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Chemical Vapor Deposition of Two-Dimensional Materials and the Investigation of Applications and Properties

by

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ABSTRACT

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Two-Dimensional Transition metal dichalcogenides (TMDs) have attracted significant research attention due to their appealing electronic, optical and catalytic properties. In order to probe and utilize some of the unique properties of TMDs there must be a scalable approach to growing large area monolayers. The research presented will be in regards to the development of chemical vapor deposition techniques for TMDs, specifically ReS$_2$, and the development of a metrology tool for experimentally determining band alignments for layered materials. We intensively characterize the first monolayer grown ReS$_2$ crystals using various spectroscopy and microscopy techniques and investigate the electronic and catalytic properties. Furthermore, we experimentally determine band alignments for various TMDs using a novel photoemission electron microscopy technique with deep ultraviolet light. Band alignments experimentally determined using this technique provide essential information to the scientific community for building complex electronic and optoelectronic devices with TMDs.
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**Nomenclature**

TMDs-Transition Metal Dichalcogenide

2D-Two Dimensional

3D-Three Dimensional

CNTs-Carbon Nanotube

C60-Fullerene

CVD-Chemical Vapor Deposition

ALD-Atomic Layer Deposition

GDP-Gross Domestic Product

EPA-Environmental Protection Agency

HER-Hydrogen Evolution Reaction

EFM-Electrostatic Force Microscopy

SKPM-Scanning Kelvin Probe Microscopy

HOPG-Highly Ordered Pyrolytic Graphite

AFM-Atomic Force Microscopy

UV-Ultra Violet

FET-Field Effect Transistor

PEEM-Photoemission Electron Microscopy

XPS-Xray photoelectron spectroscopy

CCD-chargecouple device

PMMA- Poly(methyl methacrylate)

TEM-Transmission Electron Microscopy
STEM - Scanning Transmission Electron Microscopy

SEM - Scanning Electron Microscopy
Chapter 1

Introduction and Background

1.1. Scope of this Thesis

This thesis consists of the study of transition metal dichalcogenides (TMDs) specifically the growth and synthesis of these novel layered materials. The growth will specifically delve into the bottom up approach via chemical vapor deposition of various TMDs specifically ReS₂. Growth parameters and details on the experimental setup will be highlighted and its effects on the physical structure and properties will be delved into. Various characterization techniques will also be discussed to understand these materials on a physical, optical, and electronic sense.

1.2. Layered Materials

Layered materials are materials that have strong covalent bonding in two-dimensions and weak bonds in the third-dimension which we commonly refer as van der Waal interactions. This anisotropy in the three-dimensional (3D) space results in materials such as graphite to be useful as lubricants and pencils due to the
planes of atoms being allowed to slip past one another due to the weak bonding in the third dimension. Since the 1930s the common thought was that isolating or synthesizing two-dimensional (2D) crystals were unstable thermodynamically and would never exist.\textsuperscript{1,2} Underlying experimental observations were rooted in the fact that the melting point of thin films rapidly decrease compared to their bulk counterpart, therefore an atomic layer of a material would become completely unstable and decompose.\textsuperscript{3,4} Atomic monolayers were thought to only be a part of a larger 3D structure such as graphite or films that are grown epitaxial on top of a 3D crystal that have matching crystal lattices. Even if a stable 2D form of a 3D material existed the basic properties were thought to not be any different from the 3D counterpart. With the heightened interest in nano-engineering and nano-materials with the discovery and synthesis of carbon nanotubes (CNT’s) and buckminsterfullerene (C\textsubscript{60}) in the new fullerene structural allotrope of carbon, carbon began to be heavily investigated.\textsuperscript{5-7} It wasn’t until 2004 when the experimental discovery of graphene negated the commonly accepted beliefs of 2D materials.

1.2.1. Graphene

With heightened interest in nanomaterials like carbon nanotubes, the concept of ‘metallic electronics’ to replace silicon and a review article from Millie Dresselhaus on intercalated graphite compounds highlighting how graphite was still a material that was understood very little, Andre K. Geim at University of
Manchester along with his first PhD student Da Jiang set out to carefully investigate graphite.\textsuperscript{8,9} Geim initially provided Da a small piece of highly oriented pyrolytic graphite (HOPG) but was actually was just high density graphite and asked him to make thin films. About a month later Da was only able to achieve thicknesses that was roughly 10\textmu m using an optical microscope to estimate thickness based on focusing adjustments. One of the underlying reasons Geim and Da were not able to achieve thinner films was because Geim didn't provide Da with highly oriented pyrolytic graphite and that they were mainly focused on traditional polishing techniques to thin out graphite. It wasn't until later when discussing with a senior fellow, Oleg Shklyarevskii an expert at scanning tunneling microscopy (STM) that maybe just bringing a piece of scotch tape over graphite would do the trick. HOPG was commonly a standard reference material for STM and usually the surface was prepared by using scotch tape to remove the top layers to expose a fresh layer. They usually throw out the used scotch tape and don't think twice but Oleg provided some of this used scotch tape from the trash to Geim. From there Geim managed to refine the process down to few layers. The end goal was to explore the electrical properties of graphite and with that they transferred the graphite flakes from the scotch tape onto oxidized silicon wafers (\textbf{Figure 1-1}).\textsuperscript{9} What they soon realized that under an optical microscope they could make out distinct interference colors which soon could be related to the thickness of your material. This methodology is now considered one of the quickest methods of analysis for the field of 2D materials.
With atomic force microscopy (AFM) and the transfer on flat surfaces (SiO$_2$) they could identify monolayers and few layers of graphite (Figure 1-1).^9^  

Figure 1-1 (a) HOPG flakes on scotch tape (b) HOPG crystals that are optically transparent under the optical microscope (c) HOPG flakes placed on oxidized Si/SiO2 wafer highlighting various crystal thickness from the various shades of blue (d) First device made using silver paint, tweezers, and toothpicks
Initial work delved into the electrical properties of few-layer graphite found on the scotch tape by transferring flakes with tweezers and using silver paint and toothpicks to form contacts on the small flakes (Figure 1-1). With refinements in device fabrication using e-beam lithography and improvement in exfoliating technique using scotch tape the team managed to cohesively study monolayer and multilayer electrical performance. The essential part of their work on monolayer graphite or what is known as graphene was reported in Science in 2004. At its core graphene is a sheet of carbon atoms arranged in a honeycomb lattice exhibiting a sp2 hybridization with in plane $\sigma_{c-c}$ bonds and out of plane $\pi$ bonds. Carbon-carbon bonds (1.42 Å) in this arrangement is one of the strongest bonds exhibited amongst all the allotropes of carbon. The delocalized $\pi$ bonds that are half filled are responsible for the most notable electronic properties of graphene which allows for free-moving electrons. Graphene is considered a zero-gap semiconductor due to its conduction bands and valance bands meeting at dirac points. Due to this interesting band structure graphene exhibits immensely large electron mobilities in excess of $15000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Graphene also is also highly thermally conductive measured to $5000\text{Wm}^{-1}\text{K}^{-1}$ due to the fact that this material is mainly phonon dominated. Optically a single layer of graphene is almost transparent absorbing only 2.3% of the light, therefore if graphene was suspended there would be no color to it. Graphene is also considered the strongest material ever to be tested with tensile strengths of 130GPa and a Young’s modulus (stiffness) of 1TPa. In essence these mechanical properties could be imagined as a 1m²
hammock of graphene being able to hold a 4kg cat while being transparent to the naked eye and weigh less than 1mg or the weight of a cat's whisker.

