Epitaxy of 2D Chalcogenides (Epi2DC)

External User Publications (Epi2DC)

G. Kim, H.M. Kim, P. Kumar, M. Rahaman, C.E. Stevens, J. Jeon, K. Jo, K.-H. Kim, N. Trainor, H. Zhu, B.-H. Sohn, E.A. Stach, J.R. Hendrickson, N.R. Glavin, J. Suh, **J.M. Redwing**, D. Jariwala, "High-Density, Localized Quantum Emitters in Strained 2D Semiconductors" *ACS Nano* (2022). 10.1021/acsnano.2c02974.
This study demonstrates a bottom-up, scalable, and lithography-free approach for creating large areas of localized emitters with high density (~150 emitters/um^2) in a WSe_2 monolayer. This approach of using a metal nanoparticle array to generate a high density of strained quantum emitters will be applied to scalable, tunable, and versatile quantum light sources. WSe_2 use in this study was grown using the 2DCC MOCVD1 equipment.

- External User Project S0065

A. Basiri, M.Z.E. Rafique, J. Bai, S. Choi, Y. Yao, "Ultrafast Low-pump Fluence All-optical Modulation Based on Graphene-metal Hybrid Metasurfaces," *Light: Science and Applications* 11, 102 (2022). 10.1038/s41377-022-00787-8.
All-optical graphene modulators reported so far require high pump fluence due to the ultrashort photo-carrier lifetime and limited absorption in graphene. This study presents modulator designs based on graphene-metal hybrid plasmonic metasurfaces with highly enhanced light-graphene interaction in the nanoscale hot spots at pump and probe (signal) wavelengths. The proposed designs hold the promise to address the challenges in the realization of ultrafast all-optical modulators for mid-and far-infrared wavelengths. The 2DCC contributed graphene using faculty equipment.

- External User Project S0036

M.H. Alam, S. Chowdhury, A. Roy, X. Wu, R. Ge, M.A. Rodder, J. Chen, Y. Lu, C. Stern, L. Houben, R. Chrostowski, S.R. Burlison, S.J. Yang, M.I. Serna, A. Dodabalapur, F. Mangolini, D. Naveh, J.C. Lee, S.K. Banerjee, J.H. Warner, D. Akinwande, "Wafer-Scalable Single-Layer Amorphous Molybdenum Trioxide," *ACS Nano* 16 (3), 3756-3767 (2022). 10.1021/acsnano.1c07705.
Molybdenum trioxide (MoO_3), an important transition metal oxide (TMO), has been extensively investigated over the past few decades due to its potential in existing and emerging technologies, including catalysis, energy and data storage, electrochromic devices, and sensors. This study demonstrates a facile route to obtain wafer-scale monolayer amorphous MoO_3 using 2D MoS_2 as a starting material, followed by UV–ozone oxidation at a substrate temperature as low as 120 °C. This simple yet effective process yields smooth, continuous, uniform, and stable monolayer oxide with wafer-scale homogeneity, as confirmed by several characterization techniques, including atomic force microscopy, numerous spectroscopy methods, and scanning transmission electron microscopy. The 2DCC contributed materials in this study from MIP equipment MOCVD1.

- External User Project S0047

O.O Ayodele, S. Pourianejad, A. Trofe, A. Prokofjevs, T. Ignatova, "Application of Soxhlet Extractor for Ultra-clean Graphene Transfer," *ACS Omega* 7 (8), 7297-7303 (2022). 10.1021/acsomega.1c07113.

This study reports a simple, economical, and highly efficient approach for obtaining pristine graphene on a suitable substrate (e.g., SiO_2/Si) by utilizing Soxhlet extraction apparatus for delicate removal of the polymer with a freshly distilled ultrapure solvent (acetone) in a continuous fashion. Excellent structural and morphological qualities of the material thus produced were confirmed using optical microscopy, atomic force microscopy, scanning electron microscopy, and Raman spectroscopy. Compared to the conventional protocol, graphene produced by the current approach has a lower residual polymer content, leading to a root mean square roughness of only 1.26 nm. Graphene materials provided in this study were created using non-MIP faculty equipment.

- External User Project R0062 (Non-R1)

T. Ignatova, S. Pourianejad, X. Li, K. Schmidt, F. Aryeetey, S. Aravamudhan, *S.V. Rotkin*, "Multidimensional Imaging Reveals Mechanisms Controlling Multimodal Label-Free Biosensing in Vertical 2DM-Heterostructures," *ACS Nano* 16 (2), 2598-2607 (2022). 10.1021/acsnano.1c09335.
In this work, a multidimensional optical imaging technique is developed in order to map subdiffractional distributions for doping and strain and understand the role of those for modulation of the electronic properties of the material. As an example, vertical heterostructures comprised of monolayer graphene and single-layer flakes of transition metal dichalcogenide MoS_2 were fabricated and used for biosensing. The 2DCC contributed materials for this study using the MIP equipment MOCVD1.

- External User Project Collaboration between S0016 (Non-R1) and S0034 (Non-R1, MSI/HBCU)

P. Kumar, J. Lynch, B. Song, H. Ling, F. Barrera, K. Kisslinger, H. Zhang, S.B. Anantharaman, J. Digani, H. Zhu, **T.H. Choudhury**, C. McAleese, X. Wang, B.R. Conran, O. Whear, M.J. Motala, M. Snure, C. Muratore, **J.M. Redwing**, N.R. Glavin, E.A. Stach, A.R. Davoyan, D. Jariwala, "Light–matter coupling in large-area van der Waals superlattices," *Nature Nanotechnology* 17, 182-189 (2021). 10.1038/s41565-021-01023-x.
This study presents optical dispersion engineering in a superlattice structure comprising alternating layers of 2D excitonic chalcogenides and dielectric insulators. By carefully designing the unit cell parameters, we demonstrate greater than 90% narrow band absorption in less than 4 nm of active layer excitonic absorber medium at room temperature, concurrently with enhanced photoluminescence in square-centimeter samples. These superlattices show evidence of strong light–matter coupling and exciton–polariton formation with geometry-tuneable coupling constants. The results demonstrate proof of concept structures with engineered optical properties and pave the way for a broad class of scalable, designer optical metamaterials from atomically thin layers. Materials in this study were provided by the 2DCC using MIP equipment MOCVD1.

