Surface Science Division
Room: 107 - Session SS1-WeM

Atomistic Control of Structure & Evolution
Moderator: T.S. Rahman, University of Central Florida

8:40am **SS1-WeM3 Destabilization of Ag Nanoislands on Ag(100) by Adsorbed Sulfur**, *M. Shen*, ***S.M. Russell***, Iowa State University, *D.-J. Liu*, Ames Laboratory - US DOE, *P.A. Thiel*, Iowa State University & Ames Laboratory - US DOE

Studies of chalcogen (O, S) interactions with coinage metal surfaces elucidate how those interactions affect mass transport on the surface and whether a general mechanism exists for these systems. Sulfur accelerates coarsening of Ag nanoislands on Ag(100) at 300 K, and this effect increases with sulfur coverage over a range spanning a few hundredths of a monolayer, to nearly 0.25 monolayers. We propose that acceleration in this system is strongly tied to the formation of AgS$_2$ complexes at step edges. These complexes can transport Ag more efficiently than Ag adatoms (due to a lower diffusion barrier and comparable formation energy), hence leading to enhanced coarsening. The mobility of isolated sulfur on Ag(100) is very low, so that complex formation is kinetically-limited at low sulfur coverages, and thus enhancement is minimal. However, higher sulfur coverages force the population of sites adjacent to step edges, so that formation of the complex is no longer limited by diffusion of sulfur.

9:00am **SS1-WeM4 Pt Terminated Mono- and Multilayer CuPt Alloys Supported on Ru(0001) Single Crystals as Model System for Core Shell Particles**, ***A.K. Engstfeld***, *R.J. Behm*, Ulm University, Germany

A popular concept to improve the catalytic activity of metal particles is the utilization of core shell particles. This means that a metal/alloy core is encapsulated by an additional metal in the shell of the particle. An interesting example has recently been published by R. Srivastava et al. [1], who found that Pt enclosed alloy particles containing Cu, Co and Pt, have a much better activity towards oxygen reduction than pure Pt. Whereas the principle concept is thus proven to work, the "optimum catalyst" for oxygen reduction has not yet been found.

For a better understanding of the structure and the formation of such core shell particles we prepare nanostructured planar model surfaces under well defined conditions, such as in ultra high vacuum (UHV). The surfaces consist of mono- and multilayer CuPt alloys on a Ru(0001) single crystal. They can be prepared by subsequent evaporation of the single metals and annealing at elevated temperatures. By this means the composition of the core can be well defined. The shell can be achieved by terminating the alloy by an additional Pt layer.

In this work we focus on the preparation of mono and bimetallic CuPt layers. They are characterized via STM to elucidate the morphology as well as the atom distribution. From the atom distribution within the alloy we will discuss the dominant factor for alloy formation, in view of the different size of the atoms and difference in their intermetallic bonding. Furthermore we will elucidate the surface segregation behavior of Pt in the bilayer alloy during the alloying process.

[1] Strivastava.R, P. Mani, N. Hahn, and P. Strasser, 'Efficient Oxygen Reduction Fuel Cell Electrocatalysis on Voltammetrically Dealloyed Pt–Cu–Co Nanoparticles', *Angewandte Chemie*, 8988 (2007).

9:20am **SS1-WeM5 Carbon-induced Nano-Faceting of Re(11-21): Synthesis and Performance of a Pt ML-C/Re(11-21) Electrocatalyst**, *X.F. Yang*, Lehigh University, *H. Wang*, Columbia University, *W. Chen*, *R.A. Bartynski*, Rutgers University, ***B.E. Koel***, Princeton University

