

# Wednesday Morning, November 12, 2014

## Surface Science

Room: 312 - Session SS+AS-WeM

### Atomistic Modeling of Surface Phenomena

**Moderator:** Carol Hirschmugl, University of Wisconsin Milwaukee, Eddy Tysoe, University of Wisconsin-Milwaukee

8:00am **SS+AS-WeM1 Oxidation of Cu Surfaces with Step-Edge Defects: Insights from Reactive Force Field Simulation**, *Qing Zhu, W.A. Saidi, J. Yang*, University of Pittsburgh

Defects on metal surfaces can induce non-canonical oxidation channels that may lead to the formation of novel nanostructures. Cu surfaces have been actively researched in the surface science community due to their wide range of applications in many fields. Recently, *in situ* TEM experiments showed that the oxidation of stepped surfaces promotes the formation of a flat metal-oxide interface through the Cu adatoms detachment from steps and diffusion across the terraces. In order to better understand these results, and to provide a tight bridge between the experiment and theory, we have investigated the Cu (100) oxidation using ReaxFF method as implemented in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). Using models for both defect-free flat and stepped surfaces, our study shows that the step-edge defects induce markedly different oxidation dynamical behavior compared to the flat surface. Additionally, on the stepped-surfaces, we show that the oxidation of the upper-terrace are more favored than the lower-terrace, which we validated by depositing oxygen homogeneously on the surface or by using a biased-mechanism where the oxygen atoms target either the top or lower terraces. This favoring of the oxidation of the top terrace drives Cu diffusion flux from the upper-terrace to the lower-terrace that explains the recent TEM experiments. We additionally show that the oxidation behavior of the stepped Cu (100) bears many similarities with the formation of the metal-oxygen "added-row" structures on the (110) surfaces of several metals. Future studies include the investigation of vicinal surfaces with different morphologies and different metals.

8:20am **SS+AS-WeM2 The Role of Time-scale Analysis in Simulation of ALD and CVD Surface Reaction Kinetics**, *Raymond Adomaitis, E. Remmers, C.D. Travis, D. Arana-Chavez*, University of Maryland, College Park

In this paper, we will describe our research on the mathematical structure of atomic layer deposition (ALD) and chemical vapor deposition (CVD) surface reaction kinetics models. Our primary objective is to investigate the mathematical structure of the differential-algebraic (DAE) systems of equations describing surface reaction species dynamics during these thin-film deposition processes. The research is motivated by the challenges presented by writing a well-posed DAE model for surface reaction species dynamics as well as the difficulties encountered when numerically solving these systems. Using a perturbation analysis approach, we demonstrate that the deposition kinetics decomposes naturally into slow (deposition reactions), fast (equilibrium reactions), and instantaneous (conserved quantities) time scales. A key contribution of our work is the development of a reaction network factorization procedure that partitions the surface reaction and deposition species dynamic balances into the distinct time scale ranges described. Under what conditions this procedure works, understanding the implications of fixed points for dynamic ALD processes, interpreting reaction fluxes, and extending the methods to spatially distributed processes in the context of representative thin-film application domains will be discussed. Physical interpretation of DAE system initial conditions for these surface processes constitutes another important research direction in this project; results will be presented which illuminate alumina ALD growth surface dynamics at the start of each exposure (TMA and water) and purge period.

8:40am **SS+AS-WeM3 Hydrogen Production from Formic Acid on Transition Metals and Alloys: A Selectivity Challenge**, *Manos Mavrikakis, J. Scaranto, J.A. Dumesic, S. Singh, S. Li, J.A. Herron, R. Carrasquillo, L. Roling, B. O'Neill, G. Peng*, University of Wisconsin - Madison

**INVITED**

Formic acid (HCOOH) is a simple molecule that is an abundant product of biomass processing and can serve as an internal source of hydrogen for oxygen removal and upgrading of biomass to chemicals and fuels. In addition, HCOOH can be used as a fuel for low temperature direct fuel

cells. We present a systematic study of the HCOOH decomposition reaction mechanism starting from first-principles and including reactivity experiments and microkinetic modeling. In particular, periodic self-consistent Density Functional Theory (DFT) calculations are performed to determine the stability of reactive intermediates and activation energy barriers of elementary steps. Pre-exponential factors are determined from vibrational frequency calculations. Mean-field microkinetic models are developed and calculated reaction rates and reaction orders are then compared with experimentally measured ones. These comparisons provide useful insights on the nature of the active site, most-abundant surface intermediates as a function of reaction conditions and feed composition. Trends across metals on the fundamental atomic-scale level up to selectivity trends will be discussed. Finally, we identify from first-principles alloy surfaces, which may possess better catalytic properties for selective dehydrogenation of HCOOH than monometallic surfaces, thereby guiding synthesis towards promising novel catalytic materials.

