PCSI

Room Ballroom - Session PCSI-TuM

Oxides II & Energy Materials

Moderator: Alex Demkov, The University of Texas

8:30am **PCSI-TuM-1 Electron-Phonon Interactions in Oxide Materials from First Principles: Implications for Exciton Properties and Superconductivity**, ***Antonios Alvertis,*** University of Texas at Austin **INVITED**

Polar metal oxides form an ideal testbed for electron-phonon physics. The strong ionic character of these materials produces a stark contrast between the static dielectric constant , which includes ionic contributions, and the high-frequency dielectric constant . This in turn results in significant long-range Fröhlich coupling between charge carriers and longitudinal optical phonons.

In this talk I will explore a number of implications of the long-range electron-phonon interaction in oxides, for superconductivity in $SrTiO_3$ – a long-standing puzzle for condensed matter theory – and for excitonic effects in a wide range of oxides. I will demonstrate a first-principles theory of superconductivity in $SrTiO_3$, which results in good agreement to experiment for the superconducting dome, wherein superconductivity arises from the interplay of the significant Fröhlich interaction with the strong deformation potential coupling associated with the Ti-O bond [1,2].

Apart from mediating the formation of Cooper pairs, as in $SrTiO_3$, this interplay of Fröhlich interaction and strong deformation potential coupling that is present in several oxides, can have a strong impact on the excited state properties of these materials. I will present a first-principles theory for including phonon effects in excitonic calculations within the GW-BSE framework [3], and apply it to a range of oxides that include MgO, TiO_2, $BiVO_4$, and $SrTiO_3$. I will demonstrate that this results in greatly improved agreement to experiment for a number of quantities, including the exciton binding energy and the optical absorption spectra [3,4].

I will close my talk with a discussion of the validity of perturbation theory for electron-phonon interactions in oxide materials, which is almost universally employed in theoretical studies. I will show that low-order perturbation theory can frequently fail catastrophically, and I will present an approach for incorporating non-perturbative electron-phonon interactions from first principles, which results in large corrections to excited state properties in a wide range of properties, compared to low-order perturbative approaches [5].

References

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9:00am **PCSI-TuM-7 Interfacial Redox Stabilization in High-Entropy Garnet Electrolytes**, ***Zhezhen Fu,*** *Fernando Soto,* Penn State Harrisburg

Interfacial reduction limits the stability of garnet electrolytes in lithium-metal batteries. Here, we examine how multication substitution regulates redox evolution at the lithium-garnet interface during electrochemical cycling. We compare the high-entropy garnet $Li_6La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$ (LLZNTH) with conventional Ta-doped $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (Ta-LLZO), which exhibit comparable room-temperature ionic conductivities.Despite similar initial interfacial resistances, LLZNTH reaches a critical current density of 0.8 mA cm^-2, twice that of Ta-LLZO. After critical-current testing, its interfacial area-specific resistance increases from 16 to 20 Ω cm^2, compared with 14 to 75 Ω cm^2 for Ta-LLZO. LLZNTH also sustains stable lithium plating and stripping for 500 h at 0.1 mA cm^-2.X-ray photoelectron spectroscopy reveals progressive Ta and Zr reduction in Ta-LLZO during cycling, while reduced Ta, Zr, and Nb components show little further evolution in LLZNTH. Raman spectra indicate better preservation of the LLZNTH garnet framework. Molecular dynamics simulations suggest that cation mixing and surface lithium enrichment limit reactive Li(metal)-O contacts on the modeled (001) interface. These findings support self-limiting reduction in LLZNTH and show that Nb incorporation need not cause progressive degradation. They highlight the local cation environment as a design variable for stabilizing lithium-garnet interfaces.

