

## Applied Surface Science Room 117 - Session AS-TuA

### Theory, Surface Structure and Processes

**Moderators:** Paul S. Bagus, University of North Texas, Jodi Grzeskowiak, Tokyo Electron America, USA

#### 2:15pm AS-TuA-1 Advances in Understanding Structure and Electron Transfer Dynamics at Iron Oxide/Water Interfaces, *Kevin Rosso*, Pacific Northwest National Laboratory

**INVITED**  
Structure and dynamics at iron oxide/water interfaces, which govern rates of adsorption, electron transfer, growth/dissolution, have long been challenging to accurately simulate because of the prominent role of iron cation valence on acidity and ligand exchange behavior, and unique electronic structure considerations in the solid state. Iron oxides are wide band gap semiconductors with a narrow conduction band arising from strongly localized 3d orbitals. Consequently, charge carriers tend to self-trap as polarons whose mobilities are controlled by thermally activated site-to-site hopping. Proper theoretical description of such properties requires thoughtful trade-off's between necessary accuracy versus efficiency.

I will provide a decadal perspective on computational efforts applied to processes at hematite/water interfaces, highlighting the importance of steady methodological improvements. The talk will feature 1) how water organizes and is dynamically stabilized at distinct hematite facets, 2) the structure and hopping kinetics of electron and hole polarons, and 3) the free energies of ferrous iron adsorption and valence interchange electron transfer with the surface. It will be shown that ab initio molecular dynamics is now both a viable and essential tool for accurately determining the H-bonding network of adsorbed water and the acidity constants of surface hydroxo groups, while static density functional theory is still a useful tool for water binding energetics. Gap-optimized hybrid functionals show that while the hole polaron generally localizes onto a single iron site, its mobility is limited by the tetragonal distortion it induces, whereas the electron polaron induces a smaller distortion resulting in delocalization over two neighboring Fe units and a factor of three higher mobility. Finally, for computationally intensive processes such as ferrous iron adsorption, it will be shown that use of neural network potentials such as the Behler-Parrinello type is a promising alternative to classically parameterized molecular dynamics, offering both the precision of first principles calculations and the same order of computational efficiency to that of classical simulations. The collective findings bode well for ultimately enabling a robust basis for interpretation of experimental observables near the atomic-scale including complex multi-step processes such as redox-catalyzed dissolution and growth.

#### 2:45pm AS-TuA-3 Manifestation of Correlated Electronic Structure in a Kagome Metal $\text{YbTi}_3\text{Bi}_4$ , *Anup Pradhan Sakhya*, University of Central Florida; *B. Ortiz*, Materials Science and Technology Division, Oak Ridge National Laboratory; *B. Ghosh*, Northeastern University, US; *M. Sprague, M. Mondal*, University of Central Florida; *M. Matzelle*, Northeastern University, US; *I. Elius, N. Valadez*, University of Central Florida; *D. Mandrus*, University of Tennessee Knoxville; *A. Bansil*, Northeastern University, US; *M. Neupane*, University of Central Florida

Kagome lattices have emerged as an ideal platform for exploring various exotic quantum phenomena such as correlated topological phases, frustrated lattice geometry, unconventional charge density wave orders, Chern quantum phases, superconductivity, etc. Here, we report the discovery of a new Ti-based kagome metal  $\text{YbTi}_3\text{Bi}_4$  which is characterized using angle-resolved photoemission spectroscopy (ARPES) and magnetotransport, in combination with density functional theory calculations. Our ARPES results reveal the complex fermiology of this system along with the spectroscopic evidence of four flat bands. Furthermore, our electronic structure measurements show the presence of multiple van Hove singularities originating from Ti 3d orbitals. We have identified that the system exhibits topological nontriviality with surface Dirac cones at the  $\Gamma$  point and a bulk linearly dispersing gapped Dirac-like state at the K point as indicated by our theoretical calculations. These results establish  $\text{YbTi}_3\text{Bi}_4$  as a novel platform for exploring the intersection of nontrivial topology, and electron correlation effects in the wider  $\text{LnTi}_3\text{Bi}_4$  ( $\text{Ln}$ = lanthanide) family of materials.

