Live Session

Room Live - Session LI-TuA1

Tuesday Afternoon Live Session I: Harnessing and Understanding Interfacial Chemistry

Moderators: Donna Chen, University of South Carolina, Zhenrong Zhang, Baylor University

12:50pm **LI-TuA1-1 Welcome and Opening Remarks***, **Donna Chen,*** University of South Carolina

Welcome to the AVS 67 Virtual Symposium. I will review the structure of this week's program. We hope you will enjoy the event!

12:55pm **LI-TuA1-2 High-Throughput Computational Screening of Diamond Like Semiconductors and Ordered Vacancy Compounds for Thermoelectrics***, J. Xu,* University of Illinois at Urbana-Champaign*; C. Porter, J. Adamczyk, E. Toberer,* Colorado School of Mines*; **Elif Ertekin,*** University of Illinois **INVITED**

Computation-driven search for thermoelectrics (TEs) has recently shown several successes, but a principal bottleneck appears to be that predicted materials often prove to be difficult to dope in the lab. Here we will present our recent computational and experimental efforts to tailor the defect chemistry and dopability of a set of ordered vacancy compounds that are of interest for their TE potential. Ordered vacancy compounds (OVCs) are a family of materials whose structure is closely related to diamond like semiconductors, but contain an ordered array of vacancies. Diamond like semiconductors and OVCs are typically observed to be p-type, but our TE materials descriptor suggests that they would be more effective as thermoelectrics if they could be doped n-type. Therefore, we screen through a chemically-diverse set of 54 OVCs to assess their TE potential and dopability. For the most promising candidates, using calculations of phase stability defect formation energies, we comprehensively establish the achievable range of carrier concentrations achievable. Using phase boundary mapping, experimental carrier concentrations are measured and compared to the predicted values, typically showing correspondence within a few orders of magnitude. For all compounds, we find that a delicate competition between a set of dominant, competing defects governs the achievable range of carrier concentrations. For instance in the II_2-IV-VI_4 OVC structural prototype, enhancing n-type dopability requires suppressing the IV_{II} antisite and promoting the formation of the group II vacancy. Using this observation as a design strategy, we identify candidates that may be more amenable to n-type doping. The results of this search are used to generate a chemically intuitive framework for predicting dopabilities in this family of materials without the need to carry out full-scale first-principles analysis.

1:15pm **LI-TuA1-6 Towards a Mechanistic Understanding of Next-Generation Particle Accelerator Materials Growth: Nb Hydride Growth and Suppression and Nb_3Sn Formation on (3×1)-O Nb(100)***, **Rachael G. Farber**, S. Willson, R. Veit,* University of Chicago*; N. Sitaraman,* Cornell University*; A. Hire, R. Hennig,* University of Florida*; T. Arias,* Cornell University*; S. Sibener,* University of Chicago **INVITED**

Niobium (Nb) is the current standard material for superconducting radio frequency (SRF) accelerator cavities due to its ultra-low surface resistance and high cavity quality factor (*Q*) at operating temperatures of ~ 2 K. However, prohibitively expensive operating and infrastructure costs prevent the implementation of accelerator-based technologies across a variety of sectors. Nb_3Sn is a promising next-generation material for SRF cavities and can operate at ~ 4.2 K, significantly reducing operating costs of cryogenic infrastructure. To increase the efficiency and accessibility of accelerator-based technologies, SRF materials must be developed that can reliably produce intense particle beams above 4 K.

Nb surface composition and contaminant incorporation directly affect *Q*. Hydrogen incorporated during Nb cavity fabrication results in the formation of Nb hydrides, which lower *Q* at high fields and reduce cavity performance. Nitrogen infusion of Nb cavities mitigates hydride formation, but the growth and suppression mechanisms of Nb hydrides are not thoroughly understood. Utilizing low-temperature scanning tunneling microscopy (LT-STM), scanning tunneling spectroscopy (STS), and density functional theory (DFT) calculations, we have investigated the growth and suppression mechanisms of Nb nano-hydrides on (3×1)-O Nb(100). STM and STS results identified the structural and electronic evolution of undoped, hydrogen doped, and co-doped Nb(100) resulting from Nb nano-hydride growth and suppression. DFT calculations corroborate experimental data and identified unique near-surface phases stabilized by dopant incorporation. These results provide the first *in situ*, real-time nanoscale characterization of the effects of dopant incorporation on Nb nano-hydride growth and suppression, elucidating the interplay between nitrogen and hydrogen regarding Nb SRF materials performance.

The latter part of this presentation will focus on the interaction of Sn with Nb substrates leading to the formation of Nb-Sn alloys. Nb_3Sn films are grown *via* Sn vapor deposition on preexisting Nb cavities. Sn homogeneity, surface roughness, and alloy thickness must be well controlled for high *Q* film growth, but the Nb_3Sn growth mechanism resulting in optimal film formation is not well understood. In this work, we have visualized Sn adsorption and diffusion behavior on (3×1)-O Nb(100) at the nanometer scale. STM data revealed preferential adsorption of Sn along the (3×1)-O unit cell. Annealing the Sn/Nb(100) sample resulted in the formation of hexagonal and rectangular Sn adlayer structures for all Sn coverages studied. STS measurements of these adlayers demonstrated thickness-dependent electronic properties that are distinct from the underlying Nb substrate. Genetic algorithm calculations and DFT based descriptors aim to determine energetically preferred Sn binding sites on the (3×1)-O surface. This spatially resolved mechanistic information of Sn adsorption and diffusion on an oxidized Nb surface guides the development of predictive Nb_3Sn growth models needed for the further optimization of Nb_3Sn growth procedures