### 1.2.2. Beyond Graphene

With the discovery of graphene and the novel properties that materials in their 2D form could bring to the scientific community, exploration into other layered materials took off at a rapid pace. Now there are various classes of layered materials that are researched to date (Figure 1-2). With every 2D material comes a variety of challenges. For example, phosphorene in the X-ene class of 2D materials (same class

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**Figure 1-2 Various families of 2D materials**
as graphene) is the monolayer form of black phosphorous composed of phosphorus atoms in an anisotropic orthorhombic structure has been found to extremely high carrier mobilities, high optical, UV absorption, and many other properties that is of interest in the optoelectronics field. This so called miracle material however is not at all stable in air unfortunately, where monolayers of this material immediately absorb moisture from the air and degrade. Therefore, determining the fundamental and eccentric properties of the material have been a challenging and irreproducible nightmare. Even though these materials seem impossible to ever scale to actual devices and products, it is still crucial to fundamentally understand these materials, in hope down the road challenges can be overcome. For example, some work on phosphorene capping agents during device fabrication is currently being looked into.

1.2.3. Transition Metal Dichalcogenides

One such broad family of 2D materials that has caught the eyes of the scientific community, primarily as a candidate to replace silicon in electronics is known as transition metal dichalcogenides. Transition metal dichalcogenides exhibit a very large range of unique electronic, mechanical, chemical, thermal, and optical properties. Due to the novel and simple preparation of monolayers pioneered by Geim and his colleagues with graphene, there has been intense study of all the various transition metal dichalcogenide crystals and their properties at the monolayer regime. Transition metal dichalcogenides have gained a keen interest in
electronics and optoelectronics primarily due to the crystals exhibiting a band gap
(1-2eV) unlike graphene, which makes these materials a perfect candidate for
channel materials.\textsuperscript{22}

Transition metal dichalcogenides is a class of materials with the formula MX\textsubscript{2}
where the M consists of a transition metal and the X contains a chalcogen (\textbf{Figure 1-3}).\textsuperscript{23} A monolayer of this material consists of a stack of 3 layers of X-M-X with the
chalcogens in two hexagonal planes. This unit composes the bulk crystal where the
units are held weakly together by Van der Waals interactions. The bulk crystals may
have various polytypes based on the stacking order of the individual layers. As an
example, the two main polytypes of molybdenum disulfide is 2H (trigonal prismatic
coordination) or 1T (octahedral coordination) (\textbf{Figure 1-3}).\textsuperscript{23}
Figure 1-3 (a) 40 different layered transition metal dichalcogenides (b) Transition metal dichalcogenide monolayer structure as a trigonal prismatic coordination (c) Transition metal dichalcogenide monolayer structure as an octahedral coordination\textsuperscript{23}
Due to the fact that the majority of semiconducting transition metal dichalcogenides are similar to silicon which has a band gap of approximately 1.1eV, these materials can potentially be suitable candidates for field-effect transistors. Currently channel length scales are reaching the limits due to quantum and statistical effects and the difficulty in dissipating heat. Transition metal dichalcogenides are candidates that do no exhibit these short channel effects. Initial reports of field-effect transistor performance for MoS2, reached mobilities of 0.1-10cm²V⁻¹s⁻¹. These values have been increasing with better fabrication and top gate designs (Figure 1-4), devices were able to reach >200 cm²V⁻¹s⁻¹ and on/off currents ratios of 10⁸. With performances highlighted and resilience to short channel effects, transition metal dichalcogenides are great candidates to replace silicon. With this there is a great need to scale the growth of large area monolayers of these materials for wafer scale fabrication of devices.
Figure 1-4 Schematic illustration of HfO$_2$ top gated monolayer MOS$_2$ FET device.$^{23}$
A novel behavior of transition metal dichalcogenides such as MoS2 is the change from indirect band gap to direct band gap and band gap tunability, when going from bulk to monolayer thicknesses. This behavior primarily due to the confinement of carriers within the monolayer and presents a perfect opportunity to exploit these materials for optoelectronic applications. Photovoltaics, photodetector, LEDs, and diode laser have all been demonstrated with transition metal dichalcogenides. The breadth of applications that these atomically thin transparent materials is immense (Figure 1-5). Furthermore there is an inherent realization of flexible and transparent electronics and optoelectronics being feasible with these materials. One of the major inhibitors in using these materials for actual commercial products is the inherent lack of scalable processes for growing these materials.
Figure 1-5 Map of various unique properties of TMDs and the potential applications.
1.3. Synthesis Techniques of Transition Metal Dichalcogenides

1.3.1. Top Down Approach

As discussed prior regarding the discovery of graphene, layers of TMD can be cleaved off a bulk crystal using scotch tape. By applying it to substrates such as Si/SiO$_2$ one can identify the number of layers by the light interference through the layers which Geim pioneered with graphene.$^{32,33}$ This method can be quite useful for fundamental studies since usually the flakes are high in crystal quality. Other methodologies to cleave off layers is through lithium intercalation by immersing bulk materials in n-butyllithium and allowing lithium ions to intercalate within the layers of your TMD. This is followed by immersing the intercalated material in water, in which the lithium reacts with the water to form H$_2$ gas separating the layers.$^{34}$ Another methodology is to exfoliate by using ultrasonication and appropriate surfactants and solvents to stabilize the flakes in solution and prevent re-aggregation.$^{35}$ However, with all these methods there is an inherent lack of scalability since you cannot systematically cleave off large flakes and thicknesses (Figure 1-6).
Figure 1-6 The low yield of monolayer MoS$_2$ with AFM results via scotch tape mechanical cleavage$^{78}$

Figure 1-7 Example of bulk single crystal growth of TMD$^{196}$
Furthermore, the growth of single crystal bulk materials of TMDs requires weeks of growth time and very high temperatures. The process starts out by pre-reacting the stoichiometric ratios of the desired product. The pre-reaction is done at very high temperatures. From there by using a temperature gradient and a transport agent such as a halogen under vacuum you slowly crystalize on the cold end resulting in a bulk single crystal of your material (Figure 1-7). This crystallization can take weeks and months to complete. This process is known as chemical vapor transport.

