Thin Films
Room Naupaka Salons 4 - Session TF-WeE

Emerging Topics: Growth and Properties of Electronic Materials, 2D Layers, and Metallic-glass Thin Films

Moderator: Lars Hultman, Linkoping University

5:40pm **TF-WeE-1 Novel Metallic-Glass Nanotube Arrays: Synthesis, Characterization and Applications**, ***Jinn P. Chu,*** National Taiwan University of Science and Technology, Taiwan, Republic of China **INVITED**

Thin film metallic glass (TFMG) is a new class of metallic thin film with unique characteristics, including high strength, high ductility, smooth surface, absence of grain boundaries, low coefficient of friction, and corrosion resistance, though their bulk forms are already well-known for properties such as because of their amorphous structure. Thin films prepared by vapor-to-solid deposition are expected to be further from equilibrium than those prepared by liquid-to-solid melting or casting processes. This is expected to further improve the glass forming ability and widen the composition range for amorphization. In this talk, we successfully fabricated the first-ever metallic glass nanotubes (MGNTs) on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter [1]. The MGNT surface becomes hydrophobic and repels water. Upon heating and cooling the array, water can be repelled and attached to the surface [1]. Two examples will be presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. With a detection time of 10 min, the detection limit for streptavidin is estimated to be 25 nM. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Further, the array is prepared on a heating device on Si and, with an applied electric voltage to the heating device underneath, the MGNT surface was heated to generate an extending force from these nanochambers up to ~75°C in order for the array to be functioned as biomimetic artificial suckers for thermally adhesion response in biological systems [3]. As a result, the adhesive forces of the MGNT arrays can be as high as 11.2 N cm^{-2}.

References

[1] J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, Metallic glass nanotube arrays: preparation and surface characterizations, Materials Today, 21 (2018), 178-185.

[2] W. T. Chen, S. S. Li, J. P. Chu, K. C. Feng, J. K. Chen, Fabrication of ordered metallic glass nanotube arrays for label-free biosensing with diffractive reflectance, Biosensors and Bioelectronics, 102 (2018), 129-135.

[3] W. T. Chen, K. Manivannan, C. C. Yu, J. P. Chu and J. K. Chen, Fabrication of an artificial nanosucker device with a large area nanotube array of metallic glass, Nanoscale, 10 (2018) 1366-1375.

6:20pm **TF-WeE-3 Growth and Characterization of Atomically-thin MoS_2-$MoSe_2$ Hetero-Junctions Synthesized by Vapor-Phase Chalcogenization**, ***Andres De Luna Bugallo,*** CINVESTAV Querétaro México, Mexico*; I Bilgin, D Rubin,* Northeastern University*; K Fujisawa,* Penn State University*; M Terrones,* Pennsylvania State University*; S Kar,* Northeastern University

Junctions between disparate electronic materials have been a focus of fundamental and applied research for over a century, and with the emergence of two dimensional (2D) semiconductors this focus has only intensified. In particular, the electronic and optical properties of 2D hetero-junctions synthesized directly from vapor-phase growth depend on the atomically-sharp interface. In this work, we present an in-depth characterization of vapor phase chalcogenization (VPC) synthesized of 2D molybdenum disulfide/molybdenum diselenide (MoS_2/$MoSe_2$) hetero-junctions exhibiting multiple morphologies. We investigated both, lateral in-plane heterojunctions and vertical out-of-plane heterojunctions with morphologies that range from being atomically-abrupt interfaces with varying degrees of doping, mixing, and alloying. High-resolution microscopy/spectroscopy performed on well-defined regions of these samples show distinguish among these regions, which also exhibit novel physical phenomena. In particular, we demonstrate strong supported-or-suspended sample dependent suppression of certain photoluminescence (PL) and Raman vibrational modes. We also describe atomically-resolved scanning transmission electron microscopy of these hetero-junctions, revealing defects, doping, and formation of different types of Moiré superlattices. This works aims at providing a comprehensive multi-probe high-resolution characterization of TMD heterojunctions.

