, we have studied the formation of Cu islands on TiO@sub2@(110)-(1x1) in ultrahigh vacuum using scanning tunneling microscopy for Cu coverages up to 1.25 ML. The formation of 3D islands at all the coverages reflects the relatively high mobility of Cu atoms on TiO@sub2@ at room temperature and the weak interactions between Cu and TiO@sub2@. Surprisingly, the island diameter remains almost constant for all coverages. Furthermore, the Cu islands exhibit self-limiting growth at low coverages (0.5 ML), the average island size scales with coverage, but this increase in island size is primarily due to an increase in height not diameter. Although larger islands can be formed by annealing, the average size of the islands is independent of coverage for any given annealing temperature. We propose two general schemes that could lead to the observed self-limiting growth. The first is that the attachment rate of adatoms drops as the island size increases. The second is that the rate at which adatoms reach existing islands drops as the islands grow. We will discuss physical scenarios under which each of these effects may be dominant. This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported in part by the USDOE-OBES-Division of Materials Sciences.

2:20pm **SS1+EM-MoA2 Influence of Surface Reactions on Morphology: Ag Nanoclusters on TiO@sub 2@(110)***, **X. Lai**, T.P. St. Clair, D.W. Goodman,* Texas A&M University

The effects of in situ O@sub 2@ exposure on TiO@sub 2@(110)-supported Ag nanoclusters were investigated using x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). An oxygen-induced cluster ripening was observed by STM after exposing Ag/TiO@sub 2@(110) to 10.00 Torr O@sub 2@ in an elevated-pressure reactor. A bimodal size distribution of Ag clusters was evident after a 10 minute O@sub 2@ exposure at room temperature. Time-dependent studies of the ripening process indicated that the majority of the ripening occurred within the first hour of exposure. The cluster density also increased 5-15%, indicating that redispersion simultaneously occurred with ripening. For comparison, a reduced, roughened TiO@sub 2@(110) and a fully oxidized TiO@sub 2@(110) were prepared and used as Ag supports. Propylene exposure was also studied to further investigate adsorbate-induced morphological changes. Issues relevant to the stability of Ag catalysts for general oxidation reactions were addressed.

2:40pm **SS1+EM-MoA3 Kinetics and Dynamics of Substrate and Metal Atoms on TiO@sub2@***, **G. Thornton**, I. Brookes, H. Raza, C.L. Pang, S. Haycock,* Manchester University, UK **INVITED**

TiO@sub2@ substrates have been used as platforms to test ideas about oxide surface reconstruction and metal growth on oxides. This work is motivated by the importance of such interfaces in a number of applications which include catalysis and gas-sensing. As part of this work we have recently studied two aspects of TiO@sub2@ surface science associated with temperature and time dependent structural changes using STM and non-contact AFM. The first involves the study of the 1x1 to 1x3 phase transition of TiO@sub2@(100). In addition to the 1x1 and the high temperature equilibrium 1x3 microfacet termination previously observed, intermediate 1x3 structures are imaged. The relationship between the 1x1 termination and the 1x3 microfacet phase suggests that the latter reconstruction is formed by removing material rather than growing from a lower lying terrace. Intermediate structures point to a mechanism of the phase transition which involves discrete bond breaking steps. Turning to Cu growth on TiO@sub2@(110), at room temperature and at <0.1 ML most of the metal atoms are initially mobile, with some 2D island formation. The cluster size of about 6 Å diameter suggests that they consist of 7 atoms arranged in a centred hexagon. Such an arrangement fits between the bridging O rows. 3D clusters are formed at higher coverage consistent with Volmer-Weber growth. At lower temperatures 1D metastable strings of Cu atoms are formed in the [001] direction, which collapse to 2D islands and subsequently 3D clusters at higher coverage.

3:20pm **SS1+EM-MoA5 Nucleation and Growth of Pt Nanoclusters on TiO@sub 2@ Rutile and Anstase Surfaces***, **Y. Liang**,* Pacific Northwest National Laboratory*; A.W. Grant,* University of Washington*; D.R. Baer, S. Gan,* Pacific Northwest National Laboratory

