The Pennsylvania State University
The Graduate School
Intercollege Program of Materials Science and Engineering

PROPERTIES OF SYNTHETIC TWO-DIMENSIONAL MATERIALS AND HETEROSTRUCTURES

A Dissertation in
Material Science and Engineering
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2017
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ABSTRACT

Graphene and other two-dimensional semiconductors have established their own research field, “2D Materials” that covers all of subjects related to fundamental and applied science, engineering, biology, medicine, and etc., where their layered structures and anisotropic properties can help to create interesting results. In particular, they play an important role as electronic materials because that their ultra-thin nature and excellent electrical properties make themselves prominent candidates for the next-generation electronics in the digital industries.

However, many researchers using 2D materials are suffering one common issue: limited size of the samples prepared by exfoliating bulk layered crystals. Besides limited size, tape-assisted exfoliation usually leaves the contamination on the surface of 2D materials. Due to the disadvantages of exfoliated samples, the research community has moved on to synthetic 2D materials prepared by thin film deposition techniques, such as chemical vapor deposition (CVD). For material engineers working on synthetic 2D materials, several challenges posed in front of them include: how to make them scalable and large area, how to grow these layers with high-quality and low-defect density, and how to integrate them with other substrates that have dissimilar features in terms of crystal structure and surface chemistry. This thesis is made to address the mentioned challenges thoroughly, or answers the questions associated with them.

This thesis covers two main discussions: 1) Vertical integration of 2D layers for van der Waals heterostructures and 2) Investigation on the properties of synthetic semiconducting 2D layers fabricated on insulating substrates. Each research chapter generally has three components in its experiment: 1) material synthesis by thin film deposition techniques, including CVD; 2) property investigation of the synthetic materials using spectroscopic, surface-probing, and electron microscope techniques; and 3) demonstration of optoelectronic devices made of 2D layers.
The first two chapters, Chapters 1 and 2, cover fundamental knowledge and short review on 2D semiconductors, heterostructures, and thin film, synthesis techniques; Chapter 3 has two parts covering the properties of synthetic WSe$_2$: The first part is for the first demonstration of the metallic-organic chemical vapor deposition (MOCVD) process for WSe$_2$; the second part covers an improved MOCVD process for WSe$_2$ on insulating substrate and studies the interface of transition metal dichalcogenides (TMDCs)/substrate and their devices. Chapter 4 discusses the direct synthesis of a variety of 2D layers on graphene, and how surface morphology and quality of graphene would impact their nucleation and growth; Chapters 5 and 6 discuss epitaxy relationship between monolayer WSe$_2$ and graphene, the electrical transport through their junction vertically, and modulation of the Fermi level of graphene to improve the performance; In Chapter 7, the resonant tunnel diodes made of TMDC bilayer (MoS$_2$/WSe$_2$ and WSe$_2$/MoSe$_2$) will be thoroughly discussed, including material preparation, property investigation, and device transport; In Chapter 8, 2D TMDCs integrated on VO$_2$, a phase transition material, and the phenomena arising from their interaction are discussed. Finally, Chapter 9 provides a summary for my dissertation.
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ACKNOWLEDGEMENTS

My time in Materials Science and Engineering at Pennsylvania State University was an invaluable research experience where I obtained both technical and professional skills. Most importantly, through this experience I was able to realize my childhood dream: to become a doctor. However, I would not have been able to achieve all of these goals without a good mentor and a group of wonderful and important friends. I would like to acknowledge Professor Joshua Robinson for offering me opportunities to exploit novel layered materials and optoelectronics and also for providing me the necessary support and guidance for success in this field. He is a great mentor and always a wonderful academic father with good nature and enormous patience with me. I would like to recognize both Dr. Amy Robinson and Professor Joshua Robinson for offering me teaching assistant opportunities that allowed me to interact with undergraduate students at PSU, providing them short courses and laboratory instruction. I would also like to recognize Professor Lain-Jong Li at KUAST, who first introduced me to materials science research when I was pursuing a master degree at National Taiwan University, and to thank Professor Joan Redwing and Dr. Sarah Eichfeld for introducing me to metal-organic chemical vapor deposition for electronic materials. I am thankful for my past and current colleagues in graduate school for assistance in research and insightful discussion. In particular, I would like to express my appreciation to Ganesh Bhinamapati, Brian Bersch, Kehao Zhang, Shruti Subramanian, Jennifer DiStefano, Maxwell Wetherington, Chia Hui Lee, Lorain Hossaine, Donna Deng, Bhaktiben Jariwala, and Rosemary Bittel for their instrumental and administrative help within the group. I also thank to my outside PSU collaborators, Professor Robert Wallace, Professor Susan Fullerton-Shirey, Professor Randall Feenstra, Professor Kyeongjae Cho, and their students and postdocs for unselfish collaboration and input on our collaborations in the SRC LEAST program. There are also important friends outside my research, including Jeremy Schreiber, Alperen Ayhan, Ece Alat, Isolina Preciado, and Ana De La Fuente whose friendship are always dear to my heart. In particular, I would like to deliver my sincere gratitude to Birgitt Boschitsch Stogin for her great support and firm friendship throughout my school years in which we shared many challenges and successes together. Finally, I would like to thank my parents, Chih-An Lin and Mei-Ying Lin, my sister Mei-Xuan Lin, and many of my close friends from my hometown whose tireless support and endurance in my long-term absence enabled me to pursue my dreams in academia on the other side of the Pacific Ocean. Especially, I want to recognize my Dad and Mom for instilling in me the motivation, drive, and diligence that have served me well in my graduate education and in life in general.
Chapter 1

Two-dimensional materials

Where do two-dimensional materials originate from?

Size effect can dictate the properties of the materials. At the nanoscale, changing the number of atoms and molecules forming the materials leads to qualitative changes in physical and chemical properties because the length of interaction from one atom (molecule) to another is approaching to the size of the entire materials. One well-known examples of size-dependent phenomena is the quantum confinement effect in ultra-small semiconducting materials.¹ The term “nanomaterial” is used to describe the materials that have at least one of their dimension in the nanometer scale. Prior to 1980s, nanoscale materials and technology was only conceptual (i.e., The lecture “There is plenty of room at the bottom” by Richard Feynman in 1959 and the term “Nano-technology” proposed by Norio Taniguchi in 1974)²,³ because manipulating atoms and molecules of the materials precisely and achieving high resolution images in the small scale were difficult at the time. Besides experimental challenges, it was commonly acceptable that a material in such scale may not be stable in room temperature due to large atomic displacement caused by thermal fluctuation. Even Feynman himself also claimed in his lecture that glass and plastic are better candidates than metal and crystals for machines and electronics in the small scale because the later ones will separate into domains to make their lattice structure stronger.²

Thanks to the rapid development in the field of surface probe technique, including scanning tunneling microscopy invented by Gerd Benning and Heinrich Rohrer in the early 80s,⁴ the public and science community was able to look into colloidal and interface sciences more effectively. For the nanomaterials, this breakthrough in surface science began at the exploration of fullerene (C60)
in the 80s, carbon nanotubes in the early 90s, and continued all the way to semiconducting quantum dots in the late 90s.

At the time they were explored, each class of these nanomaterials exhibit unprecedented properties arising from their dimensionality. If one dimension is restricted, a layered shape or 2D material can be made; if two dimensions are limited in size, a wire or 1D material can be found; if all dimensions are in the range of a few nanometers, 0D material is then produced. The most representative case can be seen on the sp² carbon materials, where graphite (3D), fullerenes (0D), nanotubes (1D), and graphene (2D) were typically presented in the chronological order of their earliest findings. Driven by the novelty that nanomaterials provide, and also significantly by ample curiosity, scientists, particularly solid state physicists, had been trying to thin down graphite aggressively by many means, including intercalation or rubbing graphite on a substrate. However, the properties of monolayer hexagonal carbon atoms was not fully explored until it was successfully isolated and thoroughly characterized by Geim and co-workers at Manchester University in 2004. Beyond Feynman and others scientists’ understanding, not only graphene can be stable on a substrate at room temperature and have high crystal quality, but also exhibits unprecedented properties that are very different to its counterparts in another dimensionality.

This single event in 2004 was indeed the birth of the field of two-dimensional materials and its preparation method also triggers the exploitation of other non-graphene 2D layered materials, like hexagonal boron-nitride (hBN), transition metal dichalcogenides (TMDC), and 2D black phosphorus (phosphorene). 2D materials exhibits numerous exceptional properties. First, quantum confinement effect in the direction perpendicular to the basal plane leads to unprecedented electronic and optical properties that are absent in their parental crystals. Second, unlike traditional 3D materials such as gallium arsenide (GaAs) and silicon (Si), their surfaces are free of dangling bonds and their structure is mechanically robust, and henceforth makes it easy to integrate 2D materials with functional structures such as cavities and photonic crystals. In addition, its van
der Waals interaction enable 2D materials to construct a vertical heterostructure without suffering the lattice mismatch issues when using layers with different lattice constants. Third, the light-matter interaction in many 2D semiconductor is strong, despite their atomic thickness (i.e., 1L MoS\(_2\) absorbs 10% of vertically incident light at its excitonic resonance).\(^{14}\) The energy bandgap of these 2D layers constituted a continuous energy spectrum in the ranges from infrared to visible wavelength, as shown in **Figure 1-1**. In other words, 2D materials not only extend the frontier of fundamental science but also serve as components in optoelectronics and photovoltaic devices used in our daily life.

**Figure 1-1:** The electromagnetic wave spectrum and the band gap ranges of various types of 2D materials. NIR, MIR and FIR indicate near-, mid- and far-infrared, respectively. The atomic structures of hBN, MoS\(_2\), black phosphorus and graphene are shown in the bottom of the panel, left to right. The crystalline directions (\(x\) and \(y\)) of anisotropic black phosphorus are indicated.\(^{12}\) (Reproduce from Ref. 12)
The rapid growth of the field of 2D materials can be reflected by the increasing number of publication within the last ten years (Figure 1-2). Especially, after graphene gained international attention at the Nobel prize in 2010, the number of research papers related to graphene increased by tens of thousands annually. Similarly, papers that reported other 2D layers including TMDC, monochalcogenides (i.e., InSe, GaSe, etc.), monoelemental 2D semiconductors (i.e., silicene, phosphorene, germanene), and MXenes also has been steadily increasing since 2011. Needless to say, 2D materials have become indispensable in academia and will soon be utilized in every aspect of our daily life in the near future.

Figure 1-2: Publication trends in 2D materials beyond graphene updated to 2014. (Reproduce from Ref.15)
Classification and thermal stability of 2D materials

Two-dimensional materials exhibit fundamental properties that are absent in their bulk counterparts. After the successful isolation of graphene, which is one carbon thick layer, the research that focused on 2D materials has been growing rapidly with an eye towards applications in semiconductors, energy-harvesting, electrodes, and membranes for water purification. In order to fully explore the total number of 2D materials, 65,000 inorganic crystal compounds with crystallographic and thermodynamic data in online the Materials Project (MP) database had been examined by Hennig and co-workers using topology-scaling algorithm (TSA) to verify layer compounds. TSA is able to simultaneously identify bonded networks of any dimension and classify structures in the MP database systematically. One task of TSA is to identify structural patterns that are separated from each other by distances larger than the bond length of atoms within the pattern. Their theoretical efforts identified 826 stable or semi-stable layered materials (LM). According to their stoichiometric ratios, 826 2D materials can be grouped into several categories. Among those, more than 50% of LM are presented by AB₂, ABC, AB, AB₃, and ABC₂, in decreasing frequency inversely proportional to their complexity (Figure 1-3A). The percentages of unary, binary, ternary, and more complexed types stable layered compounds are compared with the percentages of all stable compounds. It shows that binary, ternary, and quaternary compounds comprise ~ 98% of the stable layered compounds. In addition, the percentages of unary and ternary compounds among layered materials are close to their percentages among all materials in the MP database (Figure 1-3, B-C). The thermodynamic stability of layered materials determines if their 2D counterpart can be isolated. They are always metastable and not true thermodynamic ground states, as the total energy of the system is always lower when two layers are brought together. Despite of the oppositions from theoretical perspective, 2D materials have been proved to be
kinetically stable by themselves. The thermodynamic stability of a 2D material can be described by the difference in the energy of a 2D material and the lowest value for its bulk part:\textsuperscript{17}

$$\Delta E_f = \frac{E_{2D}}{N_{2D}} - \frac{E_{3D}}{N_{3D}}$$

where $E_{2D}$ and $E_{3D}$ are the energies of the single-layer and bulk (or mixture of bulk) materials, respectively, and $N_{2D}$ and $N_{3D}$ denote the numbers of atoms in the respective unit cells. In general, lower the exfoliation energies of 2D materials are, higher their thermodynamic stability would be. Previously, the materials in 2D form were presumably impossible because the theory stated that the thermal fluctuations in low-dimensional crystal lattices would make displacement of atoms exceed their interatomic distances at any temperatures.\textsuperscript{18} Owing to this reason, atomically thin films had only been considered as an integral surface of 3D crystals. This knowledge had been revisited after Novoselov and Geim at the University of Manchester successfully discovered graphene and other 2D crystals on the top of non-crystalline substrates.\textsuperscript{19} Arguably, the strong in-plane interatomic bonds of 2D crystals would ensure that thermal fluctuations cannot generate crystal dislocations and defects.\textsuperscript{18}

The exfoliation energies for all 826 compounds have been calculated (Figure 1-3D).\textsuperscript{16} It shows 680 layered materials have exfoliation energies below 150 meV/atom and 612 of those have the energies below 100 meV/atom. Those associated with low exfoliation energies within 200 meV/atom have been extracted as free-standing or suspended monolayers, such as those have been experimentally demonstrated like graphene, hBN, and 2D transition metal chalcogenides. On the other hand, 2D materials exfoliation energies more than 200 meV/atom (above SnSe in (D)) are unlikely to be synthesized and need a suitable stabilizing substrate, such as silicene, 2D oxides, 2D group III–N (Figure 1-3E).\textsuperscript{17}
Figure 1-3: The classification and stability of 2D materials. (A) Distribution of stoichiometries of the 826 layered compounds. The top 5 most common stoichiometries are ABC, AB2, AB, AB3, and ABC2.  represent half of all compounds. (B) Distribution of comparison of the compositional complexity among the stable layered materials identified by this work. (C) Distribution of all materials in the MP database. The percentage of binary compounds (one cation and one anion) among layered materials is significantly higher than among all materials. It indicates that binary compounds are relatively conducive to creating interlayer interactions. (D) Histogram of calculated exfoliation energies for 826 layered materials is compared to the range of calculated exfoliation energies for synthesized 2DM. Most of compounds have the energies below 100 meV/atom and could be easily exfoliated. (E) All 2D materials that have been synthesized as freestanding films have formation energies below 200 meV/atom, illustrated by the horizontal dashed line.16,17 (Reproduce from Ref.16,17)

From graphite to graphene

Graphene and hBN are isostructural layered materials with strongly anisotropic chemical bonds. In the basal plane of graphite (h-BN) carbon atoms (boron and nitrogen atoms) construct a 2D honeycomb structure with strong covalent bonds, while the basal planes interact weakly with each
other via van der Waals (vdW) bonds (Figure 1-4). Therefore, many of their physical properties, such as energy band structure, electrical conductivity, thermal conductivity, Debye temperature, phonon type, and magnetism type are highly anisotropic. Their basal plane has surface energy much lower than the other surfaces have due to the absence of dangling bond and, hence, makes integration of basal planes with various solid surfaces possible. From a mechanical aspect, the above-mentioned 2D bonds exhibit a high flexibility for bending their basal plane. The restoring force for mild bending of the basal plane is smaller than that of 3D crystals because the polarized transverse acoustic mode normal to the basal plane has parabolic dispersion the regime of longer wavelength, instead of the linear one that is common in 3D crystals. This mechanical robustness consequently enable the 0D and 1D nanostructures of graphite and hBN such as C60 and multiwall nanotubes made by rolling their basal planes. The epitaxial films of ultra-thin graphite and hBN had been studying for decades before their 2D allotrope, owing to their interesting characters. For example, thin film of graphite was grown on transition metal substrates (i.e., Ni, Pt, Ir, Pd) and carbide substrates (i.e., TiC, TaC, HfC) via chemical vapor deposition techniques, and subsequently probed by low-energy electron diffraction, Auger electron spectroscopy, and high-resolution electron energy-loss spectroscopy for understanding phonon dispersion, band structures, and epitaxial relationship, etc.

Geim and Novoselov used the “Scotch tape” for graphite exfoliation in order to create ultra-thin graphite layers on an insulating substrate. Tapes have been used to clean residue off TEM grids and happen to provide just enough force to decouple vdW interaction between graphene layers in graphite (Figure 1-5A). An atomically thin layer was successfully extracted by the exfoliation technique and its size is typically ranging from sub-μm to 100 μm (Figure 1-5B). In graphene, each carbon atom provides 3 electrons that bound with the nearest-neighbor electrons, thus creating a covalent bond (sp²). For each atom, a fourth electron (π) is delocalized on the whole graphene, which enables the conduction of current. If the energy of the electron is represented in function of
their momentum, the bands are in a parabola shape. The energy bands form two circular cones, connected one with the other at their extrema. They are called Dirac cones (Figure 1-5, C-D). Graphene presents an uncommon behavior because it does not have a gap, unlike the insulators, but also no partially filled band, unlike metals. Layered materials enabled the realization of pure 2D systems and present peculiar phenomena. While a traditional 2D electron gas (2DEG) is confined to the interface of two tandem epitaxial III-V semiconductors, graphene has been regarded as “real” 2DEG system. Since 2004, numerous interesting electrical phenomena raising from its Dirac cone band structure, such as ambipolar transfer characteristics, a mobility of $10^6$ cm$^2$/Vs at room temperature, and only 2% absorbance in the whole range of visible wavelength (Figure 1-5, E-F). Although great advantages that it provides to science and engineering community, its gapless nature raises the concerns for realization of graphene-based digital applications.

**Figure 1-4:** Graphite (3D) and its one basal plane (2D). Graphene can be further rolled into 1D and 0D structures. (Reproduce from Ref.18)
**Figure 1-5:** (A) The “Scotch tape” procedure isolates graphene on a substrate, reported by Novoselov and Geim in 2004. (B) Scanning electron microscopic image of a graphene, which shows that most of its faces are zigzag and armchair edges as indicated by blue and red lines and illustrated in the inset. (C) Band structure of graphene shows conductance band touches the valence band at the K and K' points, which is so-called the Dirac point. (D) Ambipolar FET in graphene. The insets show its conical low-energy spectrum E(k), indicating changes in the position of the Fermi energy $E_F$ with changing gate voltage $V_g$. Positive (negative) $V_g$ induce electrons (holes) in concentrations $n = \alpha V_g$ where the coefficient $\alpha$ depends on the use of dielectrics ($7.2 \times 10^{10} \text{ cm}^{-2} \text{ V}^{-1} 300 \text{ nm SiO}_2$). The rapid decrease in resistivity $\rho$ on adding charge carriers indicates their high mobility (in this case, $\mu \approx 5,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). (E) Mobility versus density at room temperature (solid black curve). Dashed black curve indicates the theoretical mobility limit due to acoustic-phonon scattering. Graphene FET is in comparison with the range of nobilities reported in other semiconductors. The inset shows that both sides of graphene have been encapsulated by hBN. (F) Transmittance spectra of single and bilayer graphene shows that every one layer absorb 2.3% of incident white light as a result of graphene’s electronic structure.\textsuperscript{18,21,23} (Reproduce from Ref.18, 21, 23)
Two-dimensional transition metal dichalcogenides

Semiconducting 2D materials like TMDC came into the play and fill in applications and science that gapless graphene cannot achieve. They have the common chemical formula MX$_2$ where M is for a transition metal (i.e., Mo, W, Ta) and X is for S, Se or Te atoms. Bulk TMDC crystals are formed by vertical stacking of monolayers separated by $\sim$6.5 Å. One monolayer contains a 3-layer stack of X-M-X (Figure 1-6A).$^{25}$ Mono- and few-layer flakes of TMDC can be easily extracted from bulk crystals in the same way that graphene, was deposited on a cleaned substrate (Figure 1-6, B-C). The bandgap of bulk TMDC crystals is around 1 eV but can further increase to 1.5-2.2 eV once they are thinned down to monolayer. O. Yazyev and A. Kis in their review has shown MoS$_2$ is an indirect gap semiconductor with valence band maximum (VBM) located at the $\Gamma$ point and conduction band minimum (CBM) located at a low-symmetry point of the Brillouin zone.$^{25}$ Upon thinning MoS$_2$ layers, the shapes of valence and conduction bands undergo changes, such that the positions of both of its VBM and CBM shift to the $K$ point making an indirect-to-direct bandgap crossover.

The change in the band structure with layer number is due to quantum confinement and the resulting change in hybridization between $p_z$ orbitals on S atoms and $d$ orbitals on Mo atoms. The electronic distributions are also spatially correlated to the atomic structure. Density functional theory (DFT) calculations for MoS$_2$ (Figure 1-6, D,F) show that the states of conduction-band at the K-point are mainly introduced by localized $d$ orbitals on the Mo atoms. These states are located in the middle of the “S-Mo-S” sandwiches and relatively intact to interlayer coupling.$^{25}$ On the other hand, the states near the $\Gamma$-point are the combined efforts of the antibonding $p_z$ orbitals on the S atoms and the $d$ orbitals on Mo atoms, and have a strong interlayer coupling effect. Therefore, as the layer numbers change, the direct excitonic states near the K-point are relatively unchanged, but the transition at the $\Gamma$-point shift significantly from an indirect one to a larger, direct one. All
semiconducting MX$_2$ compounds are expected to undergo a similar transformation with decreasing layer numbers, covering the bandgap that ranges from 1.1–1.9 eV.

Significant efforts to open the bandgap of graphene using graphene nanoribbons, AB-stacked bilayer graphene, and chemical doping (i.e., substituting C of graphene with B and N) had negligible success, providing the bandgap opening up to 200 meV as the best. This challenge serves as a driving force in developing 2D TMDC with a finite bandgap. 2D TMDs reveal a wide range of bandgap covering all visible and infrared range with the choice of material. Most semiconducting 2D TMDC reveal direct bandgap in monolayer, whereas their bulk counterparts are indirect bandgap (exceptional cases are InSe and ReSe$_2$). For example, 2D MoS$_2$ (1.8 eV), MoSe$_2$ (1.5 eV), (2H)-MoTe$_2$ (1.1 eV), WS$_2$ (2.1 eV) and WSe$_2$ (1.7 eV) show direct bandgap.\textsuperscript{25} Depends on the structures, constituent elements and amounts of electron in $d$ orbitals of transition metal elements, 2D TMDC layers can exhibit metallic/semiconducting behaviors, charge density wave (CDW), magnetism (ferromagnetic and anti-ferromagnetic), and superconductivity (Figure 1-7).\textsuperscript{27} The tremendous diversity of their properties indeed enriches the knowledge of the solid-state physics and enables numerous applications.
Figure 1-6: (A) Schematic representation of the structure of a TMDC material with a formula MX$_2$ where metallic atoms are shown in black and chalcogens (X) in yellow. (B) Photograph of a bulk crystal of MoS$_2$ that can be used as a starting point for the exfoliation of single layers. (C) Optical image of a monolayer MoS$_2$ deposited on the surface of SiO$_2$. (D-E) Electronic band structures of bulk MoS$_2$ and monolayer MoS$_2$ calculated from first principles using density functional theory (DFT) within the generalized gradient approximation (GGA). Valence band maxima (VBM) and conduction band minima (CBM) are indicated by red and blue circles, respectively. Energies are given relative to the VBM. Schematic drawings of low-energy bands in (F) bulk MoS$_2$ and (G) monolayer MoS$_2$ showing their band gaps (E$_g$) as well as the valence band spin–orbit splitting $\Delta_{so}$ and the $\Gamma$ valley band offset $\Delta_{\Gamma–K}$ for the case of monolayer MoS$_2$. The band structure parameters have been obtained at the DFT–GGA level of theory. The orbital composition of electronic states at band extrema is indicated. (Reproduce from Ref.25)
Opportunities for 2D semiconductors in electronic applications

As the scaling task on traditional semiconductors (e.g., Si for logic electronics, GaAs for communications, and GaN for high power devices and solid-state lightning) becomes increasingly challenging due to the fundamental limits from both of chosen materials and device physics, new materials and critical engineering breakthrough is in demand to achieve the future high performance and low power electronics. For example, a field effect transistors fabricated on bulk Si will not offer significant performance improvement below 22 nm-node devices; thinning gate dielectric can improve electrostatic control to but also increase leakage current, which would eventually degrade carrier mobility.24 2D TMDC and other 2D semiconductors provides several advantages for new device concepts. They provide ultrathin channel for good electrostatic control in transistors and also opportunity for new device concepts, one of these is tunneling field-effect transistors (TFET); One advantage using 2D semiconductors as FET is their dangling bond-free surface that helps lowering interface trapping states.; A finite bandgap between 1.5-2.2 eV means the stand-by-
current (off-state) would be much lower than that of Si FETs.; Most of 2D TMDC have large relative effective mass for holes and electrons, between 0.55 – 0.66 for all carriers in MoX$_2$. This brings an advantage over 3D semiconductors (0.3 for Si and 0.15 for GaAs) when the channel length is ultimately narrow: a reduced source-drain tunneling current.$^{24}$ (4 nm channel of MoS$_2$ FET has been achieved by Xie et al.$^{28}$)

For high-performance devices, 2D TMDC cannot compete directly with Si- and III-V materials due to relatively low carrier mobility (TMDC: < 100 cm$^2$V$^{-1}$s$^{-1}$, Si: few hundreds of cm$^2$V$^{-1}$s$^{-1}$, III-V: few thousands of cm$^2$V$^{-1}$s$^{-1}$)$^{24}$ However, their high on/off ratio (> 10$^6$, MoS$_2$) and low SS (< 80 mV/dec, MoS$_2$) make them possible to outperform existing Si-based low-power devices.$^{29}$ One of leading transistor candidates for lower-power device is TFET, which can achieve low SS by creating band-to-band tunneling via field control.$^{24}$ Several theoretical and experimental works have predicted the feasibility of using 2D TMDC for TFET (Figure 1-8A),$^{24}$ considering their excellent electrostatic control and possible low trapping states on surface. For next-generation flexible electronics, 2D materials can also be ideal candidates because they can be synthesized in polycrystalline form and in large-area, and are also mechanically flexible. In addition, 2D materials may have better mobility and high on/off ratio, compared to organic semiconductors (Figure 1-8B)$^{24}$

Although 2D materials offer tremendous opportunities to device applications, growth of large-area, high-quality, and single-crystal 2D semiconductors remains a daunting task. Processing of 2DMs is still in its infancy because the nucleation phenomena and associated surface science and defect control at the monolayer are yet understood. The community is still understanding baseline properties by using micromechanical cleaving method that provides high-quality but small size samples. The most common methods for synthetic films are Chemical Vapor Deposition (CVD), molecular beam epitaxy (MBE), and physical vapor processing (Figure 1-8C)$^{24,30}$ Single-crystalline graphene can be grown up above 1 cm$^2$ in diameter on Cu, Cu-Ni alloys, germanium
(110), and SiC via high temperature process.\textsuperscript{24,31} Although current deposition techniques are able to grow single domains of 2D semiconductors with the edge size up to hundreds of \( \mu \text{m} \) below 1000 \(^\circ\text{C} \), the uniformity and crystallinity of these results are yet to meet the industrial standard for massive device fabrication. The other engineering questions, such as layer thickness control, defect density control, forming ohmic contact, and doping engineering also need to be answered before high-performance electronics can be made on synthetic 2D materials.
Figure 1-8: (A) Measured subthreshold swing (SS) as a function of drain current for experimental tunnel field-effect transistors (TFET) versus simulations. The dashed line refers to the lowest SS, 60 mV/dec, achievable in thermionic devices. (B) Trade-off between field-effect mobility and On/Off ratio for materials typically used in flexible electronics versus organic materials. (C) Mobility of 2D materials as a function of preparation method. Images from left to right: low-energy electron microscopy image of epitaxial graphene on SiC; large graphene domains grown on Cu; High-resolution transmission electron microscopy (HRTEM) image showing graphene grown by plasma-enhanced CVD (PECVD); scanning transmission microscopy image of graphene grown by MBE; HRTEM image of graphene prepared by liquid phase exfoliation; and an atomic force microscopy (AFM) image of graphene prepared by micromechanical cleavage (MC). The red curve shows the mobility of graphene on SiO₂ and the blue curve is for MoS₂ on SiO₂, extracted from FETs. The mobility of MoS₂ is less dependent on the preparation process (blue curve; images from left to right: optical micrograph of MoS₂ made by CVD; AFM image of MoS₂ prepared by LPE; AFM image of MoS₂ prepared by MC).²⁴ (Reproduce from Ref.24)
Heterostructures based on van der Waals solids

A heterostructure consists of different electronic materials and has a varied energy gap. In principle, a heterostructure utilizes its energy gap variations to control electrons and holes in terms of their flow and distribution, in addition to electrical fields. Since the proposed design principle of heterostructure devices in 1957 by Kroemer, it has been an essential requirement for high performance transistors, semiconducting lasers, and optical devices made out of conventional semiconductors. Graphene and beyond-graphene layered materials, especially atomically thin TMDCs, have created a vast field that generates more than a thousand of publications on the study of their fundamentals and material applications each year. These publications provide throughput fundamental understandings on every aspect of each layered materials and enable people to select specific layered materials for their needs. While new opportunities of discovering exotic phenomena in one layered material itself are running low, a new focus going beyond this field has been initiated. Various isolated monolayers of TMDCs and other vdW crystals are assembled into a sophisticated structure made into a layer-by-layer sequence that is purposely designed. These vdW heterostructures have been synthesized and investigated extensively since 2010, and already revealed new properties and exotic phenomena yet presented in their constituent layers. While most of ultra-thin layered crystals have been explored and demonstrated in optoelectronics, the emerging vdW heterostructure is raising a “layered renaissance” for the next-generation devices.

Van der Waals (vdW) heterostructures consist of a variety of 2D layered crystals that have strong in-plane covalent bonds and weak out-of-plane vdW interaction. The key feature that distinguishes vdW heterostructures (Figure 1-9, A,C) from conventional heterostructures (Figure 1-9, B,D) is the vdW gaps presenting in between constituent layers. While the convenient heterostructures derived from 3D solids, such as III-V compounds, SiGe epitaxy layers,
and oxides (i.e., perovskites, spinels, and dielectrics) involve covalent bonds to bridge the constituent materials. vdW heterostructures bridge their constituent layers merely with weak vdW forces. Without physical bonds involved, their interfaces can tolerate a highly lattice mismatch combination (Figure 1-9C).

![Figure 1-9: (A) Schematic illustration of “van der Waals” (vdW) heterostructures; and (B) “conventional” heterostructures. The symbolic feature of a vdW heterostructure is the presence of vdW gaps (Arrows in a) in between constituent 2D layers, which attract to their adjacent layers by a weak vdW force, shown in (C). (D) On the other hand, the heterostructures derived from ionic and covalent compounds have physical bonds at their interfaces connecting each constituent 3D building block. Dangling bonds would be caused if there’s a large lattice mismatch between grown material and growth template in the 3D cases. (Reproduce from Ref.40)](image)

To build vdW heterostructures mechanically

When reliable techniques to synthesis high quality vdW heterostructures are still under development, the simplest fabrication technique is to mechanically transfer one 2D crystal onto another in a step-by-step manipulation. The easiest report of this route is from Dean et al on graphene and hBN stacks, in which a micromanipulator was used, under an optical microscopy, to precisely deposit graphene that is closely aligned to a hBN flake (Figure 1-10A). The electrical transport measurement on the graphene integrated with hBN flakes shows a significant improvement in the field effect mobility of graphene (Figure 1-10B). These results indicate that hBN serves as a substrate better than SiO₂ for graphene electronics due to their closely matched lattice constants, an atomically flat surface, and lack of dangling bonds. The stacking methods can
apply to layered materials that are not structurally compatible or unlikely can be grown on each other. This method had inspired numerous works that built exotic vdW heterostructures to discover the new properties and applications.\textsuperscript{35,45,46} There have been many new prototypes of vertical devices made from stacked exfoliated layers, while the synthesis techniques for ultra-high quality heterostructures are under development.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{(A) Schematic flow of the transfer process used to deposit exfoliated graphene on hBN flakes. (B) Top: The field effect mobility of graphene-hBN devices achieved 60,000-80,000 cm\textsuperscript{2}V\textsuperscript{-1}S\textsuperscript{-1}, a significant improvement compared with graphene-SiO\textsubscript{2} devices. Bottom: The atomically flat and dangling bond-free surface of hBN attribute to the success of the high mobility.\textsuperscript{36} (Reproduce from Ref.36)}
\end{figure}

There are a wide variety of devices demonstrated with vdW heterostructures utilizing a variety of 2D crystal categories including conductors, insulators, and semiconductors. The groundbreaking work by Britnell \textit{et al.}\textsuperscript{46,47} utilized hBN flakes ranging from 5-7 layers as a tunneling barrier between two sheets of graphene serving as the top and bottom electrodes in the vertical field effect tunneling transistors in hBN-Gr-hBN-Gr-hBN (Gr: graphene) vertical heterostructures (\textbf{Figure 1-11, A-C}). The amount of tunneling current density of the vertical devices can be tuned by controlling finite doping density and applied bias (\textbf{Figure 1-11, D-G}). The transistors show a tunneling $I$-$V$ characteristics and orders of the on/off ratio, which address the weakness of planar graphene field effect transistors due to lack of on/off ratio. In addition to rigid devices, flexible devices and technology utilizing 2D crystals are also emerging. The strain limit of thin-film devices
made of TMDCs and other monolayers possess a value 3-5 times greater than that made from III-V compounds, metal oxides, and crystalline silicon.

Similar to the first prototype of Gr-hBN-Gr devices, Georgiou et al.\textsuperscript{48} prepared a Gr-WS\textsubscript{2}-Gr vertical heterostructure fabricated on a flexible polyethylene terephthalate films using the same transfer methods (Figure 1-12, A-B). The device exhibits tunneling characteristics under applied characteristics (Figure 12C) and maintains its electrical performance subjected to a strain up to 5% (Figure 1-12D).\textsuperscript{48} The flexible structures also demonstrate a transistor effect (Inset, Figure 1-12D) and may have improved performances with the optimal thickness of dielectrics.

