New Horizons in Coatings and Thin Films
Room San Diego - Session F3

2D Materials: Synthesis, Characterization, and Applications

Moderators: Eli Sutter, University of Nebraska-Lincoln, USA, Liping Wang, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences

8:00am **F3-1 Crystallization Kinetics of Photonically Annealed Two Dimensional Materials and Heterostructures**, *R Vila,* Stanford University, USA; *R Rao, B Maruyama,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *E Bianco,* Air Force Research Laboratory, Materials and Manufacturing Directorate/Rice University, USA; *N Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; ***Chris Muratore,*** University of Dayton, USA

Synthesis capability for uniform growth of two-dimensional (2D) materials over large areas at lower temperatures without sacrificing their unique properties is a critical pre-requisite for seamless integration of monolithic van der Waals materials or their heterostructures into novel devices, especially on flexible substrate platforms. Developing effective strategies to synthesize 2D materials, such as MoS_2 and other transition metal dichalcogenides necessitates a fundamental understanding of the thermodynamics and kinetics controlling nucleation and growth processes. To elucidate crystallization mechanisms we utilize *in situ* Raman spectroscopy during photonic crystallization of amorphous 2D films to directly probe the diffusion-limited kinetics while eliminating contributions from factors adding extreme variability to growth mechanisms such as precursor delivery and gas-phase reactions. We employ a high-throughput autonomous experimentation technique to perform studies in rapid succession on the same substrate, while precisely monitoring temperature by analysis of Stokes/Anti-Stokes peak shifts on rigid (SiO_2/Si) or flexible (polydimethylsiloxane or PDMS) substrates. Preliminary results during isothermal heating reveal that nucleation of amorphous 2D MoS_2 occurs very rapidly and the crystallization rate follows an Arrhenius temperature relationship, yielding an energy barrier of 1.03 eV/atom that corresponds to sulfur diffusion. A correlation between crystallization rate and crystal quality was also observed, as the technique allows *in situ* measurement of atomic defect concentrations. materials. Comparison to theororetical results will allow use of the empirically determined activation barrier for diffusion-limited crystallization as a mechanistic fingerprint in TMD compounds with varying degrees of atomic mass-mismatch. Photonically annealed crystalline 2D materials derived from amorphous precursor films demonstrate device-quality performance, enabling correlation of device properties (i.e., lateral photodetectors and others) to the structure, composition and defect density resulting from different crystallization conditions.

8:20am **F3-2 The Application of Pulsed Laser Deposited a-BN for Temperature and Oxidation Resistance of 2D $MoTe_2$ Semiconducting Devices**, ***Benjamin Sirota,*** University of North Texas, USA, United States of America; *N Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *C Muratore,* University of Dayton, USA; *S Krylyuk, A Davydov,* National Institute of Standards and Technology, USA; *A Voevodin,* University of North Texas, USA

Pulsed laser deposition (PLD) of ultra-thin (2-10 nm) amorphous boron nitride (a-BN) films was previously shown to provide a wide band gap insulating material with excellent breakdown and dielectric characteristics [1,2]. The process enables large area coverage at near room temperatures which make it an attractive deposition technique for the use in with two-dimensional (2D) semiconducting materials; such as few monolayer thick transition metal chalcogenides (TMDs). 2D TMDs provide unique physical properties needed for electronic and opto-electronic devices, however they are also prone to degradation by oxidation, especially at elevated temperatures in atmospheric conditions. This study explores the benefit of a-BN for environmental stability of 2D TMDs, using an example of few monolayer thick exfoliated 2H-$MoTe_2$ capped with a PLD-grown a-BN top layer to create a 2D BN-$MoTe_2$ heterostructure. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements demonstrated a significant improvement in chemical stability and resistance to oxidation for BN-$MoTe_2$ hetrostructures as compared to uncoated $MoTe_2$ samples when heating in air up to 300 °C. Both XPS and Raman analysis showed a rapid oxidation and structural degradation for uncapped $MoTe_2$ while BN-$MoTe_2$ demonstrated significant durability after one hour of heating at 100 °C. This was correlated with heating in air experiments with BN-$MoTe_2$ 2D filed effect transistor (FET) devices. Uncapped $MoTe_2$ FET devices heated in air for 1 minute showed a polarity switch from n- to p-type at 150 °C, while BN-$MoTe_2$ devices switched only after 200 °C of heat treatment. Time dependent experiments at 100 °C in air showed that uncapped $MoTe_2$ FET devices exhibited the polarity switch after 15 minutes of heat treatment while the BN-capped device maintained its n-type conductivity for the 60 minutes of the heating exposure. This work demonstrates the effectiveness of an amorphous BN capping layer in preserving few-layer $MoTe_2$ material quality and controlling its oxidation rate at elevated temperatures in an atmospheric environment.

