2D Materials Technical Group
Room C123 - Session 2D-WeM

2D-Materials: Defects, Dopants, and Modifications

Moderators: Jin Myung Kim, University of California, Irvine, **Stuart Parkin**, MPI Halle

8:00am **2D-WeM-1 Developing Quantum Photon Sources from 2D Semiconductor Materials***, **Xuedan Ma**,* Argonne National Laboratory **INVITED**

Optical photons are ubiquitous in quantum communication and storage applications due to their long coherence times and ease to travel over long distances. On-demand quantum photon sources that may emit single photons as quantum information carriers are especially sought after for quantum-related applications. In this talk, I will present our recent effort in the development of solid-state quantum photon sources based on low-dimensional semiconductor materials. By atomic defect creation [1,2] and local strain field engineering,[3-7] we demonstrate versatile approaches for efficient single photon generation and modulation.

References:

[1] W. Wang et al, *ACS Nano*, 16, 21240 (2022)

[2] Q. Qian et al. *ACS Nano*, 16, 7428 (2022)

[3] M. I. B. Utama et al. *Nat. Commun*. 14, 2193 (2023)

[4] X. Li et al. *J. Phys. Chem*. C 126, 20057 (2022)

[5] D. J. Morrow et al. *Phys. Rev. B* 104, 195302 (2021)

[6] W. Wang et al. *ACS Photon*. 7, 2460 (2021)

[7] L. Peng et al. *Nano Lett*. 20, 5866 (2020)

8:40am **2D-WeM-3 Bandgap Modulation of Graphene by Boron Nitride Doping***, **Sergi Campos Jara**,* Leiden University, The Netherlands*; L. Caputo,* Université Catholiqué de Louvain, Belgium*; T. Roorda, T. Benschop, A. Mozes,* Leiden University, The Netherlands*; V. Calvi, R. van Rijn,* Delft University of Technology, Netherlands*; M. P. Allan, I. M.N. Groot,* Leiden University, The Netherlands

Since its discovery, graphene has shown to exhibit remarkable electronic properties.[1] Numerous techniques have been devised to create high-performance devices by manipulating the bandgap in order to enhance their semiconducting properties.[2]

Doping has proven to be one of the most effective methods for bandgap engineering. Experimental and theoretical studies on graphene doping show the possibility of making p-type and n-type semiconducting graphene by substituting C atoms. Boron and nitrogen have been specifically studied during the last years due to the interesting insulating behavior of h-BN. Boron, nitrogen, and carbon can be atomically mixed to form various semiconducting, hexagonal, layered structures. Experimental and theoretical studies have indicated that BNC nanostructures show semiconducting properties with small bandgaps.[2,3] Low concentrations of borazine rings within the graphene structure can modify graphene's electronic properties to form a 2D semiconductor material with homogeneous patterns.[4,5]The intercalation of hexagonal BN (h-BN) within the graphene lattice has already been successfully achieved, however, segregation of both materials has been the main issue. Recent research has demonstrated that incorporating borazine-like molecules with carbon structures into graphene can result in reduced segregation of h-BN domains.[5,6] Herrera Reinoza et al. demonstrated a notable example by depositing hexamethylborazine onto Ir(111), which yielded numerous boron-nitrogen-carbon (BNC) domains exhibiting low BN segregation and an estimated bandgap ranging between 1.4 and 1.6 eV.[6]

To grow our boron nitride-doped graphene nanomaterial (Figure 1a) we first synthesized graphene via chemical vapor deposition (CVD) by cyclic exposures to 10^{-5} mbar of ethylene for 10 minutes with subsequent annealing at 1100 K for 10 minutes. We have successfully doped our graphene by exposing it to hexamethylborazine right after the 3rd cycle of graphene synthesis. Auger electron spectroscopy depicted in Figure 1b demonstrated the presence of B, C and N in the sample. As depicted in Figure 1c, a bandgap was opened on our BN-doped graphene, forming a semiconductor material.