\textbf{Figure 1-11:} Field effect tunneling transistors on vertical hBN-graphene-hBN-graphene-hBN heterostructure (A) Optical image of the final device. (B) Electron microscopic image captured prior to evaporation of the Au electrodes shows 2 Hall bars made from graphene are shaded in green and orange. (C) Schematic structure of the experimental vertical devices. (D) The corresponding band structure without applied gate voltage; (E) the same band structure subjected to a finite gate voltage ($V_g$) and zero bias ($V_b$); (F) Both of $V_g$ and $V_b$ are applied. (Only the tunnel barrier for electrons is considered in the illustrations.) (G) Tunneling characteristics for the vertical tunneling device with 5-7 layers of hBN as the tunnel barrier. $I$-$V$ curves for different $V_g$, in a 10-V step. Due to finite doping, the minimum tunneling conductivity is achieved at $V_g$ around 3 V. The inset compares the experimental $I$-$V$ curves at $V_g = 5$ V (red curve) with theory (dark curve, which takes the linear density of state in the two graphene layers into consideration and assumes no momentum conservations.\textsuperscript{47} (Reproduce from Ref.47)
Figure 1-12: A transistor Gr-WS$_2$-Gr built on a flexible polymer substrate: (A) Optical image and (B) Image of the device under bending, (C) $I$-$V$ plot at $T = 300$ K for the bended device with $V_g=0$. Curvature is 0.05 mm$^{-1}$. (D) Relative current variation versus applied strain. Standard variations for several consecutive measurements are shown in error bars. Inset is the gating transport of the device under strain.\(^{48}\) (Reproduce from Ref.48)

Besides vertical tunneling devices, engineering the band structures of heterostructures can also lead to practical lightning devices using TMDs (MoS$_2$, WS$_2$, WSe$_2$) as light emitter.$^{49,50}$ The work by Withers et al.$^{49}$ fabricated single quantum well (SQW) emitters made from a stack of hBN/Gr$_{Bottom}$/3L hBN/1L MoS$_2$/3L hBN/Gr$_{Top}$/hBN (Figure 1-13, A-B), in which 1L MoS$_2$ serves as a light emitter excited by an applied bias and operates at 300 K (Figure 1-13, C-G). One of the demonstrated devices in this work achieved extrinsic quantum efficiency nearly to 10%, and the emission can be tuned over a wide range of wavelength by choosing different types and thickness of 2D semiconductors. By stacking more repetitive SQW, a multiple quantum well (MQW) vdW heterostructure with enhancement emitting intensity was realized.
Figure 1-13: Heterostructure devices with a single quantum well (SQW), made from hBN/Gr\textsubscript{Bottom}/3L hBN/1L MoS\textsubscript{2}/3L hBN/Gr\textsubscript{Top}/hBN, shown in (A), the optical image. The inset of (A) is electroluminescence (EL) image from the same device, under $V_b=2.5$ V, $T=300$ K. (B) The schematic structure of the same SQW device; (C-E) Band alignment for the case of zero applied bias (C), intermediate applied bias (D), and high applied bias (E), for the heterostructure presented in (B). (F) EL spectra as a function of applied bias ($V_b$) for the SQW device made from MoS\textsubscript{2}. White curve is its current density versus applied bias characteristics ($j$-$V_b$), and (G) Comparison of the PL and EL spectra for the same devices.\textsuperscript{49} (Reproduce from Ref.49)

Combining different TMDC monolayers can lead to a new class of van der Waals solids that exhibits new optical and electrical properties. The theoretical work by Terrones \textit{et al.}\textsuperscript{51} predicted that stacking MoS\textsubscript{2}-WSe\textsubscript{2} heterostructures (Figure 1-14A) will yield electronic properties that are entirely different from their constituent layers, such as a significantly reduced bandgap energy (Figure 1-14, B-C). This exciting theoretical work got support from many experimental works aiming to realize the theoretical results through manual stacking of different TMDC layers.\textsuperscript{52-54} For example, a manually stacked MoS\textsubscript{2}-WSe\textsubscript{2} heterostructure made by Fang \textit{et al.}\textsuperscript{52} exhibits an interlayer exciton at 1.55-1.59 eV (Figure 1-15),\textsuperscript{47} in addition to intralayer excitons of (1.87 eV) MoS\textsubscript{2} and (1.65 eV) WSe\textsubscript{2} monolayers.\textsuperscript{52} More interestingly, adding electrically insulating hBN monolayers into MoS\textsubscript{2}-WSe\textsubscript{2} heterostructures can modify strength of the interlayer coupling and result in decoupling of the layers, as evident by a decreased intensity of the interlayer excitons.\textsuperscript{52}
Figure 1-14: (A) Simulated MoS$_2$-WSe$_2$ heterostructure yields a new direct bandgap, which is shown in (B). (C) Bandgap of monolayer and bulk TMDCs and their heterostructures.\textsuperscript{55} (Reproduce from Ref.55)

Figure 1-15: (A) Band diagram of WSe$_2$/MoS$_2$ heterobilayer under photo excitation, illustrating (1) exciton generation in 1L WSe$_2$ and MoS$_2$, (2) relaxation of excitons at the MoS$_2$-WSe$_2$ interface where band has been offset, and (3) radiative recombination of spatially indirect excitons. (B) 1L MoS$_2$, WSe$_2$, and their heterolayer exhibit PL spectra created by radiative recombination of intralayer and interlayer excitons. (C) Normalized PL (solid lines) and absorbance (dashed lines) spectra of 1L WSe$_2$, MoS$_2$, and their corresponding heterolayers, where the spectra are normalized to the height of the strongest PL/absorbance peak.\textsuperscript{55} (Reproduce from Ref.55)

Crystallographic rotation impact on the properties of vdW heterostructures

Transition metal dichalcogenides based heterostructures can “feel” different force fields by different patterns of their superlattice, where rotational angles between two TMDC monolayers determine the features of the optical properties in their vdW heterostructures.\textsuperscript{54,56} van der Zande \textit{et al.}\textsuperscript{56} made a series of artificial MoS$_2$ bilayers with twisted-angle ranging from $0^\circ$ to $60^\circ$ (Figure 1-16, A-B).\textsuperscript{56} He found that the intensity and peak position of their indirect transition (indirect bandgap) are highly tunable in PL measurements for 532 nm excited wavelength (Figure 1-16C).\textsuperscript{56}
The combined study of experiments and theoretical calculations confirmed the changed distance between inner sulfur atoms in MoS\(_2\) bilayer would modify the indirect transition in their band structures due to a changed interaction between the \(p\) orbitals form sulfur atoms (Figure 1-16, D-E). Given by these examples, ones can say the rotation angle between stacked 2D lattices is an additional degree of freedom for whom are engineering the properties of vdW heterostructures.

Figure 1-16: (A) Optical microscope image of two overlapping CVD MoS\(_2\) monolayers, forming a bilayer with a twisted angle. The dashed lines are plotted to indicate the different orientations of the triangle edges. (B) Top and side view of the aligned bilayer MoS\(_2\) with rotation angles of 0°, 30°, and 60°. The 0° and 60° alignments match the 2H and 3R phase of nature MoS\(_2\) crystals, respectively. (C) Photoluminescence spectra for the bottom (as-grown, gray line, one at the most top in (C)) and top (transferred, green line) MoS\(_2\) monolayers, and twisted-bilayers at different twist angles. The spectra are normalized and offset for clarity and color-labeled by the angle with black and yellow corresponding to 0° and 60°, respectively. The black dashed line highlights relevant tuning features of the MoS\(_2\) indirect bandgap, alone with increased twisted angles. (D) Calculated electronic structures of 60° and 30° bilayers are presented in solid pick lines and broken black lines, respectively. (E) The partial charge density of states corresponding to 1-3 in (D) show only the inner sulfur atoms in the structures and their separation are the main factors involved in the indirect transition. The twisted-angle dictates the separation of sulfur atoms, which is the key parameter for this optical modulation.\(^{56}\) (Reproduce from Ref.56)
Interface imperfection in the vdW heterostructures made mechanically

The manual stacking process is indeed a practically useful for integrating various 2D materials to create a variety of proof-of-concept van der Waals heterostructures. However, the process requires multiple steps to complete an assembly, including isolating a 2D layer in micro-size, transferring it onto polymer-supporting films, stacking 2D crystals repeatedly, repeating standard clean room procedure in terms of cleaning, dissolving, resist spinning, and so on, and a precision-demanding alignment under a microscope with a micromanipulator. These multiple steps, carried out in ambient, unavoidably introduce contaminations at the interfaces of constituent layers (Figure 1-17A), which could be due to the presence of adsorbents and the usage of polymer films in the transfer process. Although a clean and sharp interface in these heterostructures are still obtained by confining trapped residues into “bubbles” with van der Waals forces that bonds adjacent constituent layers, a sophisticated process is still needed in order to fabricate a useful device. The visual example of the bubbles is shown in Figure 1-17B, where the top gate contact was deposited in a shape that the “bubbles” would be avoided. In order to make van der Waals heterostructures practically useful for digital industries, an alternative for the synthetic vdW heterostructures with clean interfaces needs to come out.

Figure 1-17: (A) “Bubbles” and wrinkles in manually stacked van der Waals heterostructures formed due to segregated residues at their interfaces after the transfer process. Each stacked layer and their overlap is highlighted, and none of them are completely free of imperfection. (B) While fabricating devices on the heterostructures, the top contacts are shaped irregularly to avoid the polymer residue (black dots in figure) that is common in this technique. (Reproduce from Ref.58)
Conclusions

In this chapter, brief history of the development for 2D materials and vdW heterostructures, and their basic properties are provided and serve as the background for the following chapters. A heterostructure made of 2D semiconducting materials is an important remark towards flexible and low-power opto-electronics in the future. Analogously, 2D TMDC represent a new class of building blocks. However, current methods for making a vdW heterostructure couldn’t always provide good material interfaces. These challenges would lead to the core focus of this dissertation: synthetic 2D layers and heterostructures made by thin film deposition techniques.
Chapter 2

Material processing and properties of 2D semiconductors

Thin film deposition steps

The thin-film process sequence contains six substeps. First, the deposited atoms and molecules adsorb on the surface. Second, they often diffuse certain distance and then incorporate into the film. Third, in the incorporating process, the adsorbed species reacted with each other and also with the surface to form the film materials. Fourth, the initial cluster of the film materials is called nucleation. Fifth, when the film grows thicker, it establishes a structure that includes roughness and crystallography. And, sixth, diffusional interactions occur within the bulk of the film or with the substrate. (This section is referenced to the book “Thin-Film Deposition: Principle & Practice by Donald L. Smith)\textsuperscript{59}

Molecule absorption on a surface

When a molecule approaches the surface within a few atomic distances, it will start to feel an attraction by interacting with the surface molecules. It happens because the molecules and atoms act as oscillating dipoles, and this behavior induces dipole interaction known as van der Waals force/London dispersion force. If the molecule is a polar one and has permanent dipole, the attraction is stronger. This molecule is trapped in a weakly-adsorbed state in the beginning called physical adsorption (physisorption). The fraction of approaching molecules so adsorbed is called the trapping probability ($\delta$). Intuitively, the fraction of the molecules that reflect or escape is $1-\delta$. Generally, the substrate is at an elevated temperature and is thermally accommodated to the molecules during the deposition process. This thermal energy makes the physisorbed molecules
mobile so they will diffuse between surface atomic sites. After a while, it may either desorb by gaining enough energy or undergo a further interaction including the formation of chemical bonds with the surface atoms; this is, chemisorption. Chemisorption involves the electron sharing in new molecular orbitals and is much stronger than physisorption, since the later only involves dipole interactions. Not all of the vapors would trap and condense on a foreign substrate. The physisorbed molecules will eventually escape the substrate before they become chemisorbed ones. Thus, the chemisorption reaction probability, \( \eta \), is defined as the fraction of the arriving vapor that becomes chemisorbed on a foreign substrate.

Some of the physisorbed species eventually escape back to in the vapor phase, the sticking coefficient, \( S_c \), is used to denote the fraction of the arriving vapor that remains adsorbed for the entire duration of the experiment. \( S_c \) is very useful in thin-film deposition, since its equal to the fraction of arriving that becomes “incorporated” as part of the film. The incorporation means this arriving vapor becomes adsorbed and subsequently buried before it can desorb. The precursor adsorption can also be simply described by a diagram of the potential energy versus molecular distance from the surface (z). The potential energy is commonly expressed as the molar quantities \( (E_p) \). One curve shown is for the precursor state and another one is for the chemisorbed state in the \textbf{Figure 2-1}. The tails of the two curves will intersect at a certain distance from the surface forming an energy barrier, \( E_a \), which is an activation energy that the arriving vapor needs to overcome in order to become dissociatively chemisorbed.

Typically, the \( E_p \) of the element involved in deposition processes is set to zero as it is in thermodynamic standard state \( (Y^{2(g)} \) in this case, lining at zero \( E_p \)). One main advantage of the energy-enhanced deposition processes (i.e., perform deposition at higher temperature) is that the arriving molecules can conquer the \( E_a \) barrier. There are two ways in which arriving vapor can have \( E_p > 0 \) at the surface, either as high kinetic energy of accelerating molecules or high potential energy of dissociated ones (i.e., formation energy provided to \( 2Y^{(g)} \)). Gases have their \( E_p \) raised by being
dissociated. Solids and liquids have theirs raised by being evaporated. If the Ep of the arriving vapor is high enough, direct chemisorption can happen without going through the precursor state. That is to say, the atoms and molecules of the arriving vapor instantly react with the surface and then make film deposition. (This section is referenced to the book “Thin-Film Deposition: Principle & Practice by Donald L. Smith)\textsuperscript{59}

Figure 2-1: (A) Adsorption processes and important quantities. (B) Energetics of the precursor adsorption model.

**Nucleation and growth**

The fundamental concept for nucleation behavior is surface energy, which is the work energy stored in a new surface after it was created. For solids, surface energy tends to minimize itself by surface diffusion. This process subsequently determines the structure of thin films. In thin film growth, area of surface topography and surface energy per unit area (γ) vary in accord to many properties of the exposed surface in terms of chemical composition, crystallographic facet, and
atomic reconstruction and roughness. In most crystalline solids, $\gamma$ is anisotropic and only one or two of many facets provide low $\gamma$. For example, an exposed \{111\} face of Si and Ge that have Diamond structure has a lower $\gamma$ than other faces because this face has fewer unsatisfied dangling bonds sticking out.

In layered materials like graphite and TMDC, there are no chemical bonds between the atomic layers of the basal plane and thus the basal plane is their low-energy facet. For deposition of thin films onto a substrate, nucleation behavior has a strong dependence on the $\gamma$ of the substrate ($\gamma_s$), deposited film ($\gamma_f$), and their interface ($\gamma_i$). With an assumption that there is enough surface diffusion so that depositing materials can rearrange themselves to minimize $\gamma$, there are two situations on a bare substrate for nucleation. In **Figure 2-2A**, the film wets the substrate because $\gamma_f + \gamma_i < \gamma_s$, so that the growth occurs in a layer-by-layer manner, which is so called “Frank-van der Merwe” growth mode. The key to let this growth mode occur is there must be strong enough bonding between film and substrate to reduce $\gamma_s$. On the other hand, if the substrate bonding is insufficient, the total surface energy will become $\gamma_f + \gamma_i = \gamma_s$, so that the film does not wet the substrate but forms 3D islands. This mode is referred to the “Volmer-Weber” growth mode, as shown **Figure 2-2B**. The third growth mode that often comes along with the previously mentioned ones is “Stranski-Krastanov” growth mode, in which the growth changes from layer to island after one layer or two due to changing energy situation with successive monolayers. (This section is referenced to the book “Thin-Film Deposition: Principle & Practice by Donald L. Smith)\textsuperscript{59}
Epitaxy (Registry)

Epitaxy means a crystalline overlayer deposited on a crystalline substrate. The crystallographic order of the deposited film is significantly influenced by the crystallinity of the substrate thus achieving certain degree of matching between the two along the interface. Crystal symmetry is one fundamental criteria for epitaxy. If it is interrupted, its potential energy (Ep) increases because the angle and length of bonds and the number of bonds attached to an atom of the crystal change. Consequently, this interruption introduces excess energy to surface and interface per unit area (γ). In order to minimize the γ when one crystal is deposited on a crystalline substrate, the density of bonds of appropriate length and angles needs to be maximized in an attempt to merge symmetries between themselves. The way that the deposited material minimizes the γ is to crystallographically align itself with the substrate as to match the substrate’s bonding symmetry and crystal periodicity, in another word, is to grow epitaxially. As long as the substrate symmetry will not be screened by any interfacial disorder and the growth temperature is high enough so that the depositing atoms can rearrange themselves into equilibrium position before incorporating into the film. In general, epitaxy can be either homo-type or hetero-type- the former type is for the growth of material onto
itself, whereas the latter is for the one on other substrates that results in $\gamma > 0$. The preferred crystallographic orientation of the heteroepitaxial film is often that which $\gamma$ can be minimized. One fundamental criterion for epitaxy is relatively small lattice (frictional) mismatch in the atomic periodicities of the material/substrate along the interface, which is defined as:

$$f = \frac{(\alpha_e - \alpha_s)}{(\alpha_e + \alpha_s)/2}$$

, where $\alpha_e$ and $\alpha_s$ are the atomic spacings along one particular crystallographic direction in the film crystal and in the substrate surface, respectively. Despite $f$ can change at different growth temperature due to the difference in the thermal-expansion coefficients of the film and substrate, the room temperature value is the generally discussed. If $f$ is too high ($> 0.1$), only a few interfacial bonds are aligned well that $\gamma$ cannot be minimized. The option of good single-crystal substrates for epitaxy is limited because it is not easy to find a large-area substrate that also has low defect density. They are also required to be chemically robust or damage-resistant. Some of the commercially available that have reasonable quality, size, and cost include Ge, GaAs, sapphire, mica, and SiC.

In order to achieve an idea epitaxial film with atomically sharp interface, one must consider chemical compatibility in reaction, a deposition process that is not operating near equilibrium, whereby the incorporation flux of adsorbed vapor into the film is larger then re-evaporation flux of film material, and also small a lattice mismatch. The attractive combinations for device applications of heteroepitaxy are those that obtain large band-gap difference and low $f$ simultaneously. For example, heteroepitaxial films integrating group-III nitride (N) semiconductors including GaN, AlN, InN and their alloys are common nowadays for compact, energy-efficient, light-emitting diodes as well as for high-power electronic devices. Heteroepitaxial films made of group III-N substrates and 2D TMDC (e.g., WSe$_2$/GaN) is getting more popular because their mutually small lattice mismatch and the possibility to create a large band edge offset can result a high-performance semiconductor devices with high quality interface (Figure 2-3A). Similarly, a verity of
semiconducting TMDC with different band gap size and position can also create high-quality heteroepitaxy with a significantly large band offset well suited for optics and electronics (Figure 2-3B). (This section is referenced to the book “Thin-Film Deposition: Principle & Practice by Donald L. Smith)  

![Figure 2-3: (A) Bandgap versus in-plane lattice parameter for III-nitrides and TMDC (B) Band alignment of TMDC in hexagonal (H) and trigonal (T) phase](image)

Deposition techniques for TMDC  

Synthesis of bulk TMDCs has been explored for many years and already had many routes (Figure 2-4). For example, chemical vapor transport has been used to synthesis a variety of TMDC under equilibrium conditions using a transport agent (B₂ or I₂) to transport transition metals and chalcogens atoms across a thermal gradient in a vacuum-sealed ampule. Despite this process requires days and weeks, the resulted bulk crystallites provide ultra-high quality for researchers. Similarly, direct vapor transport utilizes a thermal gradient to vaporize stoichiometric TMDCs (many times in powder form) and to recrystallize them at the cold end of the furnace. Although this route has been successful for production of a wide variety of materials (MoS₂, WS₂, MoS₂, WSe₂, TaSe₂, etc.) that can be further mechanically exfoliated to monolayers, it is not scalable and thus cannot fulfill many applications that require large-area samples.
In order to increase the area size and uniformity of film thickness for synthetic TMDC thin films, researchers came out the chalcogenization process, in which thin films made of transition metal/transition metal oxide were converted into MX$_2$ after exposure to chalcogen vapor, such as S$_2$(g), Se$_2$(g), and H$_2$Se(g). Despite this process indeed provides excellent uniformity along both of lateral and vertical direction, its nanoscale domain size and nearly-amorphous nature is the main detriment to high-performance opto-electronics.

Current state-of-the-art techniques for high-quality monolayers are powder vaporization (PV) and metal-organic chemical vapor deposition. Both of these two methods have demonstrated large domain (edge length > 100 μm) and wafer-scale size films deposited on insulating substrates. Therefore, they will be further discussed and implanted in this thesis.

![Figure 2-4: Summary of primary growth techniques for the formation of TMDC atomic layers. These methods include chemical vapor deposition, powder vaporization, metal transformation, chemical vapor transport, chemical exfoliation, pulsed laser deposition, molecular beam epitaxy, spray pyrolysis, and electrochemical synthesis.](Reproduce from Ref.30)
Powder vaporization

The vapor-phase reaction, or powder vaporization (PV) was developed for vapor-phase growth of crystalline MoS$_2$ monolayer on SiO$_2$ in the first paper of synthetic monolayer. This technique provides the easiest method for scalable deposition of high-quality TMDC films on any arbitrary substrate (Figure 2-5A). Taking MoS$_2$ as an example, sulfur and MoO$_3$ powders were chosen as the precursors because they can be vaporized easily at low elevated temperature. The Mo–O–S ternary phase diagram in Figure 2-5B indicates that the gas-phase MoO$_3$ precursors may undergo a two-step reaction during the growth:

\[ \text{MoO}_3 + (\text{x}/2) \text{S} \rightarrow \text{MoO}_{3-x} + (\text{x}/2) \text{SO}_2, \text{ and then } \text{MoO}_{3-x} + (7-\text{x}/2) \text{S} \rightarrow \text{MoS}_2 + (3-\text{x}/2) \text{SO}_2 \]

The transition metal sub-stoichiometric oxides are also formed during the reaction. As illustrated in Figure 2-5C, the intermediated adsorbates diffuse to the substrate surface and further react with sulfur vapors to grow MoS$_2$ layers. MoS$_2$ clusters may also form before it lands on the surface and becomes adsorbate. The partial pressure (which is dictated by temperature) of S and MoO$_3$ governs subsequent adsorption on the substrate and film morphology when they are traveling towards the downstream.

An investigation performed by Vila et al. shows a high MoO$_3$:S$_2$ partial pressure near the front of the substrate promotes MoO$_2$ growth, whereas MoS$_2$ monolayers grow near the end of the substrate, whereby the partial pressure is lower. Besides, the excess in sulfur supply will suppress the volatilization of MoO$_3$, make the partial pressure of vaporized MoO$_3$ low, thus make domain size small. Therefore, a more controllable vapor pressure is in demand in order to have a more consistent morphology and quality.
Figure 2-5: (A) Schematic illustration of commonly PV method for TMDCs monolayers. (B) Phase diagram and possible reaction routes for MoS$_2$ growth. (C) Schematic illustration of the gas-phase reaction and surface epitaxy of MoS$_2$. (D) During PV of MoS$_2$, a transition from vertical domains, to a mixture of vertical and horizontal domains, and finally only horizontal domains, as the partial pressure ratio of MoO$_x$:S$_2$ decreases towards the end of the reactor. $^{65,66}$ (Reproduce from Ref.65-66)

**Metal-organic chemical vapor deposition**

To ensure a consistent precursor supply and improve the scalability and controllability for TMDC deposition, Metal-organic chemical vapor deposition (MOCVD) was developed. It uses organic compounds that contain transition metal and chalcogen elements as the precursors for synthesis. The system for MOCVD process can be hot-wall and cold-wall type (Figure 2-6).$^{30,67}$ The precursors with a high equilibrium vapor pressure are required for MOCVD process so that they can be delivered through mass flow controller. Molybdenum/tungsten hexacarbonyl (Mo(CO)$_6$/W(CO)$_6$) and dimethyl/diethyl- sulfide/selenide ((CH$_3$)$_2$S, (C$_2$H$_5$)$_2$S, (CH$_3$)$_2$Se, (C$_2$H$_5$)$_2$Se) are common options for making TMDC in MCOVD. By using mass flow controller and controlling vapor pressure of each precursor with a bubbler, MOCVD process has been proved to
have better control than the PV and other chalcogenization, in terms of ratio of partial pressure and flow rate, and deposition rate.

One concern on the MOCVD process for TMDC is unintentional carbon incorporation. Chalcogen source such as (CH$_3$)$_2$Se will crack at high temperature in the growth and unavoidably deposit carbon thin layers on the substrate surface and interrupt the film morphology.$^{68,69}$ Due to this reason, the alternative precursor like carbon-free H$_2$Se and H$_2$S has gradually been adopted. A comparison between using H$_2$Se and DMSe by Zhang et al. shows that the carbon incorporation has been removed and the film morphology has also been improved in Raman spectrum and AFM topography (Figure 2-7).$^{69}$ Despite the carbon-contained precursors can diminish the quality of growth on sapphire, it may not severely affect the growth of TMDC on other substrates.

![Figure 2-6: (A) A hot wall MOCVD reactor and (B) A cold wall reactor that uses induction heating and graphite susceptor during the growth.$^{30,67}$ (Reproduce from Ref.30,67)]
Figure 2-7: Raman spectra of WSe$_2$ grown using (A) DMSe and (B) H$_2$Se. The insets are zoom-in regions showing the D and G peaks of carbon in WSe$_2$ grown with DMSe; and the AFM topography of WSe$_2$ grown using (C) DMSe and (D) H$_2$Se.$^{69}$ (Reproduce from Ref.69)

Epitaxial graphene synthesis

In order to provide optoelectronic applications with uniform and large-scale graphene, the synthesis of epitaxial graphene (EG) on silicon carbide (SiC) has been developed.$^{70}$ SiC wafer can be fabricated in the range of 2-6 inches in diameter using standard industrial semiconductor synthesis techniques. The very first growth of graphene on SiC was performed in ultra-high vacuum demonstrated by Van Bommel et al. in 1975.$^{71}$ Silicon sublimation from the SiC cause a carbon rich surface that provides nuclei for graphene growth. However, the electrical transport of epitaxial graphene by UHV method did not look great mainly because of high Si sublimation rate, which results a poor topography. Hence, it is necessary to lower the rate at which silicon sublimes. Among many proposed methods for controllable Si sublimation, one promising route is” confinement controlled sublimation”,$^{72}$ which encloses SiC in a graphite crucible during silicon sublimation
The SiC substrate is first cleaned via chemical solutions and then H-etched at 1500 °C in 700 Torr of H₂/Ar, which removes polishing damages and resulting in a surface with atomically flat terraces. The graphene is then obtained on a SiC substrate via the solid-state decomposition of the substrate, which is achieved by annealing the material in elevated temperatures in the ranges of 1600 - 2000 °C in partial pressures of Ar, driving the sublimation of Si atoms from the surface slowly.²³ The C atoms left behind would reorganize themselves in a hexagonal fashion forming graphene.²³ By optimizing the synthesis conditions of EG, mono- to few-layer graphene deposited on the wide terraces of SiC, separated by a few unit cell high of SiC, and the conjunctions of SiC step/terrace, respectively (Figure 2-9).²⁴

Figure 2-8: (A) If SiC is annealed in UHV, silicon sublimation is not confined and causing rapid growth of graphene; The confinement controlled sublimation method uses a graphite crucible to provide an over-pressure of Si vapor so that the growth rate can be controllable. (B) Using this method, mono-to-few-layer graphene grows on Si-face, whereas thin graphite grows on C-face of SiC. (C) AFM images provide topography of graphene/SiC made by i) UHV; ii) the confining method: Si-face and iii) C-face.²² (Reproduce from Ref.72)
Figure 2.9: (A) Topography of graphene/SiC cannot identify the layer number, which can be revealed by the Raman spectroscopes in (B) The ratio of the intensity of graphene 2D to G peaks ($I_{2\text{DG}}/I_G$) can identify graphene ($I_{2\text{DG}}/I_G \geq 2$) and the fewlayers ($I_{2\text{DG}}/I_G \leq 1$). (Reproduce from Ref.74)

**Progress of synthetic vdW heterostructures updated to 2015**

The practically useful heterostructures made of III-V compounds, such as heterostructure bipolar transistors, phototransistor with wide-gap emitters, and double-heterostructure lasers, hadn’t appeared until the growth technologies of MOCVD and MBE were developed in early 1970s. Similar to the early development on their conventional counterparts, vdW heterostructures haven’t been practical since its demonstration in 2010 due to limited size of clean interface obtained and absence of techniques for the large area growth. Although the vdW epitaxy, growing one vdW solid on another, have already been recognized in 1980s, many were by Koma, it did not get much attention from the research societies until the breakthrough results exploited in manually stacked vdW heterostructures. Recently, the emergence of direct synthesis of vdW solids, utilizing CVD, MOCVD and MBE, also made impressive progress in synthetic vdW heterostructures like graphene-hBN transistors, graphene-TMDC photosensors, and TMDC p-n junctions and tunneling diodes grown on graphene and insulating substrates. In view of these recent results, synthetic vdW heterostructures appear to revolutionize the digital electronics and their industries.
In order to synthesize crystalline TMDC layers, lattice of the selected substrate is critical for the epi-growth of vdW heterostructures. Shi et al.\textsuperscript{81} initiatively used CVD graphene grown on copper foils as the template for MoS\textsubscript{2} growth (Figure 2-10A). The reported process utilizes (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} precursors that was thermally decomposed into MoS\textsubscript{2} in vapor phase and then subsequently deposited on CVD graphene/Cu foil. The as-grown MoS\textsubscript{2} domains on graphene adopted the same orientation of underlying graphene. This experiment indicated that a epitaxial vdW heterostructure can be realized still, even the lattice mis-match can be 20 to 23\%.\textsuperscript{30,81} Similarly, the study in this thesis used epitaxial graphene (EG)/SiC as the growth template for monolayer MoS\textsubscript{2} made via powder vaporization (Figure 2-10B). We also found morphology and defects of EG/SiC can significantly impact the nucleation density and thickness of MoS\textsubscript{2} layers.\textsuperscript{74} Scanning transmission electron microscopy (STEM) images show that the atomically sharp interface is possible to achieve through vapor deposition techniques (Bottom, Figure 2-10B). In addition, it is also possible to grow larger domain of WSe\textsubscript{2} monolayers on EG/SiC via vdW epitaxy.\textsuperscript{77} Following vdW epitaxy, monolayered WSe\textsubscript{2} domains grown on graphene consistently align at either the same direction or 180° rotated and thus achieve a commensurability between WSe\textsubscript{2} and graphene (scanning electron microscopy (SEM) image in Figure 2-10C), as evident by low-energy electron diffraction (LEED) patterns, which roughly shows that 4 transition metal atoms can align with 9 carbon atoms in a long-range order (Inset, Figure 2-10C). The vdW heterostructures can be put on a more sophisticated level by stacking other types of TMDs layers. Two-step growth of MoS\textsubscript{2} and WSe\textsubscript{2} was carried out to create MoS\textsubscript{2}-WSe\textsubscript{2}-graphene and WSe\textsubscript{2}-MoSe\textsubscript{2}-graphene that have clean and sharp interfaces without Mo-W and Se-Se alloys, as evident in STEM images (Figure 2-10, D-F). Besides the techniques of pyrolysis, PV, CVD, and MOCVD, MBE is also emerging for synthetic 2D crystals. Bradley et al.\textsuperscript{82} synthesized 1L to 3L MoSe\textsubscript{2} on bilayer graphene through MBE. Albeit the domain size of the MoSe\textsubscript{2} is typically less than 1 μm in scanning tunneling microscopy (STM),
performing scanning tunneling spectroscopy (STS) on these films is able to obtain the quasi-particle
bandgaps and exciton binding energy of 1L-3L MoSe₂.

