Surface Science

Room 104E - Session SS+HC-FrM

Deposition and Analysis of Complex Interfaces

Moderators: Bruce D. Kay, Pacific Northwest National Laboratory, Daniel Killelea, Loyola University Chicago

8:20am **SS+HC-FrM1 A Quantitative, Experimentally Supported Model for Surface Energy (SE) as a Function of Surface Defect Density (DD): the SEDD Model - Comparison with Three Liquid Contact Angle Analysis and AFM***, **Abijith Krishnan**,* Arizona State University/BASIS HS Scottsdale/SiO2 Innovates LLC*; N.X. Herbots,* Arizona State University/SiO2 Innovates LLC*; Y.W. Pershad,* Arizona State University/BASIS HS Scottsdale/SiO2 Innovates LLC*; S.D. Whaley,* SiO2 Innovates LLC/Arizona State University*; R.J. Culbertson, R.B. Bennett-Kennett,* Arizona State University

Metal Oxide Semiconductor Field Emission Transistors (MOSFETs) have been key to micro- and nano-electronics for the past six decades, but electrically active defects resulting from dangling bonds (unbounded electrons) or mobile ions create parasitic charges, known as surface charges (Q_{ss} for dangling bonds and Q_o for mobile ions), that limit performance. Passivation via oxygen and hydrogen species can reduce surface defects. However, surface state charge analysis via capacitance-voltage (C-V) curves is used to evaluate the extent of passivation but does not accurately reflect the number of structural defects. On the other hand, surface characterization by Tapping Mode Atomic Force Microscopy (TMAFM) can be used for topographic observation and surface roughness measurements but has not been used to measure surface defect density. The new theoretical model proposed the Surface Energy Defect Density (SEDD) Model [1] aims to relate surface defect density to surface energy, a macroscopic quantity measured via high statistics Three Liquid Contact Angle Analysis (3LCAA) metrology [2,3]. Three Liquid Contact Angle Analysis (3LCAA) conducted in a class 100 clean-room using the Sessile Drop method and the Van Oss theory enables for accurate and reproducible contacts angles analysis within 1°, and a reproducible relative error lower than 2-3% for the total surface energy. These results have led to the conception a new theoretical model, the Surface Energy -Defect Density Model (SEDD) which relates the macroscopic surface energy density to the microscopic defect density. To test this model with experimental defect densities, this work uses PIXNANOVERT, a new algorithm to extract defect densities from high resolution large area (1 x10 μm^2) TMAFM topographs taken on Si(100) passivated by the Herbots-Atluri process [5-7]. Analysis using surface effect density extracted. PIXNANOVERT shows that the SEDD Model predicts, within 5 the measured surface defect densities of oxidized Si surfaces with known surface energies. With this model, MOSFET manufacturers can determine the defect density in the oxide interface of their transistors by measuring the surface energy of the oxide. Testing transistor effectiveness for computers and other electronic devices would thus become more accurate than relying on C-V curves to quantify surface charge density. The SEDD Model would also allow us to determine the surface chemistry (e.g. hydrophobicity) of many other crystalline or amorphous materials, such as polymers and glasses, by measuring the surface energy.

[1] AS Krishnan, Senior Thesis (2016)

[2] Pat. pend., Herbots et al. (2011,2012,2016)

[3] SD Whaley, PhD, ASU (2013)

8:40am **SS+HC-FrM2 Ab initio Analysis of Elementary Reactions during ALD Tungsten Nucleation on Selective Substrates***, **Mariah King**, G.N. Parsons,* North Carolina State University