Understanding the interaction of ultra-thin metal overlayers with oxide surfaces impacts a wide range of technological applications. One of those is the oxide-supported metal catalysts where unusual surface chemisorption and activity have been observed. In this presentation, we report an investigation of nucleation and growth of Pt on rutile and anatase surfaces using scanning tunneling microscopy, x-ray photoelectron spectroscopy, and low energy electron diffraction. Results show that vapor deposition of 0.1 ML of Pt on a rutile TiO@sub 2@(110) surface at ambient temperature leads to the formation of randomly distributed three-dimensional Pt nanoclusters on the 1x1 surface. However, this random distribution is strongly perturbed by the presence of surface line defects produced by extended sputtering and annealing cycles. As the density of the line defect increases, majority of Pt nanoclusters are preferentially attached at the ends of line defects instead of randomly distributed on the rutile surfaces. This result suggests that the line defects on TiO@sub 2@(110) surfaces have stronger interaction with Pt and thus serve as nucleation sites for Pt growth. Based on the change of distribution of Pt clusters as a function of line defect density, the diffusion length of Pt on rutile surfaces is obtained. In addition to rutile, we also investigate the nucleation and growth of Pt on anatase surface. We have successfully grown anatase single crystal thin films on SrTiO@sub 3@ substrates using oxygen plasma assisted molecular beam epitaxy. Investigation of nucleation and growth of Pt on anatase surface is currently in progress. The results will be presented at the meeting and compared with those obtained on the rutile TiO@sub 2@ surfaces.

3:40pm **SS1+EM-MoA6 Role of Surface Vacancies and Water Products in Metal Nucleation: Pt/MgO(100)***, A. Bogicevic, **D.R. Jennison**,* Sandia National Laboratories

Metal atom adsorption on oxide surfaces, resulting in clusters or thin films, involves a variety of structure-determining chemical interactions. While surface steps have long been known to promote nucleation, it has been speculated in several experimental studies that the most common defect in well prepared surfaces, isolated surface oxygen vacancies, may act as nucleation sites. However, this has not been substantiated via experiment or theory. Here we examine this question and, for completeness, how water dissociation products affect nucleation, since there have been several reports that these are common low-density contaminants on prepared oxide surfaces. Our density-functional calculations reveal that isolated F@sub s@ and V@sub s@ surface vacancies on MgO(100) ionize single Pt atoms, roughly tripling their adsorption energy. This trapping inhibits Pt atoms from binding to other Pt atoms, resulting in a negative addimer binding energy. Hence, isolated surface vacancies demote nucleation, contrary to popular belief. A defect that does promote nucleation is the F@sub s@V@sub s@ divacancy, which increases the addimer binding energy by 20%. Amongst water and its dissociation products, adsorbed hydroxyl ions are found to have a similar but even stronger effect. We discuss the implications of these results for the temperature dependence of nucleation and the generality of these results for other metals and oxides.@footnote 1@ @FootnoteText@ @footnote 1@ Sandia is operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE under Contract DE-AC04-94AL85000.

4:00pm **SS1+EM-MoA7 Metal Particles on Single Crystal Oxides as Model Catalysts***, **J.H. Larsen**, J.T. Ranney, A.W. Grant, D.E. Starr, J.E. Musgrove, C.T. Campbell,* University of Washington

The growth morphology and reactivity of model oxide-supported metal catalysts are intimately connected. On some well-defined oxides, vapor-deposited metals form two-dimensional islands, typically up to a critical coverage below 1 monolayer (ML). The local electronic environment of the supported metal particles is modified as compared to the surface of the bulk metal, and so changes in reactivity are expected. Above the critical coverage, three-dimensional growth sets in and it becomes possible to measure reactivities as a function of island thickness. Several metal on metal oxide systems were studied. The surface growth mode was investigated using low energy ion scattering (LEIS) and x-ray photoelectron spectroscopy (XPS). In order to probe the nature of the reaction sites on the surface, the decomposition of hydrocarbons was also studied with temperature programmed desorption (TPD). From these experiments, the dependence of the metal reactivity on the lateral dimensions of the two-dimensional metal islands and the thickness of three-dimensional metal clusters was determined. It was found that Pt particles on ZnO(0001)-Zn exhibit reactivity towards methanol decomposition which is characteristic of low-index Pt facets, even below the critical coverage of ~ 0.6 ML where only two-dimensional islands are present. The adsorption energy of some metal on metal oxide systems was furthermore measured as a function of coverage using single crystal adsorption calorimetry. The adsorption energy is a fundamental quantity that gives important insight into the energetic origins of the growth and reactivity of metal particles supported on metal oxides.