- External User Project Collaboration among S0065, S0070 and S0077 (Industry)

X. Chen, **B. Huet**, **T.H. Choudhury**, **J.M. Redwing**, T.-M. Lu, G.-C. Wang, "Orientation domain dispersions in wafer scale epitaxial monolayer WSe_2 on sapphire," *Applied Surface Science* 567, 150798 (2021). 10.1016/j.apsusc.2021.150798.

Azimuthal reflection high-energy electron diffraction (ARHEED) is demonstrated to be a powerful technique to measure the symmetry, lattice constants, and in-plane orientation domain dispersion in wafer-scale, continuous monolayer WSe_2 epitaxially grown by metal organic chemical vapor deposition on c-plane sapphire substrate. The constructed 2D reciprocal map from ARHEED reveals few degrees' dispersion in WSe_2 orientation domains due to the step meandering/bunching/mosaic of sapphire substrate. Minor 30° orientation domains are also observed. The methodology can be applied to study other TMDCs epitaxial monolayers, graphene, and confined atomically thin hetero-epitaxial metals. Materials in this study were provided by the 2DCC using MIP equipment MOCVD1.

- External User Project S0048

H. Kim, K. Lu, Y. Liu, H.S. Kum, K.S. Kim, K. Qiao, S.-H. Bae, S. Lee, Y.J. Ji, K.H. Kim, H. Paik, S. Xie, H. Shin, C. Choi, J.H. Lee, C. Dong, **J.A. Robinson**, J.-H. Lee, J.-H. Ahn, G.Y. Yeom, D.G. Schlom, J. Kim, "Impact of 2D-3D Heterointerface on Remote Epitaxial Interaction through Graphene," *ACS Nano* 15 (6), 10587-10596 (2021). 10.1021/acsnano.1c03296.
This study unveils the respective roles and impacts of the substrate material, graphene, substrate–graphene interface, and epitaxial material for electrostatic coupling of these materials, which governs cohesive ordering and can lead to single-crystal epitaxy in the overlying film. Results demonstrate that simply coating a graphene layer on wafers does not guarantee successful implementation of remote epitaxy, since atomically precise control of the graphene-coated interface is required and provides key considerations for maximizing the remote electrostatic interaction between the substrate and adatoms. This was enabled by exploring various material systems and processing conditions, and we demonstrate that the rules of remote epitaxy vary significantly depending on the ionicity of material systems as well as the graphene–substrate interface and the epitaxy environment. The 2DCC provided graphene through use of faculty equipment.

- External User Project S0097

F. Aryeetey, S. Pourianejad, K. Nowlin, T. Ignatova, S. Aravamudhan, "Bandgap recovery of monolayer MoS_2 using defect engineering and chemical doping," *RSC Advances* 11 (34), 20893-20898 (2021). 10.1039/D1RA02888J.
This paper reports on the successful growth and modification of monolayer MoS_2 (1L MoS_2) by controlling carrier concentration and manipulating bandgap in order to improve the efficiency of light emission. Atomic size MoS_2 vacancies were created using a Helium Ion Microscope, then the defect sites were doped with 2,3,5,6-tetrafluro7,7,8,8-tetracyanoquinodimethane (F4TCNQ). The carrier concentration in intrinsic (as-grown) and engineered 1L MoS_2 was calculated using Mass Action model. The results are in a good agreement with Raman and photoluminescence spectroscopy as well as Kelvin probe force microscopy characterizations. The 2DCC provided MoS_2 materials in this study synthesized by MIP equipment MOCVD1.

- External User Collaboration S0016 (Non-R1) and S0034 (Non-R1, MSI/HBCU)

M. Hilse, X. Wang, P. Killea, F. Peiris, **R. Engel-Herbert**, "Spectroscopic ellipsometry as an in-situ monitoring tool for Bi2Se3 films grown by molecular beam epitaxy," *Journal of Crystal Growth* 566-567, 126177 (2021). 10.1016/j.jcrysgro.2021.126177.

In-operando spectroscopic ellipsometry used in this study enabled determining the dielectric function of substrate and growing film unobscured by surface or interface reactions. Its sensitivity to sample temperature and film thickness variations allows determining growth temperature, absolute film thickness, and growth rate in real time, rendering it a reliable and universal approach for a direct comparison of growth conditions between different growth campaigns, thus offering the potential to improve reproducibility of the growth conditions for Bi_2Se_3 based films and heterostructures. Materials in this study were synthesized using the 2DCC MIP equipment MBE2 and its onboard spectroscopic ellipsometer.

- External User Project S0013 (non-R1, PUI)

J. Li, J. Wang, X. Zhang, C. Elias, G. Ye, D. Evans, G. Eda, **J.M. Redwing**, G. Cassabois, B. Gil, P. Valvin, R. He, B. Liu, J.H. Edgar, "Hexagonal Boron Nitride Crystal Growth from Iron, a Single Component Flux," *ACS Nano* 15 (4), 7032-7039 (2021). 10.1021/acsnano.1c00115.

This paper reports on the synthesis of hexagonal boron nitride bulk crystal at room temperature using a single component iron flux which is simpler and more cost effective than current multi-component flux processes. A low nucleation density for WSe_2 was observed on the hBN surface indicating a low defect density. The hBN exhibits excellent structural and electrical properties. (WSe_2 growth by MIP equipment MOCVD1 was carried out in the 2DCC facility.)