6:40pm **TF-WeE-4 Band-engineering of $(TiO_2)_{1-x}(TaON)_x$ Thin Films for Photochemical Applications**, ***Tetsuya Hasegawa,*** University of Tokyo, Japan

Titanium dioxide (TiO_2) has been extensively studied for photocatalytic applications. Recently, we synthesized epitaxial thin films of anatase tantalum oxynitride (TaON), which has a smaller bandgap and larger refractive index than TiO_2 [1,2]. Alloying of anatase TiO_2 and TaON would enable band structure engineering of TiO_2 in a controller manner. In this study, we have grown thin films of an anatase $(TiO_2)_{1-x}(TaON)_x$ (TTON) solid solution and investigated their optical properties and band alignment. Epitaxial thin films of TTON ($0.1 \leq x \leq 0.9$) were deposited on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ substrates by nitrogen plasma-assisted pulsed laser deposition technique. X-ray diffraction confirmed epitaxial growth of phase-pure anatase TTON, of which lattice constants changed with x in agreement with Vegard's law. Optical properties and band alignment were examined spectroscopic ellipsometry and X-ray photoelectron spectroscopy, respectively. The bandgap of TTON systematically decreased with increasing x, mainly due to upward shift in the valence band maximum through evolution of shallow N 2p band. Meanwhile, the position of the conduction band minimum was insensitive to x. The band alignment of anatase TTON was found to be suitable for photocatalytic water splitting with visible light. The refractive index of anatase TTON monotonically increased with x, possibly originating from the higher covalency of metal-N bonds than that of metal-O bonds.

References

[1] A. Suzuki, Y. Hirose, D. Oka, S. Nakao, T. Fukumura, S. Ishii, K. Saso, H. Matsuzaki, and T. Hasegawa, Chem. Mater.**26**, 976 (2014)

[2] A. Suzuki, Y. Hirose, D. Oka, S. Nakao, T. Fukumura and T. Hasegawa, Jpn. J. Appl. Phys. **54** 080303 (2015).

7:00pm **TF-WeE-5 Exploring Mechanical and Liquid-phase Exfoliation of HOPG through Low-energy Ion Beam Analysis**, ***Paolo Branchini,*** INFN RomaTre, Italy*; S De Rosa,* National Institute of Nuclear Physics Roma Tre, Italy*; L Tortora,* INFN RomaTre, Italy*; R Yivlialin, G Bussetti,* Politecnico di Milano, Italy

Among two-dimensional semiconductors, graphene is universally recognized as an emerging material having potentials for a wide range of applications including organic electronics and photonics. Graphene flakes can be produced following different preparation protocols,[1] such as: dry and liquid-phase exfoliation, growth on SiC and metal substrates, CVD, molecular beam epitaxy, atomic layer epitaxy, chemical synthesis etc.. Within the European Graphene flagship program, different analytical techniques [SEM/FIB, TEM, EDS, SPM, XPS, XRD, Raman] are routinely adopted to provide the structural and chemical characterization and to validate the production process.

Here, we propose ToF-SIMS combined with multivariate analysis as validation tool for monitoring the graphene production. In particular, we focused the research on most diffused production methods: (i) the mechanical exfoliation by adhesive tape and (ii) the dispersion of graphene flakes inside an electrochemical bath after the intercalation of ions inside a graphite (HOPG) sample.

The (i) preparation protocol foresees the deposition of graphene onto a silicon wafer, which is then cleaned with acetone, ethanol, and deionized water and dried on a hot plate maintained at 300°C for 1min. The (ii) procedure requires an acid media (e.g. sulphuric or perchloric solutions), purified by bubbling Ar gas inside a separator funnel for several hours. A three-electrode cell is then exploited for inducing ion intercalation in graphite, used as a working electrode, which expands the crystal helping the weakening of the layer-layer interaction.