**Figure 2-10:** (A) Multilayer MoS₂ grown on CVD graphene/Cu through the thermal decomposition of ammonium thiomolybdate. (B) Mono- and few-layer MoS₂ grown on epitaxial graphene (EG) from powder vaporization (PV) process. (C) WSe₂ monolayers grown EG through PV process or metallic-organic CVD (MOCVD). The WSe₂ lattices are fully registered to the graphene lattices, as evident by low-energy electron diffraction pattern (LEED, Inset). (D) The flow for growing “trilayer” vdW heterostructures. MoS₂-EG was converted into MoSe₂-EG during the growth of WSe₂ layers via a Se-S ionic exchange occurring in high temperatures. (E-F) STEM image confirms these trilayer stacks exhibits pristine interfaces without W-Mo or S-Se formation. (G-I) MoSe₂ layers ranging 1L-3L grown on bilayer EG by MBE. EG serves as bottom electrodes for STS in (I), which measures the quasi-particle bandgap of 1L-3L MoSe₂. 83 (Reproduce from Ref.83)

Although TMDC-graphene heterostructures can be useful as electrical diodes, photosensors, and platforms for STM/STS measurements, majority of devices research are focusing on metal-oxide-semiconductor device geometry. (e.g., TMDCs deposited on SiO₂/Si.) To fulfill this need, many efforts had been made to grow high quality and large size TMDC-based vdW heterostructures on SiO₂/Si, sapphire, and other insulating substrates, mainly through a CVD
Among insulating growth templates, the most popular one is SiO$_2$/Si since it is easy to prepare and immediately makes a metal-oxide-semiconductor (MOS) devices after the material growth. Gong et al.\textsuperscript{79} used Te-assisted powder vaporization involving the reaction of MoO$_3$, W, and S powders to grow both of the lateral and vertical MoS$_2$-WS$_2$ heterostructures in an \textit{in-situ} process. The role of Te powders involved is for lowering the melting point of W powders via forming metastable Te-W alloys during the reaction.\textsuperscript{79} The lateral MoS$_2$-WS$_2$ grows at 650 °C (\textbf{Figure 2-11, A-B}), while the vertical one grows at a higher temperature, at 850 °C (\textbf{Figure 2-11, C-D}).\textsuperscript{79} Besides the a heterostructure that uses single chalcogen atom, Li et al.\textsuperscript{80} also developed a two-step \textit{ex-situ} process using the edges of the WSe$_2$ monolayers pre-grown at 950 °C as nucleation sites and then growing MoS$_2$ monolayers epitaxially around the MoS$_2$ monolayers at 700 °C to obtain MoS$_2$-WSe$_2$ lateral heterostructures (\textbf{Figure 2-11E}). The order for material growth, that is WSe$_2$ 1$^{st}$ and MoS$_2$ 2$^{nd}$, is deliberately decided to avoid the ionic exchange of Se-S occurring above 800 °C. The STEM performed on MoS$_2$-WSe$_2$ confirmed that the lateral interface is atomically abrupt and no sign of Mo-W and Se-S formation in a micro-meter range in parallel to the junction (\textbf{Figure 2-11, F-H}).\textsuperscript{80} Besides the above “flat” cases, vdW heterostructures can also exist in a vertically aligned fashion. Jung et al.\textsuperscript{86} sulfurized (selenized) patterned Mo/W arrays to synthesize MoS$_2$-WS$_2$ (MoSe$_2$-WSe$_2$) heterostructures in large area (\textbf{Figure 2-11I}). Functionality and properties of this type of structures may be completely controllable because the dimension and thickness of Mo/W arrays can be controlled by the lithography and sputtering time, respectively. Although electrical transports don’t favors the vertical formation, as evident in STEM images (\textbf{Figure 2-11J}), (the measured mobility is < 0.01 cm$^2$V$^{-1}$S$^{-1}$ in both of the direction vertical and parallel to the array), preferably exposed dangling bonds on the edge sites are useful for hydrogen-evolution-reaction.\textsuperscript{86}
Electrical transport for 2D semiconductor-based transistors

Atomically-thin TMDC layers has been considered as prominent alternatives of bulk Si, Ge, and III-V compound semiconductors (Figure 2-12, A-B) for future low-power electronic technology and because their ultra-thin nature and leads to excellent carrier confinement effects (Figure 2-12, C-D). In addition, comparing to 3D elemental and compound semiconductors, TMDCs have no dangling bonds that could potentially lead to traps that reduce the mobility of electrons and holes in devices.
Figure 2-12: The inherent difference in surface properties between (A) 3D materials and (B) 2D materials significantly impacts performance of the devices fabricated on them. Mobile charge distribution in (C) 3D and (D) 2D materials indicates a pristine surface without dangling bonds has a good carrier confinement effect that leads to excellent gate electrostatic control. The blue plumes inside the wells of c and d are electron density waves and $V(x)$ stands for a potential well. $^{87}$ (Reproduce from Ref.87)

In graphene- and 2D TMDC-based transistors, transport and scattering activities are confined to their plane. Wang et al. summarized the scattering mechanisms that affected the mobility of carriers: $^{88}$ acoustic and optical phonon scattering; Coulomb scattering at charged impurities; surface interface phonon scattering; and roughness scattering. In the electronics of 3D materials, interfacial roughness scattering can dominate because they mainly rely on the quantum well structure. In the electronics of 2D materials, on the other hand, the effect of surface phonon scattering and Coulomb scattering can be very important in 2D materials electronics. 2D TMDC have partial ionic bonds between the metal and chalcogen atoms, crystal deformation would lead to polarized fields that scatter carriers. The phonon scattering has a strong relationship with the carrier mobility and heavily depends on operating temperatures. Calculation from first principles by Kaasbjerg et al. shows the temperature dependence of carrier mobility in 1L MoS$_2$ with a constant carrier concentration (Figure 2-13A). $^{88}$

Coulomb scattering in 2D semiconductors is caused by random charged impurities located within the layer or on its surfaces. This Coulomb effect also limits the mobility of graphene on SiO$_2$
to values less than $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. A 20x improvement to mobility can be achieved by placing graphene on hBN, which has much less Coulomb scattering on graphene than many substrates due to its excellent surface inertness. Engineering the dielectric environment can enhance the carrier mobilities of TMDC transistors, from $\sim 0.1-3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $\sim 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (MoS$_2$ as an example) at room temperature. Screening the Coulomb scattering from the charged impurities by using the materials with a high dielectric constant. The combined effect of phonons and charged impurities on the mobility of 1L- and few-layer MoS$_2$ and other TMDC is summarized in **Figure 2-13B**.

Theoretical simulation shows that 2D TMDC can make transistors with excellent performance. The operation of 1L MoS$_2$ field-effect transistor (FET) predicted by Yoon *et al.* using the non-equilibrium Green function formalism demonstrate that the top-gated MoS$_2$ transistors with gate lengths of 15 nm can reach on-current as high as 1.6 $\mu \text{A} \cdot \mu \text{m}^{-1}$ during operation, subthreshold swing (SS) as low as 60 mV/dec, and current on/off ratio up to 10 orders. The illustration and the simulated transfer characteristics (gated voltage versus drain current, $I_d-V_g$) for a 1L MoS$_2$ FET at different drain voltage are shown in (**Figure 2-13, C-D**). The high-$k$ dielectric simulated in this device, HfO$_2$, also improves the mobility of monolayer MoS$_2$ owing to the screening of Columbic scattering. The first experimental demonstration of a top-gated transistor based on 1L MoS$_2$ by Kis and co-workers in 2011 has verified the theoretical simulation and showed the use of dielectric layer is effective for performance enhancement. Their devices showed high on/off current ratio ($\sim 10^9$), room-temperature mobility $\sim 40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and SS of 60 mV/dec.
Figure 2-13: (A) Carrier mobility in 1L MoS$_2$ as a function of temperature calculated from first-principles DFT calculation for the electronic band structure, phonon dispersion and electron–phonon interactions. The grey band shows the uncertainty in calculated mobility values due to a 10% uncertainty in computed deformation potentials associated with phonons (B) Calculated and measured carrier mobility in multilayer MoS$_2$ as a function of temperature, showing the scattering contributions from charged impurities (red line), homopolar out-of-plane phonons (green lines) and polar-optical phonons (blue line), as well as the total mobility due to the combined effects (dashed line). (C–D) $I_D$-$V_D$ characteristics at $V_{d} = 0.05$ V and 0.5 V on logarithmic (left axis) and linear scales (right axis). For the nominal device simulated, a maximum ON current close to 1.6 mA/μm and a subthreshold swing (SS = $V_{gg}/\partial I_D/\partial \log_{10}(I_D)$) close to 60 mV/dec are achieved. Drain-induced barrier lowering (DIBL) is as small as 10 mV/V even with very short channel length.88,89 (Reproduce from Ref.88-89)
Conclusions

This chapter covers the fundamentals of thin film deposition and the methods commonly used for TMDC. The transport mechanisms for 2D materials are dominated by a few scattering events, which are also introduced in this chapter. The following chapters are comprised of my research articles that studied the properties, devices of synthetic 2D layers, 2D/2D vdW heterostructures, and 2D/3D heterostructures.
Chapter 3

Properties of atomically thin WSe₂ grown via metal-organic chemical vapor deposition

Part I: Understanding how process and substrate impact property and morphology of film

Tungsten diselenide (WSe₂) is a 2D material that is of interest for next-generation electronic and optoelectronic devices due to its bandgap of 1.65 eV in the monolayer and excellent transport properties. However, technologies based on this novel 2D material cannot be realized without scalable synthesis processes. First part of this chapter talks about the first scalable synthesis of large-area, mono and few-layer WSe₂ via metal organic chemical vapor deposition (MOCVD) using tungsten hexacarbonyl (W(CO)₆) and dimethylselenium ((CH₃)₂Se). In addition to being intrinsically scalable, this technique allows for the precise control of vapor-phase chemistry, which is unobtainable using more traditional oxide vaporization routes. Growth parameters such as temperature, pressure, Se:W ratio, and substrate choice have a strong impact on the resultant atomic layer structure, with optimized conditions yielding > 8 µm size domains. (Collaborators in Part I: The WSe₂ thin films investigated in this study were prepared by Dr. Sarah Eichfeld and Ms. Lorraine Hussain in Materials Science and Engineering. Parts of device fabrication was done by Dr. Jie Li in Electrical Engineering at Penn State University.)
Introduction

Chemical vapor deposition of thick (>100 nm) but non-crystalline TMDC has been successful using a variety of metal-organics (W(CO)$_6$, Mo(CO)$_6$, etc.)$^{90-92}$ and metal-chlorides (MoCl$_5$, WCl$_5$, WOCl$_5$, VOCl$_5$)$^{90,93-95}$ combined with wide range of chalcogen precursors.$^{90-95}$ These early processes, while not refined to synthesize atomically thin layers, provide important insight into precursor chemistries suitable for monolayer TMDC synthesis, and have led to a variety of reports on synthesis of monolayer MoS$_2$, MoSe$_2$, and WS$_2$.$^{96-104}$ Additionally, synthesis of WSe$_2$ has been reported via various techniques including pulsed laser deposition,$^{105}$ amorphous solid-liquid crystalline solid,$^{106}$ and powder vaporization (PV).$^{74,107,108}$ These methods, while important for understanding the properties of monolayer TMDC, lack the control and reproducibility of the precursors needed for a truly scalable synthesis process. Thus, in order to advance technology, developing a scalable process that allows for more precise control of both the metal and chalcogen precursors is requisite.

This part presents the first MOCVD process for synthetic atomically thin WSe$_2$, including synthesis on a wide variety of substrates including sapphire, graphene, and amorphous boron nitride (aBN) and also provides evidence how layer properties could be controlled by varying the Se:W ratio. Characterization of the films using Raman spectroscopy, atomic force microscopy (AFM), and field emission scanning electron microscopy (FESEM) correlate domain size, layer thickness, and morphology of the synthetic WSe$_2$ monolayers with Se:W ratio. Growth conditions necessary to obtain large (5-8µm) domains are discussed including the effect of temperature, pressure, and Se:W ratio. Conductive AFM (CAFM) and current-voltage ($I_{ds}$-$V_{ds}$) measurements on WSe$_2$/epitaxial graphene (EG) also provide evidence that the MOCVD process leads to electronic-grade heterostructures, suggesting a pristine interlayer gap is present between the WSe$_2$ and EG.
**Experimental methods**

**Material synthesis**

Tungsten selenide was synthesized using tungsten hexacarbonyl (Sigma Aldrich 99.99% purity) and dimethylselenium precursors (SAFC (99.99% purity) or STREM Chemical (99% purity)) in a vertical cold-wall induction heated susceptor. The precursors were dispensed into the system via a bubbler manifold allowing for independent control over each precursor concentration. The carrier gas included H₂/N₂ mixtures, with 100% H₂ being optimal. The samples were heated to 500 °C at 80°C/min and annealed for 15 minutes to drive off any water vapor. Samples were then heated to growth temperature (600 - 900 °C) at 80°C/min. Upon reaching growth temperature the W(CO)₆ and DMSe were introduced into the reaction chamber. Growth took place at total pressures from 100-700 Torr and growth times were 30 minutes. The Se and W concentrations were varied by changing the H₂ carrier gas flow rate or bubbler temperature. Samples were cooled to room temperature. (Note: This process was developed by Dr. Sarah Eichfeld, Dr. Joshua Robinson, and Dr. Joan Redwing, with significant assistance provided by Ms. Lorraine Hossain, who is currently a graduate student at UCSD)

Epitaxial graphene is grown on diced SiC wafers via sublimation of silicon from 6H-SiC (0001) at 1700 °C for 15 min under 1 Torr Ar background pressure. CVD Graphene was prepared via a catalytic CVD method on 25-µm 99.999% pure Cu foils at 1050 °C, 1 Torr and transferred onto SiO₂/Si via PMMA membrane. Boron-nitride was deposited on sapphire substrates via a pulse laser deposition (PLD) technique.
**Materials characterization**

The as-grown samples are characterized using Raman spectroscopy, atomic force microscopy (AFM), and transmission electron microscopy (TEM). A WITec CRM200 Confocal Raman microscope with a 488 nm and 633 nm laser wavelength is utilized for structural characterization. A BRUKER Dimension 3100 with a scan rate of 0.75-1 Hz was utilized for the AFM measurements. The scanning electron microscopy was carried out on a Zeiss MERLIN FESEM. TEM cross-sectional samples were made by FEI Nova 200 dual-beam FIB/SEM with lift-out method. A carbon layer was deposited on the WSe$_2$ surface to avoid electron charging. In FIB, SiO$_2$ and Pt layers were deposited to protect the interested region during focused ion beam milling. A JEOL ARM200F transmission electron microscope operated at 200 kV with probe aberration corrector was used for high-resolution TEM (HRTEM) imaging and energy-dispersive X-ray spectroscopy (EDS) analysis.

**Device Fabrication and I-V measurement**

The vertical diode was fabricated with electron beam lithography and lift-off of evaporated metal contacts. In the first step, the graphene contact is patterned and developed with electron beam (e-beam) lithography. Subsequently, metal contacts Ti/Au (10nm/40nm) are deposited with low pressure electron beam evaporation ($10^{-7}$ Torr) after an oxygen plasma treatment to reduce the contact resistance (45s at 100 W, 50 sccm He, 150 sccm O$_2$ at 500 mTorr). Then a layer of 30 nm Al$_2$O$_3$ is deposited conformally over the entire substrate with atomic layer deposition (ALD), which serves as a protection layer for subsequent processing steps and a passivation layer. ALD deposited Al$_2$O$_3$ capping layer has been reported as an effective film to substantially block influence of ambient. In the second e-beam lithography step, a pattern of etch regions are defined, including an
opening on the Ti/Au pads, and regions for the later WSe₂ contacts. The Al₂O₃ capping layer on these regions are first removed with hydrofluoric acid followed by oxygen plasma etching to remove the monolayer WSe₂ and few layers of graphene. This step prevents shorting through the underlying graphene layer after depositing the WSe₂ contacts. In the third e-beam step, the WSe₂ contact pads and thin lines are defined, and the Al₂O₃ layer on the WSe₂ triangular sheets is removed by hydrofluoric acid prior to the metal deposition. Then 50 nm thick Palladium (Pd) layer is deposited by electron beam evaporation at 10⁻⁷ Torr. The high work function Pd contacts with WSe₂ have been reported to produce a smaller Schottky barrier, and many orders higher current density compared to Ti/Au contacts.

Results and discussion

The synthesis of WSe₂ was carried out via metal organic chemical vapor deposition (MOCVD) in a vertical, cold wall system using tungsten hexacarbonyl (W(CO)₆) and dimethylselenium (DMSe, (CH₃)₂Se) as the W and Se sources, respectively (Figure 3-A-B). The precursor purity has significant impact on the resultant film quality, where 99% pure (CH₃)₂Se exhibits much higher carbon contamination compared to 99.99%, regardless of H₂ concentration (Figure 3-1C). While previous reports suggest adding small amounts of H₂ promotes WSe₂ growth,¹¹¹ synthesis using metal-organics requires the use of 100% hydrogen to minimize the carbon impurity incorporation from the W(CO)₆ and (CH₃)₂Se precursors (Figure 3-1D).¹¹²

The choice of substrate clearly has a significant impact on the morphology of atomically thin WSe₂ domains. This is apparent in Figure 3-2, where AFM confirms that EG, CVD graphene, sapphire, and amorphous boron nitride substrates all yield distinct morphologies and thicknesses when grown under the same conditions. This suggests that there may be significant interaction between the WSe₂ and substrate during synthesis, even when the WSe₂ should have no dangling...
bonds out-of-plane when formed. Epitaxial and CVD graphene yield the highest nucleation density of monolayer WSe$_2$ domains, while amorphous boron nitride yields the lowest nucleation density with a strong preference for vertical (3D) growth of WSe$_2$ versus lateral (2D) growth. The presence of reactive defects and wrinkles in graphene is known to provide low energy nucleation sites for the growth of MoS$_2$. This is also the case in this work for WSe$_2$, where graphene defects and surface contamination from the transfer process results in a high density of 3D-WSe$_2$ structures at the center of most 2D-WSe$_2$ domains. Growth on sapphire substrates yields the largest domains (5 - 8 µm) with additional layers growing from edge sites or defect sites on the monolayer. This suggests that the sticking coefficient for Se and W atoms on the surface of sapphire is greater than the other substrates, providing a means to achieve larger triangles through diffusion of source material across the substrate surface.

Finally, the presence of the E$_{2g}$ and A$_{1g}$ peaks of WSe$_2$ in Raman spectroscopy (Figure 3-2E) are observed, confirming the presence of WSe$_2$. Similar to previous reports, the synthesis of the WSe$_2$ on graphene to form a vdW heterostructure does not appear to significantly degrade the underlying graphene based on the minimal “D” peak at 1360cm$^{-1}$ in the Raman spectra.
Figure 3-1: (A) Schematic of MOCVD process allowing for precise precursor control in a vertical cold wall system for the investigation of the synthesis conditions. (B) AFM of WSe$_2$ on sapphire after growth showing monolayer WSe$_2$ was achieved. (C) Impact of the impurity in Se precursor on the WSe$_2$ monolayer under the same growth conditions. The red line indicating a Se source purity of 99.0% and the black curve indicating a purity of 99.99%: Raman spectra indicating that the Se precursor with higher impurity yielded carbon impurity incorporation in the WSe$_2$ layers. (D) The impact of H$_2$ on the growth of WSe$_2$ Raman spectra comparing 100% H$_2$ versus 1:3 H$_2$:N$_2$ as the carrier gas for synthesis of WSe$_2$. A H$_2$:N$_2$ mix for the carrier gas shows the carbon impurity as seen by D and G peaks. The PL is also quenched under the presence of carbon in the WSe$_2$. (Reproduce from Ref.68)

Metal-organic chemical vapor deposition yields crystalline WSe$_2$ atomic layers with a tunable optical bandgap based on substrate choice. Cross-sectional transmission electron microscopy (TEM) of WSe$_2$ on EG and sapphire (Figure 3-2F) confirm the presence of crystalline WSe$_2$ with pristine interfaces. In the case of growth on epitaxial graphene, TEM confirms the presence of three layers of epitaxial graphene and a single monolayer of WSe$_2$, with a clean interface and no observable defects. In contrast, for the case of multilayer WSe$_2$ on sapphire, TEM reveals some disorder at the WSe$_2$/sapphire interface suggesting a reaction during growth, which is similar to that found for WSe$_2$ films synthesized via selenium-oxygen ion exchange of tungsten oxide. In the case of CVD graphene, Raman spectroscopy provides evidence that, while no additional defects
are formed in the graphene during growth, there is a significant amount of strain introduced into the graphene following the deposition of WSe$_2$.

Figure 3-2: (A-D) AFM scans showing differences in the WSe$_2$ morphology when grown on (A) epitaxial graphene, (B) CVD graphene, (C) sapphire, and (D) Amorphous boron nitride. (E) Raman spectra for synthetic WSe$_2$ on the various substrates showing similar quality. (F) Top: Cross-sectional TEM showing high quality WSe$_2$ grown on epitaxial graphene. Bottom: Cross-sectional TEM of high quality, multilayer WSe$_2$ on sapphire. (Reproduce from Ref.68)

This was further investigated by examining shifts in the Raman 2D and G peaks in Figure 3-3A. The data are vector decomposed (Figure 3-3B) to correlate peak shifting to tensile and compressive strain (“eT” and “eC”, respectively), Fermi velocity reduction (eFVR), and hole doping (eH), using methods by Ahn et al. Therefore, it is likely that the WSe$_2$ is also strained due to interlayer interactions, which ultimately reduces the bandgap by 30 meV.$^{115,116}$
Figure 3-3: The presence of strain in WSe$_2$ on CVD graphene. (A) Raman spectra of CVD graphene compared to WSe$_2$ on CVD graphene normalized to the SiO$_2$ at 520 cm$^{-1}$ showing significant G and 2D peak shifts to higher frequency. (B) Plot of Raman 2D frequency vs. G peak frequency for CVD graphene on SiO$_2$ (black) compared to annealed CVD graphene/SiO$_2$ (blue) and WSe$_2$ growth on CVD Graphene/SiO$_2$ (red). The WSe$_2$ growth resulted in 0.4% compressive strain, while the same growth condition without W and Se sources introduced resulted in 0.2% compressive strain comparing to a freestanding graphene. This indicates that the WSe$_2$ deposited on CVD Graphene contributes additional 0.2% strain in addition to the strain from the thermal effects. The strain in monolayer CVD Graphene is calculated according to Ferralis et al.$^{117,68}$ (Reproduce from Ref.68)

Growth conditions, including temperature and total pressure, have a strong impact on the overall domain size, domain shape, and nucleation density. Focusing on sapphire and EG, we find that the WSe$_2$ domain size increases with increased temperature and pressure. This is shown for growth on epitaxial graphene in Figure 3-4A (The temperature is held at constant in the top row; and the pressure is held at constant in the bottom row). While the temperature is held constant at 750 °C, and Se:W ratio held at 100, the domain size increases from roughly 250 nm to 700 nm when the total pressure is increased from 500 to 700 Torr. Likewise, when the pressure is held constant at 650 Torr, and Se:W ratio held at 100, an increase in temperature of 100°C (800→900 °C) yields a 200% increase in domain size (700→1500 nm). Synthesis at high pressure also results in the formation of particulates on the sample surface, which were subsequently identified as W-rich WSe$_2$ via cross-sectional TEM (Inset in Figure 3-4A. The presence of such particles indicates a
lack of Se in the vapor phase during the growth of WSe$_2$, and therefore merited an investigation into the impact of Se:W ratio.

The Se:W ratio is a critical factor in controlling defect formation in WSe$_2$. This is evident in Figure 3-4B, where a surface plot of temperature and pressure versus Se:W ratio clearly demonstrates that domain size increases significantly as the Se:W ratio is increased to 800. Additionally, as the Se:W ratio increases, there is a decrease in the density of W-rich WSe$_2$ particulates. This further supports the TEM analysis determining the particulates to be due to an imbalance in Se:W ratio and led to more detailed analysis of Se:W including “extreme” ratios.

Figure 3-4C plots the domain size as a function of Se:W ratio. Extreme MOCVD ratios of up to 20,000 Se:W allows for a dramatic increase in domain size from 1 micron to 5 micron WSe$_2$ domains. We hypothesize that pushing the Se:W ratio to high values through a reduction in W(CO)$_6$ also leads to a decrease in the amount of nucleation sites and a reduced tendency to form Se vacancies which lead to secondary nucleation sites. Above a ratio of 20,000, however, the domain size begins to decrease again, suggesting that there is an ideal ratio for large domain growth.

Beyond temperature, pressure, and precursor ratios, the total flow through the system can also have a large impact. Figure 3-4D demonstrates the impact of total flow on the domain size and shape. Temperature, pressure, and Se:W ratio were held constant at optimized conditions (800 °C, 700 Torr, and 20,000 Se:W) while the total flow through the system was increased from 100-500 sccm. A total flow of 250 sccm yields 8 µm WSe$_2$ domains, while higher flow rates of 500 sccm result in a decrease in domain size and less defined WSe$_2$ edges. Increased total flow from 100 to 250 sccm increases the gas velocity in the system and leads to increased gas flux at the sample surface and higher lateral growth rates. However, increasing the total gas flow from 250 to 500 sccm leads to a decrease in domain size suggesting the gas velocity does not allow sufficient time for reaction of species at the substrate surface.
Figure 3-4: (A) AFM of WSe$_2$ on EG showing increased domain size with increasing temperature and pressure. (B) Plot of temperature, pressure, and low (<1000) Se:W flux ratios as a function of domain size for sapphire substrates showing the impact of Se:W flux ratio on domain size. (C) Plot of extreme Se:W flux ratios as a function of domain size for both sapphire and epitaxial graphene indicating an optimum Se:W flux ratio around 2x10$^4$. (D) FESEM showing the change in domain size as a function of total flow rate.\textsuperscript{68} (Reproduce from Ref.68)
In addition to synthesis of WSe$_2$, the synthesis of vdW heterostructures is also of increasing importance in the advancement of the field. Synthesis of WSe$_2$ on graphene via MOCVD leads to an electronic-grade heterostructure. Comparing surface topography and conductivity acquired at $V_{\text{bias}} = +0.8$ V clearly indicates that a barrier to transport exists in the heterojunction regions. Current mapping reveals that both of 1L WSe$_2$ and multilayer WSe$_2$ is uniformly resistive, while high conductivity is observed on the graphene area, with graphene wrinkles (Bright stripes in Figure 3-5B) exhibiting enhanced conduction through the AFM tip. Vertical diode structures (Figure 3-5, C-D) structures confirm the presence of a tunnel barrier creating by the WSe$_2$ to vertical transport. The barrier is persistent under an increasing $V_{\text{bias}}$ up to $\pm 2$ V prior to turn-on, while the area only having graphene clearly exhibits linear I-V behavior (Inset, Figure 3-5D). A resistance of $\sim 10^{10}$ $\Omega$ prior to turn-on suggests suggesting that the interlayer gap at the WSe$_2$/graphene interface.

Figure 3-5: (A) WSe$_2$-EG AFM correlated with (B) conductive-AFM mapping. (C) The schematic structure (side view) of 1L WSe$_2$-EG diode using Au/Ti and Pt as source and drain contact, respectively. (D) WSe$_2$-EG diodes display a thermionic emission-like tunnel current turning on before 2 V, while WSe$_2$ grown on EG as a barrier reduced the current by 6 order (Inset of D).$^{68}$ (Reproduce from Ref.68)
Part I conclusions

In summary of this part, a process for MOCVD was developed to synthesize highly crystalline monolayer and multilayer WSe$_2$ and WSe$_2$/Graphene heterostructures. This is the first known report to achieve monolayer control of large domain TMDC structures via MOCVD, and this process allows for excellent control over the process conditions which is necessary to tune domain size, shape and nucleation density. Synthesis via MOCVD offers a highly scalable process with precise control over the gas phase chemistry, which cannot be accomplished using powder vaporization methods.
Part II: Large-area and Electronic-grade epitaxial WSe$_2$

In the second part of the study on the properties of MOCVD WSe$_2$, the breakthroughs in the knowledge of synthesis and material process lead to a device-ready, large-area epitaxial WSe$_2$ film on a crystalline substrate. When epitaxy is achieved, the sapphire surface reconstructs, leading to strong 2D/3D (i.e., TMDC/substrate) interactions that impact carrier transport. Even with 2D/3D coupling, transistors utilizing transfer-free epitaxial WSe$_2$/sapphire exhibit ambipolar behavior with excellent on/off ratios (~$10^7$), high current density (1-10 μA·μm$^{-1}$) and good FET mobility (~30 cm$^2$·V$^{-1}$·s$^{-1}$) at room temperature. This work establishes that realization of electronic-grade epitaxial TMDC must consider the impact of the substrate and 2D/3D interface as leading factors in electronic performance.

Introduction

As previously mentioned, there are extensive efforts to synthesize large-area atomically thin TMDC by a variety of thin film deposition techniques, including powder vaporization (PV) selenization of W/WO$_x$ thin films pre-deposited on arbitrary substrates, MBE and MOCVD. Owing to the ease of preparation and setup, PV using WO$_3$ and Se powders has been widely adapted to produce large WSe$_2$ domains with edge length between 1-100 μm on both crystalline and non-crystalline substrates. Although the PV process provides the scientific community the fastest and most convenient route for obtaining materials for proof-of-concept demonstrations, its limited scalability will inevitably make itself obsolete for large-area commercial applications. On the other hand, MOCVD is an established manufacturing process for traditional compound semiconductors that enables the precise control of thermochemical reactions over an arbitrary size and time scales. The capability to control the defect density and stoichiometry of
synthetic TMDC by MOCVD is continually evolving an improving to the point where large-area films are readily available. Eichfeld et al. extensively studied MOCVD of WSe$_2$ using W(CO)$_6$ and DMSe and demonstrate that optimized growth windows utilize very high Se:W ratios for achieving large domains on sapphire and epitaxial graphene.$^{68}$ Similarly, Kim et al. synthesized large area polycrystalline MoS$_2$ and WS$_2$, demonstrating uniform electrical and optical properties across 4-inch wafers.$^{67}$ In this study, by utilizing high purity precursors and substrate surface engineering, we are able to achieve atomically thin epitaxial WSe$_2$ films with excellent chemical, structural, and electronic uniformity.

Previously reported MOCVD process of WSe$_2$ mainly used carbon-contained MO precursors, such as DMSe or DESe as the Se source.$^{68,124}$ In particular, the use of DMSe frequently leads to nano-size particles deposited on the surface of WSe$_2$ or deposition of amorphous carbon layers at the interface between the substrate and WSe$_2$. Similarly, other MOCVD works for TMDC use alkali metal halide salts such as NaCl and KI to increase domain size and improve film morphology, which inevitably contaminate substrate and as-grown film.$^{67,125}$ In order to suppress the carbon and other impurity contamination caused by the previous precursors, hydrogen selenide (H$_2$Se) was selected as the Se source for this work, while W(CO)$_6$ is the source for W. Instead of using the alkali metal halide salt, the reactor is filled with 100% H$_2$ during the growth to eliminate residual ambient molecules and also carbon contamination.
Experimental methods

**Materials characterization**

Atomic force microscopy (AFM) micrographs were taken with a Bruker Dimension at a scan rate of 0.5 Hz and 512 lines per image resolution. Peak Force KPFM mode using PFQNE AL probe on the same instrument was used to obtain the KPFM data. Lift height of 30 nm (or lower) and AC bias of 4 V were used during the surface potential measurement. The surface potentials of WSe$_2$ measured on the flat surface decreased monotonically with increasing layer number due to the enhanced screening of electronic trap states and dipole moments from the sapphire surface. The screening effect reaches a saturation on 3-4L WSe$_2$ and is consistent with that observed on 1-4L TMDs exfoliated on different surfaces. Scanning electron micrographs (SEMs) are taken in a LEO 1530 scanning electron microscope that uses a Schottky type field-emission electron source and in-lens detector that receives the secondary electrons from the imaged sample. Raman and photoluminescence (PL) spectroscopy measurements (Horiba LabRam) were performed with 532 nm excitation wavelength, 100x objective lens.

*Micro-size* selected-area low-energy electron diffraction (LEED) is performed on WSe$_2$ films in an Elmitec III system. In the experiment, a collimating aperture can restrict the area of the electron beam to size between 1-7 $\mu$m in diameter, allowing us to locally probe the crystallinity across the surface.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) with detection limit of 0.1 part-per-million (ppm) were carried out by the Balazs Nanoanalysis lab on three different samples: sapphire substrate (used as background reference), and two WSe$_2$ films grown by DMSe and H$_2$Se. The impurities detected by LA-ICPMS are well below the X-ray photoemission spectroscopy (XPS) detection limit. XPS of all impurities as well as relevant core
levels (W 4f, Se 3d, C 1s, O 1s, and Al 2p) were measured via a monochromated Al Kα source with takeoff angle of 45° and Omicron EA125 hemispherical analyzer with ±0.05 eV resolution, and acceptance angle of 8°. (26) The analyzer was calibrated with Au, Ag, and Cu foils according to “ASTM E2108-16 2016 Standard Practice for Calibration of the Electron Binding Energy Scale of an X-Ray Photoelectron Spectrometer (West Conshohocken, PA: ASTM)”.

The STM/STS experiments were carried out with a cryogenic STM operated in ultrahigh vacuum at 5 K. Electrochemically etched tungsten tips cleaned in UHV by Ne ion bombardment and electron beam heating were used. STM images were recorded in constant-current mode; bias voltages refer to the sample with respect to the STM tip. STS measurements of the differential tunneling conductance dI/dV were carried out with lock-in technique (modulation frequency 675 Hz at a peak-to-peak modulation of 10 mV) to probe the local density of electronic states. The STS spectra were recorded in a linearly varying tip height mode to improve the dynamic range in the band gap region. All the spectra shown in the paper have been normalized to the constant tip height spectra.

To transfer WSe₂ onto a TEM grids or a fresh substrate, WSe₂/sapphire was spin-coated with 950 K PMMA using 2000 rpm for 30 sec. After that, 16% HF solution was used to release PMMA/WSe₂ from sapphire. Once part of the substrate is merged in HF solution while the sample surface is above the solution surface, the solution will infiltrate into the interface between WSe₂ and sapphire substrate by capillary force to weaken the bond. The total releasing process takes around 1 min. At the end, the released specimen was positioned and captured on the target substrate and the supporting PMMA film was dissolved using acetone and iso-propyl alcohol. All atomic resolution aberration corrected HAADF STEM images were taken with a FEI Titan3 G2* with a resolution of 0.07 nm using 80 kV acceleration voltage.
Impurity of precursor and growth steps of epitaxial WSe$_2$

To understand the impact of precursor on film purity in MOCVD, WSe$_2$ films are deposited using two different chalcogenide precursors, dimethylselenium (DMSe, 99.99% purity) and hydrogen selenide (H$_2$Se, 99.9% purity), while keeping the metal precursor as tungsten hexacarbonyl (W(CO)$_6$). Utilization of DMSe leads to the deposition of carbon as confirmed by x-ray photoelectron spectroscopy (XPS) (Figure 3-6A), which is likely due to an undesirable carbon layer that deposits on the sapphire simultaneous with growth of the WSe$_2$ film. Additionally, using ICPMS, we identify impurities including Fe, Na, Mg, Mo, Co, Zn, Cu, Au, Sb, As, Cr, Ga, Mn, Ni, Nb, Th, Sn, Y, Zr that are not detectable in XPS, indicating that the DMSe precursor exhibits high concentrations of impurities. After switching to a “carbon-free” chalcogenide precursor, H$_2$Se, the C- peak intensity is reduced by ~2-3X and the WSe$_2$ is stoichiometric. In addition, use of the H$_2$Se leads to significant reduction of impurity elements, with the complete elimination of Sb, As, Cr, Ga, Mn, Ni, Nb, Th, Sn, Y, Zr (Figure 3-6B) and reduction in Fe, Na, Mg, Mo, Co, Zn, Cu, Au concentrations to < 10$^{13}$/cm$^2$. Impurities may originate from the H$_2$Se, W(CO)$_6$, the growth chamber itself or post-growth sample handling.