- External User Project S0087

E. Thompson, E. Manzella, E. Murray, M. Pelletier, J. Stuligross, B.C. Daly, **S.H. Lee**, **R. Redwing**, "Picosecond laser ultrasonic measurements of interlayer elastic properties of 2H-$MoSe_2$ and 2H-WSe_2," *Materials Today Chemistry* 18, 100369 (2020). 10.1016/j.mtchem.2020.100369.

This project explored the use of pump-probe measurements to study the interlayer elastic properties of TMD flakes exfoliated from bulk crystals. Undergraduate students from Vassar College (external user) received training and worked on-site at the 2DCC facility during the summer to synthesize and characterize TMD films which were used during the academic year to carry out the ultrasonic measurements in the lab at Vassar College. Five of the co-authors including the first author are undergraduate students as Vassar.

- Also Science Driver AdvCM
- External User Project R0027 (non-R1, PUI)

G.G. Jernigan, J.J. Fonseca, C.D. Cress, M. Chubarov, **T.H. Choudhury**, J.T. Robinson, "Electronic Changes in Molybdenum Dichalcogenides on Gold Surfaces," *Journal of Physical Chemistry C* 124 (46), 25361-25368 (2020). 10.1021/acs.jpcc.0c07813.

This study employed x-ray and UV photoelectron spectroscopy to study possible charge transfer between TMD monolayer and gold surfaces and revealed that shifts in the XPS spectra were due to interactions of defects in the TMD monolayer with the gold surface. Wafer-scale MoS_2 monolayers from the 2DCC Thin Films facility were supplied to NRL (external user) for this study.

- External User Project R0024 (National Lab)

Y. Xiang, X. Sun, L. Valdman, F. Zhang, **T.H. Choudhury**, M. Chubarov, **J.A. Robinson**, **J.M. Redwing**, **M. Terrones**, Y. Ma, L. Gao, M.A. Washington, T.-M. Liu, G.-C. Wang, "Monolayer

MoS_2 on sapphire: an azimuthal reflection high-energy electron diffraction perspective," *2D Materials* 8 (2), 025003 (2020). 10.1088/2053-1583/abce08.

This study employed x-ray and UV photoelectron spectroscopy to study possible charge transfer between TMD monolayer and gold surfaces and revealed that shifts in the XPS spectra were due to interactions of defects in the TMD monolayer with the gold surface. Wafer-scale MoS_2 monolayers from the 2DCC Thin Films facility were supplied to NRL (external user) for this study.

- External User Project S0048 (non-R1)

J. Li, C. Yuan, C. Elias, J. Wang, X. Zhang, G. Ye, C. Huang, M. Kuball, G. Eda, **J.M. Redwing**, R. He, G. Cassabois, B. Gil, P. Valvin, T. Pelini, B. Liu, J.H. Edgar, "Hexagonal Boron Nitride Single Crystal Growth from Solution with a Temperature Gradient," *Chemistry of Materials* 32 (12) 5066-5072 (2020). 10.1021/acs.chemmater.0c00830.

Large hexagonal boron nitride crystals were synthesized by solution growth with a temperature gradient. The crystals have low defect density and narrow Raman peak width, providing an alternative method to high-pressure synthesis. Epitaxial growth of TMDs on hBN was carried out in the 2DCC to assess the defect density.

- External User Project S0087

D.J. Pennachio, C.C. Ornelas-Skarin, N.S. Wilson, S.G. Rosenberg, K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy Jr., C.J. Palmstrom, "Tailoring commensurability of hBN/graphene heterostructures using substrate morphology and epitaxial growth conditions," *Journal of Vacuum Science & Tech*. A, 37, 51503 (2019). 10.1116/1.5110524.

Demonstration of the ability to select different rotational alignments by changing epitaxial growth conditions. This may be used in future wafer-scale growth of hBN/graphene heterostructures to achieve varying degrees of graphene band structure modulation. The project utilized non-MIP equipment to provide epitaxial graphene to external users for hBN growth.

- External user project S0018 (Users from MSI)

K. Zhang, **Y. Wang**, J. Joshi, F. Zhang, S. Subramanian, M. Terrones, P. Vora, **V. Crespi**, and **J.A. Robinson**, "Probing the origin of lateral heterogeneities in synthetic monolayer molybdenum disulfide," *2D Materials* 6 (2) 025008 (2019). 10.1088/2053-1583/aafd9a.

Joint experiment/theory study of the distribution and the origin of inhomogeneities in monolayer MoS_2 of relevance for understanding and optimizing the quality of materials supplied by 2DCC.

- Also science driver AdvCM
- External User Project R0016

X. Zhang, **T.H. Choudhury**, **M. Chubarov**, Y. Xiang, B. Jariwala, F. Zhang, N. Alem, G.C. Wang, **J.A. Robinson**, and **J.M. Redwing**, "Diffusion-Controlled Epitaxy of Large Area Coalesced WSe_2 Monolayers on Sapphire," *Nano Lett*., 18(2), 1049–1056 (2018). 10.1021/acs.nanolett.7b04521.

Development and study of a multi-step process to grow coalesced epitaxial monolayer 2D chalcogenide films on scalable substrates in collaboration with external user.

- External User Project S0014 (User from non-R1).

Local User Publications (Epi2DC)

Q. Qian, W. Wu, L. Peng, **Y. Wang**, A.M.Z. Tan, L. Liang, S.M. Hus, K. Wang, **T.H. Choudhury**, **J.M. Redwing**, A.A. Puretzky, D.B. Geohegan, **R.G. Hennig**, X. Ma, *S. Huang*, "Photoluminescence Induced by Substitutional Nitrogen in Single-Layer Tungsten Disulfide," *ACS Nano* 16 (5), 7428-7437 (2022). 10.1021/acsnano.1c09809.
This study combines experiment and theory in the 2DCC. The electronic and optical properties of two-dimensional materials can be strongly influenced by defects, some of which can find significant implementations, such as controllable doping, prolonged valley lifetime, and single-photon emissions. In this work it is demonstrated that defects created by remote N_2 plasma exposure in single-layer WS_2 can induce a distinct low-energy photoluminescence (PL) peak at 1.59 eV, which is in sharp contrast to that caused by remote Ar plasma. The WS_2 thin films in this study were grown by 2DCC MOCVD equipment.