#### 3:00pm AS-TuA-4 Impact of Surface Pretreatment on $\text{Al}_2\text{O}_3/\text{GaN}$ and $\text{HfO}_2/\text{GaN}$ Band Offsets Measured by X-Ray Photoelectron Spectroscopy, *Melissa Meyerson, P. Dickens, J. Klesko, B. Rummel, P. Kotula, A. Binder*, Sandia National Laboratories

The need for modern power devices with lower ON-resistances, higher breakdowns, and improved efficiencies is increasing as power demands in electronics continue to rise. Gallium nitride (GaN) has emerged as a promising candidate to satisfy these demands due to its advantageous material properties as a wide bandgap semiconductor (e.g., high breakdown electric field, enhanced mobility, and a high saturation velocity). The use of GaN in power electronics often relies on the interactions between the GaN and a dielectric layer, such as  $\text{Al}_2\text{O}_3$ , which are highly dependent on the properties of the materials at the interface. Variations in the band offset and interface trap state densities can be impacted by a variety of processing factors, including the surface chemistry of the GaN prior to dielectric deposition. Since the surface chemistry of the GaN is affected by the methods used to clean the surface prior to deposition of the dielectric, it is expected that these interfacial properties will also be affected by the cleaning method used. Here, we study the interfacial properties of  $\text{Al}_2\text{O}_3/\text{GaN}$  and  $\text{HfO}_2/\text{GaN}$  films using X-ray photoelectron spectroscopy (XPS) to measure the band offsets as a function of GaN cleaning method. Additionally, a  $\text{Ga}_x\text{O}_y$  interlayer has been identified at this interface by XPS, which is correlated with interface trap state densities measured from capacitance-voltage measurements of subsequently fabricated MOS-capacitors.

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#### 3:15pm AS-TuA-5 Absence of Electronic Structure Reconfiguration in $\text{EuSnP}$ Across the Antiferromagnetic Transition, *Milo Sprague, A. Sakhya*, University of Central Florida; *S. Regmi*, Idaho National Laboratory; *M. Mondal, I. Bin Elius, N. Valadez*, University of Central Florida; *T. Romanova, A. Ptok, D. Kaczorowski*, Polish Academy of Sciences, Poland; *M. Neupane*, University of Central Florida

Magnetic ordering in lanthanide-based metals is commonly attributed to RKKY interactions, where localized magnetic f electrons interact magnetically with itinerant conduction electrons through exchange interactions. Due to the intricate interplay between the electronic band structure and magnetic ordering, many lanthanide magnetic metals undergo significant changes in their electronic spectrum. In our study of the europium-based antiferromagnetic metal  $\text{EuSnP}$ , employing angle-resolved photoemission spectroscopy (ARPES) and first-principles density functional theory (DFT) calculations, we surprisingly found no modifications to the band structure upon cooling below the paramagnetic to antiferromagnetic transition temperature. We discuss potential reasons for this absence of observed reconstruction in this compound.

#### 4:00pm AS-TuA-8 Calculation of X-Ray Absorption Spectra of f-Element Compounds from First Principles, *Jochen Autschbach*, University at Buffalo, SUNY

**INVITED**  
This talk will be concerned with calculations of X-ray absorption near-edge structure (XANES) spectra for f-element compounds using multi-configurational wavefunction methods (using complete and restricted active space self-consistent field (CAS/RASSCF) methods and variants thereof), along with supporting density functional calculations. A focus of our research has been the connection of the observed spectral features and the underlying covalent bonding in the systems, in particular, the involvement of the valence f-shells of lanthanides and actinides. The talk will cover published studies of actinyl(VI) species, actinide hexa-chlorides, cerocene vs.  $\text{CeO}_2$ , as well as on-going research on a variety of Ce(IV) materials.

