

Tuesday Morning, October 27, 2020

Virtual Showcase

Room Live - Session VS1-TuM

It's All in the Details: Mechanistic Understanding of Materials Fabrication and Analysis

Moderators: Mariadriana Creatore, Eindhoven University of Technology, The Netherlands, Dan Killelea, Loyola University Chicago

10:00am **VS1-TuM-1 Welcome Address from the AVS President, Amy V. Walker**, University of Texas at Dallas, USA

The AVS President, Amy V. Walker, welcomes you to the AVS 67 Virtual Showcase. We hope you will enjoy the event!

10:10am **VS1-TuM-3 Welcome Message from the AVS 67 Program Chair, Daniel Killelea**, Loyola University Chicago; **A. Creatore**, Eindhoven University of Technology, The Netherlands, Netherlands

The AVS 67 Program Chair, Dan Killelea welcomes you, thanks all presenters, sponsors, and the community for their support and participation.

10:15am **VS1-TuM-4 Gaede-Langmuir Award Lecture: How Advances in High-Power Magnetron Impulse Sputtering (HiPIMS) Can Control Ion Energy, Ionization, and have High Deposition Rates, David Ruzic**, University of Illinois at Urbana-Champaign **INVITED**

High-Power Magnetron Impulse Sputtering (HiPIMS) is a pulsed physical vapor deposition (PVD) technique which creates a dense plasma near the sputtering target resulting in high ionization of the target material. Normally, most of these ions return to the target and can not be utilized for thin film deposition. However recent advances have changed this picture. The waveform can be altered to provide a short fast negative spike leading to higher energy electrons which cause more ionization. Then, if a positive pulse "kick" immediately follows, the plasma near the target is expelled ionizing even more of the sputtered atoms. Furthermore, by controlling the height and length of the positive kick, the plasma potential is increased. By controlling the magnitude of that plasma potential, the energy of the ions reaching the substrate can be controlled. Further developments allow for additional plasma to be created sustaining the higher plasma potential, and even allowing HiPIMS devices to be used for etching. Deposition rates and ionization fractions can be raised even higher through magnet design. The history of these advances, their underlying physics, and their applications will be presented.

11:05am **VS1-TuM-14 Ru Precursors for Photoassisted Chemical Vapor Deposition: Comparison of Allyl and Diene Complexes, Christopher Brewer**, N. Sheehan, University of Florida; **B. Salazar**, A. Walker, University of Texas at Dallas; **L. McElwee-White**, University of Florida

Chemical vapor deposition (CVD) is a potentially attractive technique for the metallization of organic thin films. However, thermal CVD processes often require high temperatures which are incompatible with organic substrates. Photochemistry provides an alternative means of initiating precursor decomposition without heating the substrate. Readily available Ru precursors, such as (η^3 -allyl)Ru(CO)₃X (X = Cl, Br, I), have been used to deposit Ru on functionalized self-assembled monolayers by means of photochemical CVD as a model system for deposition of metal on a thermally sensitive substrate. Quantum yields for loss of a single CO ligand in alkane solutions were determined for the (η^3 -allyl)Ru(CO)₃X complexes, to elucidate the photochemistry that initiates the deposition process. As a comparative study, the quantum yields for various (diene)Ru(CO)₃ complexes were determined. These (diene)Ru(CO)₃ undergo mixed photolytic decomposition pathways, making them attractive precursors for photochemical CVD. This talk will discuss the photochemistry of the (diene)Ru(CO)₃ complexes relative to the (η^3 -allyl)Ru(CO)₃X complexes with respect to their deposition results.

11:25am **VS1-TuM-18 Rhodium Copper Single-Atom Alloys for Selective and Coke-Free C-H Activation, Ryan Hannagan**, C. Sykes, Tufts University

Due to the recent prevalence of small hydrocarbons, there has been renewed interest in direct dehydrogenation of small alkanes to the corresponding alkenes. One of the major issues in this reaction is the deactivation of catalysts due to coke formation. Here, we report a new RhCu single-atom alloy which displays considerable activity for C-H activation without coke formation. First, using a combination of scanning tunneling microscopy, temperature programmed desorption, and infrared spectroscopy, we characterize the model catalyst surface. We find that Rh atoms exist as isolated sites in the Cu host. We correlate this structure with the binding energy and vibrational frequency of CO on the isolated Rh sites.

With knowledge of the atomic-scale structure, we then examine how the isolated Rh sites promote C-H activation. Using methyl iodide as a reporter on C-H activation, we find the isolated Rh sites promote C-H activation at a significantly lower temperature than Cu(111). We observe the formation of methane (from the hydrogenation of methyl groups) in addition to the formation of ethene (via coupling of CH₂ to CH₃ followed by beta-dehydrogenation). This is in strong contrast to extended Rh ensembles where coke formation is apparent. Together, these results indicate that RhCu single-atom alloys offer significant opportunities for efficient and coke-free C-H activation.