- Also science driver AdvCM
- Local User Project S0023

A. Dodda, *S. Das*, "Demonstration of Stochastic Resonance, Population Coding, and Population Voting Using Artificial MoS_2 Based Synapses," *ACS Nano* 15 (10), 16172-16182 (2021). 10.1021/acsnano.1c05042.
This study demonstrates how a population of stochastic artificial neurons based on monolayer MoS_2 field effect transistors (FETs) can use an optimum amount of white Gaussian noise and population voting to detect invisible signals at a frugal energy expenditure (~10s of nano-Joules). The findings can aid remote sensing in the emerging era of the Internet of things (IoT) that thrive on energy efficiency. MoS_2 materials in this study were synthesized using MIP equipment MOCVD1.

- Local User Project S0084

R.C. Haislmaier, Y.F. Lu, J. Lapano, H. Zhou, N. Alem, *S.B. Sinnott*, **R. Engel-Herbert**, *V. Gopalan*, "Large Tetragonality and Room Temperature Ferroelectricity in Compressively Strained $CaTiO_3$ Thin Films," *APL Materials*, 7 (5), 051104 (2019). 10.1063/1.5090798.

Demonstration that sizeable epitaxial strain can stabilize a tetragonal distortion and lead to ferroelectric ground state of $CaTiO_3$ at room temperature.

- Local User Project R0002

T.N. Walter, S. Lee, X. Zhang, **M. Chubarov**, **J.M. Redwing**, T.N. Jackson, and *S.E. Mohney*, "Atomic layer deposition of ZnO on MoS_2 and WSe_2," Appl. Surface Sci. 480, 43-51 (2019). 10.1016/j.apsusc.2019.02.182.

Investigation of ALD growth of ZnO on TMD monolayers grown in the 2DCC Thin Films facility.

- Local User Project S0035

In-house Research Publications (Epi2DC)

Y. Lin, R. Torsi, N.A. Simonson, A. Kozhakhmetov, **J.A. Robinson**, "Chapter 6 - Realization of Electronic-grade Two-dimensional Transition Metal Dichalcogenides by Thin-film Deposition Techniques," *Materials Today*, edited by Rafik Addou and Luigi Colombo, Elsevier, 159-193 (2022). 10.1016/B978-0-12-820292-0.00012-4.
This book chapter was contributed based on synthesis techniques used by the 2DCC in-house research team. The chapter discusses challenges in synthesizing high-quality TMDs and provides an overview on the thin-film deposition techniques that show a great potential for making electronic-grade 2D TMD, including powder-based and metal-organic chemical vapor deposition (CVD), as well as molecular beam epitaxy. Second, the chapter discusses several aspects of 2D crystals growth in CVD that would impact the material quality, such as substrates, precursor dissociation dynamics, as well as nucleation and growth kinetics in detail. Lastly, a review of the engineering methods for controlling their heterogeneity through controlling defect type and density, heterostructure formation, and substitutional doping.

S. Lee, X. Zhang, T. McKnight, B. Ramkorun, H. Wang, **V. Gopalan**, **J.M. Redwing**, T.N. Jackson, "Low-temperature Processed Beta-phase In_2Se_3 Ferroelectric Semiconductor Thin Film Transistors," *2D Materials* 9 (2), 025023 (2022). 10.1088/2053-1583/ac5b17.
Ferroelectric semiconductor field effect transistors can be key enablers to improve energy efficiency and overall chip and memory performance. In this work, low-temperature processed, back-end-of-the-line compatible transistors were demonstrated by depositing a layered chalcogenide ferroelectric semiconductor, beta-phase In_2Se_3, at temperature as low as 400 °C. Top gate n-channel In_2Se_3 thin film transistors were fabricated with field-effect mobility ∼1 cm^2 V^{-1} s^{-1}, and simple polarization switching based memory results are presented. The In_2Se_3 in this study was grown by a high-pressure chemical vapor deposition (HPCVD) system, faculty equipment.

- External user collaborator S0069 (National Lab)

M. Hilse, K. Wang, **R. Engel-Herbert**, "Molecular Beam Epitaxy of $PtSe_2$ Using a Co-deposition Approach," *2D Materials* 9 (2), 025029 (2022). 10.1088/2053-1583/ac606f.
The structural properties of co-deposited ultrathin $PtSe_2$ films grown at low temperatures by molecular beam epitaxy on c-plane Al_2O_3 are studied. Postgrowth anneals under a Se flux was found to dramatically improve the crystalline quality of the films. Even before the postgrowth anneal in Se, the crystallinity of $PtSe_2$ films grown with the co-deposition method was superior to films realized by thermal assisted conversion. Postgrowth annealed films showed Raman modes with narrower peaks and more than twice the intensity. Transmission electron microscopy investigations revealed that the deposited material transitioned to a two-dimensional layered structure only after the postgrowth anneal. $PtSe_2$ growth was found to start as single layer islands that preferentially nucleated at atomic steps of the substrate and progressed in a layer-by-layer like fashion. Materials in this project were grown by 2DCC equipment MBE2.

A. Bansal, X. Zhang, **J.M. Redwing**, "Gas source chemical vapor deposition of hexagonal boron nitride on C-plane sapphire using B_2H_6 and NH_3," *Journal of Materials Research* 36, 4678-4687 (2021). 10.1557/s43578-021-00446-5.
Chemical vapor deposition (CVD) of hexagonal boron nitride (hBN) using diborane (B_2H_6) and ammonia (NH_3) is reported. The effect of growth conditions on hBN growth rate using continuous vs. flow modulation epitaxy (FME) method is investigated to gain insight into the role of gas-phase chemistry during film deposition. The results provide additional insight into the

effects of gas-phase reactions on CVD of hBN. The 2DCC provided materials in this study from non-MIP faculty equipment.