Selected relevant references:

- [1] Sergentu, D.-C.; Autschbach, J., 'Covalency in Actinide(IV) Hexachlorides in Relation to Chlorine K-Edge X-ray Absorption Structure', *Chem. Sci.* 2022, 13, 3194–3207. <https://doi.org/10.1039/D1SC06454A>
- [2] Sergentu, D.-C.; Autschbach, J., 'X-ray absorption spectra of f-element complexes: Insight from relativistic multiconfigurational wavefunction theory', *Dalton Trans.* 2022, 51, 1754–1764. <https://doi.org/10.1039/d1dt04075h>

[3] Sergentu, D.-C.; Booth, C. H.; Autschbach, J., 'Probing multicongfigurational states by spectroscopy: The cerium XAS L<sub>3</sub>-edge puzzle', Chem. Eur. J. 2021, 27, 7239–7251. <https://doi.org/10.1002/chem.202100145>

**4:30pm AS-TuA-10 The XPS of Ni Compounds – A Comparative Study, Paul S. Bagus**, University of North Texas; *C. Nelin*, Consultant; *N. Lahiri*, Pacific Northwest National Lab; *E. Ilton*, Pacific Northwest National Lab

The Ni 2p XPS of the ionic compounds NiO, Ni(OH)<sub>2</sub>, and Ni(CO)<sub>3</sub> are analyzed, interpreted, compared with each other and, as well, the theoretical results are compared with XPS measurements. The main features as well as the satellite, shake, features are considered. The theoretical analysis is based on the properties of ab initio molecular orbital wavefunctions, WFs, for cluster models of the compounds. We distinguish two theoretical approaches. The first is where only the angular momentum coupling of the core 2p open shell and the valence open shell which contains 8 dominantly Ni 3d orbitals is considered to form the ionic wavefunctions, WFs. The second is where excitations from closed shell orbitals into the valence open shell space is added. The second approach properly describes the XPS satellites and puts, for the first time, the concept of "charge transfer" in the core ionic states on a firm theoretical basis. It is important to choose orbitals and WFs which allow the mixing of normal and shake character and novel methods are used to characterize the orbitals and to describe the WF character. The consequences for the XPS of the variation of the Ni-ligand distance are examined. Three key results are: (1) The extended theoretical approach must be used to describe the satellites and it also somewhat modifies the main XPS peaks. (2) The choice of orbitals is critical to properly describe the XPS, especially the satellites, and this can be related to the electronic structure of the excited states. The differences between the XPS of the different compounds are mainly for the satellite features and the reasons for this are explained.

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**4:45pm AS-TuA-11 The Experimental Asymmetry of the 2p, 3d, and 4f, Photoemission Spectra of the Elements of the 3<sup>rd</sup>, 4<sup>th</sup>, and 5<sup>th</sup> Periods, Alberto Herrera-Gomez**, Cinvestav, Mexico; *A. Dutoi*, University of the Pacific; *D. Guzman-Bucio*, CINVESTAV-Queretaro, Mexico; *D. Cabrera-German*, Universidad de Sonora, Mexico; *A. Carmona-Carmona*, Benemerita Universidad Autonoma de Puebla, Mexico; *O. Cortazar-Martinez*, CINVESTAV-Unidad Queretaro, Mexico; *B. Crist*, The XPS Library; *M. Mayorga-Garay*, CINVESTAV-Unidad Queretaro, Mexico

We carried out a peak-fitting analysis of the 2p, 3d, and 4f, spectra of the elements of the 3<sup>rd</sup>, 4<sup>th</sup>, and 5<sup>th</sup> periods, respectively. We found that the Double-Lorentzian lineshape (DL) [1] closely reproduces the asymmetry in all cases. Moreover, the DL asymmetry shows clear trends with atomic-number. This contrasts with the Doniach-Sunjic lineshape, which, in most cases, does not reproduce the experimental data; besides, it cannot be used in quantitative studies because it is not integrable.

The asymmetry parameter ( $a_{DL}$ ) for the 2p<sub>3/2</sub> photoemission line shows a decreasing trend with increasing atomic number, with a pronounced shoulder in the region of the ferromagnetic metals. For the 2p<sub>1/2</sub> photoemission line, the DL asymmetry increases for the ferromagnetic metal. This indicates a relationship between the asymmetry and the electronic structure of the metals.