9:00am **2D-WeM-4 Wafer-Scale Photoluminescence Enhancement for MoS_2 Monolayers Through Simple Wet-Chemical Defect Passivation in Acidic Hydrogen Peroxide Solution***, **Dennis H. van Dorp**,* IMEC Belgium*; L. van der Krabben,* Radboud University Nijmegen, Netherlands*; A. Brady-Boyd,* Aberystwyth University, UK*; C. Gort,* TU Darmstadt, Germany*; S. Arnauts, T. Nuytten, H. Medina Silva, E. Altamirano Sanchez,* IMEC Belgium*; J. Hofmann,* TU Darmstadt, Germany*; S. Brems,* IMEC Belgium

It is expected that in the 2030 timeframe, CMOS technology nodes could include not only Si based transistors, but also possible 'Beyond-CMOS' devices that are co-integrated with the classical CMOS-based solutions. The alternative devices could be used along CMOS for specific functions. For instance, devices are being explored that have two-dimensional transition-metal dichalcogenides (2D TMDCs) as their conduction channel.

While device processing strategies for conventional CMOS technologies are well established, the use of TMDCs as atomic channel material poses new problems. In such applications, both dry and wet etching are essential processing steps for nanodevice fabrication, e.g. for patterning, contacting, layer selective etching, and surface engineering purposes. In contrast to dry etching, that may induce surface damage in the form of chalcogenide vacancies, wet-chemical methods provide an attractive alternative that avoids the problem of surface damage. However, the atomic scale dimensions of the 2D layer require ultimate selectivity and control to maintain and or improve the electronic and optical properties at wafer-scale level. To meet these goals, in-depth insight is needed in the compatibility of TMDC's with wet-chemical solutions.

In this work, we will show the first semiconductor ICP-MS results on the atomic-scale etching kinetics of MoS_2 in acidic solutions. Despite the very small dimensions of TMDC atomic layers, a surprisingly high chemical stability is demonstrated for both multilayer and monolayer MoS_2. Controlled wet etching of the layers was achieved for dilute HCl/H_2O_2 solutions without significantly modifying the surface chemistry. In addition, it was found that wet-chemical treatment of MoS_2 can dramatically enhance the photoluminescence properties on wafer-scale level using simple acidic solutions that contain a strong oxidizing agent.

We will show that wet-chemical processing can be utilized to significantly lower defect related non-radiative decay in the monolayers through passivation of sulphur vacancies. Room temperature PL measurements were used to optimize the passivation step. PL enhancements of up to 3 orders of magnitude were consistently achieved. Wafer-scale PL mapping showed good uniformity across the 2-inch wafer. Cryo-PL measurements confirmed effective defect passivation through the quenching of the bound exciton peaks.

The data presented indicate a good wet-chemical compatibility of the atomic layer TDMC material which is highly relevant for future developments in the CMOS industry.

9:20am **2D-WeM-5 Metal-to-Semiconductor Transition Observed in the Surface Density of States of Ti-Te Layered Monoclinic Crystals via Forced Atmospheric Exposure***, **Bishal Pokhrel**, J. Quarnstrom, S. Shrestha, H. Helfrich, E. Echeverria, D. McIlroy, M. Borunda, A. Yost,* Oklahoma State University

Transition metal chalcogenides are promising 2D materials due to their unique properties and emerging phenomena such as charge density waves, superconductivity, ferroelectricity and ferromagnetism. Specifically the transition metal trichalcogenides of the form AX_3 (A=Ti, Zr, Hf, X=S, Se, Te) exhibit a quasi 1-D nature with anisotropic bandstructure which leads to preferential charge transport along the chain direction and minimal edge scattering effects suitable for fabricating high-performance devices. In this study, we examine the surface sensitivity of a high pressure grown Ti-Te transition metal chalcogenide using the chemical vapor transport (CVT) technique and study the surface changes in the sample upon exposure to air. The high-pressure growth results in the formation of silvery mirror-like sheets and nanowhiskers atypical of bulk 1T-$TiTe_2$ growth, which is usually black and non-reflective. The silvery materials are capable of mechanical