1. Glavin et al, Thin Solid Films, 572 (2014), 245-250.

2. Glavin et al, Adv. Funct. Mater. (2016) 26: 2640–2647.

8:40am **F3-3 A Predictive Thermokinetic Model of Friction in MoS_2**, ***John Curry,*** *A Hinkle,* Sandia National Laboratories, USA; *T Babuska, B Krick,* Lehigh University, USA; *M Dugger, N Argibay, M Chandross,* Sandia National Laboratories, USA

Building on more than a century of concerted effort to understand the friction behavior of 2D materials, we present a thermokinetic model for predicting the shear strength of MoS2 based on energetic barriers to sliding. This model accounts for a wide range of factors underlying the interaction between molecularly thin lamellae, including defects, temperature, crystallite size and commensurability. Findings are supported by results from thermally ramped sliding experiments and molecular dynamics simulations.

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9:00am **F3-4 Supercritical Fluid Assisted Synthesis of V_2O_5/VS_2 Nanocomposites for use in Supercapacitor**, ***Yen-Chun Liu,*** *J Ting,* National Cheng Kung University, Taiwan

A novel one-pot Supercritical fluid (SCF) CO_2 synthesis method was used to fabricate V_2O_5/VS_2 nanocomposite. VS_2 was first synthesized using a microwave assisted hydrothermal technique. The obtained VS_2 powders were then mixed with an oxidizing agent and subject to the SCF treatment to form V_2O_5/VS_2 nanocomposites as follows. During the SCF process, the VS_2 was exfoliated to form nanosheets of VS_2 by the SCF CO_2. In the meantime, V_2O_5 nanoparticles (NPs) were formed due to the partial oxidation of the VS_2. The formed V_2O_5 NPs were intercalated into the VS_2 nanosheets also with the assistance of the SCF CO_2. The effects of the SCF condition and the strength of the oxidizing agent on the formation and characteristics of V_2O_5/VS_2 nanocomposites were investigated. Supercapacitor cells were assembled using the resulting V_2O_5/VS_2 nanocomposites as the electrodes. The cells were evaluated using cyclic voltammetry, and electrochemical impedance spectroscopy, and subjected to cycle life and charge-discharge cycling tests.

9:20am **F3-5 2D and Layered Metal Chalcogenide Semiconductors: Growth, Electronic Structure, Light-Matter Interactions**, ***Peter Sutter,*** University of Nebraska-Lincoln, USA **INVITED**

Metal chalcogenides have received attention as layered crystals and as 2D materials beyond graphene. Semiconducting chalcogenides show promise for applications in energy conversion and next-generation low-dimensional (opto) electronics benefiting from carrier confinement and other unique characteristics, such as a thickness dependent or anisotropic electronic structure, non-charge based degrees of freedom, and strong light-matter interactions. Here, I discuss recent work using novel high spatial resolution probes to study the properties of 2D semiconductors and their variations on the nanometer scale.

Real-time microscopy provides insight into the microscopic mechanisms governing the bottom-up growth and transformation of 2D semiconductors. Local band structure measurements are used to establish the thickness dependent electronic properties, as well as other key aspects such as the interlayer coupling as a function of layer orientation. Finally, I present nanometer-scale measurements of light-matter interactions in 2D semiconductors, which offer a way to probe and manipulate optical excitations far below the diffraction limit near defects, edges, or engineered interfaces.

