2D Materials Focus Topic
Room 15 - Session 2D+AS+SS-ThA

Dopants, Defects, and Interfaces in 2D Materials
Moderator: Aubrey Hanbicki, Naval Research Laboratory

2:20pm **2D+AS+SS-ThA-1 Electron Irradiation-induced Defects and Phase Transformations in Two-dimensional Inorganic Materials**, ***Arkady Krasheninnikov,*** Helmholtz Zentrum Dresden-Rossendorf, Germany

Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN, transition metal dichalcogenides (TMDs) and silica bilayers were manufactured. All these systems contain defects and impurities, which may govern the electronic and optical properties of these materials, calling upon the studies on defect properties. In my talk, I will present the results [1-6] of our first-principles theoretical studies of defects (native and irradiation-induced) in inorganic 2D systems obtained in collaboration with several experimental groups. I will further dwell on the signatures of defects in Raman spectra and discuss defect- and impurity-mediated engineering of the electronic structure of inorganic 2D materials. I will also present the results [7] of our theoretical studies of electron-beam induced phase transformations in 2D TMDs when electric charge, mechanical strain and vacancies are present. Based on the results of our calculations, we propose an explanation for this phenomenon which is likely promoted by charge redistribution in the TMD monolayer combined with vacancy formation due to electron beam and associated mechanical strain in the sample.

References

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2. T. Björkman et al., ACS Nano 10, 10929 (2016).

3. M. Ghorbani-Asl et al., 2D Materials 4 (2017) 025078.

4. H.-P. Komsa and A.V. Krasheninnikov, Adv. El. Mat. (2017) 1600468.

5. L. Nguyen, et al., ACS Nano 11 (2017) 2894.

6. C. Herbig, et al. Nano Letters (2017) DOI: 10.1021/acs.nanolett.7b00550.

7. S. Kretschmer et al., submitted.

2:40pm **2D+AS+SS-ThA-2 Key Role of Rotated Domains in Oxygen Intercalation at Graphene on Ni(111)**, ***Luca Bignardi,*** *P Lacovig, M Dalmiglio,* Elettra-Sincrotrone Trieste, Italy*; F Orlando,* Paul Scherrer Institut (PSI), Switzerland*; A Ghafari,* Helmholtz-Zentrum Berlin, Germany*; L Petaccia,* Elettra-Sincrotrone Trieste, Italy*; A Baraldi,* University of Trieste, Italy*; R Larciprete,* Istituto dei Sistemi Complessi - CNR, Italy*; S Lizzit,* Elettra-Sincrotrone Trieste, Italy

In this contribution I will provide a description of the oxygen intercalation at the strongly interacting graphene on Ni(111) and of the role of rotated graphene domains in triggering the intercalation. The system was studied by a combination of high-resolution x-ray photoelectron spectroscopy (HR-XPS), photoelectron diffraction (XPD) and angle-resolved photoemission (ARUPS) performed with synchrotron radiation. The HR-XPS measurements provided a full characterization of the interface at each stage of the intercalation, revealing the formation of an oxide layer between graphene and the metal substrate. The ARUPS data showed that the oxide layer efficiently decouples graphene from the substrate, restoring the Dirac cone and providing a slight n-doping. The C1s XPD measurements revealed that the graphene domains not aligned with the Ni substrate are the first to be intercalated with oxygen. At the same time, these domains are also preferential regions under which the oxygen is retained during the deintercalation process.

3:00pm **2D+AS+SS-ThA-3 Atomic Structure of Defect and Dopants in 2D Semiconductor Monolayer MoS_2 and WS_2**, ***Jamie Warner,*** University of Oxford, UK **INVITED**

Defects impact the properties of materials and understanding their atomic structure is critical to their interpretation and behaviour. I will discuss how aberration corrected TEM can be used to resolve the detailed structure of Sulfur vacancies and grain boundaries in CVD grown MoS2 and WS2. I will present our latest results on detecting single Cr and V impurity dopants that substitute Mo and W sites. Electron energy loss spectroscopy is used to map out the spatial position and confirm the contrast profiles from HAADF STEM images. Single Pt atimsnare added to the surface of MoS2 and we study the dynamics of hopping between S vacancies. finally I will discuss in situ observations of Pt nanocrystal formation on MoS2 using high temperature annealing.