4:20pm **SS1+EM-MoA8 High-Pressure STM Studies of Pt Nano-clusters on Al@sub 2@O@sub 3@/NiAl(110)**, ***L. Österlund**, M.O. Pedersen, P. Thostrup, K.H. Hansen, E. Laegsgaard, I. Stensgaard, F. Besenbacher,* University of Aarhus, Denmark

A novel system in which an STM is incorporated into a high pressure cell has been constructed. The system permits in-situ studies of surfaces with atomic resolution at pressures ranging from UHV to one atmosphere. In the present paper, we have investigated the morphology and structure of well-ordered Pt nano-clusters deposited on thin layers of aluminum oxide created by oxidation of NiAl(110). >From the shape, i.e. the height and width, and from atomic resolved images of the top facets of the clusters, we can quantitatively determine the adhesion energy of the metal cluster to the oxide, using calculated surface free energies for the cluster facets. We have investigated the change in the morphology of the Pt nano-clusters exposed to up to 1 bar of hydrogen and oxygen.

4:40pm **SS1+EM-MoA9 Cu Interaction with Al@sub 2@O@sub 3@ Substrates: Effects of Defects and Coverage**, *C. Niu, K. Shepherd, **J.A. Kelber**,* University of North Texas

We report UHV surface science studies of the wetting and nucleation behavior of Cu on sapphire(0001). Such fundamental wetting and nucleation interactions are of increasing importance in microelectronics, joining and brazing, as well as in catalysis. This study focuses on the effects of defects and kinetic factors for well-defined systems that are critical to an understanding of behavior for "real world" systems. On clean sapphire, Cu is initially present as Cu(I) to a coverage of 0.35 ML [ML = monolayer], after which a second, metallic Cu layer begins to grow. This behavior is in agreement with recent theoretical calculations by A. Bogicevic and D. R. Jennison[Phys. Rev. B (in press)]. The behavior of Cu on sapphire at elevated temperatures is coverage dependent. For @theta@@sub Cu@ < 0.35 ML, Cu(I) remains stable on the surface for temperatures up to ~ 1000K. However, in the presence of Cu(0), e.g. @theta@@sub Cu@ = 0.75 ML, Cu(I) reacts to form additional Cu(0) at about 500K. Pre-sputtering of the sapphire surface prior to Cu deposition inhibits Cu(I) formation and enhances Cu(0) formation at low coverage, correlating with the sputter-induced dehydroxylation of the sapphire surface and creation of oxygen vacancies. These data indicate that variations of a small number of surface defect densities can explain the large number of contradictory results obtained for the Cu/alumina systems. The significance of these findings to "real world" applications (e.g. Cu on oxidized Ta and other microelectronics diffusion barriers) will be discussed.

5:00pm **SS1+EM-MoA10 Nucleation and Growth of Tungsten on SiO@sub 2@ During Atomic Layer Deposition Using Sequential Surface Reactions**, ***J.W. Elam**, C.E. Nelson, R.K. Grubbs, S.M. George,* University of Colorado, Boulder

The atomic layer deposition of tungsten (W) can be achieved by separating the binary reaction WF@sub 6@ + Si@sub 2@H@sub 6@ --> W + 2SiHF@sub 3@+ 2H@sub 2@ into two half-reactions. Successive application of the WF@sub 6@ and Si@sub 2@H@sub 6@ half-reactions in an ABAB... sequence produces W atomic layer controlled growth. The nucleation and growth of W on SiO@sub 2@ was examined during alternating exposures to Si@sub 2@H@sub 6@ and WF@sub 6@. Auger electron spectroscopy studies at 573 K revealed an initial nucleation phase that was followed by a layer-by-layer W growth regime. Nucleation occurred during the first 10 sequential Si@sub 2@H@sub 6@ and WF@sub 6@ surface reactions. Layer-by-layer W deposition then proceeded at a growth rate of 2.5 Å per AB reaction cycle. This W growth rate is consistent with one W monolayer per AB reaction cycle. The Auger data was fit well assuming Frank-van der Merwe layer-by-layer growth. These studies reveal that the sequential surface reactions can facilitate metal wetting of oxide surfaces and conformal layer-by-layer metal growth. Additional Auger experiments yielded the adsorption kinetics for both Si@sub 2@H@sub 6@ and WF@sub 6@ during W atomic layer deposition. The WF@sub 6@ half-reaction had an activation energy E=7 kcal/mol and required WF@sub 6@ exposures of 30 L for the WF@sub 6@ half-reaction to reach completion. The Si@sub 2@H@sub 6@ had virtually no temperature dependence and the Si@sub 2@H@sub 6@ half-reaction saturated following 200 L Si@sub 2@H@sub 6@ exposures at 573 K.

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