9:20am **SS+AS-WeM5 Elucidating Atomic-scale Wear Processes in Hydrocarbon-based Materials via Molecular Dynamics and AFM**, *Judith Harrison*, United States Naval Academy, *T.D.B. Jacobs*, University of Pennsylvania, *P.L. Keating, M. Fallet*, United States Naval Academy, *J.D. Schall*, Oakland University, *Y. Jiang, K.T. Turner, R.W. Carpick*, University of Pennsylvania, *K.E. Ryan*, United States Naval Academy

Molecular dynamics (MD) simulations are unique in their ability to elucidate atomic-scale phenomena because the positions, velocities, and forces of all atoms in the system are known as a function of time. Atomic-scale wear in nanoscale contacts is of particular importance for tip-based nanomanufacturing applications. As a result, wear resistant materials, such as diamond-like carbon (DLC), have been used to coat AFM tips to improve the lifespan and reliability of AFM probes. We have performed atomic force microscope (AFM) experiments and MD simulations aimed at examining adhesion and wear in diamond, ultrananocrystalline diamond (UNCD), and amorphous carbon (a-C:H) materials. Specifically, we examined the normal and sliding contact of differently shaped axisymmetric tips, composed of a-C:H and UNCD, with hydrocarbon-based substrates. Specific attention was paid to elucidating specific atomic-scale wear mechanisms and their dependence on tip shape, material, surface termination, impact point, and roughness. To examine the effect of the potential energy function on wear mechanisms, identical simulations were performed with the AIREBO potential and the REBO+S potential. The AIREBO potential is based on the reactive empirical bond-order potential (REBO), which was developed to model CVD growth of diamond. Recently, it was demonstrated that the short-range cut-off for covalent bonding in the REBO potential resulted in bond-breaking forces that are an order of magnitude larger than those predicted by DFT calculations. A screening function was added to the REBO potential (REBO+S) to alleviate this situation. Simulations were carried out using each potential, and wear mechanisms identified in each set of simulations were compared.

9:40am **SS+AS-WeM6 Theoretical Investigation of the Structure and Properties of Titania/Graphene Hybrid Materials**, *Ivan Iordanov, C.J. Karwacki*, Edgewood Chemical And Biological Center, *G.M. Mogilevsky*, Booz Allen Hamilton

We are using modeling to understand the properties of complex materials that show promise for catalysis, filtration and decontamination. These materials are of interests both for chemical defense, as well as in many industrial applications. The main focus of our modeling so far has been determining the structure and properties of mixtures of TiO<sub>2</sub> nanoparticles (NPs) and small sheets of graphene. The synthesis technique for these materials was pioneered at ECBC. It involves synthesizing graphene from alizarin molecules in close contact with TiO<sub>2</sub> NPs. This was expected to create a close connection between the graphene and TiO<sub>2</sub> NPs, and improve their catalytic properties. However, the exact structure of the small graphene patches and how and where they bind to TiO<sub>2</sub> is difficult to characterize experimentally. Our models have shown that the binding between graphene TiO<sub>2</sub> is quite weak (on the order of 0.01eV/Carbon atom), and that it is not strongly dependant on the addition of O and OH to the surface of the graphene, or to the size of the graphene patches. This appears to confirm the experimental finding that the surface graphene can be removed from the TiO<sub>2</sub> particles simply by rubbing. We also modeled the case where graphene is surrounded by TiO<sub>2</sub> on both sides, and the binding in this case increases by nearly 2x, suggesting that graphene would prefer to bind between TiO<sub>2</sub> NPs. This may be the explanation for the disappearance of the smallest (~5nm) sized pores from the TiO<sub>2</sub> NP agglomerates upon addition of graphene. We also find that there is a non-trivial degree of charge transfer between graphene and TiO<sub>2</sub>, which can be expected to improve TiO<sub>2</sub>'s photo catalytic properties.