4:00pm **2D+AS+SS-ThA-6 Interaction of an Energetic Ar Molecular Cluster Beam with Graphene**, ***Songkil Kim,*** *A Ievlev, J Jakowski, I Vlassiouk, M Burch, C Brown, A Belianinov, B Sumpter, S Jesse, O Ovchinnikova,* Oak Ridge National Laboratory

Manipulation of low dimensional nanomaterials provides intriguing opportunities to design new functional materials as well as to develop next-generation device applications. To manipulate properties of low dimensional nanomaterials, extensive study has been conducted so far for interaction of energetic particles with low dimensional nanomaterials. However, most of the research has been focused on utilizing electron or light/heavy ion beams to study irradiation effects on alternation of structural, mechanical and electrical properties of nanomaterials. In this study, we investigated the effect of Argon molecular cluster beam irradiation on both defect formation and removal of organic contaminants on graphene. An Argon cluster beam was generated using the Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) combined with Atomic Force Microscopy (AFM). The ToF-SIMS allows for conducting in-situ monitoring of defect formation as well as organic contaminants removal. This leads to accomplishments of a high degree of controls over modification of graphene. A systematic study has been conducted to provide in-depth understanding about defect formation of graphene by synergistic theoretical and experimental approaches. Raman spectra clearly indicate that suspended graphene is more susceptible to Ar cluster beam irradiation than supported graphene on a SiO_2/Si substrate under the same irradiation conditions. The underlying mechanisms for the experimentally observed phenomena are demonstrated by theoretical analysis using the first-principles molecular dynamics calculations.

This work was supported by the Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

4:20pm **2D+AS+SS-ThA-7 Efficient and Low-Damage N-doping of Graphene by Nitrogen Late-Afterglow Plasma Treatment**, ***Xavier Glad,*** *G Robert-Bigras, P Levesque, R Martel, L Stafford,* Université de Montréal, Canada

Graphene already shows promises for the next generation of electronics and optoelectronics devices and other applications where a band gap or magnetic response is necessary [1]. The availability of versatile processing techniques is thus crucial to the development of these graphene-based technologies. An ideal and efficient nitrogen doping would precisely tune the N-doping and keep a minimal defect density. In this work, we explore the potential of the late afterglow of a microwave N_2 plasma at reduced pressure (6 Torr) for post-growth tuning of CVD-grown graphene films on copper foils.

A single graphene sample received five subsequent 30-second plasma treatments between which X-Ray photoelectron spectroscopy (XPS) and Raman spectroscopy (RS) were carried out. XPS measurements confirmed a strong N-incorporation increasing with the plasma treatment time (up to N/C = 29%) while RS assessed an uncommonly low damage generation (D/G ratio below 0.4) for such incorporation.

XPS, RS and ultraviolet photoelectron spectroscopy (UPS) were also performed on the sample after transfer to an Si/SiO_2 substrate via the PMMA method [2]. The results show a strong decrease of the N content (N/C = 6%) which is attributed to the desorption of out-of-plane adsorbed N due to the transfer. RS and UPS techniques both support an n-doping which is associated to the different aromatic N-incorporations deconvoluted from the high resolution XPS spectra.

The low ion density ($< 10^7$ cm^{-3}) and the high density of reactive neutral ($> 10^{14}$ cm^{-3}) and metastable species ($> 10^{10}$ cm^{-3}) of the nitrogen late-afterglow in our conditions [3] are believed to be the key of such efficient and low-defect N-incorporation in graphene.

[1] Vashist SK, Luong JH (2015) *Carbon* **84** 519-550.

[2] Suk JW, Kitt A, Magnuson CW *et al.* (2011) *ACS Nano* **5**(9):6916-6924.

[3] Afonso Ferreira J, Stafford L, Leonelli R, Ricard A (2014) *Journal of Applied Physics* **115**(16) 163303.

