Thin Films
Room Naupaka Salon 5-7 - Session TF-ThM

Nanostructured Surfaces and Thin Films: Synthesis and Characterization

Moderator: Jyh-Wei Lee, Ming Chi University of Technology

8:00am **TF-ThM-1 Electronic Interaction in Graphene/WS_2 Assisted by the Interlayer Rotation Angle**, ***Cecelia Noguez,*** UNAM Mexico **INVITED**

Two-dimensional (2D) van der Waals (vdW) heterostructures are a new realm of materials with potential applications and fascinating physical properties. Besides graphene (G), transition metal dichalcogenides (TMDCs) have been considered promising building blocks in 2D vdW heterostructures with improved and new properties. The vertical stacking of at least two atomic monolayers bonded by vdW forces with different electronic behavior, i.e., G/TMDC, leads to new hybrid nanostructures. In principle, hybrids could retain the main advantages of pristine monolayers at the same time that they might achieve superior and unusual properties which cannot be obtained otherwise. In recent years, the combination of G and TMDCs, such as tungsten disulfide (WS_2) and molybdenum disulfide (MoS_2) has attracted increasing interest as promising building blocks for future electronics, photonics, and optoelectronic devices. First, we present a general unfolding method for the electronic bands of systems with double-periodicity. Within density functional theory with atomic orbitals as basis-set, our method takes into account two symmetry operations of the primitive cell: a standard expansion and a single rotation, letting to elucidate the physical effects associated with the mutual interactions between systems with more than one periodicity. As a result, our unfolding method allows studying the electronic properties of vertically stacked homo- or heterostructures.

We apply our method to study G/WS_2 heterostructures with different interlayer angles. This allows observing typical mini gaps reported in heterostructures, as well as other electronic deviations from pristine structures, impossible to distinguish without an unfolding method. Electronic minigaps, band hybridization, and splitting occur in graphene supported on tungsten disulfide (G/WS2). These are studied by employing periodic first-principles calculations and an unfolding method to interpret the supercell's crowded-band structure. Electronic alterations because of the interlayer interactions identified as Bragg diffractions, electronic repulsions or avoided crossings, and replicas due to the Moiré potential, all of them depending on the interlayer angle. The results indicate that out-of-plane orbitals interactions from different layers, depending on energy and k-region, induce the avoided crossings, band hybridization, and splitting. At the same time, Moiré replicas emerge because of the superperiodic potential associated with patterns. Finally, the minigaps energy position is intrinsically related to the interlayer angle and the commensurate conditions.

8:40am **TF-ThM-3 Atomic-Scale Probing of Chemically Modified Borophene via Tip-Enhanced Raman Spectroscopy**, ***Nan Jiang,*** University of Illinois - Chicago

Two-dimensional boron monolayers (i.e., borophene) hold promise for a variety of energy, catalytic, and nanoelectronic device technologies due to the unique nature of boron−boron bonds. To realize its full potential, it is desirable to chemically modify borophene either by Van der Waals interactions or covalent modification. In this context, the atomic-scale chemical study of functionalized borophene is of critical importance to the understanding of local interfacial characteristics and site-specific chemical properties.

Tip-enhanced Raman spectroscopy (TERS), which couples scanning tunneling microscopy (STM) and surface-enhanced Raman spectroscopy, provides such a powerful capability to concurrently harvest topographic and chemical information with single-bond sensitivity at the angstrom-scale. Herein, we use ultrahigh vacuum (UHV) TERS to measure the angstrom-scale interfacial interactions of a vertical Van der Waals heterostructure of borophene with tetraphenyldibenzoperiflanthene (DBP) molecules. TERS reveals subtle ripples and compressive strains of the borophene lattice underneath the molecular layer. The induced interfacial strain is demonstrated to extend in borophene by ∼1 nm beyond the molecular region by virtue of 5 Å chemical spatial resolution. Next, weuse our method to probe the local chemical properties of oxidized borophene. The results show that single oxygen adatoms on borophene can be identified and mapped with ~4.8 Å spatial resolution and single bond (B–O) sensitivity. Furthermore, we reveal the propensity of borophene towards molecular oxygen activation at room temperature and phase-dependent chemical properties.