1.3.2. Bottom Up Approach (Chemical Vapor Deposition)

In order to realize any of the unique applications of TMDs there is an inherent need to synthesize these materials with large areas and uniform layers. This is crucial to utilizing these materials in actual future electronics, especially developing growth techniques that can grow 300mm wafer scale layers. A Bottom up approach of growing films that is currently used in the semiconductor industry and even for sunglasses to potato-chip bags is known as chemical vapor deposition (CVD). Generally speaking CVD uses precursors of the desired material, which is heated to relatively high temperatures in order for either thermal decomposition or redox reactions to occur and crystallize the desired product onto a substrate. An intensive amount of research is being conducted on developing methods and processes for controllably growing monolayer and few layer TMDs. Overall this top down methodology exhibits more control in thickness and lateral sizes however
the crystal quality is not as uniform compared to the top down bulk crystal growth. Growth methods have primarily been developed for Mo and W systems primarily using sulfur powder and MoO$_3$ (Figure 1-8).

Figure 1-8 Example CVD growth of MoS$_2$ on SiO$_2$
1.3.2.1. Basics of Chemical Vapor Deposition

CVD processes comprise of the following steps\textsuperscript{46} (Figure 1-9):

1. Convective and diffusive transport of the reactant species to the reaction zone
2. Gas phase reactions
3. Transport of reactants to the substrate surface
4. Chemical and physical adsorption to the surface
5. Surface reactions leading to film synthesis
6. Desorption of volatile byproducts
7. Convective and diffusive transport of by-products away from the reaction zone

Choosing the chemical species is very important for chemical vapor deposition to take place. Precursors must be volatile and or easily able to volatilize. A prime example is SiH\textsubscript{4} commonly used to deposit silicon in the semiconductor industry. Furthermore, chemical reactions that need to take place have to be thermodynamically favorable with the resulting solid product. This means that there needs to be an energetic advantage for the desired reaction to take place where the Gibbs Free Energy decreases. Temperature and pressure can be adjusted to make sure the Gibbs Free Energy is less than zero. Another important part is making sure the byproducts be volatile.
Gas transport is another important aspect of tuning CVD growth. The flow of your reactants through the chamber is crucial when the goal is for gas to uniformly be delivered to the substrate. Flow also needs to be optimized for maximum deposition. CVD processes usually take place in the viscous or laminar regime where Reynolds Number is small <2000. Chemical vapor deposition processes can often be mass transport limited or surface reaction limited. Engineering and process tuning can aid in alleviating these issues. Mass transport limited category is where reactants are not readily available which is often an external factor in a CVD reactor such as the flow rate, or pressure, chamber size, etc. Surface reaction limited category is where enough reactants are available but the reaction at the surface is too slow. This can be alleviated by substrate temperature, catalyst.

A suitable or prepared substrate is necessary for films to grow efficiently. The barrier to nucleation on a substrate has to be overcome along with the thermodynamic barriers. There are two types of nucleation that exists, one where the nuclei does not incorporate into the crystal structure and the other incorporates in the film structure. There are three different types of nucleation that can be present on the surface. One is a three dimensional island growth or Volmer-Weber which is primarily due to impurities on the surface (dust particle). The next is layer plus island growth or Stranski-Kastanov growth and then layer by layer growth which is known as Franck-van der Merwe growth. Franck-van der Merwe growth occurs when the films atoms are less or equally bonded to each other than to the substrate.
Figure 1-9 CVD growth process steps
1.4. Transition Metal Dichalcogenide Film Processing Challenges for Large Scale Manufacturing

Two-dimensional (2D) layered dichalcogenides (TMDS) (MX2: M = Mo, W and X = S, Se, Te) have attracted unprecedented scientific & technological interests owing to their rich physical, chemical, and electrical properties. Present silicon technology has followed the famous Moore’s law for miniaturization, higher integration, higher performance, low power dissipation, and lower cost. According to International technology roadmap for semiconductors (ITRS), existing CMOS technology faces unprecedented technological challenges regarding the scaling-down of transistor, device integration process, and power consumption issues which led to technology progression that shown in (Figure 1-10).\textsuperscript{47,48} TMDs are one of the technology option to drive “More Moore” using a dual gate -2D FET that will extend MOS FET to ≤6nm gate length and shown in (Figure 1-12).\textsuperscript{49} Moreover, TMD based integrated devices for flexible electronics and photonics based applications will drive “More than Moore” shown in (Figure 1-12).\textsuperscript{48,49} MoS\textsubscript{2} and WSe\textsubscript{2} will be the first generation TMD and TFET and Photonics require the other new materials, such as ZrSe\textsubscript{2}, HfSe\textsubscript{2}, etc. These materials exhibit a very high surface-to-volume ratio, which is a natural advantage for the reduction of power consumption in the future nanoelectronics, in that the atomically thin materials enable the highly efficient modulation of charge transport via surface gates.\textsuperscript{47}
Figure 1-10 Emerging CMOS technology at 5nm and beyond, emphasis on 2TMD materials\textsuperscript{47,48}
Figure 1-11 Dual gate-FET with TMD based channel gate length ($L_{gate}$), $\leq 10$nm$^{47,48}$

