

New Horizons in Coatings and Thin Films Room Pacific Salon 6-7 - Session F3-TuA

2D Materials: Synthesis, Characterization, and Applications

Moderator: Eli Sutter, University of Nebraska-Lincoln, USA

1:40pm **F3-TuA-1 Roll-to-roll Plasma Chemical Vapor Deposition for Scalable Graphene Production**, Timothy Fisher, UCLA, USA; M Alrefae, Purdue University, USA

INVITED

Recently, roll-to-roll (R2R) chemical vapor deposition (CVD) processes have been implemented to produce graphene with substrate feed rates ranging from 5-100 mm/min. However, this production rate must increase much further to make graphene a feasible product in semiconductor and materials manufacturing industries. Plasma sources can be applied to increase the graphene deposition rate, and additionally, to decrease energy input. This work will describe the implementation of a radio frequency plasma R2R CVD process to deposit graphene on copper and nickel foils, and carbon fibers. The growth process takes advantage of the high-temperature plasma gas that produces active carbon species to accelerate growth kinetics. Thus, supplemental heating of the substrate is unnecessary when using plasma, in contrast to thermal CVD systems that consume energy to heat the substrate and to decompose the carbon gas source. *In situ* temperature measurements of the substrate in the plasma region confirm the plasma's ability to heat the substrate to the 1200-1500 K range depending on the plasma power. From these real-time temperature measurements, a heat transfer model is developed and validated to determine the substrate temperature profile during R2R graphene growth. The effects of plasma power and web speed on substrate temperature are explored and correlated to graphene quality. The results indicate that graphene growth on Cu foil is most significantly influenced by the in-plasma substrate temperature, whereas growth on Ni foil is controlled by the substrate cooling rate, which is evaluated from the heat transfer model. Furthermore, the plasma environment is characterized by optical emission spectroscopy (OES) to optimize graphene growth and assess the impact of ion bombardment. The OES results suggest that the quality of graphene deposited on Cu foil is enhanced with increased CH emission and decreased emission from O, H, Ar⁺, C₂, and CN. The process characterization techniques aid in controlling and optimizing graphene growth in a large-scale setup, including graphene quality as a function of reactor pressure and nitrogen mole fraction with associated uncertainties obtained from statistical analysis. The talk will include a discussion of applications of the resulting materials in energy and biosensing technologies, as well as plans for a new MHz plasma R2R system supplemented by solar heating.

2:20pm **F3-TuA-3 Magnetron Sputtered MoS₂/C Nanocomposites as Highly Efficient Electrocatalyst in Hydrogen Evolution Reaction**, S Rowley-Neale, M Ratova, Manchester Metropolitan University, UK; L Fugita, University of Sao Paulo, Brazil; G Smith, University of Chester, UK; A Gaffar, Justyna Kulczyk-Malecka, P Kelly, C Banks, Manchester Metropolitan University, UK

The design and fabrication of an inexpensive and highly efficient electrocatalyst for the hydrogen evolution reaction (HER), were performed by the route of magnetron sputtering. Molybdenum disulfide (MoS₂) was coated directly onto the nanocarbon (C) powder support. Sputtering time was explored as a function of physicochemical composition of MoS₂/C nanocomposites, and its performance in HER. Increased sputtering time gave rise to materials with different compositions and oxidation states of Mo ions, Mo⁴⁺ and Mo⁶⁺, associated with sulfur anions (sulfide, elemental and sulfate) and improved HER outputs. The physicochemical characterisation of the MoS₂/C nanocomposites as a function of sputtering time was evaluated using scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman Spectroscopy. An optimised sputtering time of 45 minutes was used to fabricate MoS₂/C nanocomposites. This gave rise to an optimal HER performance in regards to its onset potential (-0.44 mV vs saturated calomel electrode (SCE)), achievable current (-1.45 mVs⁻¹) and Tafel value (43 mVdec⁻¹) for the compositions rich in Mo⁴⁺ and sulfide (MoS₂). This bespoke fabricated MoS₂/C nanocomposites were incorporated into the bulk ink utilised in the fabrication of screen-printed electrodes (SPEs) to allow improved electrical wiring to the MoS₂/C and to produce scalable and reproducible electrocatalytic platforms. The MoS₂/C-SPEs displayed far greater HER catalysis with a 450 mV reduction in the HER

onset potential and a 1.70 mA cm⁻² increase in the achievable current density (recorded at -0.75 V vs SCE), compared to a bare/unmodified graphitic SPE. The approach of using magnetron sputtering to modify carbon with MoS₂ facilitates the mass production of stable and effective electrode materials for possible use in electrolyzers, which are cost competitive to platinum (Pt) and mitigate the need to use time consuming and low-yield exfoliation techniques, typically used to fabricate pristine MoS₂.