A. Sebastian, S. Das, **S. Das**, "An Annealing Accelerator for Ising Spin Systems Based on In-Memory Complementary 2D FETs," *Advanced Materials* 34, 2107076 (2021). 10.1002/adma.202107076.

In this work, subthreshold Boltzmann transport is exploited in complementary 2D field-effect transistors (p-type WSe_2 and n-type MoS_2) integrated with an analog, nonvolatile, and programmable floating-gate memory stack to develop in-memory computing primitives necessary for energy- and area-efficient hardware acceleration of SA for Ising spin systems. The hardware-realistic numerical simulations further highlight the astounding benefits of SA in accelerating the search for larger spin lattices. MoS_2 and WSe_2 materials in this study were synthesized using MIP equipment MOCVD1.

A. Bansal, **M. Hilse**, **B. Huet**, K. Wang, A. Kozhakhmetov, J.H. Kim, S. Bachu, **N. Alem**, R. Collazo, **J.A. Robinson**, **R. Engel-Herbert**, **J.M. Redwing**, "Substrate Modification during Chemical vapor Deposition of hBN on Sapphire," *ACS Applied Materials & Interfaces* 13 (45), 54516-54526 (2021). 10.1021/acsami.1c14591.
A comparison of hexagonal boron nitride (hBN) layers grown by chemical vapor deposition on *C*-plane (0001) versus *A*-plane $(11\bar{2}0)$ sapphire (α-Al_2O_3) substrate is reported. Under the typical growth conditions required for high crystalline quality hBN growth, *A*-plane sapphire provides a more chemically stable substrate. Materials (hBN) in this study were provided by 2DCC faculty non-MIP equipment and RHEED analysis was contributed using MIP equipment MBE2.

M.A. Steves, S. Rajabpour, K. Wang, C. Dong, W. He, S.Y. Quek, **J.A. Robinson**, K.L. Knappenberger, "Atomic-Level Structure Determines Electron-Phonon Scattering rates in 2-D Polar Metal Heterostructures," *ACS Nano* 15 (11), 17780-17789 (2021). 10.1021/acsnano.1c05944.
The electron dynamics of atomically thin 2-D polar metal heterostructures, which consisted of a few crystalline metal atomic layers intercalated between hexagonal silicon carbide and graphene grown from the silicon carbide, were studied using nearly degenerate transient absorption spectroscopy. Optical pumping created charge carriers in both the 2-D metals and graphene components. Wavelength-dependent probing suggests that graphene-to-metal carrier transfer occurred on a sub-picosecond time scale. These studies provided insights into electronic carrier dynamics in 2-D crystalline elemental metals, including resolving contributions from specific components of a 2-D metal-containing heterojunction. The correlative ultrafast spectroscopy and nonlinear microscopy results suggest that the energy dissipation rates can be tuned through atomic-level structures. Materials provided by the 2DCC in this study were grown on non-MIP faculty equipment.

J.A. Robinson, B. Schuler, "Engineering and probing atomic quantum defects in 2D semiconductors: A perspective," *Applied Physics Letters* 119 (14), 140501 (2021). 10.1063/5.0065185.
Semiconducting two-dimensional (2D) transition metal dichalcogenides (TMDs) are considered a key materials class to scale microelectronics to the ultimate atomic level. The robust quantum properties in TMDs also enable new device concepts that promise to push quantum technologies beyond cryogenic environments. In this Perspective, the authors review some recent results on engineering and probing atomic point defects in 2D TMDs. Furthermore, we provide a personal

outlook on the next frontiers in this fast evolving field. Materials included in the 2DCC portion of the analysis were synthesized using non-MIP faculty equipment.

M.T. Wetherington, F. Turker, T. Bowen, A. Vera, S. Rajabpour, N. Briggs, S. Subramanian, A. Maloney, **J.A. Robinson**, "2-dimensional polar metals: a low-frequency Raman scattering study," *2D Materials* 8 (4), 041003 (2021). 10.1088/2053-1583/ac2245.
This study discusses newly discovered low-frequency (LF) (<100 cm^{-1}) Raman features due to the formation of unique 2D polar metals (Ag, Cu, Pb, Bi, Ga, In) or metal alloys (In_xGa_{1-x}) intercalated at an epitaxial graphene (EG)/silicon carbide (SiC) interface and demonstrate that 2D-Ag and 2D-Ga can have spatially distinct phases with their own unique Raman responses. Additionally, the study establishes that the 2D-Ga exhibits a structural evolution as a function of temperature, independent of the SiC and EG, that can lead to nucleation of secondary phases. The newly identified LF Raman responses discussed here lay the foundation for rapid, direct, and spatially resolved evaluation of 2D polar metals in ambient. Materials provided by the 2DCC were synthesized using non-MIP faculty equipment.

M. Fromel, R.L. Crisci, C.S. Sankhe, **D.R. Hickey**, T.B. Tighe, E.W. Gomez, C.W. Pester, "User-friendly chemical patterning with digital light projection polymer brush photolithography," *European Polymer Journal* 158, 110652 (2021). 10.1016/j.eurpolymj.2021.110652.
Patterned polymeric coatings are broadly relevant for all areas of bioengineering: anti-biofouling, controlled protein adsorption, guided cell growth, and many more. This contribution describes a robust topographical and chemical patterning platform that combines an LED digital light projector with oxygen-tolerant light-mediated polymerization to design advanced surfaces on the micron scale and in mild ambient conditions. The user-friendly nature of this approach is targeted towards bringing complex chemical patterning abilities based on surface-tethered polymers into the hands of non-experts and enabling both fundamental and applied studies related to patterned surfaces in bioengineering.