There are three critical steps that we believe play an important role in achieving a high-quality epitaxial WSe$_2$ film including thermal treatment performed on as-received sapphire as the first step to create uniformly distributed step terraces; second, a “nucleation step” where the substrate is exposed to higher flow rates of W- and Se-precursors for a short period; lastly, post-growth annealing at 800 °C under H$_2$Se flow to prevent Se vacancies from forming and also to reduce particles deposited on the surface. Verified by AFM and STM, this last step anneal reduces vacancies and surface nanoparticles. By following these steps, we are able to realize large area epitaxial WSe$_2$ (Figure 3-7) with highly uniform coverage and an excellent epitaxial relationship to the underlying sapphire substrate.
Figure 3-6: (A) Binding energy of carbon measured in the XPS measurement found more carbon incorporated in WSe₂ grown with DMSe as Se source. (B) Elemental impurities detected in WSe₂ films using both H₂Se and DMSe measured by ICPMS. + marks the impurities that were also detected on the annealed c-plane sapphire used for growth.

Figure 3-7: (A,C) The topography of WSe₂ grains grown on annealed c-plane sapphire with (A) and without (C) post-growth annealing with H₂Se flow. (B) A STM view of WSe₂ monolayer grown on graphene without post-growth annealing (D) An improved surface quality of WSe₂ grown on graphene after a 10-minute post-growth annealing was introduced. The applied voltage and scanned area are below their corresponding images.
**Electrolyte-gating electrical measurement**

The preparation of the polymer electrolyte is similar to previously published procedures by Xu *et al.*\textsuperscript{126} with the exception that the electrolyte is prepared and deposited in an argon-filled glovebox where the concentrations of \( \text{H}_2\text{O} \) and \( \text{O}_2 \) are maintained to < 0.1 parts-per-million (ppm). Poly(ethylene-oxide) (PEO) (molecular weight 95,000 g/mol, Polymer Standards Service) and CsClO\(_4\) (99.9%, Sigma-Aldrich) are dissolved in anhydrous acetonitrile (Sigma-Aldrich) with an ether oxygen to Cs molar ratio of 76:1 to make a 1 wt% solution. The solid polymer electrolyte is deposited on the sample by drop-casting 25 µL onto the \( \sim 1 \text{ cm}^2 \) sample, which is enough to cover a majority of the sample surface. After a 15 min wait time to allow the majority of the solvent to evaporate, the sample is annealed on a hotplate at 80 °C for 3 min to drive off remaining solvent. The sample is then transferred from the glovebox to the probe station through an Ar-filled load lock. The entire process of electrolyte preparation, deposition, transfer to the probe station, and measurement are completed under an inert gas environment with no sample exposure to ambient. Electrical measurements are performed on a Lake Shore cryogenic vacuum probe station (CRX-VF) under \( \sim 10^{-6} \) Torr at 300 K using a Keysight B1500A semiconductor parameter analyzer. Before applying the side gate bias (\( V_G \)), ions are homogeneously distributed in the PEO:CsClO\(_4\).

The channel of the field effect transistor (FET) can be doped \( n \)- or \( p \)-type simply by applying voltages of opposite polarity to the side gate (Figure 3-8A). When a positive \( V_G \) is applied, Cs\(^+\) ions are driven to the surface of the channel, which induces electrons in the WSe\(_2\), turning it into an \( n \)-FET. Likewise, a \( p \)-FET can be realized by an opposite electrical field where ClO\(_4\)\(^-\) ions are driven to the channel and dope the channel inducing accumulation of holes. Due to the low mobility of ions in PEO at room temperature, a low sweep rate (8 mVs\(^{-1}\)) was used to provide sufficient time for the ions to respond to the applied electrical field (Figure 3-8B). At the beginning of each transfer curve (\( I_D-V_G \)) measurement, S/D were grounded and \( V_G \) was held at 4 V for 5 min before
initiating sweep to provide the ions sufficient time to reach equilibrium at positive gate bias. All of the transfer curves in the following device study are then swept from positive \( V_G \) to negative \( V_G \) under a drain bias of 500 mV because this polarity (from 4 V to -4 V) provides a more ideal transfer curve where the on-and-off states can clearly be resolved.

**Figure 3-8:** (A) A schematic for the operation of p- and n-FETs using the solid electrolyte under \( V_G > 0 \) (\( CS^+ \) ions form EDL on the channel) and \( V_G < 0 \) (\( ClO_4^- \) ions form EDL on the channel), respectively. (B) Representative dual sweep during the transfer characteristic measurement on WSe\(_2\) FET.

**Results and discussion**

Switching to H\(_2\)Se leads to dramatic improvement in WSe\(_2\) purity compared to prior works, where carbon and many elemental impurities detected in inductively coupled plasma mass spectrometry (ICPMS) are eliminated. Furthermore, utilization of MOCVD provides a means to uniformly synthesize large area monolayers across the substrate (Figure 3-9A). The substrate and the subsequent surface preparation of the substrate is fundamentally important for achieving crystallographic alignment (epitaxy) and long-range order. While epitaxial growth of TMDCs is possible on graphene,\(^{77}\), gallium nitride,\(^{127}\) and sapphire,\(^{128,129}\) c-plane sapphire [Al\(_2\)O\(_3\) (0001)] is the substrate of choice in this study because it is a commercially viable,\(^{130}\) and highly chemically
robust surface compatible with the harsh environments required for synthesis of TMDCs \(^{128,129}\). The choice of sapphire, however, does not guarantee uniformity or epitaxy of the WSe\(_2\). This is evident when growth is carried out on “as-received” c-plane sapphire, where we find optimized conditions often simply lead to multilayered, truncated domains (Figure 3-9B) due to low surface energy and potential surface damage caused by mechanical polishing. However, annealing the sapphire substrate in air leads to the reconstruction of the surface resulting in terracing and regular atomic steps (0.2-0.4 nm tall and 50-300 nm wide).\(^{129}\) The reconstruction leads to a significant enhancement in surface energy, which enables uniform film coverage and layer-by-layer growth of the WSe\(_2\) grown under the same growth conditions (Figure 3-9C). The three-fold symmetry of 2H-phase TMDCs and its long-range commensurability with the c-plane sapphire \(^{128,129}\) results in an epitaxial orientation of the WSe\(_2\) grains that is either 0° or 60° compared to each other. Importantly, subsequent layer growth also follows this relationship. Furthermore, atomic force microscopy (AFM) verifies that the atomic steps of c-plane sapphire are readily translated to the WSe\(_2\) topography (Inset of Figure 3-9C). The photoluminescence (PL) of the epitaxial WSe\(_2\) clearly identifies a direct to indirect bandgap transition as the film thickness is increased from 1L to 3L, where the peak intensity is reduced and the energy position red-shifted (Figure 3-9D).\(^{131}\) Further investigation of the WSe\(_2\) via scanning tunneling spectroscopy (STS) (Figure 3-9E) confirms that the bandgap of 1L and 2L WSe\(_2\) grown on epitaxial graphene(EG)/SiC are 1.94 and 1.64 eV, which is consistent with the MBE-grown WSe\(_2\) on EG.\(^{123}\)

While substrate surface engineering is requisite for epitaxy, it is not the only requirement. The growth temperature (T\(_{G}\)) is also a primary factor in achieving commensurability between WSe\(_2\) and (0001) sapphire. This is clear when comparing the low-energy electron diffraction (LEED) patterns of WSe\(_2\) films grown at 650 °C and 800 °C on 1x1 cm\(^2\) annealed c-pane sapphire (Figure 3-9F). The LEED patterns of films grown at 650 °C only exhibit a broad, blurred pattern, confirming the polycrystalline nature of the layers. On the other hand, samples grown at 800 °C exhibit clear
hexagonal LEED patterns across the sapphire substrate, confirming the epitaxial nature of the layers despite the large lattice mismatch between the sapphire and WSe$_2$. This is possible via the commensurability of a 3×3 superlattice of WSe$_2$ and 2×2 superlattice of c-plane sapphire, which exhibits a relatively small lattice mismatch of approximately 4.0%. However, evident from the 650 °C growth, if $T_G$ is not high enough, then the deposited atoms do not have enough surface energy for diffusion to crystallographically rearrange and align with the sapphire. In this research, temperatures > 700 °C are necessary to achieve commensurability between TMDCs and sapphire substrates, thus we focus on 800 °C for epitaxial synthesis of WSe$_2$ on annealed sapphire substrates.

Growth temperature also controls defect density in a TMDC. Scanning transmission electron microscopy (STEM) provides direct evidence that the density of point defects within the lattice of WSe$_2$ is reduced by 100x (from $\sim 10^{14}$ cm$^{-2}$ to $\sim 10^{12}$ cm$^{-2}$) when $T_G$ is increased from 650 °C to 800 °C (Figure 3-9, G-H). Additionally, there is also a greater density of multi-atom defects and defect complexes (dark regions) in WSe$_2$ grown at 650 °C compared to 800 °C. Scanning tunneling microscopy (STM) performed at 5 K on 1L WSe$_2$/EG identifies five types of defects with distinct features on the WSe$_2$ surface, labeled as A to E in Figure 1I. Such defects adversely affect carrier transport in WSe$_2$ and thus need to be minimized. In order to reduce these defects, a 10-minute annealing in H$_2$Se flow was included after the growth step. During this post-growth annealing, H$_2$Se flow is maintained at 800 °C. The surface quality was significantly improved by post-growth annealing, as the numbers of particles and point defects on WSe$_2$ surface were reduced. Quantitatively, type A and B were reduced by $\sim 10$x, and the high quality hexagonal lattice becomes more evident, and in some areas, the type C defect was entirely eliminated. On the other hand, the density of defect types D and E remained the same level after the post-growth annealing. It is possible that the increased type D and E is due to excess Se deposited during growth cooldown or impurities incorporated during growth (i.e., iron from gas pipes and sodium from quartz tubes in the reactor)). Nevertheless, the overall density of defects in an area of the sample that went through
the post-annealing is around \(7.5 \times 10^{11}\) cm\(^2\), which is compatible to the densities from MBE-grown WSe\(_2\) (\(2.8 \times 10^{12}\) cm\(^2\)) and mechanically cleaved WSe\(_2\) crystals (\(1.2 \times 10^{12}\) cm\(^2\)).\(^{123,132}\)

**Figure 3-9:** (A) \(\text{H}_2\text{Se}\) and \(\text{W(CO)}_6\) metal-organic precursors provide Se and W atoms in the growth of WSe\(_2\). The bottom optical microscope image shows a uniform WSe\(_2\) film grown on 1 cm\(^2\) c-plane sapphire. (B) Growth performed on as-received sapphire at 800 °C resulted in isolated and multilayered WSe\(_2\) islands (C) Scanning electron microscope image shows the same growth conditions performed on annealed sapphire achieved continuous 1L WSe\(_2\) film with the 2nd layer aligned and starting to coalesce. Inset: An atomic force image of the clean morphology of the epitaxial WSe\(_2\) film. (D) Evolution of the photoluminescence spectra obtained from the fully coalesced WSe\(_2\) ranging from 1L to 3L. (E) Bandgap of 1L and 2L WSe\(_2\) obtained in the STS measurement performed at 4 K. (F) Low-energy electron diffraction patterns obtained at 3 different spots on WSe\(_2\) grown on annealed-sapphire shows a sharp hexagonal pattern on 800 °C WSe\(_2\) but an unresolved pattern on 650 °C WSe\(_2\), indicating an improved epitaxial growth at higher growth temperature. (G-H) The relationship between the quality of WSe\(_2\) lattice in terms of defect density and the growth temperature was established in STEM measurement from \(> 1 \times 10^{14}\) cm\(^{-2}\) at 650 °C to \(< 1 \times 10^{12}\) cm\(^{-2}\) at 800 °C. (I) 5 most common types of defects observed in WSe\(_2\) in STM measurement. (A is Se-vacancy, B is W-vacancy substituted by a Se atom, C is double Se-vacancy, and D/E are impurity interstitials)

Even with low defect density, epitaxial WSe\(_2\), domain boundaries (DBs) can form as the films coalesce. Based on high-resolution STEM investigations, epitaxial WSe\(_2\) DBs are predominately categorized as: 1) the intersection and coalescence of domains that are oriented at 0° and atomically displaced in x or y, or 2) anti-phase domain boundaries that form when domains that are rotated 60° with respect to one another coalesce. Typically, when two aligned domains coalesce (0° DB), their joint interface predominantly remains hexagonal and uninterrupted (Figure 3-10, A,C). On
the other hand, when domains are rotated 60°, a 4|4P boundary forms, referred to here as an anti-phase domain boundary (APB), characterized by one Se atom coordinated with four W atoms (Figure 3-10, B,D). Such boundaries, in addition to containing a high density of atomic dislocations (Red squares in Figure 3-10D), are predicted to be metallic, which could impact carrier transport.

Figure 3-10: (A) Z-contrast image of two domains aligned in the same direction that have coalesced and formed a seamless DB with the WSe₂ lattice remaining hexagonal (marked in light green). Voids are marked in purple. (B) the grains aligning against each other form 4|4P 60° DB (marked in orange). (C-D) z-contrast images provide closer views on two major types of DBs. Different domains that form a DB are labeled by 1 and 2. (blue and yellow sphere represent W and Se atoms, respectively; dislocation is marked with red square)

The synthesis of vdW materials on 3D substrates is not like traditional epitaxy, in part because vdW materials do not exhibit dangling bonds like that found in 3D. In order to achieve vdW epitaxial growth of 2D materials on traditional 3D substrates, Koma et al. passivated the surface dangling bonds with chalcogen atoms prior to layered TMDC growth (i.e., GaSe/Se-GaAs (111) and TX₂/S-GaAs). Epitaxy of WSe₂ on sapphire is accompanied by a “passivation layer” (noted as P) formation between the WSe₂ and sapphire substrate. A cross-sectional image of STEM (Figure 3-11A) shows a vdW gap between the WSe₂ and sapphire surface. The sapphire surface
also exhibits a structure different from that of the bare sapphire and now includes selenium (P in Figure 3-11B), based on z-contrast intensity and the EDX mapping (Appendix Figure A2). Density functional theory (DFT) modeling of various substrate surface terminations indicates that the passivating layer consists of selenium chains attached to the sapphire surface (Figure 3-11C). The connection between the Se chain and the sapphire surface can be a direct Al-Se bonds or an Al-O-Se bridge via residual oxygen atoms on the surface (Appendix Figure A3). The randomized orientation and length of the Se chains cause the blur of the STEM images. The simulated layer closely matches the interface identified by STEM imaging. Despite DFT modeling that predicts the presence of the passivation layer leads stronger WSe$_2$-substrate bonding, the electronic properties of the WSe$_2$ are not significantly altered, as the calculated WSe$_2$ density of states (DOS) shows no new energy states inside the bandgap caused by the passivating layer (Figure 3-11C).

Substrate surface topography strongly influences the electronic properties of epitaxial WSe$_2$. Kelvin-probe force microscopy (KPFM) of an epitaxial WSe$_2$ film establishes that the topographic steps in the sapphire (Figure 3-11D) induce localized modulation in WSe$_2$ surface potential (and hence Fermi level), creating a “striping” effect in the KPFM map (Figure 3-11E). The AFM of the original growth substrate following transfer (Figure 3-11F) reveal residual stripes of Se-rich WSe$_2$ along the step edges, indicating that coupling between the WSe$_2$ and the step edge is much stronger than that found at the WSe$_2$/sapphire (0001) interface. The impact of the steps is further verified when the WSe$_2$ is transferred to a fresh SiO$_2$/Si (Figure 3-11G), where the variability in potential is reduced by 2-4x and the “striping” has disappeared. Such modulation in the Fermi level, and the presence of W/Se residue at step edges following film transfer provides direct evidence that the steps play a critical role in the growth and electronic transport of epitaxial WSe$_2$, making it essential to understand the physical source of this Fermi level variation.

Atomic steps in sapphire enable WSe$_2$ nucleation and induce structural variation. Evident from STEM (Figure 3-11, H-I), the first WSe$_2$ layer appears to nucleate at the sapphire atomic step edge.
and subsequently grows across the adjacent step edge and over the layer nucleating at that edge, similar to step-flow growth in traditional semiconductors. Beyond providing a potential source for nucleation, the presence of the steps can lead to structural mixing of WSe₂ (Figure 3-11I), that can also be accompanied by sporadic interlayers between sapphire and WSe₂ (Figure 3-11J). Such structural bonding and mixing are correlated with the presence of a step edge, and are hypothesized to be the source of the Fermi level modulation, while the sporadic interlayers lead to circular bright spots in the surface potential map at terrace centers. Interestingly, the impact of the step edges is reduced with increasing layer thickness (Figure 3-11E), indicating that each additional layer electronically screens the interface imperfections. Therefore, it is likely imperative to grow ≥ 2L to effectively realize high quality electronic transport and lateral device performance.

Electrolyte-gated bilayer WSe₂ FETs (Figure 3-12A) demonstrate the impact of material properties on electronic performance. FETs are evaluated for on/off ratio, subthreshold slope (SS), FET mobility (μFET), and threshold voltage (V_T). Prior to electrolyte deposition, the WSe₂ channel is highly resistive (Figure 3-12B), suggesting the as-grown WSe₂ is p-doped such that the threshold voltage (V_G) is > 0V. Following electrolyte deposition the contacts are ohmic (Figure 3-12B), indicating n-doping of the channel and thinning of the Schottky barrier at the WSe₂/metal interface. Furthermore, transfer curves (I_dS-V_G) (Figure 3-12C) indicate that palladium (Pd) contacts yield the highest μFET, best on/off ratio, and best SS for n-branch FETs. This is likely due to hybridization between Pd and WSe₂ surfaces that reduces the tunnel barrier at top of surface.
Figure 3-11: (A-B) indicates that the sapphire surface reconstructs to form a selenium-based passivating layer (P). DFT (C) indicates that the P consists of Al-Se that can lead to (C) energy states near the valance band edge (0 eV) of the WSe₂ DOS. Furthermore, AFM (D) and KPFM (E) provide evidence that the sapphire topography induces localized modulation of the WSe₂ Fermi level. AFM (F) of the original substrate indicates residual WSe₂ at the sapphire step edges, and KPFM (G) on the same film following transfer exhibits a 2-4x reduction in surface potential variation. Cross-sectional STEM confirms localized Fermi level modulations are likely the result of: (H) WSe₂ bound to the step edge, (I) WSe₂ layer junctions, and (J) Se-rich interlayers.

Growth temperature dramatically impacts epitaxial WSe₂ performance. This is evident when considering the transport of WSe₂ grown at 800 °C (800WSe₂) and 650 °C (650WSe₂) (Figure 3-12C). Bilayer 800WSe₂ exhibits colossal improvements in transport over 650WSe₂, with ~1000x increase in on-current, 100-1000x higher on/off ratio (10⁷), 100x higher μFET (~10 cm²/Vs), and 2-3x lower SS for the n-branch (<200 mV/dec) in long channel FETs (Figure 3-12C). In this case, the larger domains, reduced density of high-angle DBs, and dramatically reduced density of lattice point defects reduce impurity and phonon scattering. For 800WSe₂, the p-branch cannot be resolved.
using the polymer electrolyte; however, based on the hole/electron $\mu_{\text{FET}}$ ratio for $^{650}\text{WSe}_2$ ($\sim 10$), we speculate that $^{800}\text{WSe}_2$ could exhibit hole $\mu_{\text{FET}}$ as high as 100 cm$^2$/Vs at room temperature.

Substrate step edges act as doping and scattering centers in epitaxial TMDC. To determine the impact of atomic step edges, FETs are fabricated with channels parallel (FET$_\parallel$) and perpendicular (FET$_\perp$) to the step direction (Figure 3-12D; dark stripes in the inset SEM image). Average $\mu_{\text{FET}}$ (and SS) for FET$_\parallel$ and FET$_\perp$ are 5.2 ± 0.7 cm$^2$/Vs (302 ± 50 mV/dec) and 3.8 ± 1.4 cm$^2$/Vs (322 ± 16 mV/dec), respectively. However, the $V_T$ of FET$_\perp$ is shifted positive by $> 1$ V, and the saturation current is nearly 2x lower, indicating the steps hole-dope the WSe$_2$ and scatter carriers at higher rates than the (0001) Se-passivated sapphire plane. Furthermore, steps also lead to variation in the WSe$_2$ layer thicknesses, leading to modification in the bandgap thus requiring tunneling between WSe$_2$ layers to maintain electrical continuity. Importantly, however, the distribution of field-effect mobility, on/off ratio, and SS from devices across a 1 cm$^2$ WSe$_2$ film (Figure 3-13) is highly uniform. Furthermore, comparing $\mu_{\text{FET}}$ versus current on/off ratio of all “large-area” synthetic WSe$_2$ films (Figure 3-14) indicates that the $^{800}\text{WSe}_2$ with Pd contacts is comparable to the best single crystal bilayer WSe$_2$ domains reported, even though epitaxial WSe$_2$ exhibits smaller domains, domain boundaries, and many sapphire steps.
Figure 3-12: Demonstration of WSe$_2$ FET: (A) Schematic details and optical image of the WSe$_2$ FETs. (B) $I_d$-$V_d$ output characteristics indicate the electrolytic gate dopes the WSe$_2$ channel, improving contact resistance and shifting $V_T$. (C) Comparing transfer characteristics demonstrates superior performance of the 800$^\circ$C epitaxial WSe$_2$. (D) Transfer characteristics of WSe$_2$ channels parallel and perpendicular to substrate steps reveals the steps dope and scatter carriers.

Figure 3-13: (A) The layout shows the location of the 12 devices on a 1x1 cm$^2$ epi-bilayer WSe$_2$ film. (B) FET performance is uniform from the center to the edge when the channel is parallel to the substrate step edges.
Figure 3-14: Benchmarking state-of-the-art room-temperature device performance on synthetic WSe$_2$ compares the performance of epitaxial WSe$_2$ in this work. Only Hall mobilities are available for the WSe$_2$ grown on sapphire by MBE, while other mobilities are from room-temperature FET measurement. (Reference: 1. Nano Letter, 15, 709; 2. ACS Nano, 8, 923; 3. Nanoscale, 8, 2268; 4. 2D Materials, 3, 14004; 5. Nano Letter, 17, 5595; 6. ACS Nano, 9, 4346; 7. Nanoscale, 7, 4193; 8. Journal of Electronic Materials, 45, 6280)

Part II conclusions

This part provides the foundational knowledge for epitaxy of WSe$_2$ on sapphire, and the 2D/3D interactions that dominate transport in as-grown epitaxial layers. The realization that the substrate can dominate the transport of atomically thin WSe$_2$ strongly suggests that we must consider epitaxy of multilayer 2D materials if we are going to produce transfer-free, electronic grade, epitaxial 2D materials. These findings are generally applicable to other TMDCs, and thus will guide and stimulate research interests in synthesis and transport of 2D epitaxial layers for electronic applications. (More details regarding materials synthesis, device fabrication, and theoretical data/discussion can be found in Appendix A)
Chapter 4

Direct synthesis of van der Waals solids

The stacking of two-dimensional layered materials such as semiconducting transition metal dichalcogenides (TMDCs), insulating hexagonal boron nitride (h-BN), and semi-metallic graphene has been theorized to produce tunable electronic and optoelectronic properties. In this chapter, we demonstrate the direct growth of MoS$_2$, WSe$_2$, and hBN on epitaxial graphene (EG) to form large area van der Waal heterostructures. We reveal that the properties of the underlying graphene dictate properties of the heterostructures, where strain, wrinkling, and defects on the surface of graphene act as nucleation centers for lateral growth of the overlayer. Additionally, we demonstrate that the direct synthesis of TMDCs on EG exhibits atomically sharp interfaces. Finally, we demonstrate that direct growth of MoS$_2$ on EG can lead to a $10^3$ improvement in photoresponse compared to MoS$_2$ alone.

Introduction

Graphene is considered the foundation of exciting new science in two-dimensional layered materials;\textsuperscript{19} but it is only the “tip of the iceberg”. Novel device designs necessarily require additional high quality film either as the barrier or active layer. Recently h-BN has attracted attention as a gate dielectric or substrate material for integration with graphene-based electronics as a gate dielectric or substrate material because its sp$^2$ hybridized bonding and weak interlayer vdW bonds results in a pristine interface.\textsuperscript{138} This also leads to a decreased density of absorbed impurities that act as Columbic scatters when designing novel layered heterostructures.\textsuperscript{35,36,46} Additionally, two-dimensional dichalcogenide-based materials are of significant interest for their
finite bandgaps ranging from 3.5 eV for GaS\textsuperscript{139} to < 1 eV for MoTe\textsubscript{2} and WTe\textsubscript{2}.\textsuperscript{140} More specifically, 2D TMDC have gained momentum in recent years due to their applications in a variety of electronic and optoelectronic applications.\textsuperscript{3} This is also complemented by the possibility to tune the energy bandgap of TMDCs from 0.8-2.1 eV through heterogeneous integration, thus producing entirely novel electronic and optoelectronic materials not yet synthesized.\textsuperscript{141} These unique properties make TMDCs promising candidates for high performance, low cost energy materials for use in flexible electronics, photovoltaics,\textsuperscript{142} and energy storage.\textsuperscript{88,143} Development of electronically tunable vdW solids must start with high quality substrate materials. Graphene and graphite are excellent templates for the growth of bilayer AB stacked graphene,\textsuperscript{144} topological insulators,\textsuperscript{145} and other 2D materials such as h–BN and MoS\textsubscript{2}.\textsuperscript{29,81,146–148}

To date, progress in the development of vdW heterostructures have led to a variety of new phenomena.\textsuperscript{148} However, these vdW structures are primarily fabricated via mechanical exfoliation using polymer membranes and micromanipulators to stack the individual 2D crystals.\textsuperscript{36} The process of mechanical exfoliation, while often useful for demonstration purposes, can lead to interface contamination.\textsuperscript{57} These defects and adsorbates buried at the interface of the 2D crystals undoubtedly diminish the quality and performance of devices. Therefore, the development of a growth technique to assemble these systems during synthesis is requisite for large area, high quality vdW solids. Several groups have demonstrated direct growth of bi-layer vdW solids (two dissimilar layers) as the building block for further hetero-integration. Liu et al.\textsuperscript{146} used a two-step ex-situ process to grow chemical vapor deposition (CVD) graphene followed by synthesis of h-BN on the CVD graphene. Similarly, Shi et al.\textsuperscript{81} utilize CVD graphene as the growth template to grow MoS\textsubscript{2} by flowing (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} precursor. While these are significant advances in the pursuit of vdW solids, the use of CVD graphene on Cu requires sophisticated methods of Cu-etching and transferring to avoid pinholes, tears, or surface contamination in the heterogeneous structures. This may limit the applicability of heterostructures based on CVD graphene simply due to variation in electronic
properties due to polymeric contamination, mechanical strains, and substrate/vdW solid interface imperfections.

In this work, we utilize EG on 6H-SiC as the growth template for direct growth of MoS₂, WSe₂, and hBN. Quasi-freestanding EG (QFEG), a hydrogen-treated EG, is also utilized as a growing template and compared to EG to understand the impact of the EG buffer layer. Epitaxial graphene is utilized because it provides several technological advantages: 1) graphene is already on an insulating substrate, requiring no transfer processes, 2) the interface between graphene and SiC is pristine and tailorable, 3) the surface is free of polymeric and other contaminants found in transferred CVD graphene, and 4) EG is typically quite robust under standard device fabrication processes. However, there are also challenges to utilization of epitaxial graphene (uniform thickness over large areas, steps in the SiC surface) that must also be considered. Here, we utilize atomic force microscopy (AFM), Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and photocurrent measurements to elucidate the impact of EG properties on the resulting MoS₂/EG, h-BN/EG, and WSe₂/EG heterostructures.

**Experimental methods**

**Material synthesis**

Epitaxial graphene is grown on diced SiC wafers via sublimation of silicon from 6H-SiC (0001) at 1700 °C for 15 min under 1 Torr argon (Ar) background pressure. Quasi-free standing graphene is prepared by exposing EG to 600 Torr hydrogen (H₂) at 1050 °C for 120 min to intercalate hydrogen at the graphene/SiC (0001) interface. Growth of MoS₂ layers were accomplished using MoO₃ powders (0.1g) placed in a ceramic crucible located in the center of a 2” tube furnace. Sulfur powders are placed in the second ceramic crucible up stream and held at 130 °C during the reaction.
The EG/SiC for growing MoS\textsubscript{2} were put at the downstream side. The MoO\textsubscript{3} and S vapors were transported to the EG/SiC substrates by pure Ar flowing gas (Ar = 50 sccm, chamber pressure = 5 Torr). The heating zone was heated to 670 °C at a ramping rate of 15 °C/min. Growth of WSe\textsubscript{2} layers on EG were accomplished by first thermally evaporating 5 nm WO\textsubscript{3} on EG/SiC. The WO\textsubscript{3}/QFEG/SiC was subsequently exposed to selenium vapor by heating pure selenium metal to 500°C upstream in the tube furnace. This process converts the WO\textsubscript{3} to WSe\textsubscript{2}, as discussed elsewhere. Growth of hBN layers on QFEG was accomplished in a 75 mm diameter horizontal tube furnace via thermal CVD method utilizing ammonia borane (NH\textsubscript{3}BH\textsubscript{3}) precursor. Solid ammonia borane powder is sublimed at 135 °C and transported into the tube furnace by H\textsubscript{2}/Ar carrier gas (5% of total flow rate). Growth occurs at 1075 °C and 250 mTorr in 5 min. After the growth, the ammonia borane carrier gas is turned off and the furnace is allowed to cool down to room temperature slowly in a 250 mTorr Ar/H\textsubscript{2} environment.

**Fabrication and measurement of MoS\textsubscript{2} photosensor devices**

Two terminal photosensor devices were fabricated using standard ultraviolet photolithography. The sensors are with various source-drain spacing, which ranges from 1 um to 15 um. Titanium/gold (30/100 nm) ohmic contacts were deposited in a similar fashion to our graphene devices, which utilizes an oxygen plasma pretreatment. Photocurrent measurements were carried out at room temperature in ambient, and were coupled to a Renishaw micro Raman spectroscopy with a 488 nm laser. The electrical conduction data was collected with a power source and a Keithley 2400 semiconductor analyzer.
Characterization

The as-grown heterostructures are characterized using Raman spectroscopy, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). A WITec CRM200 Confocal Raman microscope with a 488 nm laser wavelength is utilized for structural characterization. For as-grown epitaxial graphene, the SiC background signal is subtracted using a direct subtraction of the SiC substrate from the spectra.\textsuperscript{153} A BRUKER Dimension with a scan rate of 0.5 Hz was utilized for the AFM measurements. A Kratos Axis Ultra XPS system utilizing an Al k-alpha source with energy of 1486.7 eV was used for XPS analysis. The TEM cross-sectional samples were made via utilizing a NanoLab dual-beam FIB/SEM system. Protective layers of SiO\textsubscript{2} and Pt were deposited to protect the interesting region during focused ion beam milling. TEM imaging was performed using a JEOL 2100F operated at 200 kV.