exfoliation via the scotch tape method and if left in atmosphere turn a darker color within a few hours. The crystal structure and size of the sheets are examined using X-Ray Diffraction (XRD), transmission electron microscopy (TEM), and select area electron diffraction (SAED). The material adopts a preferential (001) single crystalline nature with monoclinic structure and P2 1/m space group symmetry. Additionally, the SAED patterns show signs of a superlattice formation at the surface of the exposed layer. The local density of states (LDOS) of the in-situ exfoliated sample surface, measured using scanning tunneling spectroscopy (STS), exhibits a metallic to semi-conducting transition, with narrow gap, when exposed to atmosphere, suggesting the surface rapidly decomposes. The STM topography indicates a decrease in surface roughness after exposure to atmosphere reminiscent of ad-layer/s formation at the surface. X-ray photoemission spectroscopy confirms the surface of the exposed sample contains -OH, O_2, -H, H_2O ad-atom species. Stability and reactivity of such layered materials has been a field of interest to researchers lately as these materials have the ability for extreme sensitivity when incorporated into a gas sensor device. In the interest of optical and gas sensing we fabricate simple FET devices and measure the opto-electronic properties while exposing to different wavelengths of light and gases (CO_2, H_2, H_2O, and N_2).

9:40am **2D-WeM-6 Correlated KPFM and TERS Imaging to Elucidate Defect-induced Inhomogeneities in Oxygen Plasma Treated 2D MoS_2 Nanosheets**, ***Sanju Gupta***, Penn State University

Modulating physical and chemical properties of two-dimensional (2D) transition metal dichalcogenides (TMDC) by defect-engineering induced by oxygen plasma is actively pursued. In this work, exfoliated 2D MoS_2 layers treated by medium power oxygen plasma for different times (0, 10, 20, 40, and 60 s) are investigated using Kelvin Probe Force microscopy and tip-enhanced Raman spectroscopy (TERS) besides micro-Raman and photoluminescence (PL) spectroscopy. Under oxygen plasma, defects (mono- and di-sulfur vacancies) and chemical oxidation is predominant from 0s (native defects) up to 40s, while etching becomes dominant beyond 40 s, for mono- (1L), bi- (2L), and tri- (3L) layer MoS_2 with optimal defect density for four- (4L) and more layers. While Raman spectra exhibited lattice distortion (broadening of phonon bands) and surface oxidation by the presence of sub-stoichiometric molytrioxide MoO_3 (*i.e.,* MoO_{3-x} or MoS_xO_{2-x}) the increased spectral weight of trions and quenching in PL spectra are observed with treatment time. The localized nanodomains (~20-40 nm) and aggregated vacancies as nanovoids and intermixed MoS_2/MoO_{3-x} alloy are identified in near-field Raman spectra. The atomic force microscopy also showed defects aggregation and Kelvin probe force microscopy revealed the work function (WF) increase from 4.98 eV to 5.56 eV, corroborating the existence of MoO_{3-x} phase which enables doping and shift Fermi level. We also highlight the unique interaction between the gold substrate and the formed MoO_{3-x} facilitating Mo^{6+} cation reduction to lower oxidation (*i.e.*, Mo^{4+}) thereby yielding intermediate oxidation states responsible for lower WF (*ca.* theoretical 6.3 eV for stoichiometric MoO_3). Strong correlations among the work function, vibrational and optical responses are established while exploring the oxygen plasma-induced defects and changing the landscape on oxygen doping at the nanoscale with varying MoS_2 layers, which are useful for heterogeneous electrocatalysis and applicable to other 2D TMDCs.[1]

[1]S. Gupta, A. Johnston, and S. Khondaker, J. Appl. Phys. **131**, 164303 (2022) and references therein.

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11:00am **2D-WeM-10 Imaging Carrier Motion in Graphene Using Scanning Tunneling Potentiometry**, *V. Brar,* ***Zachary Krebs***, University of Wisconsin - Madison **INVITED**

In this talk I will show how scanning tunneling potentiometry (STP) can be used to directly image the motion of charge carriers in graphene, revealing the manner that they scatter off defects, pass through potential barriers, and generate Hall voltages. In the ballistic regime, STP imaging allows for the semi-classical motion of graphene quasiparticles to be visualized over large lengthscales, and for their incoming/scattered wavefunctions to be imaged locally. Near potential barriers, this allows for the direct observation of Landauer residual resistivity dipoles and scattering processes involving quasibound states. When magnetic fields are applied, the carriers generate a Hall field that can be quantified using STM, and near potential barriers they are observed to take a spiral-like trajectory in low fields, and form bound states around the potentials in the quantum hall regime. We also probe the carrier motion as the graphene is heated and the electrons enter a hydrodynamic phase. In this regime, STP can be used to image the new fluid-like flow patterns of the electrons and quantify how those new flow properties reduce the macroscopic resistivity of the sample.