S. Rajabpour, A. Vera, W. He, B.N. Katz, R.J. Koch, M. Lassauniere, X. Chen, C. Li, K. Nisi, H. El-Sherif, M.T. Wetherington, C. Dong, A. Bostwick, C. Jozwiak, **A.C.T. van Duin**, N. Bassim, **J. Zhu**, G.-C. Wang, U. Wurstbauer, E. Rotenberg, **V.H. Crespi**, S.Y. Quek, **J.A. Robinson**, "Tunable 2D Group-III Metal Alloys," *Advanced Materials* 33 (44), 2104265 (2021). 10.1002/adma.202104265.

Chemically stable quantum-confined 2D metals are of interest in next-generation nanoscale quantum devices. Bottom-up design and synthesis of such metals could enable the creation of materials with tailored, on-demand, electronic and optical properties for applications that utilize tunable plasmonic coupling, optical nonlinearity, epsilon-near-zero behavior, or wavelength-specific light trapping. In this work, it is demonstrated that the electronic, superconducting, and optical properties of air-stable 2D metals can be controllably tuned by the formation of alloys. Environmentally robust large-area 2D-In_xGa_{1-x} alloys are synthesized by Confinement Heteroepitaxy (CHet). Materials in this study were synthesized using non-MIP faculty equipment. Theoretical analysis was provided by 2DCC personnel.

- Also science driver AdvCM
- In-house Research Collaboration with External User S0048 (Non-R1)

T. Mirabito, **B. Huet**, **J.M. Redwing**, **D.W. Snyder**, "Influence of the Underlying Substrate on the Physical Vapor Deposition of Zn-Phthalocyanine on Graphene," *ACS Omega* 6 (31), 20598-20610 (2021). 10.1021/acsomega.1c02758.
This work investigates the ZnPc physical vapor deposition (PVD) on graphene either as-grown on Cu or as-transferred on various substrates including Si(100), C-plane sapphire, SiO_2/Si, and h-BN. The experiments show that, for identical deposition conditions, ZnPc exhibits various morphologies such as high-aspect-ratio nanowires or a continuous film when changing the substrate supporting graphene. ZnPc morphology is also found to transition from a thin film to a nanowire structure when increasing the number of graphene layers. The observations suggest that substrate-induced changes in graphene affect the adsorption, surface diffusion, and arrangement of ZnPc molecules. This study provides clear guidelines to control MPc crystallinity, morphology, and molecular orientations which drastically influence the (opto)electronic properties. Materials in this study were synthesized using non-MIP faculty equipment.

D.R. Hickey, N. Nayir, M. Chubarov, **T.H. Choudhury**, S. Bachu, L. Miao, **Y. Wang**, C. Qian, **V.H. Crespi**, **J.M. Redwing**, **A.C.T. van Duin**, **N. Alem**, "Illuminating Invisible Grain Boundaries in Coalesced Single-Orientation WS_2 Monolayer Films," *Nano Letters* 21 (15), 6487-6495 (2021). 10.1021/acs.nanolett.1c01517.
Engineering atomic-scale defects is crucial for realizing wafer-scale, single-crystalline transition metal dichalcogenide monolayers for electronic devices. Using electron microscopy and ReaxFF reactive force field-based molecular dynamics simulations, this study provides insights into WS_2 crystal growth mechanisms, providing a direct link between synthetic conditions and microstructure. Imaging and ReaxFF simulations uncover two types of translational mismatch, and we discuss their origin related to relatively fast growth rates. Statistical analysis of >1300 facets demonstrates that microstructural features are constructed from nanometer-scale building blocks, describing the system across sub-Ångstrom to multimicrometer length scales.WS_2 materials in this study were synthesized using MIP equipment MOCVD1 and ReaxFF simulations were conducted by 2DCC personnel.

- Also science driver AdvCM

A. Khozhakhmetov, S. Stolz, A.M.Z. Tan, R. Pendurthi, S. Bachu, F. Turker, **N. Alem**, J. Kachian, **S. Das**, **R.G. Hennig**, O. Groning, B. Schuler, **J.A. Robinson**, "Controllable p-Type Doping of 2D WSe_2 via Vanadium Substitution," *Advanced Functional Materials* 31 (42), 2105252 (2021). 10.1002/adfm.202105252.
Scalable substitutional doping of 2D transition metal dichalcogenides is a prerequisite to developing next-generation logic and memory devices based on 2D materials. In this study scalable growth and vanadium (V) doping of 2D WSe_2 at front-end-of-line and back-end-of-line compatible temperatures of 800 and 400 °C, respectively, is reported. A combination of experimental and theoretical studies confirm that vanadium atoms substitutionally replace tungsten in WSe_2, which results in *p*-type doping via the introduction of discrete defect levels that lie close to the valence band maxima. The *p*-type nature of the V dopants is further verified by constructed field-effect transistors, where hole conduction becomes dominant with increasing vanadium concentration. Therefore, this study presents a method to precisely control the density of intentionally introduced impurities, which is indispensable in the production of electronic-grade wafer-scale extrinsic 2D semiconductors. Materials in this study were synthesized using non-MIP faculty MOCVD equipment for the doping. Theoretical studies were contributed by 2DCC personnel.

- Also science driver AdvCM

D.S.H. Liu, **M. Hilse**, **R. Engel-Herbert**, "Sticking coefficients of selenium and tellurium," *Journal of Vacuum Science and Technology* 39 (2), 023413 (2021). 10.1116/6.0000736.

This work focused on the direct and quantitative determination of sticking coefficients of selenium and tellurium which provides important insights into the kinetics of chalcogenide-based film growth and points toward the need of a precise sample temperature control. Results were obtained from materials grown on the 2DCC MIP equipment MBE2.