Figure 1-12 More Moore: MoS$_2$ or WSe$_2$ based dual gate 2D FET (5nm node), WTe$_2$, MSe$_2$ (M = Zr, Hf) based dual gate-FET beyond 5nm technology, MoS$_2$ based flexible TEFs, MSe$_2$ (M = Zr, Hf) based photonics devices.$^{47,48}$
To fabricate TMD devices and measure their properties reliably, the one of the prerequisite as well as unsolved challenge is to synthesize 300mm wafer scale film with controlled layers. At present, high quality TMD materials are difficult to grow. Top-down syntheses pathways via mechanical and chemical exfoliations have results in a very low yields, poor uniformity in the film thickness and extrinsic defects. Bottom-up syntheses via chemical vapor deposition (CVD) and atomic layer deposition (ALD) with better control of chemical potentials (i.e. precursor ratio)\textsuperscript{50}. Several deposition techniques used for the targeted large area film growth are listed in (Table 1).
### Table 1 Overview of Primary TMD Growth Techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Substrate</th>
<th>Substrate temperature</th>
<th>Mo source</th>
<th>Mo source temperature</th>
<th>S source</th>
<th>S source temperature</th>
<th>Annealing</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Reaction</td>
<td>Quartz tube</td>
<td>600°C</td>
<td>Mo powder</td>
<td>600°C</td>
<td>S powder</td>
<td>600°C</td>
<td>1100°C, 10 hrs</td>
<td>MoS₂ (Bulk)</td>
</tr>
<tr>
<td>Direct Deposition</td>
<td>Sapphire, Glass, SiO₂/Si</td>
<td>650°C</td>
<td>MoS₂</td>
<td>900°C</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>Flake</td>
</tr>
<tr>
<td>Halogen Vapor Transport</td>
<td>Quartz</td>
<td></td>
<td>Br₂</td>
<td>850°C - 950°C</td>
<td>S powder</td>
<td>850°C-950°C</td>
<td>1000°C (MoS₂ to MoS₃), Ar/S₂</td>
<td>MoS₂ (bulk, thin film)</td>
</tr>
<tr>
<td>Decomposition</td>
<td>Graphene, h-BN, MoS₂</td>
<td>500°C to MoS₃</td>
<td>(NH₄)₂MoS₄</td>
<td>spin coat from solvent</td>
<td>NA</td>
<td>NA</td>
<td>1000°C in S vapor</td>
<td>MoS₂ (epitaxy)</td>
</tr>
<tr>
<td>Metal Sulfurization</td>
<td>SiO₂/Si</td>
<td>750°C</td>
<td>Mo thin film</td>
<td>pre deposited by ebeam</td>
<td>S powder</td>
<td>150°C</td>
<td>Continuous thin film (poor thickness control)</td>
<td></td>
</tr>
<tr>
<td>Oxide Sulfurization</td>
<td>Si</td>
<td>500°C, H₂</td>
<td>MoO₃ thin film</td>
<td>Pre-deposited</td>
<td>S powder</td>
<td>500°C</td>
<td>1000°C in S vapor</td>
<td>Monolayer (large area)</td>
</tr>
<tr>
<td>CVD</td>
<td>SiO₂/Si</td>
<td>650°C</td>
<td>MoO₃ powder</td>
<td>650°C</td>
<td>S powder</td>
<td>120°C, H₂</td>
<td>Monolayer (large area)</td>
<td></td>
</tr>
<tr>
<td>CVD</td>
<td>SiO₂/Si</td>
<td>850°C</td>
<td>WO₃ vapor</td>
<td>650°C</td>
<td>Se powder</td>
<td>Unknown</td>
<td>WSe₂ (epitaxial with MoS₂)</td>
<td></td>
</tr>
<tr>
<td>ALD</td>
<td>Sapphire</td>
<td>300°C</td>
<td>MoCl₅</td>
<td>?</td>
<td>H₂S</td>
<td>RT</td>
<td>800°C, S</td>
<td>MoS₂ (monolayer), low quality</td>
</tr>
<tr>
<td>ALD</td>
<td>Au/Ti catalyst</td>
<td>100°C</td>
<td>Mo(CO)₆</td>
<td>~100°C</td>
<td>(CH₃)₂S, H₂S</td>
<td>100°C</td>
<td>Post anneal</td>
<td>(MoS₂, Not stoichiometric, poor thickness control)</td>
</tr>
</tbody>
</table>

*Note: RT refers to room temperature.*
It has remained a great challenge to grow large size crystalline and high surface coverage monolayer TMD film and transfer TMDs from the growth substrate to another without compromising the quality of the TMDs. In manufacturing scale, transfer of TMDs layer will not be scalable and end up with many more defects, contaminations, crack, wrinkle related issues. Need to have controllable growth of monolayer MoS2 evolving from triangular flakes to continuous thin film. So far, chemical vapor deposition (CVD) growth has been divided into (a) vapor sulfurization and (b) vapor deposition. In the vapor sulfurization, the source materials, e.g., Mo14, MoO3 or (NH4)2MoS4, are coated on a substrate, which is followed by sulfurization in a sulfur vapor environment at high temperature. The TMDs grown by sulfurization method usually have large area and good uniformity but poor crystalline quality, small domain size, and uncontrollable layer number. In contrast, the source materials, e.g., MoO3 or MoCl5 are evaporated in the vapor deposition method, usually have relative large domain size but poor surface coverage on a substrate. These two kinds of CVD methods require high growth temperature (up to ~800 °C), which cannot meet the requirements of the back-end processing of IC technology. A nucleation-controlled strategy is established to systematically promote the formation of large-area single- and few-layered films has been presented, however, kinetic factor is not accounted via first-principles calculations.
1.5. Hydrogen Evolution Reaction and the Hydrogen Economy

Biology provides much inspiration for processes, systems, or structures that can greatly improve current technologies or lead to the invention of new ones. The slow, constant, and random development of adaptations in nature leads to multifunctional systems that would likely not be thought of by mankind’s development processes, which are often focused on unifunctional maximization. This is why biomimetics, the conscious emulation of nature’s genius, is a design methodology being utilized to solve humanity’s most pressing problems. One such problem is our unsustainable energy paradigm. Society’s dependence of fossil fuels is extremely detrimental to the environment; this environmental impact must stop if we hope to continue to live with the same luxuries and amenities that are available today. This is even more true considering the rapid growth that mankind is projected to experience in the near future.

Current global energy usage is about 20 terawatts per year, and current carbon dioxide production in the US alone is about 6,000 million metric tons of CO₂ each year. The majority of this energy use comes from transportation and production of electricity, and is expected to increase significantly in the near future due to population increase and GDP growth. An international energy outlook study by the U.S. energy information administration predicts that global energy consumption will increase by over 50 percent from 2008 to 2035, and our current energy model will be even less sustainable at this increased level. Because of this
unsustainability, is essential to consider new energy models, and biology offers an obvious one: photosynthesis.

Photosynthesis is the root of all energy production on earth. It is the process whereby plants and some other autotrophic organisms convert solar energy and carbon dioxide into chemical energy, which the organisms then use to survive, grow, and reproduce. Photosynthesis produces around 130 terawatts of energy per year, (over six times our current energy consumption), and converts over 100 thousand million metric tons of carbon dioxide into biomass every year (almost 20 times our current CO₂ production).⁶¹,⁶² Part of photosynthesis’s potential comes from the fact that it is a process which is happening at a small scale all over the world, so the individual processes combine to create a very powerful cumulative energy production system.

With the rapidly growing population there is a significant challenge for humanity to provide clean renewable energy for society. Carbon dioxide (CO₂) is one of the primary greenhouse gases emitted into the environment. In 2010 carbon dioxide accounted for 84% of all U.S. greenhouse gas emissions through human activities. The main source of this 84% is due to the combustion of fossil fuels (coal, oil, natural gas) for transportation and electricity purposes. Human activities have had an increasing temperature effect on the climate and this is primarily due to the billion tons of heat trapping greenhouse gases being emitted. There have been many strategies to reduce carbon dioxide emissions and slow down global warming. One
of the first strategies in place is using energy efficient appliances and fuel efficient vehicles. The United States Environmental Protection Agency (EPA) have set up many programs such as ENERGY STAR and various motor vehicle standards to regulate the amount of carbon dioxide emissions. Another strategy is to teach individuals at an early age to conserve electricity. For example, in various elementary schools there are units to teach children about energy conservation and methods to reduce the carbon footprint such as turning off lights and electronics when not in use. Fuel switching is another strategy that is heavily being evaluated by governments.