In addition to offering atomic-level insights into the above-mentioned systems, our studies demonstrate UHV-TERS as a powerful tool to probe the local chemistry of surface adsorbates and interfacial structures in the atomic regime with widespread utilities in heterogeneous catalysis, on-surface molecular engineering, and low-dimensional materials.

9:00am **TF-ThM-4 Thin Film Combinatorial Sputtering of Al-Ce Alloys for Mechanical Alloy Design**, ***Reece Emery,*** *M. Thompson, O. Rios,* University of Tennessee Knoxville*; D. Weiss,* Eck Industries*; P. Rack,* University of Tennessee Knoxville

Al_xCe_{100-x} thin films with a composition range of ~75.0<x<99.5 at. % (36.5<x<97.5 wt. %) were synthesized via combinatorial co-sputtering from an Al and an $Al_{50}Ce_{50}$ target. The crystal structure, phase fraction, film morphology, and temperature-dependent coefficients of thermal expansion (CTE) are all correlated to the Al_xCe_{100-x} composition. Temperature dependent x-ray diffraction (XRD) reveals that the two phases expand independently of one another, and the thin film Al temperature-dependent CTE is similar to bulk Al. The thin film $Al_{11}Ce_3$ intermetallic phase has a nearly constant CTE of ~$1.5x10^{-5}$/°C within the temperature range studied (25-550°C).To confirm the thin film $Al_{11}Ce_3$ results, bulk stoichiometric $Al_{11}Ce_3$ and +/- 1 wt.% Ce samples were prepared and the CTE of each was measured under the same conditions. A Rietveld analysis of the bulk data enabled an estimation of the CTE in each of the 3 orthorhombic lattice parameters, which displayed anisotropic behavior. The thin film and bulk CTE measurements were in very good agreement. Additionally, nanoindentation was performed to track the mechanical properties of the combinatorial library. By demonstrating the efficacy of the approach, more complex multi-component rapid materials discovery of low CTE Al-alloys can be pursued via the combinatorial thin film synthesis, TDXRD measurements, and nanoindentation.

9:20am **TF-ThM-5 Quantum Decoherence of Superconducting Quantum Circuit Interfaces: Niobium on Silicon**, ***Frank Ogletree,*** *V. Altoé,* Lawrence Berkeley Laboratory*; A. Schwartzberg, C. Song,* Lawrence Berkeley Lab*; D. Santiago, I. Siddiqi,* Lawrence Berkeley Lab, University of California, Berkeley

The performance of superconducting quantum sensors and qubits is limited by losses associated with few-nanometer amorphous oxide films at the superconductor and substrate interfaces [1,2]. We have localized 92% of the total loss of niobium-on-silicon quantum resonators to the Si substrate-air (SA) and Nb metal-air (MA) interfaces through selective chemical etching, correlated with millikelvin microwave loss measurements and materials analysis of the interfaces [3]. Interfacial materials analysis combining analytical scanning transmission electron microscopy (STEM) and x-ray photoemission spectroscopy (XPS) was used to correlate physical and chemical changes in the surface oxides with reductions in loss [4,5]. We found clear differences in the characteristic losses associated with the Si and Nb oxides. SiO_x hosted 70% of two-level system (TLS) losses, with only 24% associated with NbO_x. Although TLS losses dominated decoherence, 39% of loss did not show the expected TLS power dependence [1]. NbO_x hosted 68% of non-TLS losses, with only 17% associated with SiOx. TEM diffraction measurements showed an epitaxial relation between the Nb superconducting film and the Si substrate, with no evidence for the commonly-reported metal-substrate amorphous oxide layer. Post-fabrication surface oxide etching improved our median quantum-resonator quality factors from 0.93 to 5.26 million. Our resonator study gives insights into decoherence in other types of superconducting quantum sensors[5].

[1] Müller et al, 'Towards understanding two-level-systems in amorphous solids: insights from quantum circuits', Rep Prog Phys, 2019.

[2] Siddiqi, 'Engineering high-coherence superconducting qubits', Nat Rev Mat, 2021

[3] Altoë et al, 'Localization and mitigation of loss in niobium superconducting circuits' PRX Quantum 3, 2022.