9:05am **PCSI-TuM-8 Ultralow Loading Platinum Films by Direct Atomic Layer Processing for Efficient Hydrogen EvolutionR. Sharma1,+, M. Carnoy1, M. Ceccato2, B. Borie1, M. Baraket1, M. Plakhotnyuk11 Atlant 3d, MåRkæRvej 2b, 2630 Taastrup, Denmark2 Department of Chemistry and Inano, Aarhus University, 8000 Aarhus C, Denmark**, ***Ruchi Sharma,*** Mårkærvej 2B, Taastrup, DK-2630, Denmark

Platinum provides benchmark hydrogen evolution reaction (HER) kinetics in acid, but reducing noble-metal inventory requires deposition routes that form active, electrically continuous films at ultralow loading. Here, Direct Atomic Layer Processing (DALP), a maskless microreactor implementation of spatial atomic layer deposition, was used to deposit Pt films with nominal thicknesses of 2, 10, 20, 30, and 50 nm directly onto 1 cm^2 glassy-carbon electrodes [1]. The corresponding nominal Pt loadings were 4.29, 21.45, 42.9, 64.35, and 107.25 μg cm^{-2}. Electrochemical performance was evaluated in 0.5 M H_2SO_4 by cyclic voltammetry and linear-sweep voltammetry, with potentials referenced to the reversible hydrogen electrode. Characteristic hydrogen-underpotential-deposition and Pt oxide-reduction features confirmed electrochemically accessible Pt surfaces. The 2 nm film exhibited a roughness factor of 0.43 and required about 100 mV overpotential to reach 10 mA cm^{-2}. Increasing the film thickness to 10 nm sharply reduced this overpotential to approximately 45 mV and produced the lowest fitted Tafel slope, 21.7 mV dec^{-1}. Films from 20 to 50 nm retained near-zero HER onset, approximately 50-60 mV overpotential at 10 mA cm^{-2}, and Tafel slopes of 26.8-33.7 mV dec^{-1}, while additional Pt did not improve benchmark performance proportionally. Thus, the 10 nm film delivered activity comparable to films containing up to five times more Pt, consistent with prior low-loading Pt studies [2]. These results identify film continuity as the key transition from sparse ultralow-loading Pt to an efficient electrode and establish DALP as a digital route for screening and patterning binder-free catalysts with high precious-metal utilization.

Figure 1. DALP Pt deposition and thickness-dependent HER metrics. Overpotentials are approximate values read from the polarization results.

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+ Author for correspondence: rsha@atlant3d.com

9:10am **PCSI-TuM-9 The Role of Near-Surface Bond Energetics in Shaping Nanoalloy Transformed Configurations**, ***Micha Polak,*** Ben Gurion University of the Negev, Israel

In addition to the surface-layer composition, the subsurface layer in alloy nanoparticles is expected to affect their catalytic activity and selectivity. This theoretical-computational study focuses on the largely unexplored issue of nanoalloy compositional configurations arising from near-surface energetics and involved in thermally induced phase-separation transformations. Employing the statistical-mechanical Free-Energy Concentration Expansion Method (FCEM) [1] with Coordination-dependent Bond-Energy Variations (CBEV) [2] and Effective Pair Interactions (EPI) as part of the input, and the Coarse–Grained Layer Model for additional efficiency, atomic site-specific configurations were computed as a function of temperature for four heterogenous-catalysis-related binary alloy nanoparticles having relatively small atomic–size mismatch: **Pd-Ir, Ag-Ir, Pt-Ir, and Pd-Rh**, all as 1415-atom cuboctahedrons. We predict distinct inner-core transitions between asymmetric and symmetric configurations beneath a surface-segregated monolayer (Fig. 1): Quasi–Janus (QJ) to solid–solution (SS) in Pd-Ir; QJ to asymmetric core-shell (asy-CS-a), followed by symmetric core–shell (CS-a) in Ag-Ir, and asy-CS-a transformed to CS-a in Pt-Ir and Pd-Rh. To quantify the roles of the CBEV and EPI, we introduce a straightforwardly calculated subsurface/inner-core permutation energy factor (λ) that predicts stable configurations without the need for FCEM computations (and has a clear correlation with the transformation temperature). Thus, its magnitude reflects the identity of the transformed configuration, e.g., for QJ to SS, λ is near zero. Application of the present methodology to ternary, quaternary, and quinary (high entropy) nanoalloys composed of the same elements is underway.