When considering the energy challenges facing society, and the energy production potential of photosynthesis, it is clear that a biomimetic exploration into plants could be very useful. In this exploration, three processes within photosynthesis rise to the surface as practical, useful, and robust biomimetic possibilities to use for “artificial photosynthesis.” These three processes are solar energy capture, water splitting, and CO₂ fixation. In general, solar energy capture is focused on utilizing the renewable energy of the sun, and is by far the most well-known aspect of artificial photosynthesis. Along with producing hydrogen for fuel during water splitting, the CO₂ fixation and utilization of photosynthesis can be mimicked in order to recycle the carbon dioxide that we are emitting in such high quantities, and reused to create fuels for transportation or industry. This carbon dioxide utilization will similarly be examined closely in this paper. It is interesting to note that artificial photosynthesis has been broken down into a number of unique
processes which can be mimicked for different reasons, rather than a single process that exactly mimics plants. This allows for artificial photosynthesis to be specifically and differentially applied to society’s needs, and makes it a very robust and adaptable example of biomimicry.

The concept of a hydrogen economy, where hydrogen is the main source of fuel instead of hydrocarbons is being researched in three major categories: hydrogen production, hydrogen storage and hydrogen fuel cell technology. Water splitting has been heavily researched as a source for hydrogen. Water electrolysis is a methodology of water splitting by using an external electrical source to push the following water splitting reaction:

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2
\]

**Equation 1-1**

The thermodynamic potential required for this reaction to proceed is 1.23V and can be divided into two half reactions. The first reaction the hydrogen evolution reaction (HER) consists of the following two electron process \((2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2)\) which takes place at the cathode. The second reaction, the oxygen evolution reaction (OER) takes place at the anode \((\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^-)\).\(^{63,64}\)

For HER there are 3 steps for the reaction to successfully produce hydrogen. The first step or the Volmer step is adsorption of a proton on the surface of the
cathodic electrode \((H^+ + e^- \rightarrow H_{ad})\). The second step is or the Heyrovsky step is where the second proton is adsorbed on the surface \((H^+ + H_{ad} \rightarrow H_2)\). The third and final step is when the 2 adsorbed species form hydrogen and the desorption of hydrogen gas arises which is known as the tafel step.\(^{63,64}\) The free energy \((\Delta G_H)\) of hydrogen adsorption is crucial for effective rate of reaction. For example if the hydrogen surface bonding is strong then the rate limiting step is the desorption step and if it is too weak then the rate limiting step is the adsorption step. Therefore the Gibbs free energy must be close to zero because in that scenario the binding of hydrogen is not too strong or too weak for any optimal HER catalyst electrode.

Extensive study has been ongoing utilizing TMDs as catalysts for hydrogen evolution reaction. In their bulk form TMDs are not very effective catalysts, but by nanostructuring, the catalytic edge site can be exploited and can reach performances of platinum meanwhile being a low cost materials\(^{65–67}\). By exfoliating bulk TMDs such as MoS\(_2\) one can expose highly catalytic edge site and achieve minimal applied bias to set off hydrogen production (Figure 1-13).\(^{68}\)
An important technical problem for artificial leaf’s industry application is hydrogen storage techniques. Various issues exist for relying on hydrogen as a fuel source for transportation. Storage of hydrogen in vehicles is one of the most important issues. Figure 10 shows that, even to this day, there is not a hydrogen storage method which is suitable for feasible application in vehicles because the existing methods require either low temperature or high pressure. These problems need to be solved before the artificial leaf technology can have a broad market impact in transportation and energy industry.

Although the US government has devoted great effort and large sums of money to push renewable power plants, like solar, wind, hydroelectric and nuclear, artificial leaf technology as it stands today does not offer a comparative advantage.
Compared to the artificial leaf, conventional fossil fuel based power generation technologies are all well-established and more feasible. If the goal is to reduce greenhouse gas emissions from transportation, one promising solution is to utilize electrical cars renewable energy infrastructure. Even if we use a non-renewable energy source such as natural gas to produce power at a power plant and use it to charge electric cars, it is better than using the artificial leaf and a hydrogen economy. For example, using natural gas in a modern General Electric natural gas turbine, we can get about 60% efficiency. But if we use the same fuel in an internal combustion engine car, we can only get 20% efficiency. This is because in a stationary power plant we can take waste heat to run a steam turbine and generate a secondary power source. But we can’t do this in a vehicle because of the space issue. The development of electrical cars is accelerating. Tesla Motors’s Tesla Model S has a performance of 265 miles per charge and Nissan Company’s electrical car “Nissan Leaf” can run 107 miles per charge. This means electrical cars are ready for application.

1.6. Photoemission Electron Microscopy

Since the introduction of two-dimensional (2D) crystalline materials, with a wave of interest bolstered by the variety of electronic behavior that can be probed and engineered in graphene, the goal of understanding electronic behavior in 2D crystals continues to be construction and tailoring of complex device structures layer-by-layer. For electronic and optoelectronic applications, limitations
encountered engineering a band gap for graphene have prompted increased attention towards transition metal dichalcogenides (TMDs) in particular. TMDs are a diverse group of layered materials that have a large intrinsic bandgap in the visible frequency range that is sensitive to the number of monolayers, composition, and external fields, affording tunability.\textsuperscript{23}

Less extensively studied than graphene, there are still gaps between theoretical prediction and experimental verification left to bridge for TMDs. A systematic understanding of how electronic states develop from monolayer to multilayers of similar and dissimilar 2D crystals is currently lacking in experimental studies.\textsuperscript{23,38,72} Evolution of the electronic dispersion as a function of the layer thickness for multilayer homojunctions of MoS\textsubscript{2} has been elucidated using ARPES, but how the electronic states of heterojunctions comprised of crystals with different thicknesses would line up is still an unknown.\textsuperscript{73,74} Another important consideration for engineering heterostructures composed of 2D materials is the manner in which charge transfer and hybridization revise the alignment of the electronic states.

Experimental studies of surface potentials using scanning Kelvin probe microscopy (SKPM) and electrostatic force microscopy (EFM), often performed in ambient conditions, are perhaps the most prevalent and commonly used approaches to address these questions. However, SKPM/EFM results for prototypical TMD systems, namely few-layer MoS\textsubscript{2} structures, have yet to achieve a clear consensus.\textsuperscript{75,76} A notable example is the evolution of the work function as a function
of layer thickness that exhibits dependence on whether the sample was annealed prior to the measurement. Incongruous results reported in the literature could be attributed to the hydrophilicity of the surface and sensitivity of MoS2 to ambient conditions which would significantly influence surface measurement.