Faceted surfaces can provide unique opportunities to explore how catalytic reactions respond to changes in the catalyst surface structure. In this study, using LEED, XPS, AES, and STM, we report on how the presence of surface carbon significantly modifies the surface structure of a Re(11-21) single crystal and causes faceting, *i.e.*, an initially planar Re(11-21) surface becomes "nano-textured" to expose new crystal faces and form "pyramids" on the nanometer scale. In addition to describing these nanostructures, we identify different states of surface carbon and describe their dependence on the coverage of carbon. We also utilized the faceted Re(11-21) surface containing these nanoscale pyramids to explore for unusual catalytic properties. Here, we describe the synthesis of a model electrocatalyst by deposition of one monolayer of Pt on the faceted C/Re(11-21) surface and investigation of its performance for the hydrogen evolution reaction (HER). This Pt ML-C/Re(11-21) surface displayed higher activity for the HER than pure Pt. This is particularly promising since Re is only one-fifth the price of Pt. This study is the first application of using a nanoscale faceted surface as a template for electrocatalyst synthesis, and illustrates the potential for other such investigations. It is also of interest to further explore the catalytic activity of such faceted surfaces for heterogeneous catalytic reactions, *e.g.,* selective reduction of NO$_x$ with NH$_3$ and selective oxidation of methanol, in order to understand the various effects of facet size, orientation, and low-coordination sites that are available for reaction.

W.C. and R.A.B. acknowledge support under DOE Contract No. DE-FG02-93ER14331. B.E.K. acknowledges support by NSF Grant No. CHE-1129417.

9:40am **SS1-WeM6 Nucleation and Growth of Ag Islands on the (√3x√3)R30^{o} Phase of Ag on Si(111)**, ***A. Belianinov***, Iowa State University & Ames Laboratory - US DOE

Using STM, we measure densities and characteristics of Ag islands that form on the (√3x√3)R30o-Ag phase on Si(111), as a function of deposition temperature between 50 and 300 K. Assuming that Ag diffusion occurs via thermally-activated motion of single atoms between adjacent sites, the data can be explained as follows. At 50-125 K, islands are relatively small, and island density decreases only slightly with increasing temperature; the island density does not follow conventional Arrhenius scaling, probably due to limited mobility and lack of steady-state between deposition and consumption of Ag atoms. At higher temperatures there is a transition to conventional Arrhenius scaling, from which a diffusion barrier of 0.20-0.23 eV can be derived. At 300 K Ag atoms can travel for distances on the order of 1 µm, and they nucleate preferentially at step bunches. We have used this information to nannopattern the surface with Ag. We have done this by creating artificial defects in the √3-Ag structure with the STM tip, and then subsequently depositing Ag at 300 K. This leads to strong preferential aggregation at these sites.

10:40am **SS1-WeM9 Surface Diffusion of In and Sn on Si(001) at Room Temperature**, *N. To*, *S. Dobrin*, ***J. Nogami***, University of Toronto, Canada

A self-aligning nanostencil mask was used to pattern circular features of tin and indium on an atomically clean Si(001) substrate. The shadow mask limited material deposition to below where the membrane was open, leaving adjacent areas of clean surface for material to diffuse. STM was used to study the room temperature surface diffusion of these metals in UHV and DFT was used to calculate relevant activation barriers. The comparison of these two metals is significant since they have the same atomic structure in the first atomic layer when grown on Si(001). The diffusion of tin is limited in comparison with indium, and remains so even at increasing metal coverage. Indium forms unstable 3D islands that dissolve over time and contribute to the spreading of a single atomic layer thick film on the surrounding clean surface. The difference in behavior between the two metals can be attributed to the energy balance between 3D islands and the 2D wetting layers, as well as differences in activation energy for diffusion of atoms on top of the first atomic layer of metal. These results also show the potential for stencil patterning to provide insight into aspects of thin film growth.