The high sensitivity of ToF-SIMS technique (few ppm) reveals graphene contamination due to the presence of residual glue coming from the scotch-tape. Furthermore, PCA and K-means cluster analysis were successfully applied to ToF-SIMS high resolution images, showing three different contributions from silicon substrate, residual glue, and graphite/graphene layers. At the same way, results from the graphite mother-crystal, used in the electrochemical approach, also show residual compounds related to the production process such as SO_2^-, SO_3^-, ClO^-, ClO_2, ClO_3^-, ClO_4^-. Dual beam depth profiling experiments showed that these compounds are present not only onto the HOPG surface but also between

graphite terraces and inside the nanoprotrusions produced during the intercalation process. These preliminary results contribute to shed light on the chemistry of the intercalation process.

References

G. Bussetti, R. Yivlialin, D. Alliata, A. Li Bassi, C. Castiglioni, M. Tommasini, C. Spartaco Casari, M. Passoni, P. Biagioni, F. Ciccacci, and L. Duo, *J. Phys. Chem.* C 2016, 120, 6088−6093

7:40pm **TF-WeE-7 Altering Cu-Ni Alloy Composition to Control 2D h-BN Growth**, ***Boris Feigelson***, Naval Research Laboratory; *K Sridhara, J Hite, J Wollmershauser,* US Naval Research Laboratory

Atomically thin two dimensional hexagonal boron nitride (2D h-BN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance. Growth of single and multi-layer (2-10 layers) h-BN films of high crystalline quality in controlled manner is still a challenge.

In this work, h-BN films were grown by atmospheric-pressure CVD on metal substrates (Cu, Ni and Cu-Ni alloys). A vertical custom-made CVD reactor was used to grow h-BN films. The design of the vertical reactor allows the simultaneous growth of a few samples of h-BN on different substrates in the same run. Ni-Cu and Cu-Ni alloys were prepared by electroplating Cu on to Ni and Ni on Cu foils, respectively, followed by thermal annealing and polishing [1] to create alloy substrates with increasing Cu or Ni concentrations (at 10 wt.% increments from 10-50 wt.% Cu in Ni and 10-50 wt.% Ni in Cu).

As it was shown in our previous work [2], Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) can be used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the A_{2u}(LO) vibrational mode were found for thin 2D h-BN films in contact with Cu and Ni. The lower-energy A_{2u}(LO)1 sub-band around 819 cm^{-1} is related to 2D h-BN coupled with Cu substrate, while the higher energy A_{2u}(LO)2 sub-band around 824 cm^{-1} is related to decoupled (essentially free standing) h-BN.

The IR-active out-of-plane vibrational mode was exploited to identify and characterize 1-5 layer h-BN on metal substrates, while micro Raman spectroscopy was used to characterize thicker h-BN films. Scanning electron microscope and x-ray photoelectron spectroscopy were used to probe the h-BN crystal size and stoichiometry.

Results on how morphology and thickness of 2D h-BN films depend on Cu-Ni alloy composition will be presented.

[1] K. Sridhara, B. N. Feigelson, J. A. Wollmershauser, J. K. Hite, A. Nath, S. C. Hernández, M. S. Fuhrer and D. K. Gaskill (2017). Crystal Growth & Design 17(4): 1669-1678.

[2] B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, Nanoscale **7,** 3694 (2015)

8:00pm **TF-WeE-8 Internal Photoemission Spectroscopy Measurements of Energy Barriers between Metallic Glass Thin Films and ALD Dielectrics**, *M Jenkins,* ***John Conley, Jr.,*** Oregon State University