[4] Sheridan et al, 'Microscopic Theory of Magnetic Disorder-Induced Decoherence in Superconducting Nb Films', arXiv 2111.11684, 2021.

[5] Harrelson et al, 'Elucidating the local atomic and electronic structure of amorphous oxidized superconducting niobium films', APL 2021.

9:40am **TF-ThM-6 Structural Analysis of Few-Atomic Layered Hexagonal Boron Nitride Nanosheets Synthesized with Magnetron Sputtering and Heat Annealing Process**, ***Yuki Hirata***, *K. Yoshii, M. Yoshizato, H. Akasaka, N. Ohtake,* Tokyo Institute of Technology, Japan

Hexagonal boron nitride (*h*-BN) is composed of boron and nitrogen atoms, tightly bound in a hexagonal honeycomb lattice. Since it has the similar structure with the graphene, *h*-BN is called as "white graphene". *h*-BN is known to have excellent properties such as high heat resistance, oxide resistance, wide bandgap and luminescence in far ultraviolet region and so on. Therefore, *h*-BN are expected to applicate as an insulating layer of electronics device, far ultraviolet light emitting device. In this study, we attempted to develop the newly synthesizing process of *h*-BN with high crystallinity on Cu substrate by using magnetron sputtering while heating at 1000 degree. According to the SEM observation, white-colored domains with facets of 60 degrees were observed. That may be corresponding to hexagonal honeycomb lattice structure. Actually, auger electron spectroscopy showed the presence of boron and nitrogen on these domains. Furthermore, XPS analysis was conducted to measure the elemental composition ratio and bonding states. It was revealed the presence of equal amounts of nitrogen and boron, as well as a single peak derived from the B-N bond. In Raman spectroscopy, a peak around 1364 cm^{-1} was observed, which was corresponding to in-plane six-membered ring vibration of *h*-BN. From these results, it can be said that we succeed in to synthesize *h*-BN with several atomic layers.

10:20am **TF-ThM-8 High-Throughput Magnetron Sputtering for Microstructure and Alloy Design**, ***Andrea Hodge***, University of Southern California **INVITED**

With the rapid ascend of machine learning as part of materials development, it is important to find synergy between experimental and computational efforts for faster materials discovery.In this talk, an overview and specific methodologies will be discussed using high-throughput experimental techniques specifically thin metallic films.These techniques allow the creation of experimental data sets which can be used to construct materials libraries.

In his context, sputtered compositional and microstructure complex metallic alloys will be presented as model systems for high-throughput synthesis and characterization.We will examine the data complexity of going from four to hundreds of compositions in a single sputtering run and how machine learning can be implemented to guide both the synthesis and characterization space.

11:00am **TF-ThM-10 Magnetronsputtered Mgli Coatings and Freestanding Thin Films for Neurological Implants – Preparation and Degradation Process**, ***Lisa Hanke***, Kiel University, Germany; *K. Bhat,* Helmholtz Zentrum hereon, Germany; *L. Kalchgruber, M. Valtiner,* Vienna University of Technology, Austria; *R. Willumeit-Römer,* Helmholtz Zentrum hereon, Germany; *E. Quandt,* Kiel University, Germany

Magnesium based freestanding thin films and structures are easily fabricated by magnetron sputtering combined with UV-lithography and sacrificial layer technique [1]. Such films are of interest for temporary medical applications as biodegradable implants but can also act as a reservoir for therapeutically active alloying elements. During the degradation of the thin film devices, the ions can be released and allow for local treatment with the aim to reduce the necessarydosage and possible side effects.

Lithium (Li) is known as a treatment for mood disorders [2] and, thus, MgLi coatings and freestanding films are investigated as possible future brain implants.The cytocompatibility of the produced thin films was proven in first in vitro experiments to underline the possibility for usage as a medical implant.

The MgLi thin films are prepared using magnetron sputtering, leading to films with a lithium concentration ranging from 5.4 at% to 26.9 at%. The range of composition allows the study of the influence of Li content as well as of different phases and microstructures on the properties of the films.The structure and phases are analyzed by XRD, SEM and TEM. While low Li concentrated films show a single hexagonal phase with preferred orientation and columnar growth, for higher Li concentrations an additional Li-rich cubic phase and also Li2CO3 occur. Tensile testing data shows the highest tensile strength and elongation for Mg-5.4(at%)Li.Similar elongation results were obtained for Mg-9.8(at%)Li and Mg-26.9(at%)Li. Additionally, influences of the film thickness and sputtering parameters on the orientation and film properties are studied.