11:00am **SS+AS-WeM10 Real-Time Ab-Initio KMC Simulation of the Self-Assembly and Sintering of Bimetallic Epitaxial Nanoclusters: Au+Ag on Ag(100).** James Evans, Y. Han, D.-J. Liu, Iowa State University  
 Far-from-equilibrium shape and structure evolution of bimetallic epitaxial nanoclusters during formation by deposition or during post-assembly sintering is extremely sensitive to the details of periphery diffusion and intermixing kinetics. Precise characterization requires accurate determination of distinct barriers for many possible local environments (compositions and periphery configurations) of the diffusing adatom. This is achieved for epitaxial nanoclusters using DFT to assess adsorption energies and lateral pair- and trio-interactions both conventionally with adatoms at adsorption sites, and unconventionally with an adatom at the transition state for hopping. KMC simulation incorporating these barriers then captures structure evolution on the appropriate time-scale. The approach is applied for unstrained Au-Ag nanoclusters on Ag(100) where these can be assembled with either 2D core-ring by sequential codeposition or intermixed structures by simultaneous codeposition or annealing. This ab-initio level approach replaces typical heuristic analyses, often resorting to macroscopic concepts, e.g., for intermixing kinetics.

11:20am **SS+AS-WeM11 Progress in Characterizing Submonolayer Island Growth: Capture-Zone Distributions, Growth Exponents, and Hot Precursors.** Theodore L. Einstein, J.R. Morales-Cifuentes, University of Maryland, College Park, A. Pimpinelli, Rice Quantum Institute

We review previous results for using the capture-zone [island proximity cell] distribution (CZD) in island growth to extract information about the critical nucleus size  $i$ .<sup>1</sup> Over the experimentally accessible region, the CZD is well described by the generalized Wigner distribution  $P_p(s) = a_p s^\beta \exp(-b_p s^2)$ , dependent only on the exponent  $\beta$ . For diffusion-limited aggregation (DLA),  $\beta \approx i+2$ . We discuss recent experimental applications. For comparison with this approach, we consider the corresponding dependence of the growth exponent  $\chi$  (stable island density  $N \sim F^\chi$ , where  $F$  is the flux) for both DLA and attachment-limited aggregation (ALA). In either case,  $\chi\beta = i$ , so that for ALA, where  $\chi = 2i/(i+3)$ , we find  $\beta = (i+3)/2$ .<sup>2</sup> We compare with experiments depositing pentacene (5A) and p-hexaphenyl (6P) on sputtered mica.

Furthermore, recent experiments<sup>3</sup> studying 5A on amorphous mica gave evidence of nucleation via a hot precursor state, with an unusual relationship between  $N$  and substrate temperature. Thus motivated, we examine a model of such behavior.<sup>4</sup> We use rate equations and Walton's relation. We take deposited monomers to be hot initially, traveling ballistically with temperature-independent speed  $v$  until a time  $\tau$ , when they thermalize. For the dimensionless combination  $z := v \tau N^{1/2} \ll 1$  rapid thermalization occurs, with consequent DLA nucleation. For  $z \gg 1$  we find the novel behavior for hot-monomer aggregation (HMA):  $\chi$  has, unexpectedly, the same form as for ALA. We scrutinize behavior in both limits as well as in the crossover regime  $z \sim 1$ , in which behavior can be described using an effective  $\chi$ . At low temperatures, the behavior becomes markedly non-Arrhenius, insensitive to temperature. We conclude a discussion of more general applications of this framework.

<sup>1</sup>T.L. Einstein, A. Pimpinelli, Diego Luis González, J. Crystal Growth (2014), <http://dx.doi.org/10.1016/j.jcrysgro.2014.01.053>.

<sup>2</sup>A. Pimpinelli, L. Tumbek, A. Winkler, J. Phys. Chem. Lett. 5 (2014) 995.

<sup>3</sup>A. Winkler, L. Tumbek, J. Phys. Chem. Lett. 4 (2013) 4080.

<sup>4</sup>A. Pimpinelli, J.R. Morales-Cifuentes, T.L. Einstein, preprint.