11:45am **VS1-TuM-22 Hydrogen Migration at Restructuring Palladium-Silver Oxide Boundaries Dramatically Enhances Reduction Rate of Silver Oxide, Christopher O'Connor**, Harvard University; **M. van Spronsen**, Lawrence Berkeley National Laboratory (LBNL); **T. Egle**, **F. Xu**, Harvard University; **H. Kersell**, **J. Oliver-Meseguer**, Lawrence Berkeley National Laboratory (LBNL); **M. Karatok**, Harvard University; **M. Salmeron**, Lawrence Berkeley National Laboratory (LBNL); **R. Madix**, **C. Friend**, Harvard University

Heterogeneous catalysts are complex materials with multiple interfaces. A critical proposition in exploiting bifunctionality in alloy catalysts is to achieve surface migration across interfaces separating functionally dissimilar regions. Herein, we demonstrate the enhancement of more than 10⁴ in the rate of molecular hydrogen reduction of a silver surface oxide in the presence of palladium oxide compared to pure silver oxide using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and scanning tunneling microscopy (STM). This enhancement is attributed to the migration of surface species across the palladium-silver interface via hydrogen atoms formed on palladium and oxygen atoms associated with silver. The palladium-silver interface dynamically restructures during oxidation, resulting in palladium dewetting, and during reduction, resulting in silver-palladium intermixing. This study clearly demonstrates the migration of reaction intermediates and catalyst material across surface interfacial boundaries in alloys with a significant effect on surface reactivity, having broad implications for the catalytic function of bimetallic materials.

12:15pm **VS1-TuM-28 Chirality Detection of Surface Desorption Products using Photoelectron Circular Dichroism, J. Wega, Tim Schäfer, G. Westphal**, University Göttingen, Germany **INVITED**

Chirality detection of gas-phase molecules at low concentrations is challenging as the molecular number density is usually too low to perform conventional circular dichroism absorption experiments. In recent years, new spectroscopic methods have been developed to detect

chirality in the gas phase. In particular, the angular distribution of photoelectrons after multiphoton laser ionization of chiral molecules using circularly polarized light is highly sensitive to the enantiomeric form of the ionized molecule (multiphoton photoelectron circular dichroism (MP-PECD)). In the talk, I will present the MP-PECD as an analytic tool for chirality detection of the bicyclic monoterpene fenchone desorbing from a Ag(111) crystal. We recorded velocity resolved kinetics of fenchone desorption on Ag(111) using pulsed molecular beams with ion imaging techniques. In addition, we measured temperature-programmed desorption spectra of the same system. Both experiments indicate weak physisorption of fenchone on Ag(111). We combined both experimental techniques with enantiomer-specific detection by recording MP-PECD of desorbing molecules using photoelectron imaging spectroscopy. We can clearly assign the enantiomeric form of the desorption product fenchone in sub-monolayer concentration. The experiment demonstrates the combination of MP-PECD with surface science experiments, paving the way for enantiomer-specific detection of surface reaction products on heterogeneous catalysts for asymmetric synthesis.

12:45pm **VS1-TuM-34 Thin Film Growth One Step at a Time: Unraveling Mechanisms in Atomic Layer Deposition, Stacey Bent**, Stanford University **INVITED**

With the growing interest in functional nanoscale materials for applications such as electronics, catalysts, and batteries, methods for fabricating materials with atomic-level control are becoming increasingly important. Atomic layer deposition (ALD) is a vapor-based method that provides excellent capabilities for depositing thin solid films, nanoparticles, and other nanoscale materials. Based on sequential, self-limiting vapor-surface reactions, ALD offers exceptional conformality, thickness control at the Angstrom level, and tunable film composition. This talk will describe research into the fundamental processes that drive ALD. Two ALD systems will be presented in which a combination of characterization methods is

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applied to elucidate nucleation and growth mechanisms. In the first system, ALD of binary and ternary metal oxides using ozone as a counterreactant show unusual behavior implicating the importance of trapped reactive oxygen species in these ALD processes. For example, in the growth of ternary Ni-Al-O films using supercycles of nickel oxide and aluminum oxide ALD, Al uptake is greatly enhanced when Al₂O₃ ALD followed a NiO ALD cycle, a result that may arise from the presence of nickel superoxide species after ozone exposure. In ALD of iron oxide by t-butylferrocene and ozone, growth per cycle of greater than one monolayer of Fe₂O₃ per cycle is observed and explained by the presence of excess oxygen stored in the surface regions of deposited films. In the second system, ALD of MoS₂ thin films as well as ALD of metal oxides on MoS₂ will be described. We show that the concentration and size of ZnO nanocrystals grown on MoS₂ by ALD can be independently tuned by controlling the growth conditions. We also introduce a kinetically-driven ALD process for growing stoichiometrically controlled, crystalline MoS₂ from Mo(CO)₆ and H₂S at temperatures as low as 190 °C. Insights into the effect of ALD process conditions on growth behavior and materials properties will be presented.

1:15pm **VS1-TuM-40 Closing Remarks and Sponsor Thank Yous, *Daniel Killelea***, Loyola University Chicago

Thank you to everyone for your participation! We hope you enjoyed the first Virtual Showcase Session! Please join us tomorrow for another exciting session!

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