Photoemission electron microscopy (PEEM) is a surface sensitive technique that is governed by the photoelectric effect to gain insight on the elemental and/or electronic structure of a material. The basic principle behind photoemission uses a light source which is can be a gas discharge lamp, X-Ray tube, or synchrotron radiation which is impinged on the surface of a solid and electrons excited by the photoelectric effect is analyzed with respect to the kinetic energy and momentum via an electrostatic analyzer (Figure 1-14). In the case of x-ray excitation which is commonly known as X-ray photoelectron spectroscopy (XPS) elemental composition can be determined because of core level excitation giving rise to specific binding energies associated with each element. By using an ultra-violet (UV) source the only electrons that can be ionized are on the outermost level of the atoms (valence levels). The valence level electrons can provide insight on the electronic structure of solids. By collecting local variations of electron emission via a charge-coupled device (CCD) on can generate image contrasts that is representative of the electronic structure variation.
Figure 1-14 Schematic of a low energy electron microscope/photoemission electron microscope
Chapter 2

Chemical Vapor Deposition of Rhenium Disulphide


2.1. Motivation

When going from bulk to monolayer forms of semiconducting TMDs, a common phenomenon is a transition from an indirect to a direct band-gap.$^{78,79}$ This transition is due to the confinement of carriers in the out-of-plane direction of the TMD monolayer and results in the significant enhancement of photoluminescence and photosensitivity in monolayer TMDs.$^{23,72}$ Among CVD-grown monolayer TMDs, there is a range of band-gaps from 1.5-1.99 eV, where selenides exhibit the lowest band gap of 1.6 eV for WSe$_2$ and 1.5 eV for MoSe$_2$ (Figure 2-1).$^{45,80–83}$ Having a toolbox with a selection of TMDs with varying properties is key to building tuned heterostructure devices.$^{38}$ Rhenium disulfide (ReS$_2$) however, unlike WS$_2$ and MoS$_2$
has layers that are charge de-coupled from one another due to an additional valence electron in Rhenium which confines the charge in individual layers even when in bulk form.\textsuperscript{83} As a result, ReS\textsubscript{2} is already a direct band-gap semiconductor (1.5-1.6 eV) in the bulk and does not show any further transition when isolated to monolayer form.\textsuperscript{83,84} ReS\textsubscript{2}'s additional valence electron also causes it to stabilize into a distorted octahedral (T) phase, where the sulfur layers are buckled and rhenium forms zigzag chains along one lattice vector.\textsuperscript{84} This distortion causes symmetry splitting, which could allow the combination of a transistor and an optoelectronic device in a single monolayer.\textsuperscript{85}

Previously, 2D ReS\textsubscript{2} has only been synthesized via high temperature (>1000°C) bulk crystal growth followed by exfoliation in a non-scalable process.\textsuperscript{83,84} Here we demonstrate the first bottom-up method for a scalable synthesis of large-area monolayer ReS\textsubscript{2}. Our CVD technique is at atmospheric pressure, and occurs at the lowest growth temperature (450°C) reported for any previously synthesized monolayer CVD-grown TMDs (Figure 2-1).\textsuperscript{36,41,43,56,80,81,86–88} The detailed characterization of these 2D materials has been performed using a combination of spectroscopy (Raman and XPS) and microscopy (Optical, AFM, SEM, and TEM). Furthermore, we fabricated field effect transistors on CVD-grown monolayers to evaluate the electrical transport of the material to highlight that these monolayers can potentially be used as an n-type semiconductor.
Figure 2-1 (a) Optical band gaps of various CVD grown monolayer TMDs along with monolayer ReS$_2$. (b) Growth temperatures for various CVD grown monolayers (red) and for bulk crystal growth (blue) of various TMDs along with temperatures for ReS$_2$. 
2.2. Experimental Procedure

2.2.1. CVD Growth of ReS\textsubscript{2}

Monolayer ReS\textsubscript{2} was grown using ammonium perrhenate (NH\textsubscript{4}ReO\textsubscript{4}) and sulfur on a clean Si/SiO\textsubscript{2} wafer (Figure 2-2).

![Figure 2-2 Schematic for the CVD growth of monolayer ReS\textsubscript{2}.]

Argon was used as the carrier gas for sulfur during the deposition process. Sulfur powder (99.5-100% Sigma Aldrich purris) and ammonium perrhenate (>99% Sigma Aldrich) were used as the precursors for growth. Sulfur (2 g) in an alumina boat was placed at the opening of the quartz tube furnace where the temperature would roughly reach 300\textdegree{C} and the center hot zone of the furnace would reach
450°C. Ammonium perrhenate (0.1 g) were positioned in an alumina boat. Si/285 nm SiO$_2$ 1 cm x 2 cm wafers were placed polished side down on top of the alumina boat, was placed directly in the center of the furnace. Argon gas was purged through the furnace at 50 sccm for 15 minutes prior to ramping up the temperature. The furnace was then ramped to 450°C in 15 minutes and then held at 450°C for 20 minutes with a constant flow rate of argon gas at 50 sccm under atmospheric pressure. The furnace was then turned off and allowed to cool to 35°C.

2.2.2. TEM Sample Preparation and Characterization

By using a poly (methyl methacrylate) (PMMA) technique, ReS$_2$ was transferred onto TEM grids (Ted Pella perforated carbon film with an orthogonal array of 1.2 µm diameter holes with a 1.3 µm separation on a 200 mesh Au grid). Initially, a PMMA film was spin-coated at 3500 rpm for 40 seconds on top of the as grown ReS$_2$ samples on the Si/SiO$_2$ substrate. The samples were then immersed into KOH (2M) to etch the SiO$_2$, causing the PMMA/ReS$_2$ to be lifted off the wafer after 24 hrs. The PMMA/ReS$_2$ was then transferred into DI water and then onto the TEM grid and allowed to be naturally air-dried. Following the drying, the TEM grids were immersed in acetone for 1 hour and then 2-propanol for another hour to remove as much PMMA as possible. The TEM and STEM images were taken from a JEOL 2100 Field Emission Gun Transmission Electron Microscope at 200 kV and FEI Titan 80–300 TEM operating at 80 kV.
2.2.3. Additional Characterizations

A scanning electron microscope (FEI Quanta 400) at 15-20kV was used for determining sizes and shapes of various crystals. Raman Microscope (Renishaw inVia microscope) with a 514.5 nm laser (Renishaw) excitation was used for determining the spectrum along with PL. XPS (PHI Quantera) with MultiPak Software was used to determine elemental composition and bonding. AFM (Asylum Research Cypher S) was used for height maps and local modulus studies. Commercial AFM tips (AC200 TS and AC240-TM-R3, Asylum Research; TESPA, Bruker) were used as received. Height data were estimated through line pixel analyses across several representative images. A spin-cast polystyrene film (Bruker-Nano) with an elastic modulus of 2.7 GPa was used as a reference sample for the contact modulus calibration.