2:40pm **F3-TuA-4 HIPIMS Graphene on Copper for Heat Spreading**, C Chen, E Liao, Ping-Yen Hsieh, Y Chen, J He, Feng Chia University, Taiwan

The heat generated from electronic devices such as light emitting diodes, batteries, and highly integrated transistors is one of the major causes limiting their performance and reliability. The extraordinarily high thermal conductivity of graphene has let intensive studies for use as a heat spreader. A strategy of further enhancing the thermal conductivity by growing graphene layer on copper will thus proposed in this study. Based on our previous study, it is able to grow graphene layer on copper foil at relative low temperature by using high power impulse magnetron sputtering (HIPIMS) equipped with synchronized substrate bias. The thermal conductivity of the graphene-on-copper (GOC) layer structure was measured, here in this study, based on Angstrom's method. The thermal conductivity of GOC was significantly enhanced as compared to bare copper foil alone. This is due to epitaxial graphene on copper generated low interfacial thermal resistance, and intrinsic high thermal conductivity of graphene. Finally, a strong correlation between graphene layer thickness and thermal conductivity was reported.

3:00pm **F3-TuA-5 Tailoring Optical Properties of Two-Dimensional Transition Metal Dichalcogenides Via Photonic Annealing**, Rachel Rai, K Gleibe, University of Dayton, Air Force Research Laboratory, USA; N Glavin, Air Force Research Laboratory, Wright-Patterson AFB, USA; R Wheeler, UES, Inc., Air Force Research Laboratory, USA; R Kim, Air Force Research Laboratory, Wright-Patterson AFB, USA; A Jawaid, UES, Inc., Air Force Research Laboratory, USA; L Bissell, Air Force Research Laboratory, Wright-Patterson AFB, USA; C Muratore, University of Dayton, USA

Semiconducting transition metal dichalcogenides (TMDs) exhibit unique combinations of physical properties at thicknesses of less than 5 molecular layers. For example, mechanical flexibility and photoluminescence (PL) in the visible to near infrared (NIR) frequencies are not properties that are commonly observed in a single material, but are routinely measured for materials such as 2D MoS₂ and WSe₂. Such properties make TMDs attractive candidates for the next generation of flexible and wearable optoelectronic technologies. Incorporation of TMDs into commercial applications is currently limited, however, by challenges associated with synthesis of large area, device-quality films with tunable properties. Our work encompasses diverse innovative techniques to tailor optical properties of TMD thin films by controlling their area, thickness, crystalline domain size, defect density and uniformity during and after processing. We begin by application of thin amorphous films of WSe₂ and other TMDs on both flexible and rigid substrates via vapor phase and liquid phase application over large areas. We then illuminate the amorphous film with diverse light sources, including lasers (visible-IR), broad-band xenon lamps, and nanoscale electron beams. WSe₂ was selected as a model material due to high quantum yield at room temperature. Tailoring the 'structure' of the amorphous material via modulation of the energy flux during magnetron sputtering provides an opportunity to model homogeneous or heterogeneous crystallization during illumination by controlling the density of pre-existing nuclei. Crystallization kinetics were examined by *in situ* analysis of real-time images and electron diffraction patterns. The amorphous-crystalline conversion is correlated to 2D growth theory and contrasting elements of 2D versus 3D growth are highlighted. A significant increase in photoluminescence intensity is accompanied by a change in crystal edge density, consistent with observations that PL originates preferentially from defective regions of 2D WSe₂. Furthermore, we examine quantum confinement effects on photoluminescence yield in nanoscale crystalline areas (~10 nm) via electron beam irradiation.

Tuesday Afternoon, May 21, 2019

4:00pm **F3-TuA-8 Mechanism of Formation of Nitrogenated Doped Graphene Films, Investigated by In situ XPS During Thermal Annealing in Vacuum**, *Yannick Bleu*, Univ. Lyon, Université Jean Monnet, France; *V Barnier, F Christien*, Laboratoire Georges Friedel, Ecole Nationale Supérieure des Mines, France; *F Bourquard*, Univ. Lyon, Laboratoire Hubert Curien, Université Jean Monnet, France; *J Avila*, Synchrotron SOLEIL & Université Paris-Saclay, France; *F Garrelie*, Univ. Lyon, Université Jean Monnet, France; *M Asensio*, Synchrotron SOLEIL & Université Paris-Saclay, France; *C Donnet*, Université de Lyon, Université Jean Monnet, France

The introduction of dopants, such as nitrogen, into the graphene network, is paramount for many applications such as nanoelectronics, nanophotonics, sensor devices and green energy technology. One way consists in thermal heating of a doped solid carbon source, such as an amorphous a-C:N film, in the presence of a metal catalyst, to obtain nitrogenated graphene (NG) layers. The control of such a process requires to investigate diffusion and segregation mechanisms of the graphene precursor through the metal catalyst.