Results and discussion

The utilization of epitaxial graphene provides a near perfect template for synthesis of VdW solids due to its lack of dangling bonds, chemical inertness, and ability to remain intact under high stress. Additionally, many of the 2D layered materials are isostructural, belonging to the symmetry group P6\textsubscript{3}/mmc.\textsuperscript{154} However, based on the lattice parameters of graphene, hBN, MoS\textsubscript{2}, and WSe\textsubscript{2} (2.461 Å, 2.50 Å, 3.16 Å, and 3.28 Å respectively) one may not expect epitaxial growth to proceed for transition-metal dichalcogenides (TMDC) on graphene because a significant lattice mismatch exists. While this mismatch can be highly detrimental in 3D semiconductor epitaxy, there is a significant relaxation in the required lattice matching when growth proceeds via vdW interaction.\textsuperscript{155} Density functional theory (DFT) modeling clearly indicates poor commensurability between strain-
free graphene and MoS$_2$ (Figure 4-1, A,C), where the red dashed box is a guide to the eye illustrating the closest lattice match occurs at 3 and 4 unit cells (3-4) for MoS$_2$ and graphene, respectively. Figure 4-1C further illustrates the poor commensurability of the MoS$_2$/graphene (and other TMDC/graphene combinations) heterostructures at the (3-4) matchup. However, the weak vdW interaction provides a route for “epitaxy” to occur in these structures. Ongoing Density Functional Theory (DFT) simulations, with vdW corrections as implemented in ONETEP,$^{25}$ have already shown homogeneous-symmetrical reconstruction of the layered structures by inducing large strain on the layer of graphene; at the Local Density Approximation level of exchange and correlation functional.$^{26}$ Additionally, DFT indicates that the residual strain in epitaxial graphene (typical for graphene on SiC)$^{156}$ could impact epitaxy of the TMDC by providing a route for improved commensurability (Figure 4-1, B,D,E). Synthesis of high quality epitaxial graphene (EG) was prepared by using an in situ hydrogen etch, followed by Si sublimation from Si-face of semi-insulating 6H-SiC (II–VI, Inc.) at 1700 °C, 100 Torr. Some EG samples were further exposed to molecular hydrogen (hydrogenation) at 1050 °C, 600 Torr for 60min to passivate the graphene/SiC (0001) buffer layer - referred as quasi-free-standing epitaxial graphene (QFEG). Hydrogenation typically results in the partial relaxation of residual strain in epitaxial graphene, which is evident in the red-shifted 2D Raman peak of the QFEG (Figure 4-1D). Raman and transmission electron microscopy confirm a uniform, continuous top layer of epitaxial graphene (EG) extending over the SiC (110n) step edge and onto SiC (0001) terraces, with few-layer EG existing on the step edge after the growth. The QFEG exhibits atomically smooth surfaces on the SiC terrace, as well as atomic-scale wrinkles that result from the coefficient of thermal expansion (CTE) mismatch that exists between EG and SiC (Figure 4-1F). This provides an ideal platform for understanding the interaction of heterolayers, and the impact surface defects such as wrinkling, thickness, and surface potential variation has on the ability to form pristine vdW solids.
In addition to transforming the buffer into an additional graphene layer, Raman indicates the quality of QFEG is significantly improved compared to EG, as the D peak is suppressed. EG and QFEG are utilized as the base templates for direct integration with MoS$_2$. The nucleation and growth of MoS$_2$ is strongly influenced by the characteristics of the underlying graphene. Heterolayers were synthesized via vapour-phase reaction of sublimed MoO$_{3-x}$ and sulfur powders in a horizontal furnace, using both EG and QFEG as the growth template. Using EG as the template, there is a distinct pattern for multi-layer, pyramidal shaped MoS$_2$ to form on the SiC (0001) terrace, while smooth mono- and bi-layer MoS$_2$ forms at the SiC(1\overline{1}0n) plane and extends outward (Figure 4-2A). On the other hand, under the same synthesis conditions, monolayer MoS$_2$ dominates the surface coverage on QFEG (Figure 4-2B) and is complemented by multilayered MoS$_2$ islands nucleating on wrinkles, SiC (1\overline{1}0n) step edge, and at graphene defects. The variation in nucleation and growth of MoS$_2$ on EG and QFEG is due to the difference in graphene strain, thickness, and potentially buffer layer - all of which have significant impact on the chemical reactivity of graphene. As-grown EG is thinner, exhibits 1% residual strain, and has a buffer layer that is partially covalently bound to the SiC substrate. However, in the case of multilayer EG, where the impact of the buffer layer is expected to be significantly reduced due to increased EG thickness, MoS$_2$ tends to grow laterally rather than vertically. In the case of QFEG, the hydrogenation process passivates the buffer layer and decouples the graphene layers from the underlying SiC (Figure 4-3A). This results in some strain relief of the graphene (~ 0.3%-0.5% residual strain), increases the layer thickness, and removes the EG buffer. This suggests the chemical reactivity of EG is higher than QFEG due to strain and the presence of a buffer layer in EG, which results in a high density of TMD nucleation sites on EG.
Figure 4-1: (A-E) DFT of MoS$_2$/unstrained graphene and MoS$_2$/1% strained graphene predicts that residual strain in EG may enhance the structural symmetry in TMDC/graphene heterostructures. (F) AFM image of as-grown epitaxial graphene demonstrating a smooth surface along with 5-10 nm steps in the SiC substrate. Wrinkles in graphene grown on SiC (0001) appear due to the CTE mismatch between graphene and SiC. (G) Raman spectra of as-grown epitaxial graphene and H$_2$ treated (hydrogenated) epitaxial graphene. Following hydrogenation, the D-peak in EG is nearly eliminated by buffer layer passivation.$^{74}$ (Reproduce from Ref.74)

The MoS$_2$/EG (or QFEG) heterogeneous structures exhibit high quality structural, chemical, and interfacial properties (Figure 4-2, C-D). Upon synthesis, the samples display MoS$_2$ peaks at 386 cm$^{-1}$ and 408 cm$^{-1}$ ($E_{2g}^1$ peak and $A_{1g}$ peak respectively)$^{159}$ and EG peaks at 1590 cm$^{-1}$ (G peak) and 2740 cm$^{-1}$ (2D peak) in the Raman spectra (Figure 4-2C and the inset of it). The intense $E_{2g}^1$ and $A_{1g}$ vibration modes of the MoS$_2$ Raman spectra indicate the MoS$_2$ is of high quality.$^{159}$ The $E_{2g}^1$ and $A_{1g}$ peak spacing is also an indicator of layer thickness in TMDCs,$^{159,160}$ and is found to be 20.0 cm$^{-1}$ for monolayer MoS$_2$ on EG. This value is 2 cm$^{-1}$ larger than that in exfoliated monolayer MoS$_2$, and could be due to the stiffening of the $A_{1g}$ mode with in-situ synthesis and CTE mismatch.$^{160}$ Photoluminescence (PL) from the MoS$_2$/EG(QFEG) heterostructures also provides evidence that the films are of high crystalline quality and can range from mono- to few-layer (Figure 4-2D) under current growth conditions. Importantly, we note that Raman spectroscopy also
confirms the direct synthesis of MoS$_2$ on EG and QFEG does not impact the quality of the underlying graphene (Figure 4-2C shows no “D” peak). The element analysis on MoS$_2$/EG and MoS$_2$/QFEG via XPS also confirms a proper stoichiometric ratio between Mo and S of two, with no carbon bonding (Figure 4-3A). The Mo 3d exhibits two peaks at 229.3 eV and 232.5 eV (Figure 4-3B), which is attributed to the doublet 3d$_{5/2}$ and 3d$_{3/2}$ respectively. The peaks corresponding to sulfur 2p$_{1/2}$ and 2p$_{3/2}$ orbitals in bonded sulfide are observed at 164 eV and 162.5 eV (Figure 4-3C). It should be noted that the resulted shapes of Mo and S in XPS are very similar and thus only MoS$_2$/QFEG heterostructures case is presented. Following nucleation, there are distinct growth morphology differences between EG and QFEG. As noted Figure 4-2A, there exists a high density of MoS$_2$ islands on the terrace of EG, which are hypothesized to grow in a manner similar to that described by Stranski-Krastanov growth mode, which describes layer-plus-island growth. Here, the MoS$_2$ films form via a combination of layer-by-layer growth and 3D island growth, which is similar to synthesis of graphene on h-BN. The source of this islanding phenomenon may be related to the vertical propagation of a defect that initiates in the graphene layer (vacancy, strain-induced high chemical reactivity site, etc. – we later discuss the impact of graphene quality on MoS$_2$), which forms an additional nucleation site for adlayers to form and grow laterally outward from the central peak of the island. This phenomenon is also present in the QFEG case; although fewer isolated islands are identified on these samples where pristine QFEG exists. Rather, the QFEG wrinkles are more reactive due to the curved sp$^2$π-bonds, which again induce localized strain and modification of the chemical reactivity of the graphene films. The same phenomenon also occurs on QFEG step edges, similar to the synthesis of MoS$_2$ ribbons on highly oriented pyrolytic graphite surface (HOPG). Kelvin potential force microscopy measurements confirm the step edge and the region adjacent to the step edge, where thicker graphene exists, exhibits a lower surface potential than that of graphene on the SiC terrace, confirming graphene on the SiC step edge is more reactive.
Figure 4-2: Atomic layers of MoS$_2$ grown on (A) EG and (B) QFEG demonstrating a clear difference in nucleation and growth for two different graphene templates, which is attributed to the presence of enhanced residual strain and a buffer layer in EG compared to QFEG. In the case of QFEG, MoS$_2$ primarily nucleates on wrinkles and SiC step edges. (C) Raman spectra of MoS$_2$/EG and EG before the direct growth. Raman indicates that synthesis of MoS$_2$ does not induce additional defects in the EG or QFEG; Inset in (C) shows the E$_{2g}$ and A$_{1g}$ of the MoS$_2$ Raman features. (D) Photoluminescence from multilayer MoS$_2$ to monolayered MoS$_2$ after the growth demonstrating high quality mono-, bi-, and multilayer MoS$_2$ is possible on epitaxial graphene.\textsuperscript{74} (Reproduce from Ref.74)

Figure 4-3: X-ray photoemission spectroscopy demonstrates (A) that hydrogenation of epitaxial graphene on SiC (0001) eliminates the buffer layer (identified as S1 and S2) at the interface of graphene and SiC (0001). High resolution XPS of the Mo 3d (B) and S 2p (C) peaks MoS$_2$, indicating no Mo-C or C-S bonding following MoS$_2$ synthesis on EG and QFEG templates.\textsuperscript{74} (Reproduce from Ref.74)
The impact of MoS$_2$ synthesis on the quality of QFEG is correlated with the measured layer thickness of the MoS$_2$ overlayer. Evident in Figure 4-4, there are regions of high I$_D$/I$_G$ ratios in the Raman spectra (Figure 4-4, A-B), which closely match the presence of wrinkles in the graphene film, as well as areas of “thick” MoS$_2$ (Figure 4-4, C-E). While wrinkles are present in as-grown QFEG, the I$_D$/I$_G$ is < 0.05 indicating that high quality QFEG exists prior to MoS$_2$ synthesis. It is not until after the synthesis of MoS$_2$ that significant degradation occurs at regions of the QFEG at wrinkle locations, which also correlates with broadening of the 2D peak (Figure 4-4B). Correlating I$_D$/I$_G$ (Figure 4-4A) with the ratio of the A$_{1g}$-peak in MoS$_2$ and G-peak in QFEG (Figure 4-4C) clearly indicates that the defect level is higher along QFEG wrinkles and in locations where the Raman spectra indicates bulk MoS$_2$ (Figure 4-4, C,E). Interestingly, every MoS$_2$ island associated with a wrinkle appears to be bisected by the wrinkle shown in Figure 4-2B, suggesting that the nucleation of the MoS$_2$ occurs at the peak of the wrinkle and is followed by lateral growth of the layer. This scenario is highly plausible considering that the wrinkle apex is of highest stress –and thus the highest chemical reactivity. It has been reported that chemical functionalization on graphene is energetically preferable to happen at the site with higher chemical reactivity due to a lower formation energy. Thus, we speculate that the formation energy of MoS$_2$ nucleation is lower at the location with high chemical reactivity.
The direct synthesis of TMD on QFEG results in a pristine hetero-interface. Transition electron microscopy (TEM) cross-sectional micrographs confirm that monolayer MoS$_2$ nucleates on the (1$\bar{1}$0n) step edges and subsequently extends onto (0001) terrace in regions where the thickness of graphene doesn’t vary over the (1$\bar{1}$0n)/(0001) conjunction (Figure 4-5A). This suggests that the (1$\bar{1}$0n) step edges may play a critical role in nucleation, which is consistent with the observation in AFM images of MoS$_2$/EG(QFEG) in (A-B) of Figure 4-2. Furthermore, the MoS$_2$ layer appears to be “blind” to thickness variations in the underlying graphene when there are no defects in the top layer of the graphene (Figure 4-5B).

Apparently, in the case where additional layers of graphene are formed in a manner as to maintain a flat surface profile, the graphene appears to shield the influence from the SiC
morphology. On the other hand, when defective graphene is present at the surface of the graphene layer, there is almost always multilayered MoS$_2$ present (Figure 4-5C). Additionally, quite often it is found that MoS$_2$ nucleation and growth does not proceed on the SiC (0001) terrace when graphene is not present. Figure 4-5D demonstrates that the MoS$_2$ growth ends at the terminations of graphene, which suggests that graphene may serve as the catalytic layer for MoS$_2$ nucleation and growth. The similar case has been reported in the growth of MoS$_2$ on CVD graphene/Cu.$^{15}$

![Figure 4-5: (A) Cross-sectional HRTEM of MoS$_2$/QFEG demonstrating the nucleation and subsequent lateral growth of MoS$_2$ on a SiC step edge covered with QFEG. In this case, the graphene thickness is consistent across the step, resulting in bending of the graphene and variation in strain of the EG layer. On the other hand, when the top graphene layer remains flat (B), the MoS$_2$ grows without regard of the changing morphology below. When the underlying graphene is defective (C), additional MoS$_2$ adlayers are present, which indicate defects in the graphene can produce this MoS$_2$. Finally, MoS$_2$ nucleation and growth is promoted by the presence of graphene, while often is found to be absent on bare SiC.$^{74}$ (Reproduce from Ref.74)
Photoconductivity has been demonstrated on monolayer MoS$_2$, but the photoconductivity must be improved to be competitive to current state-of-the-art materials. Yin et al.$^{44}$ demonstrate a photoresponsivity of $\sim 0.42$ mA/W with at a photon intensity of $80 \mu$W and drain bias of 1 V, while 7.5 mA/W is achieved at $V_g = 50$ V. This was improved upon by Zhang et al.$^{45}$ with the mechanically stacked heterostructures made of synthetic MoS$_2$/graphene, where the photoresponsivity reached more than $10^7$ A/W with the electrically gating effect. We also investigate photoconductivity and responsivity using two terminal MoS$_2$/QFEG devices without back-gating fabricated via standard photolithography process to demonstrate the superiority of direct synthesis heterostructures.$^{46,47}$ The channel resistance is found to increase from hundreds of Ohms to $\sim 10^6$ Ohms as the channel length increases from 5 μm to 15 μm (Figure 4-6, A-B). Interestingly, the drain current is similar to previous reports for MoS$_2$,$^{44}$ and much lower than epitaxial graphene devices,$^{22}$ indicating that the Ti/Au metal contacts have not contacted the underlying graphene, and that transport is dominated by MoS$_2$ in the channel. This is encouraging for the development of lateral TMD devices on graphene, since the graphene has not shorted the device. This phenomenon is likely a result of the high interlayer resistance in vdW solids,$^{48}$ which provides a large potential barrier for vertical transport, and results in charge being confined to the top MoS$_2$ layers when the ohmic metallization does not contact the underlying graphene. In the case where pinholes exist in the MoS$_2$ layer under the ohmic metallization, we find that current transport is dominated by graphene, and $I-V$ curves become highly linear with channel resistances $< 500$ Ohms. These devices were not considered for photocurrent measurements. Direct growth of MoS$_2$ on EG yields significant improvement in photoconductivity and responsivity. The MoS$_2$/QFEG photosensor device was investigated by exploring photocurrent under various optical powers and bias conditions. Ideally, the generation of photocurrent needs to match the basic condition that the incident photon energy must be greater than the optical energy gap ($E_g$) of MoS$_2$. Monolayer MoS$_2$ is reported to have a bandgap of 1.83 eV corresponding to 676 nm in
wavelength. The MoS\(_2\) from the direct growth in this study shows PL at 668 nm, corresponding to an optical energy gap 1.85 eV that was confirmed previously. Under a constant excitation wavelength at 488 nm, and power ranging from 4 to 40 \(\mu\)W, the MoS\(_2\)/QFEG generates a power-dependent photocurrent ranging from 150 to 550 nA at \(V_{ds} = 1\) V (Figure 4-6, C-D). This represents a 200x increase in photocurrent compared to exfoliated MoS\(_2\). Photoresponsivity is a crucial parameter when evaluating the performance of a photosensor. It is defined as \(R = I_{ph}/P_{light}\), where \(I_{ph}\) is photogenerated current and \(P_{light}\) is the total incident optical power on the photosensor. In the current MoS\(_2\)/EG device with a 15\(\mu\)m channel length, \(V_{ds} = 1\) V, and \(V_g = 0\) V, we find \(R = 40\) mA/W when \(P_{light} = 40\) \(\mu\)W. Previously, the reported \(R\) of similarly biased monolayer MoS\(_2\) photosensor with \(P_{light} = 80\) \(\mu\)W was 0.42 mA/W, which was 2 times that of a WS\(_2\) photosensor device (0.22 mA/W). Thus the MoS\(_2\)/EG photosensor represents a minimum 100x improvement in photoresponsivity, and 1000x improvement in absolute photoconductivity, compared to exfoliated single layer MoS\(_2\) (Figure 4-6E). At \(V_{ds} = 1\) V the photocurrent increases from 150 to 230 nA when the \(P_{light}\) increases from 20 to 40 \(\mu\)W. The photocurrent further increases to 1000 nA when the \(V_{ds}\) increases from 1 to 3 V at constant \(P_{light}\) of 40 \(\mu\)W. Moreover, the stability of this switching behavior is further test by sequentially turning the illumination laser on (30s) and off (30s). Figure 4-6E shows the photocurrent stability over 1000 seconds of continuous operation. Correlating materials characterization with optoelectronic performance, the improvement can be ascribed to: 1) the high crystal quality of MoS\(_2\) grown on QFEG, the presence of pristine surfaces and atomically sharp interfaces of the MoS\(_2\)/QFEG heterostructures; and 2) The underlying QFEG screens charge scattering sites that may be present in the SiC substrate.
Figure 4-6: (A) Optical image of the fabricated MoS$_2$/Graphene photosensor. (B) Room-temperature electrical characteristic of a two-terminal MoS$_2$/QFEG photosensor shows the drain current ($I_{ds}$) vs voltage ($V_{ds}$) at different channel lengths (5, 10, 15 μm). The output characteristics of the MoS$_2$/QFEG photosensor (C-D) when illuminated with 488nm photon at increasing illuminating laser power and gate voltage. (E) Photoswitching behavior of the photosensor at different laser power ($P_{light}$) and $V_{ds}$ compared to the literature.$^{162}$ and (F) Transient measurement of the photosensor at $V_{ds}$ at 3.0 V and $P_{light}$ at 40 μW demonstrating fast, stable response.$^{74}$ (Reproduce from Ref.74)

To determine the universality of epitaxial graphene as a template for the synthesis of high quality vdW solids, we further demonstrate the integration of WSe$_2$ and hBN on QFEG substrates. Cross-sectional HRTEM of WSe$_2$/QFEG/SiC and Raman of hBN/QFEG/SiC (Figure 4-7) indicates that the underlying graphene is not damaged by the synthesis process.$^2$ Additionally, TEM confirms a clean vdW gap between the different layered materials. After the growth of hBN on QFEG, several Raman peaks are present at 1368 cm$^{-1}$, which is suggested as the combination of the $E_{2g}$ mode of B-N vibration at 1372 cm$^{-1}$ and the D peak of graphene at 1360cm$^{-1}$.$^{14}$ The very minor peak at 2950 cm$^{-1}$ (corresponding to the graphene Raman D+G mode) indicates the growth of hBN only nominally increases the defect density. Additionally, similar to MoS$_2$, there is no carbon bonding in the W-, Se-, or B- XPS peaks, indicating minimal interaction between QFEG
and the overlayer. As a result, the utilization of EG as a template may be considered as an excellent candidate for development of a broad range of vertical heterostructures.

Figure 4-7: Transmission electron microscopy of (A) WSe2/QFEG reveals that the interface within layers and between heterolayers is pristine, with no observable defects. (B) Additionally, Raman spectra of quasi-free standing epitaxial graphene (QFEG) and QFEG/hBN indicate high quality hBN has been grown on QFEG. There is also a small PL background following hBN synthesis.74 (Reproduce from Ref.74)
Conclusions

High quality EG has been synthesized and utilized as the growth template for vdW solids that include MoS$_2$, WSe$_2$, and hBN. TMDCs are synthesized by gas phase reaction of MoO$_3$ and WO$_3$ and S and Se, while hBN is synthesized on epitaxial graphene by utilizing ammonia borane as the precursor in a tube CVD chamber. This demonstrates that EG may be a universal substrate for a variety of deposition methods and materials. This is due to the presence of residual strain and wrinkles, which play an important role in the nucleation of vdW solids. It has been found that QFEG template has less MoS$_2$ nucleated on terrace than EG template due to the strain-relief and elimination of the underlying buffer – both expected to increase chemical reactivity of the graphene. Photosensors based on direct growth MoS$_2$/QFEG heterostructures exhibit an improvement in photoresponsivity by a minimum of 200x, demonstrating the high quality in heterostructures from the direct growth. Finally, we have provided strong evidence that EG can be an excellent candidate for building large area vdW solids that will have extraordinary properties and performance. The two-terminal electrical measurements on synthesized layers here show that the interlayer resistances between the graphene and top heterolayers are high enough and that the stacks are not “shorted” simply by the presence of graphene, rather it will be proper contacting of the individual layers that will be critically important.
Chapter 5

Atomically thin heterostructures based on monolayer WSe$_2$ and graphene

Heterogeneous engineering of two-dimensional layered materials, including metallic graphene and semiconducting transition metal dichalcogenides, presents an exciting opportunity to produce highly tunable electronic and optoelectronic systems. In order to engineer pristine layers and their interfaces, epitaxial growth of such heterostructures is desirable. We report the direct growth of crystalline, monolayer tungsten diselenide (WSe$_2$) on epitaxial graphene (EG) on silicon carbide. Raman spectroscopy, photoluminescence, and scanning tunneling microscopy confirm high-quality WSe$_2$ monolayers; while transmission electron microscopy shows an atomically sharp interface, and low energy electron diffraction confirms near perfect orientation between WSe$_2$ and EG. Vertical transport measurements across the WSe$_2$/EG heterostructure provides evidence that an additional barrier to carrier transport beyond the expected WSe$_2$/EG band offset exists due to the inter-layer gap, which is supported by theoretical local density of states (LDOS) calculations using self-consistent density functional theory (DFT) and non-equilibrium Green’s function (NEGF).

Introduction

Analogous to the evolution in graphene research,$^{35}$ the research community is at the initial stage of forming and characterizing vdW heterostructures, where samples are produced mainly through mechanical exfoliation and manual transfer stacking.$^{46}$ Unlike isolated monolayer samples, the transfer stacking process can lead to uncontrollable interface contamination$^{57}$ that in turn results in reduced device performance.$^{46,57}$ Therefore, developing synthetic techniques to form such heterostructures is critical for engineering pristine layers and junction interfaces. Efforts towards
this end include the vertical integration of 2D materials such as MoS$_2$ and hBN on EG.\textsuperscript{74} Similarly, CVD graphene grown on Cu foils has been utilized as “universal template” for the synthesis of vertical hBN or MoS$_2$,\textsuperscript{146,81} or lateral (in-plane) hBN/graphene systems.\textsuperscript{163} In either case, monolayer growth control is essential to exploit phenomena such as the direct-gap crossover in TMDC\textsuperscript{164} or inter-layer coupling that can hybridize the electronic structure of stacked monolayers.\textsuperscript{165} In this report, we demonstrate direct growth of high-quality WSe$_2$ monolayers on EG, and provide evidence that this heterosystem exhibits pristine interfaces, high-quality structural, chemical, and optical properties, and significant tunnel resistances due to the WSe$_2$/EG inter-layer gap.

**Experimental methods**

**Epitaxial graphene growth**

Epitaxial graphene is grown on diced SiC wafers via sublimation of silicon from 6H-SiC (0001) at 1725 °C for 20 min under 200 Torr argon (Ar) background pressure after hydrogen (H$_2$) etching at 1500 °C for 15 min under 700 Torr 10% H$_2$/Ar mixtures.

**Growth & properties of WSe$_2$ layers**

Tungsten tri-oxide (WO$_3$) powder (0.3 g) was placed in a ceramic crucible located in the center of the furnace. The Se powder is placed in a separate ceramic boat up-stream of the WO$_3$, and maintained at 270 °C during the reaction. Graphene substrates were subsequently placed down-stream of the crucible loaded with WO$_3$, and Se and WO$_3$ vapors were transported to the targeting sapphire substrates by an Ar/H$_2$ (80:20) forming gas at 1 Torr of chamber pressure. The center of the hot zone was held at 925 °C for 30 min to 1 hour and the furnace was then naturally cooled to
room temperature. The as-grown heterostructures are characterized using atomic force microscopy (AFM), Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS). A WITec CRM200 Confocal Raman microscope with an excitation wavelength (488 nm) is utilized for structural characterization. A Bruker Dimension with a scan rate of 0.5 Hz was utilized for the AFM measurements. The TEM cross-sectional samples were made via utilizing a NanoLab dual-beam FIB/SEM system. Protective layers of SiO₂ and Pt were deposited to protect the interesting region during focused ion beam milling. TEM imaging was performed using a JEOL 2100F operated at 200 kV. CAFM measurement was performed in Bruker Dimension. For surface analysis, the sample was loaded into an ultra-high vacuum (UHV) with a base pressure in low 10⁻¹⁰ mbar range described in detail elsewhere. The WSe₂/EG sample was then imaged using an Omicron variable temperature scanning tunneling microscope (STM) without any thermal treatment. The STM images were obtained at room temperature and in the constant-current mode, with an etched tungsten tip. The same system is equipped with a monochromatic Al-Kα source (E = 1486.7 eV) and an Omicron Argus detector operating with pass energy of 15 eV. The spot size used during the acquisition is equal to 0.5 mm. Core-level spectra taken with 15 sweeps are analyzed with the spectral analysis software analyzer.

Device fabrication

The hetero-junction device demonstrated is fabricated with electron beam lithography (EBL) and lift-off of evaporated metal contacts. The process flow is illustrated in Figure 5-1. In the first step, the graphene contact is patterned and developed with EBL. Subsequently, metal contacts Ti/Au (10nm/40nm) are deposited with low pressure electron beam evaporation (10⁻⁷ Torr) after an oxygen plasma treatment to reduce the contact resistance (45s at 100 W, 50 sccm He, 150 sccm O₂ at 500 mTorr). Then a layer of 30 nm Al₂O₃ is deposited conformally over the entire substrate
with atomic layer deposition (ALD), which serves as a protection layer for subsequent processing steps and a passivation layer. ALD deposited Al$_2$O$_3$ capping layer has been reported as an effective film to substantially improve carrier mobility in 2D materials.$^{168}$ In the second EBL step, a pattern of etch regions are defined, including an opening on the Ti/Au pads, and regions for the later WSe$_2$ contacts. The Al$_2$O$_3$ capping layer on these regions are first removed with hydrofluoric acid, followed by oxygen plasma etching to remove the monolayer WSe$_2$ and few layers of graphene. This step prevents shorting through the underlying graphene layer after depositing the WSe$_2$ contacts. In the third e-beam step, the WSe$_2$ contact pads and thin lines are defined, and the Al$_2$O$_3$ layer on the WSe$_2$ triangular sheets is removed by hydrofluoric acid prior to the metal deposition. Then 50 nm thick Palladium (Pd) layer is deposited by electron beam evaporation at $10^{-7}$ Torr. The high work function Pd contacts with WSe$_2$ have been reported to produce a smaller Schottky barrier, and many orders higher current density compared to Ti/Au contacts.$^{169}$

Figure 5-1: Process flow for the fabrication of the hetero-junction devices on a heterostructure based on WSe$_2$ and graphene. (A) Patterning and depositing Ti/Au for graphene contacts. (B) Coating the entire substrate with ALD Al$_2$O$_3$. (C) Define the isolation region on graphene contact pads, and later WSe$_2$ contact regions, and remove the Al$_2$O$_3$ layer. (D) Isolation etching with oxygen plasma to remove the WSe$_2$ and graphene. (E) Patterning the WSe$_2$ contacts (Pd).$^{77}$ (Reproduce from Ref.77)
LEEM for assessment of the graphene layer thickness

A false color image of the LEEM-IV along a line is used for this purpose. The example is shown in Figure 5-2, along with the individual spectra representative for 1L and 2L in (C). The electron energy of the characteristic dips for 1L and 2L are highlighted by blue and red arrows, respectively. We suspect the slight difference in the energy of the dips in 2L is due to the slight difference in the interaction between graphene and the underlying SiC substrate. The ‘narrow’ terraces located in between large terraces show multiple dips consistent the existence of many-layer EG.

![Figure 5-2](image)

**Figure 5-2:** (A) LEEM image acquired at the electron energy 1.6 eV above the vacuum level. (B) The false color image of the LEEM-IV along the green dash line in (A). (C) Representative LEEM-IV from the same dataset. (Reproduce from Ref.77)

Results and discussion

Epitaxial graphene grown from silicon carbide (SiC)\cite{70,170} is an ideal platform to investigate the nucleation and growth of vdW heterostructures. In particular, EG on SiC eliminates the need for post-growth transfer required for chemical vapor deposited graphene and therefore provides a
chemically uniform starting surface. Epitaxial graphene also enables the nucleation and epitaxial growth of WSe$_2$. Scanning electron microscopic image shows the selective growth of WSe$_2$ on graphene indicates a significant surface energy difference between SiC and EG exists, and that EG is more favorable for nucleation and growth of the WSe$_2$ (Figure 5-3A). Raman spectra shows that the WSe$_2$ ($A_{1g}/E_{2g}$ peak $\approx$ 250 cm$^{-1}$) only grows where the graphene (1580 cm$^{-1}$ and 2700 cm$^{-1}$) presents (Figure 5-3B). This phenomenon may be quite useful for developing templated growth of vdW heterostructures in the future, and requires subsequent theory to better understand the fundamental mechanisms of growth selectivity. The WSe$_2$ triangular domains seems to strictly align to the underlying graphene. Using low energy electron microscopy/diffraction (LEEM/LEED) we are able to more precisely quantify the in-plane crystalline orientation of WSe$_2$ monolayers on EG (Figure 5-3, C-E). Unlike the diffuse LEED patterns of monolayer MoS$_2$ or MoSe$_2$ on SiO$_2$, the LEED spots of monolayer WSe$_2$/EG are sharp, resembling that found for twisted bilayer graphene on SiC. The green and the blue spots in Figure 5-3D illustrate the diffraction spots for WSe$_2$ and EG, respectively. The larger WSe$_2$ lattice constant (3.28 Å) compared to graphene (2.46 Å) means the WSe$_2$ diffraction spots will be closer to the specular beam (central spot), where both crystals display hexagonal symmetry. The ratio of their lattice constants matches the ratio of the hexagons’ sizes (\~1.3, extracted from our experiment), demonstrating a 23% lattice mismatch between WSe$_2$ and graphene. Acquiring diffraction from multiple WSe$_2$ islands simultaneously reveals that the WSe$_2$ is not randomly orientated, but maintains an in-plane orientation aligned to the underlying graphene layer. A detailed inspection of the sample reveals that diffraction spots of WSe$_2$ show near-perfect alignment with the graphene spots, indicating less than $\pm$ 5° variation of the relative orientation of the WSe$_2$ islands with respect to the EG layer (not shown). The area without as-grown WSe$_2$ was also acquired and only gave the diffraction spot from the buffer layer that bonds to SiC (Figure 5-3E). This distribution of azimuthal orientation is significantly improved compared to the exfoliation samples on SiO$_2$, and
further confirms that the graphene lattice plays an important role in the growth of WSe$_2$. The notable azimuthal alignment between WSe$_2$ and EG despite a significant lattice mismatch suggests that synthesis of these pristine layers occurs via vdW epitaxy.\textsuperscript{155,175} This phenomenon is the result of a long-range commensurate structure formed between WSe$_2$ and graphene, where every third W atom in WSe$_2$ matches every fourth C atom graphene forming a heterostructure unit cell with a lattice constant equal to 9.84 Å (3 and 4 times the WSe$_2$ and graphene lattice constants, respectively). The growth rate of WSe$_2$ is slow, with monolayer coverage remaining < 75% after a 60 min exposure to the WSe$_2$ precursors. As a result, WSe$_2$ domain size is highly dependent on synthesis temperature, with the largest domains being achieved at 1000 °C. Morphological features in the EG (such as wrinkles, SiC step edges, and other surface imperfections) appear to directly influence WSe$_2$ monolayer development by acting as a barrier to further lateral growth, or by modifying the registry of the WSe$_2$ layers on epitaxial graphene. A qualitative assessment of the WSe$_2$ in-plane orientation via AFM suggests a narrow distribution with > 80% of the triangles aligned (+/- 5 degrees) to the underlying graphene.
Figure 5-3: (A) SEM image of WSe$_2$ monolayers grown on epitaxial graphene shows the WSe$_2$ triangular crystals strictly aligned on graphene due to their commensurability. (B) Evident by Raman spectroscopic measurement, WSe$_2$ monolayers only grew on the area where graphene exists. (C) LEED pattern of a selected circles with a diameter of 5 µm was obtained and shows zero misorientation between WSe$_2$ and graphene in (D) and the presence of buffer layer only on SiC in (E). (Reproduce from Ref.77)

It is well known that the electron reflectivity spectra obtained through LEEM measurements (LEEM-IV) can provide the ‘fingerprint’ of the EG thickness.$^{149,176}$ By combining the information of EG’s thickness together with the density and size of WSe$_2$ islands, we observe a distinct correlation between WSe$_2$ island density and EG thickness: The terraces area of SiC terminated with 1-2 layer EG have a higher density of larger WSe$_2$ islands. Electron reflectivity spectra reveals that this particular terrace is terminated with a monolayer of EG, while the neighboring terraces have bilayer EG. We also note that there are virtually no WSe$_2$ islands on the narrow terraces located between the larger terraces or near the step bunches originated from the morphology of the SiC substrate. LEEM-IV confirms these ‘narrow’ terraces are covered by many-layer EG, typically three to five layers. As a result, one must take care to control the layer thickness of the underlying
graphene to 1-2 layers since the surface properties and chemical reactivity of many-layer graphene layers precludes the formation of large WSe₂ domains, similar to that found for synthesis on graphite. Cross-sectional TEM reveals that the uniformity and structure of the underlying graphene can significantly impact the nucleation, growth, and quality of the WSe₂ overlayer. Wherever pristine graphene is present, the WSe₂ overlayer is crystalline, with no observable defects (Figure 5-4A). Additionally, the EG inter-layer distance is measured to be 3.64 Å (typical for EG/SiC), while the WSe₂/EG layer spacing is 5.23 Å, with a WSe₂ thickness of 6.45 Å. In the case where graphene is defective, we also observe increased disorder in the WSe₂. Unlike the MoS₂ grown on EG, in which the SiC (1̅10n) step edges and EG wrinkles serve as nucleation sites for MoS₂ growth, the WSe₂ abruptly stops at the edge of the (1̅10n) plane (Also see STM in Figure 5-4B), preferring to grow only on EG synthesized on the SiC (0001) plane. It is also useful to note that WSe₂ is sensitive to damage during TEM investigations and it is not stable under high-energy electrons (also seen in LEEM at high electron beam intensity). The height of individual WSe₂ domains measures 0.71 nm (Figure 5-4B), and atomic arrangement matches that of 2H-WSe₂, in good agreement with previous reports on CVD WSe₂. The bandgap size of the WSe₂ monolayer was measured in scanning tunneling spectroscopic measurement.

The STS profile shows 1.87 eV of the 1L WSe₂ bandgap and a parabolic curve of conductivity that belongs to few-layer graphene (Figure 5-4C). The Fermi level of WSe₂ is at the middle of bandgap, which means that its transport will not favor either p- or n-type. To better understand the impact of the graphene under the WSe₂, we compare the PL spectra of WSe₂ grown on insulating sapphire formed under the same growth conditions (Figure 5-4D). From this comparison, three features are apparent: (i) the PL intensity of
WSe$_2$/EG is quenched by a factor of three; (ii) the PL peak position of WSe$_2$/EG is up-shifted by 35 meV (from 1.625 eV on sapphire to 1.66 eV on EG); and (iii) the full width of half-maximum (FWHM) of the WSe$_2$ PL peak on EG is narrower than WSe$_2$-on-sapphire (38 meV versus 80 meV). Since the WSe$_2$ crystalline quality is known to be high on EG based on the characterization results, the PL quenching is likely a result of photo-generated charge carriers transferring from WSe$_2$ to EG.$^{24,25}$ Zhang et al.$^{180}$ proposed the observed quenching in MoS$_2$/Gr is due to the exciton splitting by the built-in electrical field between 1L CVD graphene and 1L CVD MoS$_2$. Additionally, Shim et al.$^{181}$ observed quenching in MoSe$_2$/graphene heterostructures due to a fast, non-radiative recombination process. It is likely that the quenching process for WSe$_2$/EG observed here is similar in nature, especially since there is p-type doping in WSe$_2$ when in proximity to EG. The second feature (red shift of PL peak) may be the result of strain, doping, or defects.$^{181}$ Within the resolution of our measurements (LEED, STM, and PL), we find the WSe$_2$ defect density to be low; however, there is measurable doping of the WSe$_2$ as a result of the underlying EG (based on XPS results). Doping is known to shift PL signatures in MoS$_2$,$^{182}$ and we believe is the primary contributor to the measured PL shift observed in this work. Finally, the PL properties of WSe$_2$ on an insulating substrate (sapphire) versus on graphene is very similar to a recent report comparing in MoS$_2$/SiO$_2$ versus MoS$_2$/EG and MoS$_2$/hBN.$^{183}$ The narrower peak width suggests that the interface between the WSe$_2$ and EG is pristine, with no dangling bonds contributing to interface roughness or surface optical phonon scattering that in turn leads to an improved optoelectronic quality.

