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

2D-Materials: Microscopy

Moderator: David Cobden, University of Washington

8:00am **2D-ThM-1 In and Ex Situ (S)TEM Manipulation of 2D Materials**, *J. Kotakoski,* ***Harriet Åhlgren,*** University of Vienna, Austria **INVITED**

Heteroatom implantation in 2D materials requires a delicate balance between being able to displace atoms from the target material while at same time stopping the incoming ion [1]. An additional problem is imposed by momentum and energy conservation, which fundamentally limits ion implantation of graphene to elements between Li and Ti. Nevertheless, some success has been made for light elements [2,3,4]. Unfortunately, even in the case of successful implantation, the samples suffer from surface contamination. Here, we describe how all of these issues can be overcome combining vacancy-mediated heteroatom implantation [5,6] with efficient sample cleaning [7] in a vacuum system shared with an atomic-resolution scanning transmission electron microscope [7].

References

1. Phys. Rev. B 83, 115424 (2011)
2. Nano Lett. 13, 4902 (2013)
3. 2D Mater. 4, 021013 (2017)
4. ACS Nano 12, 4641 (2018)
5. J. Phys. Chem. C 123, 13136-13140 (2019)
6. 2D Mater. 9, 025011 (2022)
7. Nano Lett. 21, 5179-5185 (2021)

8:40am **2D-ThM-3 Synthesis of Quantum-Confined Borophene Nanoribbons**, ***Qiucheng Li***, *M. Hersam,* Northwestern University

Borophene refers to synthetic two-dimensional (2D) boron, which has attracted significant attention due to its anisotropic metallicity, correlated electron phenomena, and diverse superlattice structures.[1]Reducing the dimensionality of nanomaterials imposes additional quantum confinement effects that unlock new physical phenomena, such as one-dimensional (1D) confined plasmons, spin-polarized edge states, and Luttinger liquid behavior. However, the realization of quantum-confined borophene nanoribbons (BNRs) is hampered by limited boron precursor optionsfor bottom-up synthesis. In this work, we present a substrate mediation strategy to synthesize quantum-confined BNRs onvicinal Ag(977) substrates. The resulting BNRs inherit thehigh degree of polymorphism present in borophene, resulting in $v_{1/5}$ and $v_{1/6}$-BNR lattice configurations in addition to phase intermixing.[2]Through atomic-scale imaging, spectroscopy, and first principles calculations, the edge structures of BNR polymorphs are shown to possess reconstructed armchair edges for $v_{1/6}$-BNRs and sawtooth zigzag edges for $v_{1/5}$-BNRs. The confined electron wave functions in 1D BNRs lead to the observation of energy level quantization and spatial nodes characteristic of quantum-well states.

Acknowledgement:

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References:

[1] Mannix, A. J., *et al.*, Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs. *Science*, **2015**, *350* (6267), 1513-1516.

[2] Liu, X., *et al.*, Intermixing and periodic self-assembly of borophene line defects. *Nature Materials*, **2018**, *17* (9), 783-788.

9:00am **2D-ThM-4 Formation of Multilayer Bismuthene on Hexagonal Manganese Nitride**, ***Ashok Shrestha***, *A. Abbas, A. Smith,* Ohio University

Bismuthene, a two-dimensional (2D) topological material, has attracted considerable attention due to its large bandgap compared to other 2D topological materials [1]. The structure and electronic properties of the single layer bismuthene have been studied by many authors [2, 3], but the growth, structure, and electronic properties of multilayer bismuthene have not yet been reported. We have successfully grown the multilayer of bismuthene on the hexagonal ζ- phase Mn_2N surface using molecular beam epitaxy.

In this presentation, we will briefly discuss the growth of the thin layer of ζ-phase Mn_2N in the first part, and the formation of a multilayer of bismuthene in the second part. Initially, the Mn_2N film is prepared on MgO (001) substrate under nitrogen-rich conditions at 510 ^oC. The correct phase of Mn_2N is confirmed using various *in-situ* techniques such as reflection high energy electron diffraction, scanning tunneling microscopy, and Auger electron spectroscopy. Once a high-quality Mn_2N surface is achieved, an ultra-thin layer of bismuth is deposited on its top at 150 ^oC.

The STM investigations reveal atomically flat multiple terraces and steps of bismuthene with a step height of 1.60 Å, which agrees well with the height of bismuthene reported by Sun *et al.* (2022) [2], although the atomic resolution STM image shows the nearly rectangular structure. Some other interesting features of bismuthene, such as “quantum islands”, are also observed. The *ex-situ* X-ray diffraction clearly shows the Bi 0002 peak, giving an interplanar spacing of 3.20 Å. This measurement is consistent with twice the step height observed in the STM image. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-06ER46317.