1:35pm **LI-TuA1-10 Phase Formation and Thermal Stability of Reactively and Non-Reactively Sputtered High-Entropy Metal-Sublattice Carbides***, **Alexander Kirnbauer,*** TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

High-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Within this work, we report on the phase formation and thermal stability of high entropy metal-sublattice carbides to provide a further insight to a more extensive understanding of the high-entropy effect, according to which, based on the Gibbs-free energy, such materials should be stabilised in the high-temperature regime. Therefore, (Hf,Ta,Ti,V,Zr)C coatings were reactively and non-reactively sputtered from a single powder-metallurgically produced composite target (either metallic or consisting of the respective binary carbides). Reactively sputtered coatings were synthesised using an C_2H_2 – Ar mixture with different $C_2H_2/(C_2H_2+Ar)$ ratios (f_{C2H2}). After deposition, the coatings were investigated in as-deposited state and after vacuum annealing between 800 and 1200°C. The structure and morphology, the chemical composition, the mechanical properties, and the thermal stability of the coatings were investigated by scanning electron microscopy, X-ray diffraction, and nanoindentation.

The non-reactively sputtered as well as reactively sputtered coatings with f_{C2H2}= 20 % show a single-phased face-centred cubic (fcc) structure. The hardness for the non-reactively sputtered HESCs is with ~41 GPa higher than that of the reactively sputtered one which exhibits a hardness of 35 GPa. This indicates that due to the use of C_2H_2 also regions of amorphous carbon form, which slightly weaken the coating already in the as-deposited state. After vacuum annealing up to 1200 °C the non-reactively sputtered coatings maintain a hardness of ~40 GPa indicating retarded softening mechanisms due to sluggish diffusion. This behaviour was also observed in previous studies on different material classes such as nitrides, borides, and oxides indicating a stabilisation due to the high-entropy metal sublattice.

2:05pm **LI-TuA1-16 Electronic Structure and Dynamics of Single Atom Catalysts***, **Nuria Lopez,*** ICIQ, Spain **INVITED**

Single atoms have shown different structural and catalytic properties with deep coupling between the oxide and metallic structures. This phenomenum, unraveled by theory might have a high impact in the understanding of the chemical properties of the materials and might affect our current understading for materials included those that are active in energy-conversion proceses.

2:25pm **LI-TuA1-20 Methanol Synthesis Pathways for the Selective Conversion of C-H bonds***, **Sanjaya Senanayake,*** Brookhaven National Laboratory **INVITED**

Methane remains a valuable yet underutilized resource, with great interest for the direct upgrade to valued products. Our recent studies indicate that, in spite of the high stability of methane, systems such as Ni-CeO2(111) and CeO2-Cu(111) can break C-H bonds even at room temperature, through careful manipulation of interfaces and metal-support interactions, using light oxidants (CO2, O2/H2O). the selective oxidation on the surface sites can lead to conversion steps that produce CH3OH and CO+H2. AP-XPS with the help of DFT has been essential to elucidate C-H activation and oxidation steps with high resolution C 1s and O 1s spectroscopies.

We have established a method for the direct conversion of methane to methanol building on these surface results yielding low methanol selectivity (~30%). Subsequently, and in remarkable contrast we have found that a CeO2/Cu2O/Cu(111) inverse system is able to activate methane at room temperature and then, with the help of water, performs a highly selective (70%) catalytic cycle, for the production of methanol. The interfacial interaction between CeOx-CuOx is crucial while the concentration of water has a strong effect on the selectivity towards the production of methanol.

We have used AP-XPS to track the sequence of pathways that initially activate C-H bonds into -OCH3 surface species that leads to the production of methanol. DFT and KMC were then used to evaluate the most prevalent steps that are likely essential for such selective chemistry.

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2. Liu et al. Angewandte Chemie (2016) 128 (26), 7581-7585.

3. Lustemberg et al. ACS Catalysis (2016) 6 (12), 8184-8191.

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6. Zhang et al. ACS Catalysis (2018) 8 (4), 3550–3560.

7. Lustemberg et al. JACS (2018) 140 (24), 7681–7687.

8. Liu et al. ACS Catalysis (2019) 94 3349-3359.

9. Zhang et al. J. Phys. Chem. (2019) 122 (50), 28739-28747.

2:45pm **LI-TuA1-24 Building Bridges Between University, National Laboratory, and Industrial Research*, Robert McCabe,*** National Science Foundation **INVITED**

From the earliest days of UHV single-crystal and thin-film research related to fundamental aspects of heterogeneous catalysis, researchers have recognized the need to address various technical gaps relating fundamental observations under pristine conditions to factors affecting the working catalyst.Some of those observations scale, and others do not, but in both cases the atomic/molecular scale understanding obtained from research bridging those divides has been invaluable to the advancement of heterogeneous catalysis as practiced.Nevertheless, significant technical gaps still exist in advancing catalyst technology through the concept, design, and development stages to commercial application.Catalyst technology often gets stuck at a particular level, characterized by a combination of factors best described as “knowledge gaps.”At that point, industry tends to focus on optimization around a core (often proprietary) technology, and the academic community heads off to new pastures.Federal funding agencies and our national laboratories sit in a unique position to forge research partnerships between academic and industry researchers that bridge knowledge gaps.I will provide specific examples of key knowledge gaps in heterogeneous catalysis, and how NSF is funding partnerships between academic institutions and industry to bridge those gaps.

3:05pm **LI-TuA1-28 Closing Remarks and Thank You's*, Zhenrong Zhang,*** Baylor University

Thank you for attending today's session! We look forward to seeing you tomorrow at 10:00 am EDT for a full day of Live Parallel Sessions. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

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