M. Chubarov, **T.H. Choudhury**, **D.R. Hickey**, S. Bachu, T. Zhang, A. Sebastian, A. Bansal, H. Zhu, N. Trainor, S. Das, **M. Terrones**, **N. Alem**, **J.M. Redwing**, "Wafer-Scale Epitaxial Growth of Unidirectional WS_2 Monolayers on Sapphire," *ACS Nano* 15 (2), 2532-2541 (2021). 10.1021/acsnano.0c06750.

This paper demonstrated that steps on the sapphire substrate surface can be used to achieve a preferential alignment of WS_2 monolayer domains grown by MIP equipment MOCVD1 in the 2DCC facility resulting in a dramatic reduction of anti-phase boundaries coalesced wafer-scale WS_2 films. Translational boundaries which result from coalescence of WS_2 domains with the same crystallographic direction, but sub-unit cell offsets were observed to be the predominant line defect in the films. The optical and transport properties of the MOCVD-grown TMD monolayers were comparable to that reported for exfoliated flakes.

A. Kozhakhmetov, R. Torsi, C.Y. Chen, **J.A. Robinson**, "Scalable Low-Temperature Synthesis of Two-Dimensional Materials Beyond Graphene," *Journal of Physical Materials*, 4 (1), 012001 (2020). 10.1088/2515-7639/abbdb1.

This review article summarizes recent breakthroughs in low-temperature synthesis for TMDs for semiconductor applications. It is the first review of its kind.

A. Kozhakhmetov, B. Schuler, A.M.Z. Tan, K.A. Chochrane, J.R. Nasr, H. El-Sherif, A. Bansal, A. Vera, V. Bojan, **J.M. Redwing**, N. Bassim, *S. Das*, **R.G. Hennig**, A. Weber-Bargioni, **J.A. Robinson**, "Scalable Substitutional Re-Doping and Its Impact on the Optical and Electronic Properties of Tungsten Diselenide," *Advanced Materials* 32 (50), 2005159 (2020). 10.1002/adma.202005159.

The study demonstrates a viable approach to introducing dopant-level impurities with high precision, specifically focusing on Re as the dopant atom, which can be scaled up to batch production for applications beyond digital electronics. The MIP provided support for both theory and experiment.

- Also Science Driver AdvCM

D.R. Hickey, D.E. Yilmaz, M. Chubarov, S. Bachu, **T.H. Choudhury**, L. Miao, C. Qian, **J.M. Redwing**, **A.C.T. van Duin**, **N. Alem**, "Formation of metal vacancy arrays in coalesced WS_2 monolayer films," *2D Materials* 8 (1), 011003 (2020). 10.1088/2053-1583/abc905.

This work identified a new type of structural defect – metal vacancy arrays – which form in epitaxial WS2 monolayers grown by MOCVD due to coalescence of domains that are slightly offset from one another. This study was a collaboration between 2DCC personnel in the Thin Films and In Situ Characterization Facility and the Theory/Simulation working on epitaxial growth of TMDs, advanced electron microscopy characterization and theory and simulation.

- Also Science Driver AdvCM

T.H. Choudhury, X. Zhang, Z.Y. Al Balushi, M. Chubarov, **J.M. Redwing**, "Epitaxial growth of two-dimensional layered transition metal dichalcogenides," *Annual Review of Materials Research*, 50 (2020). 10.1146/annurev-matsci-090519-113456.

Review article highlighting fundamental issues associated with vapor phase growth and epitaxy of TMDs

- Included external user from Government Lab on user project S0069 and external user from project S0067

Y.C. Lin, B. Jariwala, B. Bersch, K. Xu, Yi.F. Nie, B.M. Wang, **S.M. Eichfeld**, X. Zhang, **T.H. Choudhury**, Y. Pan, R. Addou, C. Smith, J. Li, K. Zhang, M. Aman Haque, S. Folsch, R. Feenstra, R.M. Wallace, K.J. Cho, S. Fullerton-Shirey, **J.M. Redwing**, and **J.A. Robinson**, "Realizing Large-Scale, Electronic-Grade Two-Dimensional Semiconductors," *ACS Nano* 12(2), 965–975 (2018). 10.1021/acsnano.7b07059.

Demonstration of MOCVD growth and properties of WSe_2 epitaxial films grown on sapphire in collaboration with external user. The project utilized non-MIP equipment as part of the Thin Film facility to create the 2D films.

- Included external user from project R0011

F. Zhang, K. Momeni, M. AlSaud, A. Azizi, M. Hainey, **J. Redwing**, *L-Q. Chen*, and N. Alem. "Controlled Synthesis of 2D Transition Metal Dichalcogenides: from vertical to planar MoS_2", *2D Materials* (2017), *4*, (2), 025029. 10.1088/2053-1583/aa5b01

Combined experimental and computational modeling study of powder vapor transport of MoS_2 films carried out in collaboration with local and external users.

- Included external user from project R0001 (User from Non-R1)

N. Briggs, B. Bersch, **Y. Wang**, J. Jiang, R.J. Koch, N. Nayir, K. Wang, M. Kolmer, W. Ko, A. De La Fuente Duran, S. Subramanian, C. Dong, J. Shallenberger, M. Fu, Q. Zou, Y.-W. Chuang, Z. Gai, A.-P. Li, A. Bostwick, C. Jozwiak , **C.-Z. Chang**, E. Rotenberg, J. Zhu, **A.C.T. van Duin**, **V. Crespi**, **J.A. Robinson**, "Atomically thin half-van der Waals metals enabled by confinement heteroepitaxy," *Nature Materials* 19, 637-643 (2020). 10.1038/s41563-020-0631-x.

This work introduces a new class of 2D materials – air-stable atomically thin metals encapsulated in graphene – whose discovery and development followed from a close coupling of experiment with predictive in-house first-principles calculations of formation energies, electronic properties, electron-phonon coupling, and superconductivity. The project utilized non-MIP equipment as part of the Thin Films facility to create the 2D films, and 2DCC theory. Sample provision of this emerging family of novel 2D metals will be a core future offering of the 2DCC.