11:20am **SS1-WeM11 The Effect of Surface Fluoride on the Crystallization and Photocatalytic Activity of Titania**, ***J.I. Brauer***, *G.J. Szulczewski*, University of Alabama

A two-step strategy to improve the photocatalytic activity of titania is reported. First, nitrogen doped titanium dioxide, denoted N-TiO2, has been synthesized by sol-gel methods to increase the absorption of visible radiation. Second, surface hydroxyl groups of the as-synthesized powders are replaced with fluoride ions. The two-step strategy gives independent control of "bulk" doping and surface modification. The as-synthesized and annealed powders were characterized by x-ray photoelectron spectroscopy, x-ray diffraction, diffuse reflection UV/Vis spectroscopy, IR spectroscopy, and scanning electron microscopy. Surface fluorination has two important consequences: it lowers the temperature to crystallize the as-synthesized powders into the photoactive anatase phase and improves the retention of nitrogen-dopants upon annealing. The photoactivity of the titania powders were characterized by assessing the ability to degrade aqueous solutions of methylene blue, a common dye molecule, with visible radiation greater than 420 nm. The photodegradation experiments show that the rate of methylene blue decomposition follows the trend: F, N-doped TiO2 > N-TiO2 > undoped TiO2. A mechanism to explain the observed effects will be presented.

11:40am **SS1-WeM12 Microscale Corrosion of an Aerospace Al 2024 Alloy with Low Mg and the Effect of Chromate and Cerium Based Conversion Coatings***, **J.A. DeRose**, T. Suter,* EMPA, Switzerland*, A. Bałkowiec, J. Michalski, K.J. Kurzydlowski,* Warsaw University of Technology, Poland*, I. De Graeve, H. Terryn,* Vrije Universiteit Brussel, Belgium*, P. Schmutz*, EMPA, Switzerland

An aluminum alloy, AA2024-T351 (Al 2024), with a composition having a higher proportion of Cu to Mg (Cu/Mg = 3.7), which is used in the aerospace industry, has been studied for corrosion simulation development. Results show that the Al 2024 alloy's microstructure and corrosion behavior is quite different from that reported for Al 2024 alloy with higher Mg, a more common composition (normally Cu/Mg = 2.9) [1]. Characterization of the Al 2024 indicates a dominant presence of 2nd phase (AlCuFeMnSi) intermetallic particles (>70%), but that the S phase (Al_2CuMg) and θ phase (Al_2Cu) precipitate particles are much smaller in population (<30%). Microscale corrosion studies show that open circuit (OCP) and pitting potential (PP) values extracted from micropolarization curves [2] measured for Al 2024 (Cu/Mg = 3.7) 2nd, S, or matrix phase have a large variation within a similar range of values. These results are in contrast to those already reported for Al 2024 with a more common composition (Cu/Mg = 2.9) where the electrochemical potential values separate with respect to the alloy phase and the microstructure shows S phase particles to be in the majority (>60%) [2]. Nanoscale dispersoid particles and, to a much lesser degree, nanoscale 2nd phase particles were also found present throughout the matrix of the Al 2024 studied. The impact of chromate and cerium based conversion coatings, which inhibit corrosion, on the microscale corrosion properties of the Al 2024 alloy has been studied. Electrochemical current density data extracted from micropolarization curves measured for Al 2024 2nd, S, and matrix phase exposed to electrolytic solutions containing chromate ($Na_2Cr_2O_7$) or cerium based ($Ce(NO_3)_3$) molecules show the chromate coating to be more efficient as an corrosion inhibitor. However, other cerium based molecules, such as cerium dibutylphosphate ($Ce(dbp)_3$) and cerium chloride ($CeCl_3$), which have shown more promising results [3], deserve further investigation. [1] R.G. Buchheit, R.P: Grant, P.F. Hlava, B. Mckenzie, G.L. Zender, J. Electrochem. Soc. 144 (1997) 2621. [2] T. Suter, R.C. Alkire, J. Electrochem. Soc. 148 (2001) B36. [3] S.J. Garcíaa, T.H. Muster, Ö. Özkanata, N. Sherman, A.E. Hughes, H. Terryn, J.H.W. de Wita, J.M.C. Mol, Electrochim. Acta 55 (2010) 2457.

Authors Index

Bold page numbers indicate the presenter