In the present study, the mechanism of atomic diffusion and NG film growth through a nickel catalyst thin film was investigated using in situ X-ray photoelectron spectroscopy (XPS) performed during thermal heating responsible for NG synthesis. Amorphous a-C:N films, containing 16%at. nitrogen, 10 nm thick, were synthesized by femtosecond pulsed laser ablation on fused silica substrates. A 150 nm thick nickel film was subsequently deposited by thermal evaporation on the a-C:N films. Thermal annealing at various temperatures (200, 300, 500 and 650°C), with different time durations, were performed in ultra-high vacuum during *in situ* XPS analysis, to carry out the top surface genesis of the NG film onto the nickel catalyst. FEG-SEM, Raman and X-ray absorption (XAS) spectroscopies were also performed to elucidate the nature and chemical composition of NG films. The diffusion of carbon and nitrogen through the nickel film towards the surface from 300°C was observed, without any graphene signature. Graphene films are formed at the highest temperatures, with a final 3%at. nitrogen content, in both pyrrolic and pyridinic configurations. In addition, the kinetics of carbon surface enrichment observed using in-situ XPS is discussed in the frame of the interface segregation theory and modelled using the Du Plessis approach. The solid-state transformation mechanism responsible for the formation of few-layer NG films is thus investigated.

4:20pm **F3-TuA-9 Engineering Point and Extended Defects in Transition Metal Dichalcogenides**, *Hannu-Pekka Komsa*, Aalto University, Finland
INVITED

Two-dimensional (2D) materials such as graphene, hexagonal boron nitride, and transition metal dichalcogenides have recently received lots of attention due to their unique material properties and numerous potential applications. The 2D atomic structure can also facilitate distinct defect formation mechanisms and offer new possibilities for defect engineering.

In my talk, I will present the results from layered molybdenum dichalcogenides (MoS₂, MoSe₂, and MoTe₂), where vacancy, substitutional, interstitial, and grain boundary defects are introduced by electron irradiation or by various chemical treatments. Due to the 2D nature, transmission electron microscopy and scanning tunneling microscopy imaging allows direct monitoring of formation and agglomeration of defects as well as of larger structural changes. First-principles calculations are used to provide microscopic insight into the energetics and kinetics of these processes. The gained understanding together with the computationally predicted defect properties can be used to guide future efforts in tailoring the 2D material properties via defect engineering.

5:00pm **F3-TuA-11 Physicochemical and Mechanical Performance of Nylon 6.6 Coated Thin Free-standing Boron-doped Diamond Nanosheets**, *Robert Bogdanowicz*, *M Ficek*, Gdansk University of Technology, Poland; *V Stranak, J Kratochvil*, University of South Bohemia, Czech Republic; *M Szkodo, J Ryl, M Sobaszek*, Gdansk University of Technology, Poland

In the following work, we describe studies on the fabrication and the physicochemical performance of thin and free-standing heavy boron-doped diamond (BDD) nanosheets coated by thin nylon 6.6. First, the diamond nanosheets with less than 400 nm of thickness were grown and doped by boron on Ta substrate by using microwave plasma-enhanced chemical vapor deposition technique (MPECVD) [1]. Then, the BDD/Ta samples were covered by 6.6 nylon to improve their stability in harsh environments.

The plasma polymer films, the thickness in the range 500-1000 nm, with different surface energies were obtained by magnetron sputtering of a bulk target. The hydrophilic nitrogen-rich C:H:N :O were prepared by sputtering

of nylon 6.6. C:H:N :O as films with high surface energy improves adhesion at ambient condition. However, their disadvantage lays in a natural swelling increasing its volume about of 15% after immersion into an aqueous liquid. This behavior influences diamond-C:H:N :O structure in a wet environment.

The C:H:N :O coated diamond nanosheets were delaminated from Ta substrate creating free-standing nanostructures (Diamond-on-Nylon). The C:H:N :O film fixtures the thin polycrystalline diamond sheets enhancing its mechanical stability and enabling transfer and integration with microelectronic systems.

We have manifested that investigated Diamond-on-Nylon nanostructures possess altered morphology and physicochemical properties, revealed by electron microscopy and Raman spectroscopy. Moreover, the electrical response of investigated nanostructures as conductive electrodes is time-stable and indicates the high activity of the sheets with higher dopant concentrations.

Moreover, the Diamond-on-Nylon is characterized with altered mechanical properties like Young modulus or internal stress. These properties varied strongly with the thickness and density of nylon coverage.

In summary, the Diamond-on-Nylon nanostructures show excellent electrical and thermal conductivity along with high mechanical strength. Composite diamond-on-polymer structures could be further developed for flexible and robust electronic devices or thermal heat spreaders.

Acknowledgments

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