There is a difference in energy (220 meV) between the measured optical bandgap and electrical bandgap (Figure 5-4E). The electronic bandgap characterizes single-particle
or quasiparticle excitations and is defined by the sum of the energies needed to separately
tunnel an electron and a hole into monolayer TMDC. On the other hand, the optical
bandgap is described as the energy required to create an exciton, which is a correlated two-
particle electron-hole pair, though optical absorption. The difference in these two energies
directly yields the exciton binding energy ($E_{\text{Binding}}$). This exciton binding energy is one
order larger than those of traditional semiconductors due to enhanced Coulomb interactions
due to low-dimensional effects are expected to increase the quasiparticle bandgap as well
as to cause electron-hole pairs to form more strongly bound excitons.
Figure 5-4: (A) Cross-sectional HRTEM image of WSe$_2$-EG shows the false-colored constituent layers and the separation distance of WSe$_2$-graphene and graphene-graphene. (B) AFM image shows a full coverage of 1L WSe$_2$ on graphene. 2L and thicker WSe$_2$ started to form along the step edge of SiC due to its higher surface energy. The thickness of a layer is 6.5 nm. High resolution STM image should the atomic structure of the WSe$_2$ lattice in a hexagonal pattern. (0.35 V, 1.5 nA) (C) STS profiles show gapless graphene and 1.87 eV of the WSe$_2$ bandgap in room temperatures. (D) PL spectra normalized to the WSe$_2$ Raman peak shows the PL intensity quenches on graphene due to the metallic nature of graphene. Inset is the normalized PL peaks and shows their peak positions. (E) The relationship between the optical and electrical bandgap of WSe$_2$ were tightened by a binding energy. (Reproduce from Ref.77)

Synthesis of WSe$_2$/EG results in pristine chemical, optical, and structural quality of the heterostructure layers and interfaces. Raman and X-ray photoelectron spectroscopy (XPS) confirms there is no measureable reaction between graphene and WSe$_2$, and the integrals of high resolution spectra of the Se 3d and W 4f peaks leads an estimated Se:W ratio of $\sim 2:1$. Recent reports of core-level energies of monolayer WSe$_2$ on an insulating sapphire substrate using non-monochromatic Mg K$\alpha$ x-rays are noted (W4f$_{7/2}$ and W4f$_{5/2}$ peaks are at 32.8 eV and 35.0 eV, respectively; Se3d$_{5/2}$ and 3d$_{3/2}$ peaks are at 55.0 eV and 55.9 eV, respectively). The study of bulk,
exfoliated p-type WSe\textsubscript{2} with monochromatic AlK\textalpha\textsubscript{1} x-rays indicates that these peaks are shifted to lower values by approximately 0.1 eV.\textsuperscript{179} Under identical analysis conditions and parameters to that employed by McDonnell \textit{et al.},\textsuperscript{179} we find here that the monolayer WSe\textsubscript{2}/EG exhibits a similar binding energies to the exfoliated bulk. Based on the core level measurements of the WSe\textsubscript{2} bulk crystal surface that confirm p-type doping,\textsuperscript{179} these energies are therefore representative of p-type monolayer WSe\textsubscript{2} interfacing with graphene. We also note that a shift in binding energy towards lower energies is consistent with a lower electron density in WSe\textsubscript{2}/EG.

In other words, EG withdraws electrons from WSe\textsubscript{2} monolayer, leading to p-doped behavior in the WSe\textsubscript{2} layer.\textsuperscript{179} This is confirmed via direct measurements of the occupied valance energy states by XPS showing that the Fermi level is positioned at 0.72 eV, which is 0.11 eV smaller than the mid-gap energy level in 1 L WSe\textsubscript{2} (0.83 eV). Similar shifts have been reported for other thin films on graphene recently (\textbf{Figure 5-5A}).\textsuperscript{184} Based on the Fermi level position measured in XPS and the optical bandgap and the reported Fermi level position of as-grown EG, a proposed band alignment is illustrated in \textbf{Figure 5-5B}. Due to their significant difference in carrier concentration, a large Schottky barrier is expected to form at EG/WSe\textsubscript{2} junction. Conductive atomic force microscopy (C-AFM) and vertical diode structures shown later provide a direct means to probe the nanoscale electrical properties of WSe\textsubscript{2}/graphene heterostructures, and assists in identifying the utility of these materials for advanced electronic and optoelectronic architectures. Comparing AFM surface topography and conductivity acquired at \textit{V}_{\text{bias}} = 0.1 \text{ V} (\textbf{Figure 5-5, C-D}) in C-AFM clearly indicates that a barrier to transport exists in the heterojunction regions. The mapping also reveals that the WSe\textsubscript{2} is uniformly resistive, while low resistance contact is possible on the graphene layer, with EG wrinkles and SiC step edges exhibiting enhanced conduction through the AFM tip.
Figure 5-5: (A) XPS measurement confirmed that the valence band maxima is 0.72 eV below the Fermi level. (B) Based on the measured spectroscopic results, the band alignment between WSe$_2$ and graphene (before them contact) was proposed. (C-D) The topographic image of as-grown sample and its corresponding C-AFM image (under a bias of 0.1 V) shows WSe$_2$ is highly resistive due to the presence of electrical barrier between WSe$_2$ and graphene. (Reproduce from Ref.77)

Illustrated by the DFT effective potential profile (Figure 5-6A), the WSe$_2$ and graphene are held together by the van der Waals interaction, and the resulting inter-layer gap, $d_{ILG}$, forms a finite potential barrier between them. Figure 5-6B illustrates the spatially resolved local density of states (LDOS) under zero bias. It shows that, within the inter-layer gap, $d_{ILG}$, there are no LDOS contributing to transport. Further, the projected contour line of LDOS that delineates the boundary between the negligible (close to zero) LDOS and the finite (0.02) LDOS values provides a quantitative estimate of the transport barrier height arising from the inter-layer gap. We estimate this additional barrier to be 1.85 eV above the Fermi level. While this model utilizes intrinsic WSe$_2$ with pristine contacts, it highlights that the gap between the layers plays a critical role in the determination of the turn-on voltage of the layer stack. The diode structures fabricated via electron-beam lithography and lift-off process (Figure 5-6C) confirm the presence of a tunnel barrier to vertical transport with turn-on occurring at $\pm 1.8$ V (Figure 5-6D). The inter-layer gap related
barrier to transport persists up to a bias of 1.80 V, acting like a thermionic barrier, as evidenced by no appearance of LDOS - agreeing well with experimental measurements showing device turn-on at ~ 1.8 - 2V. The inter-layer gap barrier starts to collapse at a bias beyond 1.85 V, where LDOS appears and contributes to the transport (See Figure 5-6B). We find theoretically that the barrier due to the inter-layer gap depends upon a) the inter-layer gap thickness, d_{ILG}, and b) the Coulombic interaction among the different atoms of the constituent layers. With the decrease in the inter-layer gap, the interaction increases which reduces the barrier height. For instance, in our system, we observe that, the Pd/WSe\textsubscript{2} inter-layer gap distance of 2.98Å is lower than that of the WSe\textsubscript{2}/EG 3.53Å. Hence, the Pd/WSe\textsubscript{2} inter-layer barrier height is significantly less than that of WSe\textsubscript{2}/EG. Thus, the barrier arising from the inter-layer gap at the WSe\textsubscript{2}/EG interface, dominates the electronic transport. It is to be noted that our calculations also shows existence of the conventional Schottky barrier of 0.95 eV between the Pd electrode and the monolayer WSe\textsubscript{2}.\textsuperscript{185}
Figure 5-6: (A) The effective potential profile of a pristine WSe$_2$/EG heterostructure supercell, calculated by density functional theory (DFT) along the out of plane direction demonstrates that a significant finite barrier to electron transport can exist as a result of the inter-layer gap ($d_{ILG}$). (B) The corresponding local density of states was extracted for the monolayer WSe$_2$ and the first layer of EG. (C) The side and top view of WSe$_2$-EG diode that was measured to understand the vertical electrical transport. (D) The measured current versus voltage (I-V) curves from WSe$_2$/EG diodes confirm a large barrier to transport through the heterostructure as well as $\sim 10^5$ on/off ratio and turn-on voltage of $\sim 2$ V. Inset shows a schematic different theoretical barrier height with respect to the Fermi level in this device. (Reproduce from Ref.77)
Conclusions

In this chapter, we demonstrate a synthetic route to forming WSe$_2$/EG heterostructures via vdW epitaxy. Even though the lattice mismatch between WSe$_2$ and graphene is shown to be 23 %, the heterostructure is commensurate at every 3$^{rd}$ W and 4$^{th}$ C atom, indicating the potential to grow single crystal heterostructures over large areas. Additionally, we provide evidence that the structural, chemical, and optical properties of the WSe$_2$ grown on graphene match or exceed that of mechanically exfoliated WSe$_2$ films. Finally, WSe$_2$/EG diode structures and C-AFM indicate that efficient tunneling is possible through the WSe$_2$ layer to graphene, and the primary source of tunneling resistance occurs at the inter-layer gap between the WSe$_2$ and graphene layer. The next chapter discusses an optimum vertical electrical transport achieved by modulating the Fermi level of the EG substrate.
Chapter 6

Tuning electronic transport in WSe\textsubscript{2}-graphene junction

Two-dimensional MoS\textsubscript{2} and WSe\textsubscript{2} has been used as a component in atomically thin photovoltaic devices, field effect transistors, and tunneling diodes in tandem with graphene and many other substrates. In some applications it is necessary to achieve efficient charge transport across the interface of layered WSe\textsubscript{2}-graphene, a semiconductor to semimetal junction with a van der Waals (vdW) gap. Similarly, In such cases, the band alignment engineering is required to ensure a low-resistance, ohmic contact. In previous chapter, prepartion and bas properties of WSe\textsubscript{2}-graphene is discussed. In this chapter, we investigate the impact of graphene electronic properties on the transport at the WSe\textsubscript{2}-graphene interface. Electrical transport measurements reveal a lower resistance between WSe\textsubscript{2} and fully hydrogenated epitaxial graphene (EG\textsubscript{FH}) compared to WSe\textsubscript{2} grown on partially hydrogenated epitaxial graphene (EG\textsubscript{PH}). Using low-energy electron microscopy and reflectivity (LEEM/LEER) on these samples, we extract the work function difference between the WSe\textsubscript{2} and graphene and employ a charge transfer model to determine the WSe\textsubscript{2} carrier density in both cases. The results indicate that WSe\textsubscript{2}-EG\textsubscript{FH} displays ohmic behavior at small biases due to a large hole density in the WSe\textsubscript{2}, whereas WSe\textsubscript{2}-EG\textsubscript{PH} forms a schottky barrier junction.

Introduction

Synthetic monolayer WSe\textsubscript{2} has been demonstrated as a tunneling barrier in the WSe\textsubscript{2}-EG diodes. However, large turn-on voltages (1.5 V - 1.8 V) in the I-V characteristics of this vertical diode were observed, and tentatively attributed to the unfavorable n-type nature of the EG. In this chapter, we demonstrate that the carrier type of the graphene is a critical parameter in controlling
the charge transport at the WSe$_2$/graphene (or with other TMDC) interface. Traditional mechanical transfer processes also utilized transferred graphene, which is inherently p-type due to water and environmental doping. These dopants ultimately control the electrical characteristics of the heterostructure stack. By controlling the doping type and concentration of EG from n- to p- via in-situ hydrogen intercalation during the WSe$_2$ synthesis,\textsuperscript{149} we demonstrate the origins of ohmic behaviour in TMDC/graphene structures, and obtain low resistance ohmic transport between a WSe$_2$ and graphene heterostructure. Low-energy electron microscopy (LEEM), low-energy electron reflectivity (LEER), and conductive atomic force microscopy (CAFM) were performed on monolayer WSe$_2$-EG$_{pH}$ and monolayer WSe$_2$-EG$_{FH}$, with the results showing that use of EG$_{FH}$ (p-type graphene) as the bottom electrode of WSe$_2$-graphene diodes can lead to an Ohmic I-V behavior. Thus, EG$_{FH}$ can serve as a high quality contact for heterostructures involving WSe$_2$ and additional 2D layers (located above the WSe$_2$).

**Experimental methods**

Epitaxial graphene was synthesized via silicon sublimation of the silicon face of 6H silicon carbide (6H SiC (0001)) at 1625 °C in a 200 Torr Ar environment inside a heating chamber made of pure graphite. The SiC substrates were pre-etched at 700 Torr with flowing 10 % H$_2$-Ar mixtures (total flow 500 sccm) to remove subsurface damage due to substrate-polishing.\textsuperscript{186} The WSe$_2$-EG growth is graphically illustrated in **Figure 6-1A**.\textsuperscript{58} The precursors chosen for WSe$_2$ synthesis are tungsten hexacarbonyl (W(CO)$_6$) and dimethylselenium ((CH$_3$)$_2$Se), which provide the W and Se, respectively. In order to eliminate carbon contamination from the precursor, a 100% H$_2$ environment is utilized for WSe$_2$ synthesis. This necessity of 100% H$_2$ significantly modulates the chemical environment of graphene, comparing to a dilute H$_2$ environment for WSe$_2$ growth. X-ray photoemission spectroscopy (XPS), equipped with a monochromatic Al-K$\alpha$ source (E =1486.7 eV)
and an Omicron Argus detector operating with pass energy of 15 eV, carried out on the samples grown via powder vaporization (PV) using 5% H₂ at 900 °C and MOCVD using 100% H₂ at 800 °C, both in the same growth time, shows that the C1s core level of the WSe₂-EG via MOCVD has been shifts towards a lower binding energy by 0.4 eV compared to that of WSe₂-EG grown via PV (Table S1). This shift of C1s core level in EG has been associated with hydrogen intercalation. Evident from XPS, the 100% H₂ environment leads to complete hydrogen interaction at the EG/SiC interface, fully passivating the buffer at 900 °C.

The growth of WSe₂ on EG proceeds by vdW epitaxy, mediating the high lattice mismatch between WSe₂ and graphene. Tungsten selenide (WSe₂) atomic layers are grown via MOCVD on EG/SiC substrates employing H₂ as a carrier gas at 800 °C and 930 °C in order to study how hydrogen intercalation impacts the electrical transport between graphene and WSe₂, for the different growth temperatures. (Figure 6-1B). In order to eliminate carbon contamination in the WSe₂, a 100% H₂ environment is utilized. After 30 minutes for growth, the as-grown atomic layers were confirmed to be monolayer WSe₂, 1 μm wide and 0.7 nm thick with atomic force microscopy (AFM) (Figure 6-1C). The optical bandgap of monolayer WSe₂ measured via photoluminescence (PL) spectroscopy is found to be 1.63 eV (Figure 6-2A), using a fitted Lorentzian peak function. The Raman spectra exhibits two peaks of WSe₂ at 251 cm⁻¹ and 260 cm⁻¹ assigned to E₁₂g + A₁g and 2LA, respectively (Inset, Figure 6-2A). The B₁₂g peak at 310 cm⁻¹ typically seen in bi- and multilayer WSe₂ is absent, verifying the presence of monolayer. Raman and PL measurements were performed in a WITec Confocal Raman microscope with a 488 nm wavelength laser. The topographic AFM micrographs were taken in a Bruker Dimension with a scan rate of 1 Hz. The current-to-voltage (I-V) measurements performed on the samples were done in the same AFM with a PtIr-coated tip. Low-energy electron microscopy (LEEM) characterization was performed with an Elmitech III low-energy electron microscope. From
sequences of images acquired with 0.1 eV energy spacing, Low-energy electron reflectivity (LEER) spectra were extracted at specific spatial locations on the surface.

Figure 6-1: (A) Illustration of MOCVD process of WSe$_2$ monolayer on EG-SiC and the synthesis conditions. (B) When the process of WSe$_2$ synthesis is carried out at a lower temperature the buffer layer decoupling is incomplete (Top). A higher synthesis temperature can efficiently convert the buffer layer into a layer of graphene via hydrogen intercalation. (Bottom) (C) AFM image of WSe$_2$-EG heterostructure. Monolayers are mostly 0.7 nm in height. The wrinkles of graphene can be seen, which promoted vertical WSe$_2$ growth.\(^\text{187}\) (Reproduce from Ref.187)

Results and discussion

WSe$_2$ synthesis and buffer-layer decoupling

While crystal WSe$_2$ can be synthesized over a range of temperatures, the electrical properties of EG can be greatly modified at higher WSe$_2$ growth temperatures.\(^\text{31}\) As-grown EG on SiC contains a C-rich “buffer layer” at the EC/SiC interface. The buffer layer can subsequently be converted to a new layer of graphene by passivating the interface with hydrogen atoms, at elevated temperatures.\(^\text{31,149}\) Furthermore, it has been demonstrated that the transformation of the buffer into an additional graphene layer is more efficient at a higher temperature when the hydrogenation time is fixed.\(^\text{31}\) The EG Raman spectra (D, G, and 2D peaks)\(^\text{188}\) before and after WSe$_2$ growth at 800 °C and 930 °C was compared to elucidate the impact of WSe$_2$ growth on structural properties of the EG. For the 800 °C, 30 min growth of WSe$_2$, the D-peak intensity of EG increases as evidenced by a higher D/G ratio. This phenomenon can be interpreted as partial hydrogenation of the epitaxial
graphene (EG$_{ph}$) that only converts a small portion of the buffer layer into graphene domains.$^{31,188}$ On the other hand, for the 930 °C, 30 minute WSe$_2$ growth, the D peak is suppressed and D/G ratio is notably smaller than those from the 800 °C process. This transformation of the D peak as the hydrogenation is increased is evidence of a more complete buffer elimination.$^{31}$ The Raman 2D peak of EG has been commonly used as an indicator for graphene thickness, graphene layer stacking, and a measure of compressive strain induced by graphene/SiC lattice mismatch.$^{153}$ In this work, the 2D peak of the 930 °C growth is at a relatively lower peak position, with broader full-width-half-maximum (FWHM), compared to that of the 800 °C growth. This is associated with a combination of increased layer thickness and released compressive strain.$^{31}$ This trend is evident (Figure 6-2, C-D) as an evolution of the peak position and FWHM of the 2D peak of graphene in as-grown (pre-WSe$_2$ growth), 800 °C WSe$_2$ growth, and 930 °C WSe$_2$ growth where data is accumulated in a 10μm-line with an interval of 500 nm (total 20 spots). The as-grown samples have peak position and FWHM distributions of 2765-2782 cm$^{-1}$ and 60-70 cm$^{-1}$, respectively. While the 800 °C growth only slightly shifts the distributions, the 930 °C growth leads to a shift of 40 cm$^{-1}$ and an increase of 10 cm$^{-1}$ in the 2D peak position and FWHM, respectively, indicating a complete transformation of the buffer layer to an additional EG layer. Additionally, the G peak shifts towards a higher wavenumber by 3-5 cm$^{-1}$ following the 930 °C growth, compared to as-grown graphene (1592.8 ± 3.5 cm$^{-1}$) and 800 °C WSe$_2$ growth (1593.5 ± 1.9 cm$^{-1}$). The shift of G peak has been associated with the doping effects on graphene, in which the wavenumber of the G peak increases when the Fermi energy of graphene moves away from the Dirac point towards both n- and p- type direction.$^{189}$ Since it has been reported that the buffer removal would move the Fermi energy to a point below the Dirac point,$^{190}$ the stiffening G peak of the EG from the 930 °C growth is hence contributed to a conversion from n-type to p-type graphene due to the buffer removal, as evident by the evolution of the 2D peak (Figure 6-2, C-D). Although the G peak provides information on the doping effects on graphene, the 2D peak has been chosen to be an effective
indicator since its peak position has a larger shift than G peak in respond to hydrogenation/buffer removal.

Figure 6-2: (A) PL peak at 1.63 eV corresponding to the optical bandgap of monolayer WSe₂. Inset is the Raman peaks of the same spot as PL. Peaks at 251 cm⁻¹ and 260 cm⁻¹ are assigned to E₁²Γ(A₁₁Γ) and A₁₁(M)/2LA(M) of WSe₂ crystals, respectively. (B) Higher growth temperature of WSe₂ can enhance the in-situ hydrogenation on EG, evident by comparing Raman spectra of EG from 800 °C and 930 °C process. As-grown EG is present as reference. All of the spectrums were deconvoluted with SiC background. (C) and (D) Among the Raman 2D peak positions and corresponding FWHM from as-grown, 800 °C process and 930 °C process, the 930 °C process resulted in the largest position shift as well as width broadening, indicating increased graphene thickness and strain release due to the decoupling of buffer layers. (Reproduce from Ref.187)
LEEM/LEER measurements and analysis

In order to locally study the surface and electronic structure of the heterostructure samples, low-energy electron microscopy (LEEM) with electron energies of 0-20 eV is employed. In addition, low-energy electron reflectivity (LEER) spectra provides an accurate means of counting the number of graphene layers as well as extracting the work function variation over the surface.\textsuperscript{191,192}

The LEEM images of WSe\textsubscript{2}-EG from 800 °C WSe\textsubscript{2} growth show triangular islands of WSe\textsubscript{2} with a characteristic size of 1 µm, nucleating preferentially near SiC step edge on the EG surface (Figure 6-3A). The graphene is found predominantly in monolayer + buffer form, but small bi- and tri-layer graphene crystals are also found on the surface. This indicates that the buffer is nearly intact as as-grown EG, or only a negligible portion of it has been eliminated during the 800 °C WSe\textsubscript{2} growth.

Low-energy electron reflectivity spectra (LEER) shows characteristic oscillations for graphene and WSe\textsubscript{2} for the respective regions of the surface and allow material identification in the LEEM images, as shown in Figure 6-3B for the 800°C WSe\textsubscript{2} growth.\textsuperscript{193} Such LEER curves also permit determination of the local work function on the surface, since for sufficiently low sample voltages (~2 V) the incident electrons are totally reflected from the sample, i.e. the so-called “mirror-mode” transition. This voltage of this mirror-mode transition corresponds to the work function difference, $\Delta W$, between the sample surface and the LEEM electron emitter. Detailed fitting of these transition voltages (energies) permits the extraction of the variation in work function across the surface.\textsuperscript{2} A difference of $\Delta W \approx 0.31 \pm 0.03$ eV is found between the work functions of monolayer graphene and WSe\textsubscript{2} on the sample surface (uncertainty from a combination of uncertainties in the measurement, analysis, and variations of the sample surface). It should be noted that this observed work function difference is between WSe\textsubscript{2} in contact with underlying graphene (G in Figure 6-3A) and a bare graphene region without WSe\textsubscript{2} covering the top (A or B in the Figure 6-3A). The presence of interface dipoles and a change in local work function implies charge transfer between
the WSe$_2$ and the graphene below. Consistent with this interpretation, it is noted that LEER curves measured on the WSe$_2$ islands from 800 °C growth (Figure 6-3B) display a broad, sloping feature for voltages below the mirror-mode transition. This feature also indicates the presence of charge, or more specifically, electric dipoles on the edges of the triangular crystals which displace the incident and reflected electron beam during measurement, thus reducing the reflected intensity.$^{192}$

The WSe$_2$-EG from the 930 °C WSe$_2$ growth shows similar 1 µm triangle islands of WSe$_2$ on an EG surface in LEEM (Figure 6-3C), however, the sloping features in reflectivity associated with charge accumulations are much smaller than in the sample from the 800 °C WSe$_2$ growth. In addition, the extracted work function differences between uncovered bilayer graphene and WSe$_2$ (in contact) in the sample from 930 °C WSe$_2$ growth are negligible (0.03 ± 0.03 eV) compared to the one grown at 800 °C, suggesting limited charge transfer between the layers after growth of WSe$_2$ (Figure 6-3D). These observations, along with the presence of an additional, small minimum valley near 0 eV in the reflectivity spectra near the mirror-mode transition,$^{149}$ are attributed to full hydrogenation of the SiC surface, which passivates bonds between the carbon-rich buffer layer and the SiC.

This has the effect of releasing the buffer layer and increasing the count of freestanding graphene layers in the hydrogenated regions by 1, or creating quasi-freestanding-epitaxial graphene (QFEG), which is situated on H-terminated SiC.$^{31}$ Based on the evolution of graphene Raman spectra (Figure 6-2, B-D) and the LEEM/LEER investigation (Figure 6-3), we conclude that the WSe$_2$ growth at high temperatures (> 900°C) leads to hydrogen intercalation and formation of fully hydrogenated (EG$_{FH}$) compared to those partially hydrogenated EG (EG$_{PH}$) at intermediate temperatures (750 °C to 850 °C).$^{31,149}$ Concurrently, the electrical properties of the WSe$_2$/EG interface appears to have significantly changed.
Figure 6-3: (A) LEEM image of WSe$_2$ grown on EG-SiC at 800 °C (EG$_{PH}$), acquired at sample voltage of 6.2 V. Labeled points indicate location of reflectivity spectra in (B), which are used to identify the materials in the image. Bright triangles are WSe$_2$ islands, dark regions are mono- to multi-layers graphene on carbon-rich buffer layer. $\Delta W$ value, to the left of each spectrum in (B), quantify the electrostatic potential surface variation and hence the variation of the vacuum level. (C) LEEM image of WSe$_2$ grown on EG-SiC at 930 °C (EG$_{FH}$). (D) Reflectivity spectra of the points labeled in the (C); characteristic of a released buffer layer (due to passivated SiC dangling bonds). $\Delta W$ values show smaller variation than in the WSe$_2$-EG$_{PH}$ case. (Reproduce from Ref.187)

$I$-$V$ characteristics and band alignment model

The hydrogenation process is known to have a significant impact on the electrical properties of graphene on SiC. EG residing on top of the buffer layer on 6H-SiC (0001) is n-type doped$^{31,186,194}$ due to the combination of bulk and interface donor states$^{190,195}$ and has a Fermi energy 0.45 eV above the Dirac point.$^{190}$ In contrast, QFEG is known to be p-type doped.$^{149,190}$ This change has been explained by the presence of the spontaneous polarization of the hexagonal 6H-SiC substrate,
which lowers the Fermi energy to a position 0.28 - 0.30 eV below the Dirac point for complete hydrogenation. This modification in the doping of graphene can thereby influence the electrical transport properties across the WSe₂-graphene interface on SiC. In order to elucidate the transport properties, vertical I-V measurements were performed on the 800 °C and 930 °C WSe₂ growth (labeled as WSe₂-EGₚḥ and WSe₂-EGₚḥ, respectively) in Conductive AFM (CAFM).

A CAFM tip with PtIr coating, and the graphene, serves as source and drain, respectively. While the WSe₂-EGₚḥ diode exhibits a I-V with turn-on current at bias of ≥1 V; however, the WSe₂-EGₚḥ diode turns on near zero bias (Figure 6-4A). The main component of the CAFM current near zero bias for WSe₂-EGₚḥ is due to tunneling from the CAFM tip to graphene through the WSe₂ gap. On the other hand, For WSe₂-EGₚḥ, the WSe₂ layer acts as a short between the CAFM tip and the EGₚḥ (Figure 6-4B).

Our LEEM measurements and analysis above indicate a work function difference of 0.31 eV between the WSe₂ (in contact with EGₚḥ) and the uncovered monolayer EGₚḥ, while the work function difference between the WSe₂ (in contact with EGₚḥ) and the uncovered bilayer EGₚḥ is near zero. The measured work function difference is a combination effect of intrinsic interface dipole and extrinsic interface dipole. The extrinsic dipole is due to doping caused by charge transfer between WSe₂ and graphene.

The intrinsic dipole results from redistribution of charge within the WSe₂ or graphene itself upon contact. In other words, it is the difference between vacuum level of undoped WSe₂ and that of undoped graphene when they are put in contact. Density functional theory (DFT) calculations of this intrinsic dipole are performed using the Vienna ab-initio simulation package (VASP) with the projector-augmented wave (PAW) method. The local density approximation (LDA) is used to describe the exchange-correlation functional with the partial core correction included. More DFT calculation details are provided in the supplementary material. As shown in Appendix, the vacuum
energy level above WSe$_2$ is 0.17 eV higher than that above graphene, indicating an (intrinsic) dipole from graphene towards the WSe$_2$.

Using this intrinsic dipole, along with the measured work function differences, we propose a model in which the WSe$_2$ has some unintentional p-type doping, and transfer of charge between the EG$_{PH}$ or EG$_{FH}$ and the WSe$_2$ (combined with the intrinsic dipole) produces the observed variation in work function. With knowledge of the doping density of EG$_{PH}$ and EG$_{FH}$ ($(4 \pm 1) \times 10^{12}$ cm$^{-2}$ n-type and $(1.5 \pm 0.2) \times 10^{13}$ cm$^{-2}$ p-type, respectively, from our previous electrical studies on EG$_{PH}$ and EG$_{FH}$) and using reported values of electron affinities of WSe$_2$ (3.50 eV), monolayer graphene (4.57 eV) and bilayer graphene (4.71 eV), we compute the transfer of charge between the WSe$_2$ and the EG$_{PH}$ or EG$_{FH}$. This charge transfer, for a given (unintentional) doping density of the WSe$_2$, yields theoretical values for the work function differences; the doping density is determined by matching these differences to experiment. Our model is illustrated in Figure 6-4, C-D. The dependence of the results on the electron affinities of WSe$_2$ and graphene is discussed in Appendix B.

For the charge transfer computation, we employ the standard linear band structure around the K point for the monolayer graphene from EG$_{PH}$, and hyperbolic bands near the band extrema for bilayer graphene from EG$_{FH}$ and for WSe$_2$ around K points, based on tight-binding models. The method to compute the electrostatics is similar to that described by Li et al. in Figure 6-4 shows band diagrams of the WSe$_2$-EG$_{PH}$ and WSe$_2$-EG$_{FH}$ surfaces, which are graphene partially covered by WSe$_2$. Both the intrinsic interface dipole and the charge transfer are taken into account and equilibrium is reached when the Fermi levels are aligned. The difference between the vacuum energy of WSe$_2$ (in contact with graphene) and the underlying graphene (e.g. $\Delta W_0$ in Figure 6-4C) is thus a sum of the intrinsic interface dipole effect and the charge transfer effect.

In order to match the theoretical work function difference between the WSe$_2$ (in contact) with the uncovered graphene with the experimental values (0.31 eV and 0.03 eV for WSe$_2$-EG$_{PH}$ and
WSe$_2$-EG$_{FH}$, respectively), we employ an unintentional p type doping of $1.3 \times 10^{12}$ cm$^2$ for the WSe$_2$ before charge transfer between the WSe$_2$ and the underlying graphene. When the WSe$_2$ is put in contact with EG$_{FH}$ (n-type), electrons transfer from the EG$_{FH}$ to the WSe$_2$, leading to nearly complete compensation of the p-type doping in the WSe$_2$ and a negligible carrier density in the WSe$_2$. The Fermi level ends up well inside the bandgap of the WSe$_2$ and near the charge neutrality point in the graphene \((\text{Figure 6-4C})\). For the case of the WSe$_2$ in contact with the EG$_{FH}$ (p-type), the same unintentional doping of the WSe$_2$ is employed \((1.4 \times 10^{12}$ cm$^2$, p-type). To reach equilibrium, electrons transfer from the WSe$_2$ to the EG$_{FH}$, making the WSe$_2$ more p-type (carrier density $2.9 \times 10^{12}$ cm$^2$). The resulting Fermi level of the WSe$_2$-EG$_{FH}$ remains near the top of the valence band of its WSe$_2$. In other words, the WSe$_2$ on the EG$_{FH}$ forms a Schottky barrier (i.e. relatively low conductivity), whereas the WSe$_2$ on the EG$_{FH}$ forms as ohmic contact (i.e. high conductivity), and leading to a \(~10^3\times\) increase in current drive \((\text{Figure 6-4A})\).

An additional output of our charge transfer computations is the sum of the bandgap plus electron affinity of the WSe$_2$, \(\chi_{\text{WSe}_2}+E_g\) (only the sum enters, since the electron density in the WSe$_2$ conduction band is negligible). In order to match the observed work function variations, we deduce an unintentional doping density in the WSe$_2$ of \(1.3 \times 10^{12}$ cm$^2$, and the value of \(\chi_{\text{WSe}_2}+E_g\) is determined to be 5.1 eV. This value is consistent with a recently reported electron affinity of \(~3.1\) eV for WSe$_2$ using first-principles GW calculation,\(^{205}\) together with a bandgap of \(~2\) eV, which is in agreement with several recently reported experimental values.\(^{206,207}\)
Figure 6-4: Electrical measurements (A) show that the I-V curves of EG_{PH}, EG_{FH}, WSe_{2}-EG_{PH}, and WSe_{2}-EG_{FH}. WSe_{2}-EG_{PH} is more resistive than that of WSe_{2}-EG_{FH}, indicating the barrier to transport is larger for WSe_{2}-EG_{PH}. (B) The WSe_{2}-EG_{PH} resulted in a small tunneling current (Left), while the tunneling current is magnified after the decoupling of buffer layer (Right). The yellow surface of CAFM tips symbols PtIr coatings. Band alignment and vacuum energy diagrams for the two heterostructures, WSe_{2}-EG_{PH} (C) and WSe_{2}-EG_{FH} (D), showing variations of vacuum energy of the surface due to partial WSe_{2} coverage. (Reproduce from Ref.187)
Conclusions

By varying the temperatures for growth of WSe$_2$ on EG in a pure H$_2$ environment, the electrical transport across WSe$_2$-Graphene heterostructures is controllable. The investigation combining LEED/LEEM, Raman spectra, and electrical measurements on the heterostructures confirmed the transport across the interface is controlled by the doping of the EG, which is-turn is tuned by the presence of a carbon buffer. The band alignment diagrams of two different heterostructures were constructed with the measured work function difference between the WSe$_2$ and the graphene from LEER. Taking into account their intrinsic interface dipoles and charge transfer, the diagrams show the presence of the Schottky barrier in WSe$_2$-EG$_{PH}$ and a reduced barrier in WSe$_2$-EG$_{FH}$, which are in agreement with their I-V characteristics. The work described here is foundational for understanding vertical transport in graphene-based 2D heterostructures, demonstrating that doping of the graphene plays a critical role in these novel structures. Epitaxial graphene is unique because it can be made n- or p-type based on the TMDC growth conditions, allowing for one to readily engineer the transport between graphene and to n- or p-type TMDCs with a truly pristine interface.
Chapter 7

Atomically thin resonant tunnel diodes built from synthetic vdW heterostructures

Vertical integration of 2D vdW materials is predicted to lead to novel electronic and optical properties not found in the constituent layers. In this chapter the direct synthesis of two unique, atomically thin, multi-junction heterostructures by combining graphene with the monolayer TMDC: MoS$_2$, MoSe$_2$, and WSe$_2$. The realization of MoS$_2$-WSe$_2$-Graphene and WSe$_2$-MoSe$_2$-Graphene heterostructures leads to resonant tunneling in an atomically thin stack with spectrally narrow, room temperature negative differential resistance (NDR) characteristics.