References:

[1] F. Reis, G. Li, L. Dudy, M. Bauernfeind, S. Glass, W. Hanke, R. Thomale, J. Schafer, R. Claessen, Science **357**, 287-290 (2017).

[2] S. Sun, J. Yang, S. Duan, J. Chen, and W. Chen, ACS Nano **16**, 1463-1443 (2022).

[3] J. Gou, K. Longjuan, H. Xiaoyue, Y. L. Haung, J. Sun, S. Meng, K. Wu, L. Chen, A. S. Wee, Sci. Adv. **6**, eaba2773 (2020).

9:20am **2D-ThM-5 A Combined NAP-XPS and NAP-STM Study on 2D MoS_2-based Catalysts for Hydrodeoxygenation of Organic Feedstocks**, ***Lars Mohrhusen***, *M. Hedevang, J. Lauritsen,* Aarhus University, Denmark

For the technological utilization of sustainable feedstocks such as pyrolysis oils from biomass, oxygen removal via hydrodeoxygenation (HDO) is one of the most essential steps.[1] Metal-promoted MoS_2-based catalysts are well-established for hydrode-sulphurization (HDS) of crude oil components, and thus a promising material for HDO catalysts.[2-4] This is already proven technology for simple feedstocks such as vegetable oils, but more complex compounds with high oxygen content and multiple oxygen functionalities such as bio-oils remain challenging, and thus gain increasing interest.

In contrast to the established use in (virtually oxygen free) HDS, the sulphide catalyst will be exposed to water or organic oxygenates in the herein desired HDO process. Thus, in the presence of oxygen, sulphur atoms may be partially exchanged. Thereby, active sites can become blocked, which triggers strong catalyst degradation on the long term. [5,6]

To gain an atomistic understanding of such processes, herein two-dimensional MoS_2 particles on Au (111) surfaces exposed to H_2 and/or oxygenate containing atmospheres were investigated combining microscopic (scanning tunneling microscopy (STM), see fig. 1) and spectroscopic insights (photoelectron spectroscopy (XPS)) under various conditions mimicking HDO from UHV level to the near-ambient-pressure regime (few mbar, NAP-STM, NAP-XPS).

9:40am **2D-ThM-6 NanoFrazor Technology - Fabricating Advanced 2D and Grayscale Structures for 2D Materials Using Thermal Scanning Probe Lithography and Direct Laser Sublimation**, ***Nicholas Hendricks***, *A. Ubezio, M. Käppeli, J. Vergés, J. Chaaban, E. Çağin,* Heidelberg Instruments Nano, Switzerland

Thermal scanning probe lithography (t-SPL), enabled by the NanoFrazor technology, is establishing itself as a mature and reliable direct-write nanolithography technique for generating nanoscale structures [1-4]. The NanoFrazor technology offers an alternative or complementary process for conventional lithography techniques of electron-beam lithography (EBL) or focused-ion beam (FIB). t-SPL generates patterns by scanning an ultrasharp tip over a sample surface to induce local changes with a thermal stimulus. By using thermal energy as the stimulus, it is possible to perform various modifications to the sample via removal, conversion, or addition of/to the sample surface. Along with an ultrasharp tip, the t-SPL cantilever contains several other important functions such as an integrated thermal height sensor and an integrated heating element both of which are advantageous for fabricating devices for nanoelectronics, photonics, molecular sensing, and quantum computing.

To complement the sub-100 nm patterning capabilities of t-SPL, a direct laser sublimation (DLS) module has been incorporated into the NanoFrazor platform. The DLS module allows for increased throughput by patterning larger structures, e.g. > 500 nm, with a continuous wave (CW) laser operating at a wavelength of 405 nm. Over the last several years, further developments of the NanoFrazor technology have been realized that are

enhancing the application space of nanofabrication. Such developments include the integration of the t-SPL and DLS modules into gloveboxes, active field stitching to allow seamless large area patterning with both t-SPL and DLS, and automated overlay to allow for precise nano and micropatterning on top of pre-existing structures.

Within this presentation, the background and workings of t-SPL will be introduced as well as the nanolithography and processing capabilities of both t-SPL and DLS will be presented, with a focus on patterning on topography. A workflow for detecting and correcting intentional topography (flakes of 2D materials, pre-patterned contacts, nanowires), and unintentional defects (impurities, folds in 2D material flakes) will be introduced. Device performance examples achieved using the damage-free lithography techniques will be included, in order to provide a comparison between conventional and novel nanolithography methods.