$a_{DL}$  also shows interesting tendencies for the 3d photoemission spectra of the 5<sup>th</sup>-period elements from Rb to In. There is a significant difference in the DL parameter between the two 3d branches for elements with an empty 4d band (Rb and Sr).  $a_{DL}$  is lower for the elements with a half-filled (Mo [Kr]5s<sup>1</sup>4d<sup>5</sup>), almost filled (Ru [Kr]5s<sup>1</sup>4d<sup>7</sup> and Rh [Kr]5s<sup>1</sup>4d<sup>8</sup>) and filled 4d band (Ag [Kr]5s<sup>1</sup>4d<sup>10</sup>, Cd [Kr]5s<sup>2</sup>4d<sup>10</sup>, and In [Kr]5s<sup>2</sup>5p<sup>1</sup>). These results suggest that the asymmetry is related to the 4d valence electrons.

A theoretical approach is proposed.

This work was partially funded by Grant 58518 of the Fronteras projects of Conahcyt, Mexico.

[1] A. Herrera-Gomez, D.M. Guzman-Bucio, A.J. Carmona-Carmona, O. Cortazar-Martinez, M. Mayorga-Garay, D. Cabrera-German, C.A. Ospina-Ocampo, B.V. Crist, J. Raboño-Borbolla, Double Lorentzian lineshape for asymmetric peaks in photoelectron spectroscopy, Journal of Vacuum Science & Technology A 41 (2023). <https://doi.org/10.1116/6.0002602>.

**5:00pm AS-TuA-12 Computational Exploration of Dimension Limits for Narrow Gap Transport of Reactive Species, Greg Hartmann, S. Sridhar, P. Ventzek**, Tokyo Electron America, Inc.

State of the art device fabrication is pushing the limits of etch processes in terms of achievable critical dimensions. Passing these limits requires an insight into the fundamentals of dry etch processes, i.e. fluxes of radicals and ions reaching the etch front and how they are transported into the feature. Here we discuss the 'in-feature' transport of radicals for narrow trenches beyond the limits of the conventional perspective of Knudsen diffusion. Advances in computational techniques, particularly density functional theory (DFT), enable theoretical models on the scale of a few molecular diameters to elucidate transport processes on the atomic scale. Van-der-Waals corrected DFT predicts significant intermolecular interactions provide a severely-constricted transport regime where a diffusing species is always interacting with at least one wall; surface diffusion has been identified as significant within typical process dimensions but may be the dominant mode of transport under this condition. Cessation of transport is predicted at the transition to solid-state diffusion. Multiphysics models utilizing kinetic data predicted via DFT predict a critical depth under which radical or by-product transmission is limited; the radical-starved limit is predicted to occur on the order of hundreds of nanometers. Consequently, a range of critical dimensions are predicted to create an inherently radical-starved condition. Scaling relationships provide insight into critical dimension limits across varied material selection.

**5:15pm AS-TuA-13 High-Temperature Diffraction and Surface Electron-Phonon Coupling of the Unreconstructed Metallic and (3x1)-O Reconstructed Nb(100) Surfaces by Helium Atom Scattering, Michael Van Duinen, C. Thompson**, University of Chicago; *M. Kelley, C. Mendez*, Cornell University; *S. Willson, V. Do*, University of Chicago; *T. Arias*, Cornell University; *S. Sibener*, University of Chicago