Metal/insulator/metal (MIM) structures are used as high speed diodes for rectenna based harvesting and sensing of IR radiation, capacitors, resistive memory, and hot-electron transistors. To better control electric fields and improve performance of these devices, there is growing interest in integrating metallic glassy (amorphous) thin films as smooth electrodes with uniform work function. Precise knowledge of metal/insulator barrier heights, ϕ_{Bn}, is critical for predicting, understanding, and optimizing MIM device charge transport and operation. In the simplest model, charge transfer across the interface is neglected, and ϕ_{Bn} should vary with the vacuum work function of the metal, $\Phi_{M,vac}$, so that $\phi_{Bn}=\Phi_{M,vac}-\chi_i$ where χ_i is the insulator electron affinity. In induced gap state theory, charge transfer at intrinsic interface traps which create an interfacial dipole that drives the metal Fermi level, E_{FM}, towards the charge neutral level of the insulator, $E_{CNL,i}$, the energy at which the dominant character of the interface states switches from donor-like to acceptor-like. A metal on an insulator will behave as if it has an effective work function, $\Phi_{M\text{-}eff}$, different from $\Phi_{M,vac}$, so that $\Phi_{M,eff}=E_{CNL,i}+S(\Phi_{M,vac}-E_{CNL,i})$.[1] S is the slope that describes how much $\Phi_{M,eff}$ on a given dielectric will change in response to $\Phi_{M,vac}$. Empirically, $S=1/(1+0.1(\varepsilon_{hf}-1)^2$. As the high frequency dielectric constant, ε_{hf}, increases, S decreases and the insulator more effectively "pins" E_{FM} at $E_{CNL,i}$. Finally, actual ϕ_{Bn}'s depend on deposition method and can deviate substantially due to extrinsic interface traps. Thus it is necessary to directly measure ϕ_{Bn} for a given metal-insulator combination.

In this work, we use IPE spectroscopy to measure ϕ_{Bn} of the thin film glassy metals ZrCuAlNi, TaWSi, and TaNiSi in MIM stacks with various insulators deposited via ALD.[2,3] To date, there have been few reports of IPE measurements of MIM structures and only one an amorphous metal.[4] Results are referenced to TaN, Al, and Au barriers on the same devices.

Ta-based metal ϕ_{Bn}'s change with Φ_M for Al_2O_3, but HfO_2 ϕ_{Bn} are relatively constant, likely due to pinning. The asymmetry in the I-V response is qualitatively consistent with the IPE determined ϕ_{Bn}. TaWSi and TaNiSi electrodes showed consistently higher ϕ_{Bn}'s than ZCAN electrodes and comparable performance to TaN. With low roughness and thermal stability approaching 900 °C, TaWSi is a promising electrode for MIM diodes.

[1] Yeo et al. J. Appl. Phys. 92, 7266 (2002).

[2] N. Alimardani et al. J. Vac. Sci. Technol. A **30**, 01A113 (2012).

[3] McGlone et al. MRS Commun. **7** (2017).

4. M.A. Jenkins et al. Physica Status Solidi (RRL) 12, 1700437 (2018).

8:20pm **TF-WeE-9 New Insights into the Kinetics of Chemical Vapor Deposition of Two-dimensional hBN Layers on Pd(111)**, ***Pedro Arias***, University of California, Los Angeles; *A Abdulslam,* Colorado School of Mines; *A Ebnonnasir,* University of California, Los Angeles; *C Ciobanu,* Colorado School of Mines; *S Kodambaka,* University of California, Los Angeles

Using in situ variable-temperature scanning tunneling microscopy (VT-STM) and density functional theory (DFT), we investigated the surface structure and growth kinetics of two-dimensional hexagonal boron nitride (hBN) monolayer on Pd(111). STM images of polydomain hBN monolayers, grown via dissociative chemisorption of borazine on Pd(111)/Al_2O_3(0001) thin films, reveal moiré patterns with periodicities between 0.6 nm and 2.8 nm corresponding to four different orientations on Pd(111). We observe tunneling-parameter dependent apparent surface corrugation Δz in the STM images of the hBN domains. Furthermore, for the largest moiré pattern periodicities, we observe a bifurcation behavior in which some domains are nearly flat, and others develop significant hill-and-valley geometric corrugations. We suggest that hBN/Pd can have either mainly geometric or mainly electronic corrugation, depending on the domain orientation.[1] This behavior is unlike any other monolayer hBN-on-metal system.