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Fig. 1 Representations of several configuration candidates for the four selected A-Bnanoalloy systems.

+Author for correspondence: mpolak@bgu.ac,il [mailto:mpolak@bgu.ac,il]

9:15am **PCSI-TuM-10 Hydrogen-Enhanced Schwoebel Barriers and Anisotropic Strontium Diffusion on Vicinal Si(001)***, **Jon Reising**, Alexander Demkov,* University of Texas at Austin

Functional oxides such as $BaTiO_3$ can add electro-optic functionality to silicon devices [1]. Epitaxial integration commonly uses a $SrTiO_3$ buffer [2–4], initiated by depositing half a monolayer of Sr at 625 °C to protect silicon from oxidation. Growth on vicinal Si(001) substrates [5,6] introduces terraces and steps that complicate Sr migration. We examine how hydrogen affects Sr migration on double-step Si(001) surfaces with a (2×1) reconstruction.

In this talk, we present first-principles calculations for bare and H-passivated surfaces with a 6.8° miscut and 22.59 Å terrace width (Fig. 1). On the bare surface, Sr moves from a terrace trough into a secondary minimum between step-edge dimers before descending. Hydrogen raises the initial barrier toward the step from 0.983 to 1.055 eV and adds two intermediate minima. Our multistate model predicts approximately tenfold slower step crossing. Conversely, hydrogen lowers the barrier along the trough above the step from 0.917 to 0.812 eV, yielding an approximately tenfold faster transition rate.

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Author for correspondence: demkov@physics.utexas.edu

9:20am **PCSI-TuM-11 Defect- and Interface-Driven Behavior in Oxide Thin Films***, **Andrew O'Hara**,* Western Michigan University **INVITED**

Complex and functional oxides possess a wide range of properties, providing platforms for tunable and emergent behavior via interfaces, defects, and reduced dimensionality. In this talk, I will discuss the effect of defects on magnetic properties and the emergence and role of unique phonons in thin oxide films across multiple theory-experiment collaborations.

Given the sensitivity of oxide magnetism to local crystal structure, growth conditions may lead to unexpected or undesirable outcomes. MBE-grown Co-substituted $BaTiO_3$ films remain non-magnetic due to oxygen-vacancy-mediated spin coupling. In heterostructures, thin nominally conductive magnetic layers may be especially defect sensitive. In PLD-grown $(SrTiO_3)^5$-$(SrRuO_3)^n$-$(SrTiO_3)^5$ films, transport measurements indicate that the n = 2 structure is conductive and ferromagnetic, but the n = 1 structure is insulating and non-magnetic. STEM imaging reveals Ru-Ti intermixing in the n = 1 structure, which DFT shows leads to AFM-like insulating states. For $(CaRuO_3)^n$-$(SrRuO_3)^1$-$(CaRuO_3)^n$ films, as n decreases, local structural perturbations near the SRO layer cause an insulating and magnetic state, suggesting an oxide engineering pathway. As another route, DFT predicts that carrier doping can couple magnetic and polar behavior, enabling switchable spin textures in h-$LuFeO_3$/MnSTe.

As in the examples above, decreasing superlattice thickness can also lead to emergent phonon behavior. In PLD-grown $(SrTiO_3)^n/(CaTiO_3)^n$ superlattices, STEM imaging and spectroscopy along with optical spectroscopy measurements show the emergence and eventual dominance of interfacial vibrational modes with decreasing n. These observations were corroborated by DFT calculations to understand structural changes and potential defect effects on phonon mode localization. Similar techniques were used to probe related systems like grain boundaries. The role of phonons in the non-resonant excitation and temperature dependence of emission in optically active Er_2O_3 films and how modifying the phonons may affect emission will be discussed.

Defects, interfaces, and reduced dimensionality are not just perturbations to ideal behavior, but ingredients that either prevent or enable unique properties, with their control providing routes to engineering functionality.

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