Superconducting radio frequency (SRF) cavities are the fundamental accelerating components of linear particle accelerators. Niobium is the material of choice for SRF cavities due to its high malleability, thermal conductivity, and superconducting critical temperature ( $T_c$ ). Despite Nb having a  $T_c$  of ~9 K, the practical operating temperature of a Nb SRF cavity is ~2 K, below the boiling point of He and consequently quite expensive to operate. The improvement of Nb SRF cavities and the lowering of operating costs has been focused primarily on the development of new materials on the Nb surface. Due to the ~100 nm superconducting penetration depth of Nb, only ~1 micron of material need be deposited onto the Nb surface to completely change its superconducting properties. One of the primary limitations to both Nb SRF cavities and the new materials under study is the presence of a thermally stable and robust oxide. Understanding the formation, stability, and dynamics of the oxide and its effects on the operation of Nb SRF cavities requires study both of material superconducting properties and atomic-scale surface material chemistry. Helium atom scattering (HAS) is a surface diffraction technique that has the ability to probe surface structure, bonding, and dynamics. The chemically inert He and an ultra-high vacuum (UHV) environment make HAS an ideal probe for the chemically reactive and sensitive Nb surface. Furthermore, experts in the field have developed theory involving the He-electron interaction and the surface electron-phonon interaction to formulate an equation by which HAS data can be used to determine an electron-phonon coupling (EPC) constant ( $\lambda$ ) for the surface ( $\lambda_s$ ). These data can then be used to find surface analogues for  $T_c$  along with other superconducting properties relevant to SRF cavity operation. We study the Nb(100) surface for its recognizable and stable (3x1)-O NbO oxide reconstruction. We find a  $\lambda_s$  of  $0.50 \pm 0.08$  for the metallic Nb(100) versus a bulk  $\lambda$  of ~1, demonstrating that the superconducting state is significantly modified at the surface. We also find a  $\lambda_s$  of  $0.20 \pm 0.06$  for the (3x1)-O reconstruction. Lower  $\lambda_s$  corresponds to lower  $T_c$  and overall poorer superconducting performance. Therefore, our studies strongly corroborate a strong body of previous literature that has hypothesized that the oxide diminishes superconducting performance for both bare Nb and new materials built atop it. From this fundamental starting point, we can further demonstrate the effect that doping, alloying, and thin-film material growth on the Nb surface have on its superconducting performance.

**5:30pm AS-TuA-14 The Type of Ru Oxide on Ru(0001) Determines the Activity for the Decomposition of Silane, Ester Perez Penco, R. Bliem, ARCNL**

Hydrogen plasma is commonly applied for the cleaning of functional surfaces, because it effectively removes most surface oxides and carbon-based deposits by reacting to form volatile species. However, this etching

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by hydrogen plasma also occurs for other elements, such as Si, which is widely abundant and forms silane gas ( $\text{SiH}_4$ ) when exposed to hydrogen radicals and ions. The resulting silane molecules can serve as a means to transport Si through the plasma setup and lead to Si redeposition. Typically, Si growth from silane only occurs at specific conditions, often involving high surface temperatures. However, in the presence of catalytically active materials such as Ru and Ru oxide, decomposition of silane occurs already at significantly milder conditions. The interaction mechanisms of silane with the surfaces of Ru and its oxides and the criteria for the deposition of Si, however, are unclear.

Here, we present an in situ study of the mechanism that leads to plasma-assisted deposition of Si on Ru surfaces. We isolate the interaction of the transport agent, silane gas, with Ru(0001) single-crystal surfaces using near-ambient pressure X-ray photoelectron spectroscopy (XPS). A comparison of Ru metal to a thin, defective type of Ru oxide and bulk-like  $\text{RuO}_2$  demonstrates a decisive impact of surface oxidation on the reaction with  $\text{SiH}_4$  and the nature of the deposited Si. On Ru metal, silane decomposition is barrierless and results in the formation of Ru silicide. The initial layers of a (metastable) Ru oxide structure readily catalyze the deposition of Si, forming a Ru-Si-O compound that consumes the Ru oxide phase. Already a few nanometers of the bulk-like  $\text{RuO}_2$  phase, on the other hand, are observed to be fully inert towards the decomposition of silane at room temperature. This striking difference between two similar oxides is attributed to their different density surface vacancies, which aid the dissociation of  $\text{SiH}_4$ .

Our in situ XPS results demonstrate that the type of Ru oxide and its structural integrity is decisive for surface chemistry of Ru under oxidizing conditions. The contrast of facile silane decomposition for a thin defective oxide and its full inhibition for bulk-like  $\text{RuO}_2$  serves as an illustration of the influence of seemingly subtle changes to the surfaces of materials with a wide application potential.

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