[1] S. Howell et al., Microsystems & Nanoengineering, 6, 21 (2020); [2] N. Lassaline et al., Nature, 582, 506-510 (2020); [3] X. Liu et al., APL Materials, 9, 011107 (2021); [4] M. Giordano et al., Advanced Material Interfaces, 10, 2201408 (2023)

11:00am **2D-ThM-10 Phase Transformations in 2D Van der Waals Materials: Insights from Cryogenic Atomic Resolution STEM and EELS**, ***Miaofang Chi,*** Oak Ridge National Laboratory **INVITED**

Two-dimensional (2D) van der Waals (vdW) materials and their heterostructures offer a remarkable platform for investigating intriguing physical phenomena and implementing diverse applications. A key advantage of these materials is their tunable quantum behavior, which varies with the number of layers. Notably, samples with different thicknesses, particularly in the range from monolayer to several nanometers, exhibit distinct and exotic properties such as magnetism, electronics, and optoelectronics. While it is recognized that lattice structural transformations often accompany changes in electronic and spin structures, leading to the emergence of exotic quantum phenomena, it remains uncertain whether the same structural transformations observed in bulk materials occur in thin flake samples. Consequently, a comprehensive understanding of the structure-property relationship in several-layer thick 2D vdW materials is often lacking. In this presentation, we unveil the thickness-dependent phase transformation and exciton state changes in several model 2D vdW materials using cryogenic atomic resolution scanning transmission electron microscopy (STEM) and monochromated electron energy loss spectroscopy (EELS). Through our findings, we provide precise insights into the layer-number-dependent properties that are crucial for harnessing the unique quantum characteristics of thin layer 2D vdW materials for device applications.

11:40am **2D-ThM-12 Intercalation of Transition Metals in between Bilayer-VSe2**, *V. Pathirage, K. Lasek, S. Lisenkov,* University of South Florida*; I. Ponomareva,* University South Florida*; **Matthias Batzill,*** University of South Florida

Modifications of transition metal dichalcogenides (TMD) can be achieved by metal insertion into the van der Waals gap. Those metals covalently bond to the chalcogen atoms and thus form a 3D crystal structure. For ultrathin TMD films, however, insertion of excess metals will result in pseudo-2D nanolayers that may be incorporated with other van der Waals materials. In this talk we discuss modifications of bilayer VSe_2 by insertion of different transition metals (V, Cr, Mn) to modify its magnetic properties. The excess transition metals are inserted by sequential vapor deposition onto the VSe2 bilayer film. DFT simulations indicate that excess metals diffuse readily through the VSe2 layer to occupy energetically favorable inter-layer sites. Different ordered arrangements of excess metals are obtained with a maximum occupation close to half a monolayer (here one monolayer refers to the amount of metal atoms in a TMD layer). The ordering of the inserted atoms is probed by scanning tunneling microscopy. Magnetic properties are identified by x-ray magnetic circular dichroism studies and show strong magnetic moments on dilute inserted Cr or Mn atoms. However, as ordered superstructures are formed the measured average magnetic moment per atom decreases, possibly suggesting antiferromagnetic order in the insertion layer.

12:00pm **2D-ThM-13 Atomically Resolved Imaging of CVD-Grown Thin α-Mo_2C Crystals**, ***Saima Sumaiya,*** Columbia University*; I. Demiroglu,* Eskisehir Technical University, Turkey*; O. Caylan, G. Buke,* TOBB University of Economics and Technology, Turkey*; C. Sevik,* Eskisehir Technical University, Turkey*; M. Baykara,* University of California Merced

Transition metal carbides (TMCs) have been used in bulk form in a variety of applications for decades due to their attractive mechanical and chemical properties. With the advent of nanotechnology, there is renewed interest in synthesizing these materials in thin form, with precise control of thickness for potential applications in fields such as energy storage and electromagnetic shielding. Consequently, it is of utmost importance to investigate the quality of these materials in terms of the presence of defects and their influence on properties, down to the atomic scale. Here, we present an atomic-resolution investigation of defects on thin crystals of molybdenum carbide (α-Mo_2C) grown via chemical vapor deposition (CVD), by way of conductive atomic force microscopy (C-AFM) measurements under ambient conditions. In particular, we observe a periodic modulation in the surface conductivity landscape with a periodicity that is ~5 times higher than the periodicity of the atomic lattice of the (100) surface. It is additionally observed that this electronic super-structure is rotationally misaligned with the underlying atomic lattice. Atomic-resolution imaging additionally reveals the presence of defects on the crystals, with a defect density that is similar to that reported for natural two-dimensional transitional metal dichalcogenides. We characterize defects based on the type (enhancement / attenuation) and spatial extent (compact / extended) of the effect they have on the conductivity landscape of the crystal surfaces. While some have localized influence on conductivity over several unit cells, other defects extend over ten nanometers and more. In addition to surface defects, we are also able to quantify the influence of defects that are present sub-surface. *Ab initio* calculations performed by way of density functional theory (DFT) are employed to gather clues about the identity of the defects. The findings presented here provide insights for defect engineering aimed at achieving tailored electronic properties of TMCs in thin form.

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