In 1987, selective deposition of tungsten via silane reduction was confirmed with a high deposition rate at a low temperature. Despite the numerous studies that have been conducted in the following years, many chemical processes that control selective tungsten ALD growth are not yet sufficiently understood and the leading concern remains that, past the "selective window", uniform deposition is observed on silica, the non-reactive surface. This loss of selectivity is due to the ability of the non-selective surface to promote nucleation in time due to surface processes and chemical reactions. The primary cause of tungsten nucleation on silica is a long-standing problem in the semiconductor industry that will require new fundamental understanding and an accurate description of the reaction kinetics between reactants and substrates at the atomic level**.** In this computational study, we use density functional theory to study the reaction energetics, structural stability, and electronic distribution to describe initial reactions during ALD tungsten nucleation on silicon, silica and tungsten substrates. The objective is to identify reactions that have a lower probability of occurrence, but may lead to defects that enable nucleation on otherwise non-reactive surfaces. Understanding the probability at which a species reacts with a pristine non-reactive surface will enable designers to define the limits of process defect generation, thereby identifying viable process options. Additionally, these simulations are used to suggest alternative system conditions that could lead to improved selectivity.

As a first step towards understanding the kinetics of complex deposition reactions, we present the kinetics of the elementary reactions for silane and tungsten deposition on silica and fluorinated tungsten surfaces. Along with intensive experimental data on this specific system, we have used the calculated reaction energetics to suggest the most probable series of reactions that lead to loss of selectivity. Extending these results will allow us to define viable options and directions for highly selective processes that minimize defect creation and propagation in electronic device manufacturing.

9:00am **SS+HC-FrM3 Design and Synthesis of Nanofence Cerium Oxide Coated Platinum Catalysts via Facet-selective Atomic Layer Deposition***,* ***Kun Cao****, J.M. Cai,* State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, School of Optical and Electronic Information, Huazhong University of Science and Technology, China

Sintering of Pt nanoparticles (NPs) catalysts at elevated working temperature is highly undesirable, as coalescence of NPs will cause significant decrease in the number of active sites and resulting catalytic performance degradation. Oxide overcoating techniques have been recently developed to minimize Pt sintering. However, certain trade-off has to be made between stabilization and reactivity. Stabilize metal nanoparticles and simultaneously enhance catalytic activity is still very challenging.

Here, we designed a cerium oxide nanofence coating structure to stabilize Pt NPs using facet selective atomic layer deposition. The facet selectivity is realized through differences in binding energy of Ce precursor fragments Pt surfaces. CeO_x prefers to selectively deposit on Pt (111) facets, while leaving the Pt (100) surface intact. CeO_x has synergy with metal as coating layer and creates highly active sites at Pt-CeOx interfaces. From stability point of view, CeO_x anchors Pt NPs with a strong metal oxide interaction, and nanofence coating layer provide physical blocking that suppresses NP particle migration. Such nanofence CeO_x coated Pt catalysts show both enhanced CO conversion activity and improved sintering resistance up to 700 °C under oxidative atmospheric condition.

9:20am **SS+HC-FrM4 Dehydrogenation and Rehybridization of ZnTPP on Ag(100) and Ag(111)***, C. Ruggieri, S. Rangan,* ***Robert Bartynski****,* Rutgers, the State University of New Jersey*; E. Galoppini,* Rutgers - Newark

The interactions between zinc(II) tetraphenylporphyrin (ZnTPP) molecules and the Ag(100) and Ag(111) surfaces were investigated using a combination of scanning tunneling microscopy as a local probe of the molecular adsorption configuration and X-ray, ultraviolet, and inverse photoemission spectroscopies as probes of the electronic structure. When forming a molecular monolayer by desorption of a multilayer on the Ag(100) surface, an order molecular array in registry with the substrate and having a square unit cell results. A similar preparation on the Ag(111) surface produces an overlayer that is considerably less dense but is also commensurate with the substrate having a unit cell that is slightly rectangular. Subsequent annealing leads to a transition from intact molecular adsorption to dehydrogenation and subsequent intramolecular and intermolecular rehybridization. Upon annealing, the molecule flattens as the phenyl portions of the molecule form bonds with a neighboring pyrrole group. This leads to a measurable alteration of the electronic structure. In addition, we find evidence of bonding between neighboring rehybridized molecules, consistent with the formation of biphenylene-type structures, leading to the growth of extended two-dimensional covalently bound structures. Understanding basic rules for molecule-molecule hybridization, potentially templated by prior self-assembly, could enable the directed formation of large, complex, and ordered 2-dimensional arrays of organic or metalorganic units.