11:40am **SS+AS-WeM12 Molecular Dynamics Simulation of Ge Deposition and Islanding on Amorphous Silica Substrates.** C.Y. Chuang, University of Pennsylvania, S.M. Han, University of New Mexico, Talid Sinno, University of Pennsylvania

Selective epitaxial growth (SEG) of Ge on Si substrates has proven to be a versatile pathway for producing Ge substrates to enable III-V device integration on Si. However, persistent problems remain, including dislocation formation and high stresses due to lattice parameter and thermal expansion coefficient mismatches between Si and Ge. Further optimization of the SEG process may be significantly assisted by atomistic simulation. Here, we present an atomistic analysis of Ge deposition on SiO<sub>2</sub>. We begin by describing a validation process for a Tersoff-based model for the ternary Si-Ge-O system [1,2], in which we compare simulation predictions to detailed experimental data [3,4] for a variety of properties. Using this validated interatomic potential, Ge deposition and islanding on an amorphous SiO<sub>2</sub> surface is studied with direct molecular dynamics and the results are compared to experimental measurements [4] of island size distributions as a function of deposition rate and temperature. A key aspect of our modeling approach is a procedure to accelerate the simulations. While direct molecular dynamics simulations of Ge deposition on SiO<sub>2</sub> are able to capture Ge island nucleation, growth and coarsening, the very fast

deposition rates necessary makes difficult direct comparison to experimental measurements of island density and size distributions. In particular, we show that direct molecular dynamics simulations are able to approach, but not quite reach, the deposition conditions in experiment. The accelerated simulations are based on "equation-free" coarse projective integration [5]. Here, measures of the island size distribution dynamics are obtained from short molecular dynamics simulations and then used to evolve numerically the size distribution over large time intervals. The new island size distribution is then used to reconstruct consistent atomic configurations that are subsequently evolved further with molecular dynamics and the process is repeated. Here, we show that the reconstruction of atomic configurations from size distribution moments represents the key challenge in deposition simulations and we propose approaches for achieving this in a computationally tractable manner.

[1] J. Tersoff, *Phys. Rev. B* **39**, 5566 (1989).

[2] S. Munetoh, T. Motooka, K. Moriguchi and A. Shintani, *Comput. Mater. Sci* **39**, 334 (2007).

[3] Q. Li, J. L. Krauss, S. Hersee, and S. M. Han, *J. Phys. Chem. C* **111**, 779 (2007).

[4] D. Leonhardt and S. M. Han, *Surf. Sci.* **603**, 2624 (2009).

[5] M.E. Kavousanakis, R. Erban, A.G. Boudouvis, C.W. Gear, I.G. Kevrekidis, . (2007) 382-407.

12:00pm **SS+AS-WeM13 Dimerization Induced Deprotonation of Water on RuO<sub>2</sub>(110).** R. Mu, D.C. Cantu, V.-A. Glezakou, Z. Wang, I. Lyubinsky, R. Rousseau, Zdenek Dohnalek, Pacific Northwest National Laboratory

RuO<sub>2</sub> has proven to be indispensable as a co-catalyst in numerous systems designed for photocatalytic water splitting. Here we present a first mechanistic study of water adsorption, dissociation, and diffusion on the most stable RuO<sub>2</sub> surface, rutile RuO<sub>2</sub>(110). Variable temperature scanning tunneling microscopy (STM) and ab initio molecular dynamics based density functional theory calculations (DFT) are employed to follow the behavior of small water clusters. We show that water monomers adsorb molecularly on Ru sites, become mobile above 240 K, and diffuse along the Ru rows. The monomers readily pair up and form dimers that are immobile below 273 K. Finally, the dimers deprotonate and form Ru-bound H<sub>2</sub>O-OH and bridging OH species. This is in a sharp contrast with the molecular binding of water dimers observed on isostructural TiO<sub>2</sub>(110). The onset for diffusion of H<sub>2</sub>O-OH pairs on RuO<sub>2</sub>(110) is observed at ~273 K, indicating a significantly higher diffusion barrier than that for water monomers. The experimentally determined diffusion barriers are in agreement with those obtained from the DFT calculations. The diffusion of H<sub>2</sub>O-OH pairs is found to proceed via a rollover mechanism, with a water molecule moving over OH, followed by hydrogen transfer from H<sub>2</sub>O to OH. At high water coverages, water dimers are found to be the building blocks of longer water chains on Ru rows. The observed behavior of water monomers and dimers is compared and contrasted with that previously reported on isostructural rutile TiO<sub>2</sub>(110).

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