Introduction

Resonant tunneling of charge carriers between two spatially separated quantum states can lead to a unique current transport phenomenon known as negative differential resistance (NDR). This is a key feature for novel nanoelectronic circuits that utilize bistability and positive feedback, such as novel memories, multi-valued logic, inductor-free compact oscillators, and many other not-yet-realized electronic applications. However, realizing spectrally narrow NDR in a resonant tunneling diode (RTD) at room temperature has been challenging due to carrier scattering related to interfacial imperfections, which are unavoidable in traditional semiconductor heterostructures synthesized using advanced epitaxial growth techniques. Two-dimensional (2D) materials, with no out-of-plane chemical bonding and pristine interfaces, presents an appealing alternative to traditional semiconductors, and could ultimately eliminate the interfacial imperfections that limit room temperature NDR performance to-date. Since 2004, the overwhelming majority of electronic transport and stacked in 2D materials has been reported using mechanically exfoliated flakes.
There has been a concerted effort to directly synthesize layered transition metal dichalcogenides (TMDCs), with powder vaporization (PV) synthesis paving the way for direct growth of atomically thin structures. Beyond monolayered TMDCs, vdW heterostructures (heterogeneous stacks of dissimilar atomic layers) have been predicted to lead to novel electronic properties not found in their constituent layers, where their realization has primarily come from mechanical exfoliation and stacking. Manual stacking has provided experimental verification of electronic bandgap modulations and strong interlayer coupling, but it can also lead to interface contamination that introduces additional scattering mechanisms and inhibits the NDR. Therefore, a synthetic route to achieve vdW heterostructures with pristine interfaces will be a critical step in the advancement of the field.

Here, we present the direct synthesis of MoS$_2$-WSe$_2$-Graphene and WSe$_2$-MoSe$_2$-Graphene heterostructures employing a combination of oxide PV and MOCVD. We not only demonstrate that these heterostructures exhibit the same interlayer electronic coupling found in mechanically exfoliated heterostructures but also show that they exhibit unique electronic transport properties not typically found in exfoliated structures. We discover that direct grown heterostructures exhibit resonant tunneling of charge carriers, which leads to sharp NDR at room temperature. Importantly, we identify that the peak of the resonant tunneling can be tuned by modifying the stacking order or layer composition, which will be a powerful tool toward engineering heterostructures for ultra-low power electronic devices.
Experimental methods

Epitaxial graphene synthesized on 6H-SiC

Graphene is synthesized on 6H-SiC (0001) in a graphite crucible. The 6H-SiC substrate was annealed in H$_2$ at 1500 °C for 10 min in order to clean substrate surface prior to graphene growth. At this stage the chamber pressure is 700 Torr under a H$_2$ (50 s.c.c.m)/Ar (450 s.c.c.m) flow. After H$_2$ annealing the system temperature cooled to 850 °C and pumped/purged with ultra-high pure N$_2$ at least six times to remove H$_2$ gas. Subsequently the chamber is filled in Ar gas (500 s.c.c.m.) to 200 Torr. The chamber was then heated up to 1725 °C at 100 °C/min and dwelled at this temperature for 20 min to grow three layers of graphene within the terraces of substrates via sublimation of silicon on the silicon side of 6H-SiC (0001). The system cooled down naturally to room temperature after the growth.

MoS$_2$-WSe$_2$-EG and WSe$_2$-MoSe$_2$-EG synthesis

WSe$_2$ can be grown on EG either via PV reaction of WO$_3$ and Se powders or via MOCVD. The PV reaction utilizes the vaporization of WO$_3$ powders in a ceramic boat placed at the center of 1” horizontal hot wall tube reactor with a flow of H$_2$ (10 s.c.c.m.)/Ar (90 s.c.c.m.). The EG substrates for WSe$_2$ growth were placed at the downstream side of the tube and heated to 925 °C at 25 °C/min. Samples were held at 925 °C for 15 min and then cooled naturally to room temperature. The total pressure throughout the reaction is held at 6 Torr. Utilizing MOCVD, WSe$_2$ was synthesized in a vertical cold wall reactor using W(CO)$_6$ and DMSe precursors. The metallic organic precursors were transported into the reactor by carrier gas of 100% H$_2$ via a bubbler manifold that allows for controlling each precursor concentration independently. The Se to W ratio
was fixed at 20,000. The MOCVD growth of WSe$_2$ took place at 800 to 850 °C with a total pressure of 700 Torr. The growth time varied between 15 to 30 min. After the completion of WSe$_2$-EG synthesis, the ex-situ MoS$_2$ growth via the vapor phase reaction using MoO$_3$ and S powders was carried out in a horizontal hot wall tube reactor at 700 Torr. During the MoS$_2$ growth, MoS$_3$ powder in a ceramic boat placed at the center of heating zone were heated at 750 °C for 10 min. After the MoS$_2$ growth, the reactor cooled down to room temperature naturally. The processes for WSe$_2$-MoSe$_2$-EG synthesis are similar, but steps reversed. The MoS$_2$ is grown first, followed by an ex-situ WSe$_2$ growth via the vapor phase reaction of WO$_3$ and Se. A Se-S ion exchange occurs in the MoS$_2$ converting the MoS$_2$ into MoSe$_2$. Subsequently, the WSe$_2$ layers grow on MoSe$_2$-EG as the hot zone is held at 950 °C for 45 min, resulting in WSe$_2$-MoSe$_2$-EG.

**Sample characterization**

The as-grown samples are characterized using Raman spectroscopy, atomic force microscopy/conductive atomic force microscopy (AFM/CAFM), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). A WITec CRM200 Confocal Raman microscope with 488/514/633 nm wavelength lasers was utilized for structural characterization. A BRUKER Dimension with a scan rate of 0.5 Hz was utilized for the topography image during the AFM measurement. Conductive AFM (CAFM) measurement was performed in PeakForce TUNA mode with platinum (Pt) AFM tip. The applied voltage from tips to sample was increased from 0 to 2 V. The optimized loading force of the AFM tip and sensitivity was nominally 5 nN and 20 pA/V, respectively, for the I-V measurements carried out on the novel junctions. All the AFM/CAFM measurements in BRUKER Dimension were at room temperature and in ambient. TEM cross-sectional samples were made via utilizing a NanoLab dual-beam FIB/SEM system.
Protective layers of SiO$_2$ and Pt were deposited to protect the interesting region during focused ion beam milling. TEM imaging was performed using a JEOL 2100F operated at 200 kV.

For surface analysis, the sample was loaded into an ultra-high vacuum (UHV) with a base pressure lower than 2 $\times$ 10$^{-10}$ mbar. The WSe$_2$/EG sample was then imaged using an Omicron variable temperature scanning tunneling microscope (STM) without any thermal treatment. The STM images were obtained at room temperature and in the constant-current mode, with an etched tungsten tip. The same system is equipped with a monochromatic Al-K$_\alpha$ source (E = 1486.7 eV) and an Omicron Argus detector operating with pass energy of 15 eV. The spot size used during the acquisition is equal to 0.5 mm. Core-level spectra taken with 15 sweeps are analyzed with the spectral analysis software analyzer.

**Theoretical methods**

In order to provide a theoretical explanation for the observed physical phenomena, we carry out non-equilibrium quantum transport calculations by using density functional theory (DFT) coupled with the Non-Equilibrium Green’s function (NEGF) formalism. Detailed setup for DFT and NEGF can be found in Appendix C.$^{219}$

**Results and discussion**

**Making vertical vdW heterostructures**

The heterostructure is achieved by sequentially growing two dissimilar TMDC monolayers on multi-layer (3 layers) epitaxial graphene (EG).$^{31}$ WSe$_2$ is synthesized using both routes: WO$_3$ and Se powders for the PV route,$^{111}$ and tungsten W(CO)$_6$ and DMSe for the MOCVD route.$^{68}$ MoS$_2$ is
grown via vaporization of MoO$_3$ and S.$^{64}$ The heterostructure synthesis process is summarized in **Figure 7-1**. The first TMD layer of the heterostructure, WSe$_2$ or MoS$_2$, is grown on tri-layer EG (**Figure 7-1A**) at 950 °C and 750 °C for WSe$_2$-EG (**Figure 7-1B**) and MoS$_2$-EG (**Figure 7-1, C-D**), respectively. Following this first TMDC growth step, the surface coverage of the WSe$_2$ or MoS$_2$ on EG is typically > 60 %, with a lateral size of 2 μm and 300 nm for WSe$_2$ and MoS$_2$, respectively. Subsequently, the MoS$_2$-WSe$_2$-EG vertical heterostructure is created via a second ex-situ growth of MoS$_2$ on WSe$_2$-EG at 750 °C (**Figure 7-1C**). Similar to our previous work,$^{74}$ we find that wrinkles in the graphene as well as defects and edges within the WSe$_2$ promote vertical growth of the MoS$_2$, and monolayer MoS$_2$/WSe$_2$ is primarily achieved in pristine regions of WSe$_2$ (**Figure 7-1C**).$^{74}$

**Figure 7-1**: (A) MoS$_2$-WSe$_2$-EG vertical heterostructures begins with the synthesis of 3L EG from SiC followed by (B) vapor transport or MOCVD of WSe$_2$ and (C) vapor transport of MoS$_2$. WSe$_2$-MoSe$_2$-EG heterostructures are similarly grown, except when (D) MoS$_2$ is grown first on EG followed by (E) growth of the WSe$_2$, a Se-S ion exchange occurs, leading to the formation of MoSe$_2$ from the original MoS$_2$ layer. The MoSe$_2$ domains are difficult to topographically identify; however, (F) conductive AFM clearly delineates their location due to enhanced tunneling at the heterostructures.$^{78}$ (Reproduce from Ref.78)
The formation of the WSe\textsubscript{2}-MoSe\textsubscript{2}-EG heterojunction occurs during growth of WSe\textsubscript{2} on MoS\textsubscript{2}. During the synthesis, a selenium-sulfur ion exchange occurs when the MoS\textsubscript{2} is exposed to the selenium vapor just prior to the growth of WSe\textsubscript{2} at 950 °C for 45 min.\textsuperscript{218} Standard topographic characterization via AFM cannot clearly identify the location of the heterostructures (Figure 7-1, E-F), however conductive AFM (CAFM) with Pt-Ir tip\textsuperscript{43} provides a means to map the WSe\textsubscript{2}-MoSe\textsubscript{2}-EG junctions and adjacent WSe\textsubscript{2}-EG regions due to a difference in heterostructure conductivity. Transmission electron microscopy (TEM) confirm the formation of crystalline, vertical vdW heterostructures (Figure 7-2). Scanning transmission electron microscopy (STEM) (Figure 7-2, A-B) also verifies the heterostructure is not a manifestation of the alloying of the constituent TMDs, but indeed are unique layers with pristine interfaces with atomic precision. In the case of MoS\textsubscript{2}-WSe\textsubscript{2}-EG, we have focused on a multilayer region of MoS\textsubscript{2}-WSe\textsubscript{2} to ensure pristine layer formation beyond the ML. The clean interface between layers can be observed in both of STEM image and the EDX cross-profiles (Figure 7-2C).
2D alloys on sapphire

Unlike vertical heterostructures based on a single chalcogen (i.e. MoS$_2$/WS$_2$), the ordered layering does not occur when we attempt to grow a vertical structure based on heterogeneous layers where M$_1$≠M$_2$ and X$_1$≠X$_2$ (M = Mo, W; X = S, Se) on “3D” substrates such as sapphire (Figure 7-3). Instead, all attempts to grow such a structure results in alloying or lateral heterostructures of the layers. Therefore, we hypothesize that EG plays a critical role in the formation of atomically precise vdW heterostructures where M$_1$≠M$_2$ and X$_1$≠X$_2$ by providing an atomically smooth surface that is free of dangling bonds, enabling mobility on the surface for TMDC layer growth. Sapphire surface exhibits high surface roughness, dangling bonds, and are therefore more likely to impede surface diffusion, which catalyzes the alloying process.

**Figure 7-3:** The growth of vertical heterostructures on sapphire ends up with 2D alloys. (A) shows the optical micrograph after CVD process, and the boundary of per-growth WSe$_2$ part is located with black dashed line. In some case, we observed that MoS$_2$ is growth from the edge instead on the top of the WSe$_2$, which is clearly shown in (A). The AFM image of (B) confirms that the MoS$_2$ grows from the edge. Some structural damages on per-growth WSe$_2$ are found in (B). (C-D) show the Raman and PL spectrum of the WSe$_2$ before (black) and after (blue) and new-growth MoS$_2$ (red), the examined positions are indicated in (A). (Reproduce from Ref.78)
The interlayer coupling within 2D junctions

A large fraction of the EG remains nearly defect free following the sequence of TMDC growths. However, there are regions of increased defectiveness due to either partial-passivation of the graphene/SiC buffer layer\textsuperscript{31} or formation of thick TMDC layers (Figure 7-4A).\textsuperscript{74} Raman spectroscopy (Figure 7-4B) also confirms presence of significant fractions of ML WSe\textsubscript{2} (E\textsubscript{2g} / A\textsubscript{1g} at 250 cm\textsuperscript{-1} and 2LA at 263 cm\textsuperscript{-1})\textsuperscript{111} and MoS\textsubscript{2} (E\textsubscript{2g} at 383 cm\textsuperscript{-1} and A\textsubscript{1g} at 404 cm\textsuperscript{-1})\textsuperscript{74} as well as ML MoSe\textsubscript{2} (A\textsubscript{1g} at 240 cm\textsuperscript{-1} and E\textsubscript{12g} at 284 cm\textsuperscript{-1}).\textsuperscript{218} X-ray photoelectron spectroscopy\textsuperscript{78} also corroborates the absence of any interaction between the two transition metal dichalcogenides or graphene; and indicates that that the MoS\textsubscript{2} exhibits an n-type behavior, while the WSe\textsubscript{2} layer shows a p-type behavior. Monolayer semiconducting TMDCs exhibit a direct optical band gap (E\textsubscript{opt}) (MoS\textsubscript{2} at 1.8 \textasciitilde 1.9 eV, MoSe\textsubscript{2} at 1.55 eV, and WSe\textsubscript{2} at 1.6 \textasciitilde 1.65 eV);\textsuperscript{88} therefore, photoluminescence (PL) spectroscopy (Figure 7-4C) can provide evidence of electronic coupling between the layers. In addition to the typical PL peaks from the direct bandgap transition within the individual layers, the PL spectra of the heterostructures exhibit the presence of interlayer excitons at 1.59 eV for MoS\textsubscript{2}-WSe\textsubscript{2}-EG and 1.36 eV for WSe\textsubscript{2}-MoSe\textsubscript{2}-EG. In this case, the MoS\textsubscript{2}-WSe\textsubscript{2} and WSe\textsubscript{2}-MoSe\textsubscript{2} junctions exhibit type II band alignment,\textsuperscript{51,52,54,220} where electrons in the WSe\textsubscript{2} conduction band transfer to the conduction band of MoS\textsubscript{2} (MoSe\textsubscript{2}) and the excited holes in MoS\textsubscript{2} (MoSe\textsubscript{2}) valence band transfer to the valence band of WSe\textsubscript{2}, as described in Figure 7-4D. Consistent with manually-stacked heterojunctions,\textsuperscript{52,54} the position of the PL peak is due to interlayer exciton recombination, which confirms the electronic coupling at the heterojunction between the two monolayer TMDCs. high resolution STEM.

Additional evidence of coupling comes from the topographical information of the heterostructures. Like graphene-hBN heterostructures,\textsuperscript{75} Moiré patterns of MoS\textsubscript{2}-WSe\textsubscript{2} are observed in tapping-mode AFM (Figure 7-5A), which are qualitatively consistent with rotation
angles of approximately 0 or 180° between MoS$_2$ and WSe$_2$. Furthermore, scanning tunneling microscopy/spectroscopy (STM/S) (Figure 7-5B) confirms the presence of a Moiré pattern produced by the misorientation of MoS$_2$ relative to the underlying WSe$_2$ layer. The lattice constant of the Moiré pattern is 9.8 ± 0.4 nm, which corresponds to a misorientation angle of ~1.9°. Modeling the heterostructure with this misorientation produces a consistent Moiré pattern, with a slightly smaller lattice constant of 9.6 nm (Inset, Figure 7-5B). While the mechanical stacking technique leads to a variety of rotation angles between layers, the direct growth of vdW layers using our approach appears to have a strict rotational alignment, which may be critical for achieving optimal coupling between the layers.$^{221,222}$

Scanning tunneling spectroscopy further provides evidence that the quasi-particle band gap of MoS$_2$-WSe$_2$-EG is significantly smaller than its WSe$_2$-EG counterpart (Figure 7-5C). Based on STS, we infer that, for WSe$_2$-EG, the conduction band minimum (CBM) is at a sample bias of +0.71±0.08 V and the valence band maximum (VBM) is at -1.11±0.02 V. This indicates that the quasi-particle band gap ($E_g$) of WSe$_2$ is 1.83±0.05 eV, which is higher than $E_{\text{opt}}$ (1.63 eV) due to the large excitonic binding energy in 2D TMDCs.$^{53,85,177,220}$ On the other hand, MoS$_2$-WSe$_2$-EG exhibits a CBM at +0.34±0.03 V and VBM at -1.31±0.03 V, indicating a quasi-particle interlayer $E_g$ of 1.65 eV±0.02 V, which is slightly larger than its interlayer $E_{\text{opt}}$ at 1.59 eV but smaller than the $E_{\text{opt}}$ in monolayer MoS$_2$-EG.$^{53,220}$ Mapping the tunnel current density of WSe$_2$-EG and WSe$_2$-MoSe$_2$-EG heterostructures via conductive AFM$^{43,223}$ provides strong evidence that tunneling is much more readily achieved in WSe$_2$-MoSe$_2$-EG at a tip bias of 1.5 V, indicating a smaller, resonance tunneling, or both may be occurring. Finally, we note that defects, such as grain boundaries and vacancies disrupt the continuity of the Moiré pattern, further emphasizing that imperfections in layers or the interface will significantly impact the electronic behavior of vdW heterostructures.
Figure 7-4: (A) Raman spectra indicates preservation of the graphene has occurred during the synthesis process. (B) The spectrums clearly display distinct features from MoS$_2$/WSe$_2$ and WSe$_2$/MoSe$_2$ and indicate no alloy-like features. The asterisks indicate the signatures of their strong couplings and can also be found in mechanically stacked MoS$_2$/WSe$_2$. (C) The PL properties of MoS$_2$-WSe$_2$-EG and WSe$_2$-MoSe$_2$-EG reveal significant interlayer coupling, where the MoS$_2$-WSe$_2$-EG and WSe$_2$-MoSe$_2$-EG exhibit the intrinsic PL peaks corresponding to MoS$_2$, MoSe$_2$, and WSe$_2$, and also exhibit interband PL peaks at 1.59 and 1.36 eV. The charge transfer process of the bilayer systems is illustrated in (D), in which (1) and (2) denoted for intralayer excitons and (3) is for interlayer excitons. The excitation wavelength ($) is 488 nm and 633 nm for MoS$_2$-WSe$_2$-EG and WSe$_2$-MoSe$_2$-EG, respectively. (Reproduce from Ref.78)
Figure 7-5: (A) The moiré patterns acquired via AFM in MoS$_2$ on WSe$_2$ indicates an alignment of nearly either 0° or 180° between the top and bottom layer due to their 3-fold symmetry, and (B) STM confirms the moiré pattern with a lattice constant equal to (9.8 ± 0.4) nm. This structure can be reproduced theoretically when the misorientation angle between these layers is ~1.9° (Inset). The continuity of the Moiré pattern is interrupted by the formation of a grain boundary and point defects, as indicated in the STM image. (C) STS on MoS$_2$-WSe$_2$-EG, WSe$_2$-EG, and EG (inset) provide evidence that the bandgap of the double junction heterostructure (MoS$_2$-WSe$_2$-EG) is smaller than that of the single junction (WSe$_2$-EG) heterostructure. (Reproduce from Ref.78)

**Vertical electrical transport**

Room temperature current-voltage measurements through the heterostructure (carried out via CAFM) do not exhibit the traditional p-n junction diode-like transport found in mechanically exfoliated dichalcogenide structures or direct grown single-junction (i.e. WSe$_2$-EG) structures.$^{48,52,74}$ Instead, we find that, following a “soft” turn-on, the current exhibits a peak at a certain bias voltage ($V_{\text{peak}} = +1.1$ and +0.7 for MoS$_2$-WSe$_2$-EG and WSe$_2$-MoSe$_2$-EG, respectively), then decreases to a minimum before undergoing a “hard” turn on with exponential current increase (Figure 7-6). The peak to valley current ratio (PVCR) is 1.9 for MoS$_2$-WSe$_2$-EG and 2.2 for WSe$_2$-MoSe$_2$-EG which is comparable to traditional resonant tunneling diodes.$^{208-212}$
Negative differential resistance in vdW heterostructures

Resonant tunneling between two spatially separated quantum states can be used to realize negative differential conductance. Negative differential resistance (NDR) holds the key for novel nano-electronic design options utilizing bistability and positive feedback. Novel memories, multi-valued logic and inductor-free compact oscillators and other electronic applications can benefit from a low power, low voltage negative differential conductance device. The resonant tunneling diode (RTD) has been a subject of intense study and design optimization, in Silicon Germanium and III-V heterostructure material systems for many years now. While theoretically capable of operating in extremely narrow voltage windows, the negative differential conductance of a RTD, particularly at room temperature, is limited by scattering mechanisms, related to interfacial imperfections, which are unavoidable even when utilizing high vacuum advanced epitaxial growth technique. The interface related scattering reduces the sensitivity of resonant tunneling to an external bias, thereby increasing the voltage window over which negative differential conductance regime is observed. van der Waals epitaxy of 2D materials can mitigate these issues and provide a materials platform for device engineers to obtain energetically sharp NDR features at room temperature leading to novel low power quantum tunneling devices.
Figure 7-6: Resonant tunneling and negative differential resistance in atomically thin layers. (A) Experimental $I$-$V$ traces for different combination of dichalcogenide-graphene interfaces demonstrating NDR. The inset shows schematic of the experimental setup for the $I$-$V$ measurement in this layered system. (B) Comparison of FWHM voltage of the NDR from this work with other reported results in room temperature.$^{224-233}$ (Reproduce from Ref.78)
Conclusions

We have demonstrated the direct synthesis of unique multi-junction heterostructures based on graphene (epitaxial graphene on SiC), MoS$_2$, MoSe$_2$, and WSe$_2$ that yields pristine interlayer gaps and leads to the first demonstration of resonant tunneling in an atomically thin synthetic stack with the spectrally narrowest room temperature NDR characteristics. Importantly, this work indicates that NDR at room temperature only occurs in TMDC-based heterostructures with truly pristine interfaces, which has been recently corroborated with manually stacked heterostructures where NDR is only evident at liquid nitrogen temperatures.$^{52,234,235}$ This is due to resonant tunneling being highly sensitive to interfacial perturbations such as defects or “residue” from the transfer process, emphasizing the importance of direct synthesis of multi-junction TMDC heterostructures for vertical quantum electronics applications. Interestingly, the room temperature full width at half maximum (FWHM) of the NDR in this work is more spectrally narrow than their “3D” semiconductor counterparts (silicon, germanium, III-V) and manually stacked graphene-boron nitride-graphene (Gr-hBN-Gr) heterostructures (Figure 7-6B).$^{224-233}$ This suggests that the interface of the directly grown vdW heterostructures is superior to that of many previously reported RTD structures.
Chapter 8

A 2D/3D interface made of monolayer MoS\(_2\) (WS\(_2\)) and VO\(_2\)

A phase transition material with two-dimensional (2D) semiconductors can provide a route towards tunable opto-electronic metamaterials. Here, we integrate monolayer transition metal dichalcogenides (TMDC) with vanadium dioxide (VO\(_2\)) thin films grown via molecular beam epitaxy to form a 2D/3D heterostructure. Vanadium dioxide undergoes an insulator-to-metal transition (IMT) at 60-70 °C, which changes the band alignment between MoS\(_2\) and VO\(_2\) from a semiconductor-insulator junction to a semiconductor-metal junction. By switching VO\(_2\) between insulating and metallic phases, the modulation of photoluminescence emission in the 2D semiconductors was observed. This study demonstrates the feasibility to combine TMDCs and functional oxides to create unconventional hybrid optoelectronic properties derived from 2D semiconductors that are linked to functional properties of oxides through proximity coupling.

Introduction

Integrating disparate electronic materials into functional hybrid structures will be key for next-generation optoelectronic devices. Recently, heterostructures consisting of 2D vdW solids have emerged, providing new hybrid phenomena that do not exist in conventional heterostructures.\(^{35,38}\) For example, integrating at least two different semiconducting TMDC monolayers can create a new emission band gap that is smaller than that of integrated 2D layers.\(^{52}\) Ultrathin p-n junctions and light emitting diodes can also be realized by combining TMDC monolayer with graphene or boron nitride.\(^{49,78,235}\) The same stacking strategy can be extended to other materials including metal nanostructures, 3D semiconductors, and functional oxides. Several studies have shown that
hybridizing gold and silver nanostructures with monolayered MoS$_2$ revealed enhanced light absorption and emission with exciton-surface plasmons.$^{236,237}$

In addition, stacking monolayered TMDC on 3D substrates, such as MoS$_2$/Si,$^{238}$ WS$_2$/Ga(Mn)As,$^{239}$ and MoS$_2$/GaN,$^{127}$ is also useful for light harvesting, laser emission, and light modulation application utilizing unique optical properties of TMDC monolayers. Besides these conventional semiconductor substrates, recently MoS$_2$/LiNbO$_3$ were used to realize a sound-driven battery and acoustic photodetector as well as to manipulate the electrical transport and optical properties of MoS$_2$ using the ferroelectric poling of LiNbO$_3$.$^{240,241}$

In the large class of functional oxides electronic phase change materials that exhibit an insulator-to-metal transition (IMT) are of particular interest. Among them, vanadium oxide (VO$_2$) is a widely studied material that exhibits greater than four orders of magnitude change in the resistivity when undergoing the IMT above room-temperature.$^{242}$ In VO$_2$, a first order IMT occurs at 60-70 °C from low-temperature insulating (I) phase to high-temperature metallic (M) phase, accompanied by a structural transition arising from the low-temperature monoclinic structure to high-temperature rutile structure.$^{242}$ In this study, we focus on a novel 2D/3D heterostructure consisting of TMDC monolayers and VO$_2$ thin films. We investigated how the phase transition of VO$_2$ impacts the optical properties of MoS$_2$ and WS$_2$ monolayers to understand how photo-excited carriers transfer between TMDCs and VO$_2$.

**Experimental Methods**

**MoS$_2$ and WS$_2$ Synthesis**

MoS$_2$ monolayers were grown on a 285 nm-SiO$_2$/Si substrate via a standard powder vaporization technique.$^{30,64}$ More specifically, 2 mg of molybdenum trioxide, MoO$_3$ (99.8%,
Sigma-Aldrich), was placed in the center of a single zone furnace, and 200 mg of sulfur powder (99.995%, Alfa Aesar) was placed 12 inches upstream of the MoO$_3$ crucible. In order to eliminate contaminants, such as gas molecules and water from the ambient, a 10 min vacuum (15 mTorr) anneal at 300 °C was performed before growth. Then sulfur was heated to 130 °C and the vapor was transported in an Ar flow of 100 sccm to the reacting zone. A growth temperature of 800 °C was performed for 15 min. In order to explore the direct growth of MoS$_2$ on VO$_2$ films, a piece of 30-nm-thick VO$_2$ on sapphire was also used as substrate for MoS$_2$ synthesis. The WS$_2$ monolayers were synthesized via sulfurizing WO$_3$ films. In this case, WO$_3$ films were thermally deposited on cleaned SiO$_2$/Si substrates in a high vacuum chamber (~10$^{-6}$ Torr). The WO$_3$ films were subsequently sulfurized in a quartz tube reactor at ambient pressure. During the sulfurization of the WO$_3$ films, the samples were kept at 800 °C for 30 minutes under an argon flow (100 sccm). The sulfur gas was independently controlled and generated from powder heated to 250 °C and placed upstream.

**VO$_2$ thin films preparation**

VO$_2$ thin films were grown by co-depositing vanadium and vanadium oxytriisopropoxide (VTIP) in the presence of molecular oxygen using molecular beam epitaxy (MBE). Vanadium and VTIP, (vanadium valence 5+) were supplied from an effusion cell and gas injector installed on opposite sides of the MBE reactor to create a flux gradient across the sample and build a vanadium valence state library. Optimal growth condition to achieve stoichiometric VO$_2$ films were determined from the analysis of the valence state calibration samples and a 30-nm-thick VO$_2$ film was epitaxially grown on γ-plane sapphire substrate.
Monolayer TMDCs transferred onto VO₂

As-grown TMDC monolayers were transferred from the growth substrates to the VO₂ by a wet transfer method using Poly(methyl methacrylate) (PMMA). First, TMDC monolayers on SiO₂/Si substrates were spin-coated with PMMA (Micro Chem 950K, A3); followed by baking at 130 °C for 90 seconds. The PMMA is then etched off the edge of the substrate using a razor blade to accelerate the etching rate of the oxides at PMMA-capped monolayers-SiO₂/Si interface. A NaOH solution (2 molar (2M)), mixed in deionized (DI) water) at 80 °C was used to etch SiO₂ and decouple PMMA-capped TMDCs monolayer from SiO₂/Si. After the PMMA-capped monolayers were lifted from the growing substrates, they were transferred to a bath of DI water with a glass slide to remove the etchant and residues stuck underneath. Subsequently, a VO₂ film on sapphire was used to support the PMMA-capped monolayers, followed by spinning away the remained DI water at the interface of membrane/VO₂ on a spin-coater at 4000 rpm for 2 minutes. The PMMA membrane was finally removed by dipping it in a bath of acetone and cleaned by isopropyl alcohol.

Characterization techniques

Topographic atomic force microscopy (AFM) micrographs were taken in a BRUKER Dimension with a scan rate of 0.5 Hz and 512 lines per image resolution. The current-to-voltage (I–V) measurements and conductive AFM (CAFM) performed on the samples were done in the same AFM instrument with a PtIr-coated tip. Scanning electron micrographs were taken in a LEO 1530 that uses a Schottky-type field-emission electron source and In-lens detector that receives the secondary electrons from the imaged sample. The TMDCs monolayer-VO₂ heterostructures were characterized via photoluminescence (PL). Raman spectroscopy (Horiba LabRam) has been performed using both 488 nm and 532 nm excitation wavelengths and a 50X long-working distance
objective lens. An incident laser power of 5.0 mW was chosen to acquire a single Raman spectrum. For temperature, dependent measurements samples were placed onto a heater located inside a Linkam stage. The heating and cooling rates of 10 °C/sec and 5 °C/sec were used, respectively.

Results and discussion

The hybrid structure, consisting of monolayer MoS$_2$ and VO$_2$, can be clearly seen in a scanning electron microscopy after the transfer process (Figure 8-1A). The average size of the MoS$_2$ monolayers was 10 – 20 µm, which is sufficiently large for the optical measurement in this study. Atomic force microscopy also confirms the high-quality transfer of MoS$_2$ monolayers on VO$_2$ with negligible difference in roughness (Figure 8-1B). Initial attempts were made to directly grow the MoS$_2$ on VO$_2$, however, the best quality heterostructures were found with transferred flakes. Although MoS$_2$ monolayers can be successfully deposited, the growth temperatures (> 700 °C) for MoS$_2$ from MoO$_3$ adversely affect the structure and morphology of VO$_2$ films, as the surface roughness and Raman spectroscopic signatures have been drastically altered (Figure 8-1, C-D). Hence, a synthetic technique that can grow TMDCs at low temperatures should be developed to ensure the VO$_2$ remains quality. Conductive atomic force microscopy, which uses VO$_2$ as a back electrode, was also performed on heterostructure (Figure 8-2). Although VO$_2$ at room temperature is commonly labeled as “insulating”, its electrical properties in terms of its electron concentration ($\sim 10^{18}$-$10^{19}$ cm$^{-3}$) and narrow bandgap (~0.7 eV) still provide enough conductivity for CAFM measurement. The topography and its corresponding current map from the measurement showed low surface roughness of VO$_2$ provide good electrical uniformity over the surface of MoS$_2$/VO$_2$.  