C. Ruggieri, S. Rangan, R.A. Bartynski, and E. Galoppini, J. Phys. Chem. C 120, 7575 (2016)

9:40am **SS+HC-FrM5 A Case Study of the SMSI Effects: CO Oxidation on the TiO_x/Pt(111) Model Surfaces***, **Mingshu Chen**, H. Li, X.F. Weng, H. Zhang, H.L. Wan,* Xiamen University, China

Well-ordered ultrathin TiO_x films were grown on Pt(111) as model surfaces to probe the effects of the strong metal-support interaction (SMSI) on the catalytic performance. The model surfaces of TiO_x/Pt(111) were prepared under UHV and characterized by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). CO oxidation was tested for the model surfaces in a batch reaction cell as a function of the TiO_x coverages and structures. And a home-built reflection adsorption infrared spectroscopy (IRAS) was used for *in-situ* studying the surface species and stability of the model surfaces under the reaction conditions. The results show that catalytic activity could be improved significantly on the monolayer z-TiO_x, while a maximum is achieved at 0.3~0.5 ML for the w-TiO_x. The TiO_x thin films were found to be stable under CO oxidation conditions. The activation energy for CO oxidation reaction on the 1 ML z-TiO_x/Pt(111) was found to be 46 kJ/mol, which is much lower than that of 87 kJ/mol on the clean Pt(111) surface.

10:00am **SS+HC-FrM6 Toluene and Benzyl Radical Formation during Deoxygenation of Phenylmethanol on Rutile TiO_2(110)***, **Long Chen**, R.S. Smith, B.D. Kay, Z. Dohnalek,* Pacific Northwest National Laboratory

Understanding the reaction pathways of lignin-derived molecules on catalyst surfaces is of great importance for the sustainable production of energy carriers. In this regard, the role of radicals in the reaction mechanisms leading to functionalized aromatics has been extensively argued. The involvement of radical species has been firmly established for a number of simpler reactions on high surface area oxide catalysts, such as oxidative coupling of methane and selective oxidation of propylene. However, the formation of free radicals is rarely demonstrated. In this work, the reaction pathways of simple lignin-derived aromatic alcohols, i.e. phenol, phenylmethanol, and 2-phenylethanol, on a prototypical model oxide surface, rutile TiO_2(110), are studied using a combination of molecular beam dosing and temperature programmed desorption (TPD). For phenylmethanol, the coverage dependent TPD data show that about 40% of molecules adsorbed on the surface at a saturation coverage are converted to reaction products indicating that the reactions proceed on regular five-fold coordinated Ti sites. This is in contrast to aliphatic alcohols where the reactions are shown to proceed exclusively on bridging oxygen vacancy defect sites. The studies of OD-labelled phenylmethanol demonstrate that a fraction of OD hydrogen is transferred to the benzyl group to form toluene that desorbs between 300 K and 480 K. In the competing reaction, the OD hydrogen is converted to water at ~350 K. Once the OD hydrogen is depleted above 480 K, the remaining plenylmethoxy surface species dissociate yielding benzyl radicals in the gas phase. Combined, these results show that the conversion of phenylmethanol on TiO_2(110) proceeds via a unique chemistry. In contrast, both phenol and 2-phenylethanol exhibit expected surface chemistry analogous to that of aliphatic alcohols. These findings reveal for the first time the formation of free radical species from the interaction of phenylmethanol with TiO_2(110) and demonstrate a new direct mechanism for deoxygenation of lignin-derived benzylic alcohols to aromatics on TiO_2.

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