4:40pm **2D+AS+SS-ThA-8 Exploring the Electronic Signature of Disordered Monolayer MoS_2**, ***Chinedu Ekuma,*** *D Gunlycke,* Naval Research Laboratory

Atomic defects in two-dimensional semiconductors could be used to induce insulator-metal- transitions (IMT), making it possible to have both insulating and metallic behavior in different regions of a single seamless material. Using a first-principles-based many-body typical medium dynamical cluster approach [1], we explore the electronic signature in

monolayer MoS_2 resulting from atomic defects. Analyzing the typical (geometric) density of states, which unlike the arithmetic density of states, is able to discern localized and delocalized states, our calculations show a correlation-mediated IMT at the experimentally relevant sulfur vacancy concentration ~10^{13} cm^{-2}, depending on the strength of the intrinsic electron-electron interactions. We will also discuss the role of atomic defects on the absorption spectra.

[1] C. E. Ekuma, V. Dobrosavljeví c, and D. Gunlycke, Phys. Rev. Lett. 118, 106404 (2017)

Acknowledgements: This work has been funded by the Office of Naval Research (ONR), directly and through the Naval Research Laboratory (NRL). C.E.E. acknowledges support through the NRC Research Associateship Programs.

5:00pm **2D+AS+SS-ThA-9 Heterogeneity in 2D Materials: From Localized Defects, Isoelectronic Doping to Macroscopic Heterostructures**, ***Kai Xiao,*** *X Li, M Mahjouri-Samani, M Lin, L Liang, A Oyedele,* Oak Ridge National Laboratory*; M Tian,* University of Tennessee*; A Puretzky, J Idrobe, M Yoon, B Sumpter,* Oak Ridge National Laboratory*; G Duscher,* University of Tennessee*; C Rouleau, D Geohegan,* Oak Ridge National Laboratory **INVITED**

Two-dimensional (2D) materials are intrinsically heterogeneous, therefore controlling defects, understanding the impact of boundaries and interfaces, and developing means to exploit these heterogeneities is a transformative opportunity that could underpin future technologies and energy applications. This talk will discuss the fundamental understanding of the roles of heterogeneity, atomic interface, and disorder in 2D materials and their heterostructures. Through isoelectronic doping in monolayer of $MoSe_2$, the Se vacancies are effectively suppressed and photoluminescence is significantly enhanced due to the decrease of defect-mediated non-radiative recombination. In addition, we demonstrate the non-equilibrium, bottom-up synthesis of single crystalline monolayers of 2D $MoSe_{2-x}$ with controllable levels of Se vacancies far beyond intrinsic levels. Both substitutional dopants and vacancies were shown to significantly alter the carrier properties and transport characteristics within a single monolayer (e.g., n- to p-type conduction in W-doped $MoSe_2$ and in Se-deficient $MoSe_{2-x}$). The vertical and lateral 2D heterostructures by controlled assembly and doping will be discussed. In addition, the lattice misfit heterostructures of monolayer GaSe/$MoSe_2$ were synthesized by a two-step chemical vapor deposition (CVD) method. We find the vertically stacked GaSe/$MoSe_2$ heterostructures maintain vdW epitaxy with well-aligned lattice orientation between the two layers, forming an incommensurate moiré superlattice. The bottom up synthesis of 2D materials discussed here provides excellent control over the heterogeneity in 2D materials, which can tunably modulate the optical and electrical properties in 2D materials and their heterostructure.

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5:40pm **2D+AS+SS-ThA-11 Evidence of a One-dimensional Metal in Twin-grain Boundaries of $MoSe_2$**, ***Horacio Coy Diaz,*** *M Batzill,* University of South Florida

In monolayer van der Waals-materials, grain boundaries become one-dimensional (1D) line defects. Here we show using angle resolved photoemission spectroscopy (ARPES) that twin-grain boundaries in the 2D semiconductor $MoSe_2$ exhibit parabolic metallic bands. The 1D nature is evident from a charge density wave transition, whose periodicity is given by k_F/p, where the Fermi momentum k_F is determined by ARPES. Most importantly, we provide evidence for spin- and charge-separation, the hallmark of 1D quantum liquids. ARPES shows that the spectral line splits into distinctive spinon and holon excitations whose dispersions exactly follow the energy-momentum dependence calculated by 1D Hubbard model, with suitable finite-range interactions. Our results also imply that quantum wires and junctions can be isolated in line defects in 2D materials, which may enable quantum transport measurements and devices.

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