2.2.4. FET Device Fabrication and Electronic Performance

The ReS$_2$ nanosheets were transferred to a Si substrate with a thermally grown SiO$_2$ layer of 285 nm. Electrical contacts were created by standard photolithography using a mask aligner (EVG 620 Mask Aligner) followed by metallization via e-beam evaporation (5 nm Ti / 65 nm of Au at a rate of 0.01 nm/s.) and lift off.

Electrical measurements were performed in a home-built probe station under vacuum conditions ($< 10^{-5}$). Two source meters (Keithly 2400) were used for
applying-source drain bias and for gate bias and drain current measurements. The measurements were performed with an applied gate voltage ranging from -70 to +70 V. To estimate the field effect mobility we use \( \mu = [dI_{ds}/dV_g] \times ([L/W]V_{ds}) \), where \( L \) and \( W \) are channel length and width. The capacitance/ unit area \( C_i \) of the thermally grown SiO\(_2\) gate oxide is estimated as 1.2x10\(^{-4}\) Farads/m\(^2\) \( (C_i = \varepsilon_0 \varepsilon_r / d) \) where \( \varepsilon_0 = 3.9 \) for SiO\(_2\) and \( d = 285 \) nm).

2.2.5. Computational Methods

We carried out DFT calculations as implemented in the OpenMX software. All properties were computed using the general gradient approximation (GGA) with the PBE functional.\(^{99-91}\) Norm-conserving pseudopotentials were used to describe the core electrons.\(^{92-94}\) OpenMX uses the pseudo-atomic orbitals (PAOs) to expand the electronic wave function for the valence electrons.\(^{95,96}\) To describe the rhenium (Re) we considered a basis set composed by three radial functions to describe the s orbital, two radial functions to describe the p and d orbitals and one for the f orbital (s3p2d2f1), with 11.0 Bohr for the cutoff radius. For the sulfur (S), an s2p2d2 basis set was considered and 9.0 Bohr to the cutoff radius. For the numerical integrations and for the solution of the Poisson’s equation, an energy cutoff of 250 Ry was considered. A mesh of (6x6x1) for the k-points was considered to describe the ReS\(_2\) slab. The geometry optimization was performed until the maximum force in the system was below 5.0x10\(^{-4}\) Hartree/Bohr.
2.3. Results & Discussion

2.3.1. Optical Microscopy, Scanning Electron Microscopy, Atomic Force Microscopy

The surface of the Si/SiO$_2$ after a growth at 450°C for 20 minutes is observed using a low magnification Scanning Electron Microscope (SEM) image (Figure 2-3) which shows thin and clean ReS$_2$ crystals of different sizes and shapes. The size of the crystals obtained using several SEM images varies from 2-60µm with a mean size of 40µm (Figure 2-4). In order to understand the shape and thickness of these 2D crystals, a detailed analysis using SEM, optical microscopy and Atomic Force Microscopy (AFM) has been performed. From optical images of as-grown ReS$_2$ samples, thick crystals and monolayers can be distinguished based on the contrast on 285nm SiO$_2$/Si. The optical image of monolayer hexagonal domains (Figure 2-3) appears purple, while thick platelets appear silver colored (Figure 2-3). Domains in the process of growing further layers can also be observed (Figure 2-3), which highlight the dendritic off-symmetry growth (Figure 2-5). The SEM images of 5 µm hexagonal monolayer (Figure 2-3), and a 50 µm hexagonal monolayer (Figure 2-3) exhibit highly dendritic edges which is in stark contrast to how CVD monolayer MoS$_2$ is characterized with sharp edges.$^{43,56}$ An SEM image of a 10 µm thick platelet (Figure 2-3) indicates a change into a circular shape as the thickness becomes larger. Similar to other CVD TMD domains, the monolayer 2D sheet can merge together to form continuous films (Figure 2-6) In order to observe the thickness,
morphology, and local mechanical properties of these 2D layers, AFM in intermittent contact mode as well as elastic modulus mapping was conducted on a 10 µm hexagonal monolayer. The edges of an as grown hexagon show a thickness of approximately 1nm, which approximately correspond to a single monolayer (Figure 2-3). Small particles on the surface made height profiles across the entire hexagon difficult to assess; for that reason, the height profile was performed across a relatively clean dendritic edge. AFM modulus mapping of a monolayer shows relatively compliant regions (dark areas) along dendritic patterns originating from the center of the crystal, indicating a dendritic growth mechanism/reconstruction, which will be discussed in more detail (Figure 2-3). Thick circular/hexagonal crystals can also be observed with sizes reaching 25 µm and thicknesses of 110 nm (Figure 2-3). If growth temperatures are 400-450°C, the primary morphology consists of the small flat 500 nm hexagons of 13 nm thicknesses (Figure 2-7). If growth temperatures are 450-500°C, the primary morphology consists of >10 µm circular/hexagons with a thickness of 110 nm (Figure 2-3) and out of plane growth (Figure 2-8).
Figure 2-3 (a) SEM image showing various ReS$_2$ monolayer crystals. 
(b) Optical image of a 20µm ReS$_2$ dendritic hexagonal monolayer. 
(c) Optical image of a 30µm ReS$_2$ dendritic hexagonal monolayer with secondary layer growth. 
(d) Optical image of a 25µm ReS$_2$ platelet. 
(e) SEM image of a 5µm ReS$_2$ dendritic hexagonal monolayer. 
(f) SEM image of a 50µm ReS$_2$ dendritic hexagonal monolayer. 
(g) SEM image of a 10µm ReS$_2$ platelet. 
(h) Height profile of a ReS$_2$ monolayer edge with a ~1nm step measured from the line in the 2µm$^2$ AFM height map inset. 
(i) 10µm$^2$ modulus mapping via AFM of a ReS$_2$ dendritic hexagonal monolayer, darker areas represent a relatively compliant response. 
(j) 8µm$^2$ height mapping of a ReS$_2$ platelet.
Figure 2-4 SEM images of several samples in different regions of the substrate with various magnifications revealing the various sizes and morphologies.
Figure 2-5 Optical images of several samples in different regions of the substrate revealing the various sizes and morphologies.
Figure 2-6 SEM image of a film-like growth of ReS$_2$. 
Figure 2-7 With growth temperatures ranging from 400°C-450°C the primary morphology consists of small 500nm hexagons with thicknesses of ~13nm as shown from the (a) SEM image and (b) the AFM height profile mapping.
Figure 2-8 Various SEM images highlighting out of plane grown seen at temperatures of 450-500°C
2.3.2. Raman Spectroscopy