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Figure 8-1: (A) Scanning electron microscopes provide ideal contrast to image MoS₂ monolayer transferred onto the surface of VO₂; (B) MoS₂ films transferred to VO₂ conform to the VO₂ surface, evident by negligible difference in the roughness between MoS₂-covered and uncovered area. (C) MoS₂ monolayer was synthesized directly on VO₂ at 800 °C. Thin region (dark color) in AFM is MoS₂ monolayers, whereas their adjacent rough surface (bright color) is remained VO₂ after growth. (D) After MoS₂ growth, the major characteristic peaks of monolithic VO₂ vanished and only the peaks of MoS₂ monolayer present, which could be a result of non-stoichiometry and phase change.²⁴⁷ (Reproduce from Ref.247)

Figure 8-2: (A) Schematic of CAFM setup for measuring the current flowing through MoS₂/VO₂. (B-C) Topography of MoS₂/VO₂ and its corresponding tunneling current map. The polarity of applied bias is towards VO₂. The electrical continuity of some area was affected by the presence of residues left from sample transfer process (marked by *), which block the current signal in C. (Scale bar in B-C are 500 nm)²⁴⁷ (Reproduce from Ref.247)
Raman spectra of MoS$_2$, VO$_2$ and MoS$_2$/VO$_2$ were obtained in order to validate that the transfer process did not affect the heterostructure (Figure 8-3A). The Raman peaks of VO$_2$ at room temperature confirm it is in the monoclinic phase, whereas E$_{2g}$ (385 cm$^{-1}$) and A$_{1g}$ (405 cm$^{-1}$) peaks of MoS$_2$ monolayers originate from their in-plane and out-of-plane phonon characteristics. No new Raman peaks were observed beyond the superposition of the MoS$_2$ and VO$_2$ constituent materials. On the other hand, PL quenching was found on MoS$_2$ once it was deposited on VO$_2$ (marked in red area in the inset of Figure 8-3B) compared to the PL intensity of monolayered MoS$_2$ on sapphire (Figure 8-3B, inset). This observation indicated that the MoS$_2$ and VO$_2$ were electronically coupled. The PL spectra of monolayer MoS$_2$ exhibits components from trions (at ~ 1.85 eV), A-excitons (~1.9 eV), and B-excitons (~2.01 eV). Fitting of the MoS$_2$ PL on VO$_2$ indicates that trions and A-excitons are at 1.83 eV and 1.88 eV, respectively (B-excitons were excluded in the discussion because their intensity contributed only a little to the overall PL). For MoS$_2$ deposited directly on sapphire the trion and A-exiton peaks are located at 1.83 eV and 1.89 eV. Besides the main PL peaks, there were emission peaks also at lower energy (1.6-1.7 eV). This peak has been attributed to a defect-bound exciton, and it is associated with defects in the MoS$_2$ caused by sample transfer, or inherently present after material synthesis. The energy separation between the trion and A exciton is consistent with reported values (~50 meV). MoS$_2$ and WS$_2$ monolayers are considered as n-type materials with their Fermi level located close to their conduction band. We hypothesize that the Fermi level in MoS$_2$ was shifted towards the mid-gap when placed on VO$_2$, due to substrate doping effects. In other literatures, lowering the Fermi level has been shown to reduce the spectral weight of the trion in the PL signal using back-gating with SiO$_2$/Si or by depositing molecule dopants like F4-TCNQ or metal-centered phthalocyanine molecules on the surface of TMDC.
Figure 8-3: (A) Raman spectra shows the characteristic peaks of MoS₂ monolayer (purple), monoclinic VO₂ (blue), and their heterostructures at 20 °C. (*) marks the features contributed by MoS₂, and the contribution from the sapphire substrate that VO₂ is grown on is marked by (#). (B) The PL of MoS₂/VO₂ (highlighted in the inset) has at least 3 times attenuation, compared to parts of its own attached on sapphire (The trench in inset). (C) The peak analysis on the PL spectra of MoS₂ monolayer transferred onto sapphire gave B-exciton emission at 2.01 eV, neutral A-exciton emission at 1.89 eV, negatively charged exciton emission (trion) at 1.83 eV, and defect-induced emission at 1.68 eV. (D) The peak fitting results show the presence of the same emission peaks but with reduced intensity, compared to one on sapphire. In addition to the total PL quenching, the ratio between A-exciton and trion emission peak changed from sapphire to VO₂, and A-exciton take large portion of the whole PL peak due to the change in doping levels. The spectra were obtained under 488 nm excitation.247 (Reproduce from Ref.247)
In order to understand the IMT properties of VO$_2$, the MoS$_2$/VO$_2$ was heated inside a chamber designed for optical measurements (Figure 8-4A). The resistivity versus temperature ($\rho$-T) was measured on VO$_2$ without monolayer TMDs, providing evidence that the critical temperature for IMT occurs between 64 °C and 67 °C (Figure 8-4B). Hall voltage measurements at 20 °C and 80 °C confirmed that the free carrier concentration increases from $10^{18}$ cm$^{-3}$ to $10^{22}$ cm$^{-3}$ when undergoing the IMT. The associated structural transition and its impact on the MoS$_2$/VO$_2$ hybrid structure was observed in temperature-dependent Raman spectra obtained during a heating/cooling cycle (Figure 8-4C). As the VO$_2$ transitioned into its tetragonal phase at ~60 °C, the Raman peaks of monoclinic VO$_2$ vanish. Additionally, the E$_{2g}$ and A$_{1g}$ of monolayer MoS$_2$ shifts to lower wave numbers as it was heated. This trend is reversible upon cooling the samples, suggesting a reduction in compressive strain (or increase in tensile strain) as the sample is cooled back to room temperature. This shift of Raman peaks is commonly attributed to the thermal expansion as well as the anharmonic contributions to the interatomic potential energy at high temperatures. Photoluminescence performed in parallel to Raman (Figure 8-4, D-E) reveals that as the VO$_2$ transforms to its metallic phase, the measured MoS$_2$ PL intensity gradually increased until VO$_2$ was completely metallic at 80 °C (Figure 8-4D). As the sample was cooled and transitioned back into its low temperature phase, the MoS$_2$ PL returns back to its original intensity (Figure 8-4E). Interestingly, this behavior is opposite to typical semiconductor behavior. The temperature-dependent trend of MoS$_2$ PL on VO$_2$ and SiO$_2$ is summarized in Figure 8-4F. The peak position of PL on both VO$_2$ and SiO$_2$ shifted towards lower energy due to no-radiative electron-hole recombination. However, the PL intensity of MoS$_2$ on VO$_2$ went up, in contradiction to the trend on SiO$_2$. This indicates that the traditional PL degradation of MoS$_2$ was somehow compensated by the IMT of VO$_2$. Similar results are found for WS$_2$. Detailed analysis of the PL before and after IMT/MIT indicates that the A-exciton, trion, and defect-induced exciton were enhanced due to the VO$_2$ IMT (see Appendix D).
Figure 8-4: (A) The setup for the optical measurement performed on MoS$_2$/VO$_2$ heterostructures. (B) Insulator-to-metal and metal-to-insulator transition of VO$_2$ occurs between 60 °C-70 °C and is accompanied by a resistivity drop/increase up to 4 orders. (C) The structural transition is evident in the evolution of their Raman spectra at various temperatures. The (*) marks MoS$_2$ Raman peaks. The Raman peaks belonging to insulating VO$_2$ in monoclinic phase disappeared once VO$_2$ transitions to the metallic rutile phase and then transitions back to monoclinic. (D) At 60 °C the PL of MoS$_2$ on metallic VO$_2$ is enhanced. It further reaches a maximum at 80 °C where VO$_2$ is completely metallic. (E) Upon cooling of the VO$_2$, the MoS$_2$ PL intensity returns to its origin intensity. (F) Normalized PL intensity of MoS$_2$ increases on metallic VO$_2$ at 90 °C, which is in contrast to MoS$_2$ on SiO$_2$ (dots with solid lines corresponding to the right y-axis). Peak position of the A-exciton in MoS$_2$ on both VO$_2$ and SiO$_2$ shifted to lower energies at elevated temperature (dots only corresponding to the left axis).$^{247}$ (Reproduce from Ref.247)
In order to confirm whether the trend in PL is due to electron injection from metallic VO$_2$ to MoS$_2$ at high temperature, PL measurement was also performed on MoS$_2$ monolayers transferred onto a 30nm-thick gold (Au) film. Gold was chosen due to its high concentration of free electron ($\sim 10^{22}$ cm$^{-3}$) and highly conductive. The PL measurement using the same experimental conditions was performed on both MoS$_2$/VO$_2$ and MoS$_2$/Au are presented in Figure 8-5, A-B. In the case of an Au substrate, PL intensity is reduced during heating, with the intensity being drastically reduced when temperature rises above 55 °C. On the other hand, PL in MoS$_2$/VO$_2$ was enhanced when temperature was also above 55 °C. This concluded that the PL enhancement is independent of the electron concentration of the chosen substrate. In addition, insulating and metallic phase VO$_2$ shouldn’t influence the optical strength of measured PL significantly since the absorption coefficients of insulating and metallic phase VO$_2$ are nearly identical under the incident wavelength of 488 and 532 nm.$^{246}$

Similarly, in order to understand the coupling between TMDCs and VO$_2$ from electron transport point of view, current-voltage (I-V) characteristics of MoS$_2$/VO$_2$ and WS$_2$/VO$_2$ were obtained from the CAFM measurement (Figure 8-5C). The difference between the I-V curves of MoS$_2$ and WS$_2$ in the turn-on-voltage indicates that VO$_2$ indeed coupled to MoS$_2$ and WS$_2$, respectively, and formed two different types of band alignments. It is noted that the turn-on-voltage of WS$_2$/VO$_2$ is larger than that of MoS$_2$/VO$_2$ by one-half volt, which is due to a larger Schottky barrier in WS$_2$ case. Theoretically, the electron affinity and Fermi level of monolayer WS$_2$ is closer to the vacuum level than that of MoS$_2$ and can result in a larger electrical barrier with VO$_2$. While electrical measurements confirmed a noticeable difference between MoS$_2$/VO$_2$ and WS$_2$/VO$_2$ in terms of their band alignments, the ratio of the PL intensity of MoS$_2$ and WS$_2$ before and after IMT is nearly the same and seems to be independent of the electron transfer. For example, the ratio of the total area of PL intensity of MoS$_2$ monolayer integrated from 1.6 eV to 2.2 eV before and after IMT over the total area was calculated under both 488 nm and 532 nm excitation wavelengths. The
ratio is 2.05 under 488 nm excitation and is 1.36 under 532 nm excitation. Similarly, the ratio from WS$_2$/VO$_2$ is also between 1.5-2.0 under the same incident wavelengths. Since there is no correlation between the ratio (or “PL enhancement factor”) and charge transfer, there should be other mechanisms that actually enhance the PL intensity. Very recently, Hou et al. claimed an optical interface effect between their TMDs/VO$_2$/SiO$_2$ is responsible for the PL enhancement. Their model predicted that the optical field strength for the PL of MoS$_2$ emitting at 670 nm is enhanced on metallic VO$_2$ compared to insulating VO$_2$. The main difference between insulating and metallic VO$_2$ is in the reflectivity under the wavelength of the PL of MoS$_2$ and WS$_2$. It is worthwhile to mention that the calculated ratio of PL intensity of MoS$_2$ before and after IMT is close to that predicted by Hou et al. on a 30 nm-thick VO$_2$ film, although 1 μm-SiO$_2$ was also taken into account in their theoretical models. This suggests that a similar effect is occurring here, even with dissimilar substrates.

Figure 8-5: (A) PL intensity of MoS$_2$ monolayer on a 30 nm-gold film decreased when temperature increased. (B) Under the same experimental conditions the intensity on VO$_2$ was enhanced when the temperature of the IMT was reached. The characteristic Raman peak of VO$_2$ (*) completely vanished when VO$_2$ was completely metallic (“+” labeled the Raman peak of the sapphire substrates used to support VO$_2$). (C) I-V characteristics of MoS$_2$/VO$_2$, WS$_2$/VO$_2$ were obtained in CAFM measurement. I-V of VO$_2$ was used as the reference. (Reproduce from Ref.247)
Conclusions

We have demonstrated the synthesis of TMDC/VO$_2$ heterostructures and investigated their properties at various temperatures. Photoluminescence of the monolayer TMDs quenches on insulating VO$_2$, when compared to PL intensity of TMDC monolayer on SiO$_2$/Si and sapphire. Their optical properties are different before and after the IMT. Once VO$_2$ transitions to metallic, the PL intensity of the TMD monolayer increases. The loss of PL intensity due to intensified non-radiative recombination can be compensated by the constructive optical inference. The optical modulation on MoS$_2$ and WS$_2$ monolayer is fully reversible. In the future, this study can be extended beyond the thermally driven IMT to the electrically driven IMT in order to achieve the same optical property modulation. We expect this study will open up more new studies combining VO$_2$, as well as other phase transition materials, for creating 2D/3D novel optoelectronic phenomena.
Chapter 9

Thesis summary

The big picture of this dissertation is to probe the viability of producing high-quality and large-area 2D semiconductors, with specific emphasis on transition metal dichalcogenides (TMDCs), by thin film deposition techniques. Many aspects, such as the surface termination of substrates, the crystal structure of substrates, and the thin film deposition conditions were taken into account in order to achieve ideal synthetic atomically thin films. This integration engineering leads to two types of interfaces: 2D materials on 3D substrates and 2D materials on van der Waals (vdW) type substrates.

From the growth perspective, the substrate properties play an important role for achieving scalable and stoichiometric 2D layers. This aspect is especially critical for metal organic chemical vapor deposition of TMDCs which involve harsh environments and multiple chemical precursors and is discussed in Chapter 3. Using vdW solids as the substrate was found to prevent the formation of 2D alloys, as shown in Chapter 7. This could be contributed to their lack of dangling bonds and less complicated dielectric environment for molecules during the synthesis. In order to achieve the epitaxial quality, the structure of the 2D layers needs to be highly commensurate with that of the substrate. The concept of van der Waals epitaxy is repeatedly discussed in Chapter 3, 4 and 7 due to its importance for achieving high-quality material interfaces. A variety of characterization methods, including Raman and PL spectroscopy, electron microscopes, SPM techniques, and also electrical measurements have been performed on material interfaces to understand their quality. The results from Chapter 3 to Chapter 8 show that the synthetic materials indeed can provide electronic-grade performance for transistors, optical applications, and surface science experiments.
This dissertation has made significant progress in the field of direct synthesis of 2D layers for heterogeneous integration, which are covered in Chapters 4 and 5. It is also possible to achieve more sophisticated heterostructures that go beyond only two different 2D layers and subsequently excite new phenomena that cannot be accessed through the mechanical approach, as demonstrated in Chapter 7. The properties of the supporting substrates can impact the device performance of the synthetic 2D layers. For example, Chapter 6 shows that the doping type and carrier concentration of EG can significantly modulate the electrical barrier between WSe$_2$ and EG. Similarly, the part II of Chapter 3 shows the substrate morphology and surface termination could influence the electrical transport of 2D devices on the substrates, resulting in anisotropic electrical performance.

Despite the fact that the mechanical exfoliation approach is neither scalable nor residue-free for hetero-engineering, it remains one of the only methods to integrate 2D layers with volatile substrates, such as VO$_2$ in Chapter 8. The optical properties of monolayer TMDC/VO$_2$ are still responsive to the phase transition of VO$_2$, despite the presence of interfacial residue as a result of mechanical transfer and stacking.
Appendix

Appendix A

Parameters of MOCVD process for epitaxial WSe$_2$

A controlled layer-by-layer growth of WSe$_2$, ranging from monolayer to three layers, was achieved by following the growth profile illustrated in Figure A1. Growths were done at 700 Torr using H$_2$ as a carrier gas, where W(CO)$_6$ and H$_2$Se precursors are introduced separately into the cold wall vertical reactor chamber and their respective flow rates controlled via mass flow controllers (MFCs). The optimized condition for the growth was modified from our previously reported work.$^{68}$ To achieve uniform deposition with complete coalescence over the entire substrate area, we introduce “seeding” and “annealing” at 800°C where the substrate is exposed to partial pressures of $\sim 2 \times 10^{-3}$ Torr W-precursor and 11 Torr H$_2$Se for 30 sec-2 min, named “pre-growth seeding step”. Subsequently the WSe$_2$ is anneal in in H$_2$Se to allow the nucleated domain to grow further under Se-rich environment. Also, such pre-annealing step at higher temperature act as a surface treatment on c-sapphire surface and promotes Se passivation of the sapphire, which further act as bridge for epitaxy at 2D/3D interface (detail can be find in main text). The number of layers was controlled by varying the seeding time, 30s (1L) to 2min (3L) while keeping growths time 30 min, unchanged. All growths were done at 800°C and 730 Torr total pressure with constant W:Se flux by adjusting the W(CO)$_6$/H$_2$Se partial pressure individually for the following layer number: 4.32×10$^{-4}$ Torr/10.8 Torr (1L), 6.24×10$^{-4}$ Torr/15.6 Torr (2L), and 7.68×10$^{-4}$ Torr/19.2 Torr (3L). Growth profile in Figure A1 is representative of deposition conditions for monolayer WSe$_2$ film.
Figure A1: Optimized growth profile for MOCVD process of monolayer epitaxial WSe$_2$ grown on sapphire

Theoretical modeling

The density functional theory (DFT) calculations were performed with the Vienna Ab-initio Simulation Package (VASP). The valence electronic states are expanded in a set of periodic plain waves and the ion-electron interaction is implemented through the projection augmented wave (PAW) approach. The Perdew-Burke-Ernzerhof (PBE) GGA exchange correlation functional is applied in the simulation. The wave functions are expanded in plane waves with a kinetic energy cutoff of 400 eV. The convergence criteria for the electronic and ionic relaxation are $1.0 \times 10^{-5}$ eV, $1.0 \times 10^{-4}$ eV, respectively. Integration over the first Brillouin zone is performed with a Γ-centered $3 \times 3 \times 1$ k-point mesh. A supercell consisting of $2 \times 2 \alpha$-Al$_2$O$_3$ unit cells and $3 \times 3$ 1L WSe$_2$ unit cells is built with a 4% strain on WSe$_2$. A vacuum layer of 20 Å is added to the c-direction. To avoid long-range interactions between supercells, a supercell consists of the surface and interface under study on both sides along the c-direction. The proposed WSe$_2$-sapphire interfaces based on the EDX data (Figure A2) are shown in Figure A3. Except for the Al-terminated sapphire/WSe$_2$ interface, gap states exist within the band gap of WSe$_2$ after contact. Comparing the density of states of the gap states, the four interfaces are ordered as Al-O > Al-Se > Al-O-Se > Al. The calculations indicate that the interaction (bonding) energy between WSe$_2$ and the Se-terminated
sapphire surfaces (4.23 eV for Al-Se connection in Figure A3b and 2.6 eV for Al-O-Se connection in the d) lies between that of WSe$_2$/Al-terminated (0.04 eV) and WSe$_2$/Al-O-terminated surfaces (5.4 eV). This relatively high interface bonding energy between WSe$_2$ and Al-Se connection also manifests itself mechanically, as we find that fully coalesced epitaxial WSe$_2$ layers are more difficult to mechanically transfer from the substrate than non-epitaxial WSe$_2$.

Figure A2: EDX and HAADF image captured from the same section during STEM measurement at 200 kV identify the distribution of W, Se, Al, and O.

Figure A3: DFT modeling for 2D/3D interface. The proposed interface structures and their corresponding density of state (DOS) under different terminations: (a) Al-terminated (b) Al-Se terminated (c) O-terminated (d) Al-O-Se terminated. The 0 eV is the valence band edge for an intrinsic semiconductor.
Device fabrication

Field-effect transistors were fabricated via standard photolithography to define WSe$_2$ channel dimensions, source/drain (S/D) contact electrodes, and side-gate electrodes (Figure 5a). The 4.1 x 2.5 mm die layout employed in this work consists of an array of FETs with channel width 24 µm and channel length ranging from 10 µm to 0.75 µm. With these die dimensions in mind, a 3 row x 2 column die layout is used to cover a majority of the 10 x 10 mm sample surface. In our work, the gate electrode is not directly deposited on top of the electrolyte-WSe$_2$ FETs, and instead, we utilize a side-gate geometry that establishes a lateral electric field in the PEO:CsClO$_4$ (PEO: poly(ethylene-oxide)) and drives the ions into place on the WSe$_2$ channel surface. All photolithography was carried out in a GCA 8500 i-line Stepper. WSe$_2$ channels were isolated and etched via reactive ion etching in a Plasma Therm PT-720 plasma etch tool using an SF$_6$/O$_2$/Ar gas chemistry at 10 mTorr and 100 W for 30 sec. Both 25 nm Ni and 10/10 nm Pd/Au source/drain metallizations are carried out under moderate vacuum (~10$^{-6}$ Torr) at 1.0 Å/sec dep rate. Directly prior to loading samples into evaporator for metal deposition and eventual lift-off, samples are subjected to a brief oxygen plasma treatment to remove photoresist residue that remains on the WSe$_2$ surface following photoresist development. This gentle plasma treatment/surface prep is carried out in an M4L etch tool at 50 W and 500 mTorr for 45 sec. Following this initial metal deposition, a second metallization consisting of ~ 10 nm/150 nm Ti/Au is carried out to define the side-gate and to thicken source/drain pads for probing.
Appendix B

Computational methods for the intrinsic dipoles between WSe$_2$ and graphene

The density functional theory (DFT) calculation are performed by Vienna ab-initio simulation package (VASP) with the projector-augmented wave (PAW) method. The local density approximation (LDA) is used to describe the exchange-correlation functional with the partial core correction included. Spin polarization and spin-orbit coupling are applied. The stable phase of the monolayer WSe$_2$ is trigonal prism structure. The optimized planar lattice constant of WSe$_2$ is 3.25 Å, and the optimized planar lattice constant for monolayer graphene is 2.45 Å. In order to fit the lattice constant, a super cell with $3 \times 3$ WSe$_2$ unit cells and $4 \times 4$ graphene unit cell is used, and a compressive strain of 0.4 % is applied to graphene, as the electronic behaviors of TMDC are very much susceptible to lattice strain. The super cell is shown in Figure B1a. The wave functions are expanded in plane waves with a kinetic energy cutoff of 500 eV, and the convergence criteria for the electronic relaxation is $10^{-5}$ eV. Integration over the Brillouin zone is performed with a gamma-centered $6 \times 6 \times 1$ Monkhorst-Pack k-point mesh for ionic and electronic optimization. A vacuum region of about 15 Å normal to the surface is added to minimize the interaction between adjacent slabs (Figure B1a). Dipole correction on the stacking direction is used in systems to reveal the dipole within the two layers caused by the Fermi-level alignment. The local density approximation (LDA) is found to be suitable for studying the metal-TMDC contact. The generalized gradient approximation (GGA) with the DFT-D2 method for van der Waals (vdW) corrections is also used to cross-check the structural accuracy. We find that GGA results with vdW corrections are in overall agreement with LDA results. Both the LDA method and the GGA+vdW method result in a similar structure with a distance of ~3.5 Å between graphene and TMDC, indicating a secondary bond interaction. The energy difference between the vacuum regions on the both sides of the contact
The vacuum energy level above WSe$_2$ is 0.17 eV higher than that above graphene, indicating a dipole from graphene towards the WSe$_2$ (Figure B1b).

![Figure B1: (a) Plane averaged local electric potential energy of electrons along the stacking direction. (b) After dipole correction, a difference on vacuum energy above both sides of 0.17 eV is observed (zoomed inset).](Reproduce from Ref.187)

**Computation of WSe$_2$ doping density and charge densities, and dependence on parameters**

For the computation of charge transfer and band alignment, we take the doping densities of EG$_{PH}$ and EG$_{FH}$ from our experimental values, as discussed in the main text. Parameters in the computation are the electron affinities for monolayer and bilayer graphene, with nominal values of 4.57 eV and 4.71 eV, respectively, as known from prior experiments.\textsuperscript{201} We take the sum of the electron affinity plus band gap of the WSe$_2$, $X_{WSe_2} + E_g$, to be an unknown in the computation, since a value for this sum is not accurately known from prior work (only the sum is considered here since the electron occupation in the conduction band of the WSe$_2$ is negligible). A second unknown is the unintentional doping density of WSe$_2$. Then, using the two measured work function differences for WSe$_2$ on both EG$_{PH}$ and EG$_{FH}$ compared to the bare EG$_{PH}$ and EG$_{FH}$, we can determine values for the two unknown parameters. The carrier densities for the WSe$_2$ on both EG$_{PH}$ and EG$_{FH}$ after charge transfer are then a byproduct of the computation. In all cases, the carrier
densities of WSe$_2$ in WSe$_2$-EG$_{PH}$ are very much greater than those of WSe$_2$ in WSe$_2$-EG$_{FH}$, consistent with the observed differences in the CAFM I-V results.

We note that the doping density values in Table B1 are all the same, reflecting a tight constraint on this value. This constraint arises from charge transfer between the WSe$_2$ and the EG$_{PH}$. As pictured in Figure B2a-b, since the Fermi energies of the EG$_{PH}$ and WSe$_2$ are relatively far apart prior to charge transfer, and hence the Fermi energy of the WSe$_2$ ends up well within its band gap after the transfer, then the p-type doping density in the WSe$_2$ is directly determined by the doping density of the EG together with the difference between the electron affinity of the EG$_{PH}$ and the $X_{WSe_2} + E_g$ value of the WSe$_2$. The resulting carrier densities for the WSe$_2$ on EG$_{PH}$ are negligible, again since the resulting WSe$_2$ Fermi energy is well within the gap. On the other hand, for the WSe$_2$ on EG$_{FH}$, their Fermi energies are relatively close prior to charge transfer, as pictured in Figure B2c-d. The resulting Fermi energy for the WSe$_2$ on EG$_{FH}$ ends up near or within the valence band even after the charge transfer, with concomitant large carrier density, and the value of the WSe$_2$ doping density is not so tightly constrained in this part of the problem.

We have also considered the effect on the computed carrier densities of variation in the EG$_{PH}$ and EG$_{FH}$ doping density values, as well as variation of the measured work functions differences within their experimental error ranges. Doping densities of $(4 \pm 1) \times 10^{12}$ cm$^{-2}$ for EG$_{PH}$ and $(1.5 \pm 0.2) \times 10^{13}$ cm$^{-2}$ for EG$_{FH}$ are typical measured in our samples. Considering the variations of these doping densities, the carrier density of WSe$_2$ on EG$_{FH}$ after charge transfer is computed to range from $2.5 - 3.0 \times 10^{12}$ cm$^{-2}$ while the carrier density of WSe$_2$ on EG$_{PH}$ after transfer is always less than $10^7$ cm$^{-2}$, i.e. its Fermi is well within the bandgap. For the measured error ranges ($\pm 0.03$ eV) on the work function differences, performing computations at the bounds of these values produces carrier densities in the WSe$_2$ on EG$_{FH}$ compared to WSe$_2$ on EG$_{PH}$ that continue to differ by more than a factor of $10^4$, for all cases.
Table B1: Computed dependence of electron affinity plus bandgap of WSe$_2$ ($\chi_{\text{WSe}_2} + E_g$), unintentional doping of WSe$_2$ ($N_u$), carrier density of WSe$_2$ after charge transfer between WSe$_2$ and EG$_{PH}$ ($N_{C,\text{WSe}_2-\text{EG}_{PH}}$), and carrier density of WSe$_2$ after charge transfer between WSe$_2$ and EG$_{FH}$ ($N_{C,\text{WSe}_2-\text{EG}_{FH}}$) on electron affinities of EG$_{PH}$ ($\chi_{\text{EG}_{PH}}$) and EG$_{FH}$ ($\chi_{\text{EG}_{FH}}$), respectively. An error range of $\pm 0.1$eV for the input parameters is considered. (Reproduce from Ref.187)

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<th>$\chi_{\text{EG}_{FH}}$ (eV)</th>
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<th>$N_{C,\text{WSe}<em>2-\text{EG}</em>{PH}}$ (cm$^{-2}$)</th>
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<td>0.9x10$^{4}$</td>
<td>2.9x10$^{12}$</td>
</tr>
</tbody>
</table>

Figure B2: Band alignment of WSe$_2$ and EG$_{PH}$ (a) before charge transfer (including computed intrinsic dipole 0.17 eV), and (b) after charge transfer. Band alignment of WSe$_2$ and EG$_{FH}$ (c) before charge transfer (including the intrinsic dipole), and (d) after charge transfer. Monolayer and bilayer graphene models are employed for EG$_{PH}$ and EG$_{FH}$ respectively, based on LEEM observations. Green shades in (c) and (d) represent conduction/valence subbands of bilayer graphene. The numerical values show various vacuum level differences, in units of eV. (Reproduce from Ref.187)
Appendix C

Theoretical validation for NDR transport in the trilayer structures

We perform non-equilibrium ballistic quantum transport calculations by combining density functional theory (DFT) with the non-equilibrium Green’s function (NEGF) formalism that provide theoretical $I$-$V$ curves to confirm the NDR transport mechanism in the heterostructure by comparing it against the simulated transport in the homo-structure (Figure C1). In the experimental setup, the voltage, $V_{ds}$ is applied between the $Pt$-$Ir$ tip of the conducting AFM and the electrically grounded graphene electrode. The area of the $Pt$-$Ir$ tip is approximately to 1000 nm$^2$, which in the simulation is modeled as a bulk electrode in the theoretical structure (Figure C1A). The calculation produces the bias and the transverse momentum dependent transmission probability of the carriers tunneling through the heterostructure and is used to simulate the $I$-$V$ characteristics using Landauer transport formulation:258

$$I(V_{ds}) = \frac{2q}{\hbar} \int_{BZ} dk_{\parallel} \int dE T(E, k_{\parallel}, V_{ds}) \left[ f\left(\frac{E-E_{f1}}{k_B T}\right) - f\left(\frac{E-E_{f2}}{k_B T}\right)\right]$$

(Eq.C1)

where $E_{f1}$-$E_{f2}=qV_{ds}$ represents the Fermi window; $BZ$ represents the Brillouin zone; and $T(E,k_{\parallel}, V_{ds})$ is the total transmission over the energy channels within the Fermi window calculated self-consistently for each $V_{ds}$. Within the NEGF+DFT framework for transport, the Hamiltonian of the system is solved by calculating the electronic charge distribution via the self-consistent DFT loop of the full density matrix of the device whose diagonal element describes the charge density.

This procedure produces the bias dependent transmission function, $T(E, V, k_{\parallel})$. We then extract the $I$-$V$ characteristics in the ballistic transport regime which shows a pronounced NDR in both positive and negative bias regimes of the MoS$_2$-WSe$_2$-Gr heterostructure device (Figure C1B). Within the Fermi window of 0-0.4 eV, we can see that the carrier transmission is effectively negligible due the absence of any transmission channel. Above 0.4 eV, the transmission becomes
finite and the current starts increasing with the applied bias, where the primary transmission resonance peaks (peak P1, P2 and P3 in Figure C1C) appear at approximately 1.0 V and then get suppressed with further increase in applied bias. It is this peak and valley in the transmission spectra arising from resonant tunneling phenomenon that leads to the observed NDR. When the bias is further increased, conventional tunneling occurs due to the high density of states (DOS) at higher energy levels, and the current increases exponentially thereafter. The transmission Eigen states at the energetic location of the three strong peaks for a bias of +1.0 V provides clue to the microscopic origin of the NDR in the MoS$_2$-WSe$_2$-Gr heterostructure. Inspection of the localized molecular orbitals of the Eigen states (Figure C1D) reveals that all three resonance peaks originate from a combination of the Pt electrode ($s$-orbital), WSe$_2$ ($p$-orbital of Se, W and $d$-orbital of W) and graphene layers ($p$-orbital).

In the case of MoS$_2$-WSe$_2$-Gr heterostructure, the MoS$_2$ in direct contact with the Pt electrode, and the first graphene layer closest to the WSe$_2$ do not contribute to the strong transmission peaks but serve as tunnel barriers. Furthermore, the interatomic electronic interaction between the 2D layers makes MoS$_2$ n-type and WSe$_2$ p-type, which make the WSe$_2$ valence band states as the host for the confinement of the resonant states when the system is subjected to a bias. Along with the conservation of transverse momenta and the alignment of energy levels in the constituent layers of the system, the theoretical $I$-$V$ traces are in good agreement with the measured results. On the other hand, bilayer WSe$_2$ does not offer any band offset in the energy band diagram and its bandgap acts as a regular electronic barrier in the carrier tunneling. The calculated transmission in bilayer WSe$_2$ -Gr clearly reflects this nature and shows no NDR in its $I$-$V$ characteristics. This study hence provides strong theoretical insights that show resonant tunneling is the dominant transport mechanism in a heterostructure with significant amounts of band offset.
Figure C1: (A) Schematic of the vertical nano-device setup of both of MoS$_2$-WSe$_2$-Gr and bilayer WSe$_2$-Gr system used for quantum transport calculation. $E_f1$ and $E_f2$ indicate the corresponding Fermi levels of the left and right electrodes, respectively, for an applied positive bias $V_{ds}$. (B) Theoretical $I$-$V$ curves of the vertical tunnel junctions for both the hetero- and homo- junction are simulated by the DFT and NEGF transport formalism that give resonant tunneling at specific energies and bias voltage, as shown in (C) The dotted line indicates the Fermi window for that applied bias voltage across the terminals. (D) Transmission Eigen states that contribute to the transmission in the peak P3 of the transmission at $V_{ds} = +1.0$ V in the MoS$_2$-WSe$_2$-Gr heterostructure.\textsuperscript{219} (Reproduce from Ref.219)
Appendix D

Figure D1: The evolution of Raman (A) and PL (B) spectra of monolayered WS$_2$/VO$_2$ heterostructure in increasing temperatures under 532 nm excitation provides another example in addition to monolayered MoS$_2$ and shows this universal phenomenon on sulfur-based TMDs monolayer. (C-D) The peak analysis performed on the PL of monolayered MoS$_2$/VO$_2$ at 25 °C and 100 °C, in which VO$_2$ is insulating and metallic, respectively. Under the same exciting wavelength and energy, the A-exciton (red) and trion (blue) were both enhanced when VO$_2$ was metallic. Comparing to trion, the A-excitons has a larger enhancement by hot-electron injection from metallic VO$_2$. (The excitation is 488nm. Both of the y-axis were adjusted to have the same range for clear comparison) (E-F) Same as MoS$_2$ monolayer on VO$_2$, the PL of WS$_2$ monolayer on VO$_2$ is composed of A-exciton (red), trion (blue), and defect-induced emission (purple). They were both enhanced on metallic VO$_2$ and shifted slightly toward red due to enhanced electron-phonon process at a higher temperature (The excitation is 532 nm).$^{247}$ (Reproduce from Ref.247)
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