- Also science driver AdvCM

X. Zhang, S. Lee, A. Bansal, F. Zhang, **M. Terrones**, T.N. Jackson, **J.M. Redwing**, "Epitaxial growth of few-layer beta-In_2Se_3 thin films by metalorganic chemical vapor deposition," *Journal of Crystal Growth*, 533 (1), 125471 (2020). 10.1016/j.jcrysgro.2019.125471.

First demonstration of epitaxial growth of beta-In_2Se_3 by MOCVD.

B. Huet, J.-P. Raski, **D.W. Snyder**, **J.M. Redwing**, "Fundamental limitations in transferred CVD graphene caused by Cu catalyst surface morphology," Carbon, 163, 95-104 (2020). 10.1016/j.carbon.2020.02.074.

Demonstration of effects of surface roughness and processing conditions on the transfer process for CVD graphene. Samples were grown using individual faculty equipment in the 2DCC.

T. Mirabito, **B. Huet**, A.L. Briseno, **D.W. Snyder**, "Physical vapor deposition of zinc phthalocyanine nanostructures on oxidized silicon and graphene substrates," *Journal of Crystal Growth,* 533 (1), 125484 (2020). 10.1016/j.jcrysgro.2020.125484.

CVD graphene layers (synthesized using individual faculty equipment) were used as substrates for the growth of zinc phthalocyanine nanostructures.

J. Fox, X. Zhang, Z. Al Balushi, M. Chubarov, A. Kozhakhmetov, **J. Redwing**, "Van der Waals epitaxy and composition control of layered SnS_xSe_{2-x} alloy thin films," *Journal of Materials Research*, 1-11 (2020). 10.1557/jmr.2020.19.

Layered $Sn(S,Se)_2$ alloys are of interest for the top absorber layer in tandem Si photovoltaics. This study explored the epitaxial growth and properties of these alloys across the entire composition range.

B. Huet, X. Zhang, **J.M. Redwing**, **D.W. Snyder**, J.-P. Raskin, "Multi-wafer batch synthesis of graphene on Cu films by quasi-static flow chemical vapor deposition," *2D Materials*, 6, 45032 (2019). 10.1088/2053-1583/ab33ae

Demonstration of high-throughput synthesis of uniform single-layer highly crystalline graphene on 3-inch wafers.

N. Briggs, Z.M. Gebeyehu, A. Vera, T. Zhao, K. Wang, A. Duan, B. Bersch, T. Bowen K.L. Knappenberger Jr., **J.A. Robinson**, "Epitaxial graphene/silicon carbide intercalation: a minireview on graphene modulation and unique 2D materials," *Nanoscale*, 11, 15440-15447 (2019). 10.1039/C9NR03721G

In-house research minireview on processes of epitaxial-graphene/SiC intercalation that underpin Platform advances in developing the new family of atomically, air-stable two-dimensional metals described in 10.1007/s11664-020-08087-w. The project also utilized faculty owned equipment as part of the Thin Film facility to create the 2D films.

X. Zhang, F. Zhang, **Y. Wang**, D. S. Schulman, T. Zhang, A. Bansal, N. Alem, S. Das, **V. H. Crespi**, **M. Terrones**, **J. M. Redwing**, "Defect-controlled nucleation and orientation of WSe_2 on hBN – a route to single crystal epitaxial monolayers", *ACS Nano*, 13 (3), 3341, (2019). 10.1021/acsnano.8b09230

A collaborative follow-up to initial work with MoS_2 that provides evidence for the generality of the proposed mechanism of defect-assisted epitaxial growth with orientation control, here demonstrated for WSe_2 grown on hBN with extensive characterization. Uses 2DCC facilities closely coupled to 2DCC-supported theory and informs growth of materials supplied to Platform users.

M. Chubarov, **T.H. Choudhury**, X. Zhang and **J.M. Redwing**, "In-plane x-ray diffraction for characterization of monolayer and few-layer transition metal dichalcogenide films," *Nanotechnol.* 29, 055706 (2018). 10.1088/1361-6528/aaa1bd

Demonstration of in-plane x-ray diffraction for characterization of epitaxial TMD monolayers grown at 2DCC.

A. Kozhakhmetov, **T.H. Choudhury**, Z.Y. Al Balushi, **M. Chubarov**, and **J.M. Redwing**, "Effect of substrate on the growth and properties of thin 3R NbS_2 films grown by chemical vapor deposition," *J. Crystal Growth* 486, 137-141 (2018). 10.1016/j.jcrysgro.2018.01.031

Study of epitaxial growth and properties of NbS_2 thin films.

T.H. Choudhury, H. Simchi, R. Boichot, **M. Chubarov**, *S.E. Mohney* and **J.M. Redwing**, "Chalcogen precursor effect on cold-wall gas-source chemical vapor deposition growth of WS_2," *Cryst. Growth Des.* 8, 4357-4364 (2018). 10.1021/acs.cgd.8b00306

Investigation of the effect of precursor chemistry on the growth and properties of WS_2 thin films grown by MOCVD in the 2DCC Thin Films facility.

N. Briggs, M.I Preciado, Y.F. Lu, K. Wang, J. Leach, X.F. Li, K. Xiao, S. Subramanian, B.M. Wang, A. Haque, **S. Sinnott** and **J.A. Robinson**, "Transformation of 2D group III-selenides to ultra-thin nitrides: enabling epitaxy on amorphous substrates," *Nanotechnol.* 29, 47 (2018). 10.1088/1361-6528/aae0bb

Development of chemical transformation routes towards expanding the suite of 2D systems that are synthetically accessible starting from a chalcogenide initial state. The project utilized faculty owned equipment as part of the Thin Films facility to create the 2D films.

- Also science driver AdvCM