10:00am **F3-7 Fabrication and Photocatalytic Application of Functional group Modification of Carbon Nitride Derivatives nanosheets**, ***ChunHung Chen***, *K Chang,* National Cheng Kung University (NCKU), Taiwan

Carbon nitride has recently attracted much attention owing to its visible-light-driven hydrogen evolution capability which is first published in 2009.[1] Compared with 1D-structured melon, which has already been well-studied by other research groups, the melon oligomer and poly (triazine imide) (PTI/Li^+Cl^-) are two promising structures which show a better photocatalytic property. However, there still remains some room for improvements to be done such as increasing the amount of functional groups of carbon nitride, which are known to be active sites during a photocatalytic process. These active sites are regarded as the predominant factor in the carbon nitride series.[2] Herein, two strategies were applied to modify the PTI & melon oligomer for the purpose of enhancing its photocatalytic ability. The first process is by using isopropanol (IPA) and ethanol in distinct heat treatment to accomplish surface functionalization. Solid NMR, FTIR, and EA were used to prove that additional functional groups are successfully linked. Also, the UV-Vis results indicated that the absorption range had a red-shift to a higher wavelength which is due to the change in powder color. For the second process, liquid exfoliation method was used to obtain ultrathin nanosheets in order to enhance its photodegradation ability due to the further increase in surface area and active sites. By considering that the enthalpy of mixing should be minimized, water is considered as the optimal solvent and was applied due to having a similar surface energy to carbon nitride nanosheet.[3] The BET analysis showed that the surface area has significantly increased, which brought about more than five times enhancement in its photocatalytic property. Furthermore, from the photoelectrochemistry measurement, the modified carbon nitride shows the linear relationship as the sensor of Cu ion determination, indicating that our sample is a promising candidate for ion determination in water solution.

REFERENCES

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[2] M. K. Bhunia, K. Yamauchi, K. Takanabe, Angew. Chem. Int. Ed., 126 (2014) 11181-11185

[3] K. Schwinghammer, M.B. Mesch, V. Duppel, C. Ziegler, J. Senker, B. V. Lotsch, J. Am. Chem. Soc., 136 (2014) 1730-1733

10:20am **F3-8 Enhanced Photocatalytic Performance for g-C_3N_4 through the Addition of α-MoO_3 Nanobelts and Mesoporous TiO_2 Beads**, ***Yen Duong***, *J Ting,* National Cheng Kung University, Taiwan

Multi-component photocatalysts based on g-C_3N_4 was synthesized to enhanced the photocatalytic performance of g-C_3N_4. Exfoliated g-C_3N_4 was fabricated by heating melamine at 550^0C, followed by the use of hydrogen peroxide (H_2O_2) to exfoliate bulk g-C_3N_4. Mesoporous TiO_2 beads were prepared using a two-step process. α-MoO_3 nanobelts were made by hydrothermal method. Three groups of binary-component photocatalysts of TiO_2/g-C_3N_4, TiO_2/ α-MoO_3 and α-MoO_3 / g-C_3N_4 having various compositions were then made. Based on the performance of these binary-component photocatalysts, TiO_2/ α-MoO_3/g-C_3N_4 ternary composite photocatalysts were synthesized. The photocatalytic performance of all the single-binary and ternary component phtotocatalysts were evaluated by degrading methyl blue under both UV and visible light irradiations.

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[1] Yeping Li, Liying Huang, Jingbo Xu, Hui Xu, Yuanguo Xu, Jixiang Xia, Huaming Li, Materials Research Bullentin 70 (2015) 500-505.

[2 Yiming He, Lihong Zhang, Xiaoxing Wang, Ying Wu, Hongjun Lin, Leihong Zhao, Weizheng Weng, Huilin Wan, Maohong Fan, Royal Society of Chemistry, (2014) 13610-13619.