Using the VT-STM, we investigated the chemical vapor deposition (CVD) kinetics of hBN monolayers on Pd(111). In each experiment, STM images are acquired while exposing Pd(111) to borazine (10^{-7} – 10^{-6} Torr) at temperatures 573 K and 673 K and for times up to 2500 s. The STM images reveal the nucleation and growth of two-dimensional islands on the Pd surfaces. From the images, we measure the areal coverage, island sizes, and island density as a function of time, temperature, and borazine flux. Our STM images reveal an unusual nucleation and growth mode: at lower deposition rate and higher temperature, islands form on terraces; increasing the deposition rate and/or lowering the temperature result in preferential nucleation and growth at the step edges. Interestingly, the attachment of the deposited species is observed on both up and down steps. We attribute this phenomenon to the structure and the highly anisotropic bonding of borazine on Pd(111). Our results provide new insights into the growth dynamics of two-dimensional layered materials.

[1]P. Arias, A. Abdulslam, A. Ebnonnasir, C. V. Ciobanu and S. Kodambaka, 2D Materials **5** (4), 045001 (2018).

8:40pm **TF-WeE-10 Very High Refractive Index Transition Metal Dichalcogenide Photonic Conformal Coatings by Conversion of ALD Metal Oxides**, ***Shaul Aloni***, *A Schwartzberg, C Chen, C Kastl,* Lawrence Berkeley National Laboratory

Materials for nanophotonic devices ideally combine ease of deposition, very high refractive index, and facile pattern formation through lithographic templating and/or etching. In this work, we present a scalable method for producing high refractive index WS2 layers by chemical conversion of WO3 synthesized via atomic layer deposition (ALD). These conformal nanocrystalline thin films demonstrate a surprisingly high index of refraction (n > 3.9), and structural fidelity compatible with lithographically defined features down to ~10 nm. Although this process yields highly polycrystalline films, the optical constants are in agreement with those reported for single crystal bulk WS2. Subsequently, we demonstrate three photonic structures - first, a two-dimensional hole array made possible by patterning and etching an ALD WO3 thin film before

conversion, second, an analogue of the 2D hole array first patterned into fused silica before conformal coating and conversion, and third, a three-dimensional inverse opal photonic crystal made by conformal coating of a self-assembled polystyrene bead template. These results can be trivially extended to other transition metal dichalcogenides, thus opening new opportunities for photonic devices based on high refractive index materials.

Author Index

Bold page numbers indicate presenter

— A —
Abdulslam, A: TF-WeE-9, 2
Aloni, S: TF-WeE-10, **2**
Arias, P: TF-WeE-9, **2**
— B —
Bilgin, I: TF-WeE-3, 1
Branchini, P: TF-WeE-5, **1**
Bussetti, G: TF-WeE-5, 1
— C —
Chen, C: TF-WeE-10, 2
Chu, J: TF-WeE-1, **1**
Ciobanu, C: TF-WeE-9, 2
Conley, Jr., J: TF-WeE-8, **2**
— D —
De Luna Bugallo, A: TF-WeE-3, **1**
De Rosa, S: TF-WeE-5, 1
— E —
Ebnonnasir, A: TF-WeE-9, 2
— F —
Feigelson, B: TF-WeE-7, **2**
Fujisawa, K: TF-WeE-3, 1
— H —
Hasegawa, T: TF-WeE-4, **1**
Hite, J: TF-WeE-7, 2
— J —
Jenkins, M: TF-WeE-8, 2
— K —
Kar, S: TF-WeE-3, 1
Kastl, C: TF-WeE-10, 2
Kodambaka, S: TF-WeE-9, 2
— R —
Rubin, D: TF-WeE-3, 1
— S —
Schwartzberg, A: TF-WeE-10, 2
Sridhara, K: TF-WeE-7, 2
— T —
Terrones, M: TF-WeE-3, 1
Tortora, L: TF-WeE-5, 1
— W —
Wollmershauser, J: TF-WeE-7, 2
— Y —
Yivlialin, R: TF-WeE-5, 1