The corrosion rate of the films is determined via potentiodynamic polarization in Hank's balanced salt solution at a pH of 7.4 and 37°C to investigate the ion release and, thus, therapeutic effect. Due to the different phases and microstructures, the lowest corrosion rate is measured for Mg-5.4(at%)Li. Similar corrosion rates occur for Mg-9.8(at%)Li and Mg-26.9(at%)Li, while the corrosion rate for Mg-16.9(at%)Li is three times higher.

Additional in situ measurements via inductively coupled plasma – mass spectrometry coupled with an electrochemical cell and XPS measurements give further insight into the corrosion process itself and formed surface layers. A Li rich layer can be identified on the surface of all MgLi alloys. Additionally, a difference of mainly Li driven corrosion in comparison to Mg based corrosion for lower Li concentrated films is determined.

[1] D. Haffner, C. Zamponi, et al. (2015) BioNanoMat 16:19-22 [2] C. Volkmann, T. Bschor, S. Köhler (2020) Front. Psychiatry 11:377

11:20am **TF-ThM-11 The Importance of Interface Chemistry and Island Morphology in Granular Metal Thin Films**, ***Simeon Gilbert***, *M. Meyerson, S. Rosenberg, P. Kotula, N. Madden, P. Sharma, J. Flicker, M. McGarry, T. Kmieciak, M. Siegal, L. Biedermann,* Sandia National Laboratories

Granular metals (GMs) consist of nanoscale metal islands dispersed in an insulating matrix. At low volumetric metal fraction (φ), GMs are insulating; at high φ, metallic. In the insulating regime, conduction occurs by electron tunneling and capacitive transport between metal islands. The percolation threshold (φ_c) is the metal volume fraction indicating the transition between insulating and metallic regimes. A sharp conductivity (σ) knee at φ_c, with σ increasing 4-6 orders-of-magnitude with $\Delta\phi \approx 0.1$ indicates a low-defect insulating matrix surrounding metal islands at $\varphi<\varphi_c$ and a conductive metallic film with limited insulator inclusions at $\varphi>\varphi_c$. Such 4-6 orders-of-magnitude changes in σ at φ_c are seen for Au- and Ag-based GMs with σ as low as 10^{-6} S/cm at φ=0.2. However, most other GMs exhibit 1-3 orders-of-magnitude σ changes at φ_c and comparatively high σ (10^{-2}-10^{-4} S/cm) at φ=0.2. Despite decades of research on GMs, the variations in σ for different GM systems have not been closely examined.

We synthesized several 100-200 nm thin films via RF co-sputtering of Mo or Co with yttria stabilized zirconia (YSZ) or SiN_x.[1] The resulting thin films form GMs with 1-3 nm metal islands based on scanning transmission electron microscopy (STEM). Unlike the Au and Ag GMs, the as-grown Mo- and Co-based GMs show ~1 order-of-magnitude σ changes at φ_c with σ values of 10^{-1}-10^{-3} S/cm at φ=0.2. X-ray photoemission spectroscopy (XPS) indicates deleterious metal-insulator interface states which increase the conductivity of the insulator in the region surrounding the metal islands. For Mo-SiN_x sputtered in Ar, $MoSi_2$ forms due to N vacancies in the SiN_x. By sputtering the Mo-SiN_x films in an Ar/H/N environment, the N vacancies and $MoSi_2$ formation are mitigated, as shown by optical bandgap and XPS measurements. As desired, σ is reduced by 3-4 orders-of-magnitude for $\varphi<\varphi_c$. Additionally, annealing the GM films increases the island sizes/separations, as shown by in-situ TEM annealing. Increased island separation weakens the effects of interface regions, and σ can be reduced >6 orders-of-magnitude when $\varphi<\varphi_c$. Based on this work, precise control of the interface chemistry and island morphology will be crucial for controlling the conduction mechanisms in future GMs.

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