11:40am **2D-WeM-12 Interfacial Design of 2D Materials for Energy-Efficient Nanoelectronics**, ***Huamin Li***, University at Buffalo

With the rise of graphene (Gr) since 2004, two-dimensional (2D) have been extensively explored for energy-efficient nanoelectronics due to their novel charge transport properties compared to conventional three-dimensional (3D) bulk materials. However, there are still challenges and issues for the practical implementation of 2D materials. Here from the perspective of interfacial design, we take 2D semiconducting MoS2 as an example to review our recent research on energy-efficient nanoelectronics, ranging from synthesis, metal contact, and device demonstration. First, at the interface between MoS2 and substrates, an interfacial tension can be induced during high-temperature chemical vapor deposition (CVD) synthesis. Due to a mismatch of thermal expansion coefficients, the interfacial tension creates an anisotropy of in-plane charge transport and leads to a self-formed nanoscroll structure [DRC 2019]. Second, at the interface between MoS2 and metal contact, a monolayer h-BN decoration can enable novel manipulation of charge transport through quantum tunneling, in contrast with conventional thermionic emission [IEEE NMDC 2018; Adv. Mater. 2019]. Third, at the interface between MoS2 and other 2D materials, band-to-band Zener tunneling and cold-source charge injection can be enabled, giving rise to a superior transport factor (<60 meV/decade) in transistor configurations. These novel charge transport can overcome the fundamental limitations of “Boltzmann tyranny”, and realize tunnel transistors and cold-source transistors with sub-60-mV/decade subthreshold swings [IEEE IEDM 2020; ACS Nano 2020]. Fourth, at the interface between MoS2 and ferroelectric or ionic dielectrics, excellent electrostatic gating leads to a superior body factor (<=1), and also improves the energy efficiency for transistor operation [Nano Express 2023].

12:00pm **2D-WeM-13 Substrate Van Der Waals Force Effect on the Stability of Violet Phosphorous**, ***Sarabpreet Singh***, University of Georgia*; M. GhafariAsl,* University of georgia*; H. Ko,* Cornell University*; S. Gamage,* University of Georgia*; R. Distasio Jr.,* Cornell University*; M. Snure,* Air Force Research Laboratory*; Y. Abate,* University of Georgia

The weak van der Waals (vdWs) forces between monolayers has been a unique distinguishing feature of exfoliable materials since the first isolation of graphene. However, the vdWs interaction of exfoliable materials with the substrate and how this interface force influences the interaction of vdWs materials with the surroundings have yet to be well understood. Here, we experimentally and theoretically unravel the role of vdWs forces between the recently rediscovered wide band gap p-type vdW semiconductor violet phosphorus (VP), with various substrates (including, SiO_2, mica, Si, Au) and quantify how VP stability in air and its interaction with its surroundings is influenced by the interface force. Using a combination of infrared nanoimaging and theoretical modeling we find the vdWs force at the interface to be a main factor that influences how VP interacts with its surroundings. In addition, the hydrophobicity of the substrate and the substrate surface roughness modify the vdWs force there by influencing VP’s stability. We found that VP can maintain its stability for a prolonged period if it is exfoliated on SiO_2 substrate, followed by mica and Au substrates, and is least stable when placed on a Si substrate. Our results could guide in the selection of substrates when vdW materials are prepared and more generally highlight the key role of interface force effects that could significantly alter physical properties of vdWs materials. Our findings can assist in the choice of substrates to exfoliate vdWs materials and emphasize the crucial impact that interface forces can have on altering the physical properties of exfoliable materials.

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