[3 Zili Xu, Chuansheng Zhuang, Zhijuan Zou, Jingyu Wang, Xiaochan Xu, Tianyou Peng, Nano Research 10(7), (2017) 2193-2209.

10:40am **F3-9 Fabrication of Nanostructured MoS_2 Thin Films on Porous Silicon Substrate for Ammonia Gas Sensing Properties**, *S Sharma, A Kumar,* ***Davinder Kaur***, Indian Institute of Technology Roorkee, India

In the present work, we have fabricated the molybdenum disulphide (MoS_2) nanostructure thin films on the 2×2 cm^2 porous Silicon (100) substrates using DC magnetron sputtering technique. Porous silicon was fabricated by the metal-assisted chemical etching of the Si (100) substrate using HF as etchant solution. The structural and surface morphological properties of MoS_2 nanostructure thin films were systematically studied using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and Raman spectroscopy. The ammonia gas sensing properties of porous MoS_2 thin film sensor shows the remarkable response with fast response/recovery time towards the 100 ppm ammonia gas (NH_3) at the room temperature. These sensing performances suggest porous MoS_2 thin films a potential candidate for room temperature sensor devices. The sensing mechanism and response behaviour towards ammonia gas was also discussed in detail.

11:00am **F3-10 Wettability, Sructural and Optical Examination of Sputtered Zirconium Oxide Thin Films**, ***Uttkarsh Patel***, McMaster University, Canada*; P Dave,* Gujarat forensic science university, India*; K Chauhan,* Charotar University of Science and Technology (CHARUSAT), India*; S Rawal,* McMaster University, Canada

Zirconium oxide films were deposited by reactive magnetron sputtering at different sputtering pressure values of 0.4Pa, 0.7Pa, 1.0Pa and 1.5Pa. The effect of sputtering pressure on structural, hydrophobic and optical properties of deposited zirconium oxide thin films is reported in this research work. Due to this variation during thin film growth, it is observed that zirconium oxide thin films formed has monoclinic phase with (111) orientation. Its intensity increase with increase in sputtering pressure from 0.4Pa to 1.5Pa. The contact angle values of 96º for water and 44º for aniline were observed at 0.4Pa. The band gap of zirconium oxide films increases as sputtering pressure is increased from 0.4Pa to 1.5Pa.

11:20am **F3-11 Synthesis and Characterization of Molybdenum-based Thin Films for Flexible Electronics**, *T Jörg,* Montanuniversität Leoben, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; D Music,* RWTH Aachen University, Germany*; R Franz,* Montanuniversität Leoben, Austria*; H Köstenbauer, J Winkler,* Plansee SE, Austria*; J Schneider,* RWTH Aachen University, Germany*;* ***Christian Mitterer***, Montanuniversität Leoben, Austria **INVITED**

Mechanical failure of thin metal films on compliant substrates presents a considerable challenge in the development of flexible electronics. In particular, this applies for sputter-deposited molybdenum thin films, which are frequently used as back electrode materials in flexible solar cells, as electrode materials in flexible piezoelectric micro- and nano-electromechanical systems, in the metallization of thin film transistors, e.g. as gate and source/drain electrodes, as adhesion promotion, diffusion barrier and ohmic contact layers due to their attractive combination of functional properties.

Within this work, different strategies for film synthesis and alloying are proposed to design Mo-based thin films on polymer substrates with enhanced fracture resistance. The fracture properties of pure Mo films can be tailored by their compressive residual stress state, enabling a considerable improvement in crack onset strain. Moreover, both fracture strength and crack onset strain of Mo thin films scale with their thickness. Since all Mo thin films exhibit a distinctly brittle fracture behavior, alloying with Re and Cu was explored as feasible concept to overcome their poor ductility. A substantial toughness improvement with rising Re content up to the solubility limit was obtained, which stems from the increased plasticity and bond strengthening in the Mo-Re solid solution. Furthermore, it was observed that Cu addition to Mo results in an increased ductility, which was rationalized by the low shear resistant bonding in the Mo-Cu solid solution. In general, both concepts proved to be promising in order to enable utilization of Mo based thin films in flexible electronics.

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