Samples were characterized via Raman spectroscopy using a 514.5nm laser. Spectra were collected from the monolayer hexagonal domains, few-layer, and quasi-bulk 100nm thick platelets. Raman peaks at ~162 and ~213 cm\(^{-1}\) correspond to the in-plane (E\(_{2g}\)) and out-of-plane (A\(_{1g}\)-like) vibrational modes (Figure 2-9), respectively. A series of additional Raman modes in the range of 100-400 cm\(^{-1}\) arise due to symmetry splitting in the distorted 1T structure. In monolayer samples, the A\(_{1g}\) mode red-shifts by 1.16 cm\(^{-1}\) and the E\(_{2g}\) mode red-shifts by 1.39 cm\(^{-1}\) compared to the quasi bulk. This is in contrast to previous exfoliation work where no Raman mode shifts were observed from bulk to monolayer\(^{83,84}\). Raman mapping of the A\(_{1g}\) mode highlights a homogenous nature of the hexagonal monolayer domains. The mapping can also provide insight into the crystallization of hexagonal monolayers occurring directly on the Si/SiO\(_2\) since the A\(_{1g}\) mode is only observed in the hexagonal domains.
2.3.3. XPS

The elemental composition and bonding of the CVD-grown films were examined by XPS. Re and S were seen from the survey spectra of the CVD-grown films along with Si and O from the Si/SiO₂ substrate (Figure 2-10). The core \(4f_{7/2} \)
and 4f_{5/2} level peaks for Rhenium are located at approximately 40.9 eV and 43.3 eV, respectively. The location of these core level peaks indicate Rhenium as metal species with no inherent oxide.\textsuperscript{97,98} The core 2p_{3/2} and 2p_{1/2} level peaks for sulfur are located at approximately 161.37 eV and 162.63 eV, respectively indicating sulfur as a metal sulfide due to the binding energy close to \( \sim 161.5 \text{ eV} \) for the 2p_{3/2} peak.\textsuperscript{97,98} The 1:1.9 Re/S ratio obtained from XPS suggests a slight deficiency of sulfur, which indicates defects.
2.3.4. TEM

Transmission electron microscopy (TEM) and aberration-corrected scanning TEM (STEM) were used to provide insight in the dendritic anisotropic growth directions, grains and crystal quality of ReS$_2$. By using a poly (methyl methacrylate)
(PMMA) technique of transfer, various as-grown ReS$_2$ samples were transferred onto TEM grids. Detailed imaging and diffraction have been performed on a single layer ReS$_2$ 2D sheet. The low magnification bright field TEM image shows a few micron-sized 2D sheet with similar morphology as observed in previous microscopic analysis (Figure 2-11). The SAED (selected area electron diffraction) clearly resolves the 001 orientation of the distorted 1T crystal. The Z-contrast-STEM clearly resolves a 001 lattice arrangements for a single monolayer with a few defects. The HRTEM images of the layer edges further confirms these to be single layer. These edges are observed as bended or folded. EELS (Electron energy loss spectroscopy) analysis of the sheet shows Re and S characteristic emission peaks to confirm the material composition (Figure 2-12).
Figure 2-11 (a) Bright field image of monolayer ReS$_2$ with dotted line approximately surrounding the hexagon with an inset showing SAED of the monolayer. (b) Z-contrast-STEM image resolving monolayer lattice arrangement (c, d) High magnification images of a monolayer edge region with various folds.

Figure 2-12 (e) EELS spectrum of the sample indicating presence of Re and S.
Figure 2-13 (a) Bright field TEM image of bilayer ReS$_2$ sample along with diffraction pattern covering (b) one layer and (c) secondary layers. (d) Low magnification Dark field STEM image of the samples covering many well shaped multilayered ReS$_2$ hexagons. (e) Z-contrast-STEM image at the edge of a thick crystal resolving number of layers. (f) HRTEM image at the edge of a thick crystal resolving various layers from contrast.
In order to understand the mechanism of growth, a detailed TEM investigation of the hexagonal thick platelets was performed for several samples (Figure 2-13, Figure 2-14). A representative bright field image of few layered ReS$_2$ is shown, which clearly shows the irregular morphology of the individual layers. In the SAED patterns, there are two different orientations in each of the layers as compared to the single layer. The HRTEM image and Z-contrast-STEM images of the edge of a thick crystals clearly shows that the individual layers, with differing contrast (1-4 number of layers with light to dark contrast), have rough edges that are stacked on top of each other which gives rise to a regular hexagonal or circular shape as observed in the other imaging techniques. The combination of TEM and the optical image reveals that the growth of the secondary layers initiates from the centre of the 2D sheet and then grows towards the edge. The difference in orientation of the second layer can be seen in bright field and STEM images.
Figure 2-14 (a) Bright field TEM image and (b) optical image showing initial growth of secondary layers, (c) and (d) Bright field and HADDF image of secondary layers grown on the first layer.
2.3.5. Density Function Theory

The growth of such complex shapes and morphologies is mainly due to distorted 1T structure which was further investigated by using DFT (density functional theory) calculations. In the recent past, several studies on 2D growth of TMD materials such as MoS$_2$ have been reported.$^{45,80-83}$ However, all discuss a highly symmetric crystal structure with a complete isotropy in the 001 plane which gives rise to controlled and well-defined shapes, such as a triangle, hexagon, etc.$^{56}$ In the case of ReS$_2$ (low symmetry crystal with a distorted 1T structure and a large lattice distortion along 001 plane), the growth is complex due to anisotropy in interfacial energy. The complex crystal growth of such an anisotropic crystal is understood with the help of detailed DFT calculations. DFT calculations have been used to perform an energetic analysis to address the low temperature growth and the origin of the dendritic shapes. First, we considered a supercell composed by 4x4x1 repetitions of the unit cell for our simulation. Due to anisotropy from the low symmetry crystal structure, we have considered a structure that has two distinct possibilities of growth: i) structures periodic in the x-direction (100) and non-periodic in the y-direction (010); and ii) structures periodic in the y-direction and finite in the x-direction (Figure 2-15). The details about the simulation procedure are described in the methods section. The DFT calculations show that the structure periodic in the y-direction is about 11.5 eV more stable than the structure periodic in the x-direction. For both cases, from the simulations we could observe a rearrangement in the structure in order to decrease the exposure of the rhenium
atoms. This rearrangement is more evident when the periodicity is in the x-direction; in this case, the rhenium atoms are initially on the edge of the structure in an exposed configuration. During the geometry optimization, the sulfur atoms migrate from the original position to the edge (Figure 2-16). A similar behavior of sulfur migration can be seen for the structure that is periodic in the y-direction (Figure 2-17). However, the total dislocation made by the sulfur atoms is small in comparison with the previous case. In both cases the edge atom dislocations lead to a decrease in energy, showing that the configuration where the rhenium atoms are exposed is not energetically favorable. Hence, the sulfur has a strong tendency to migrate to the edges in order to minimize the energy, which gives rise to rough dendritic edges. We carried out geometry optimization to understand the addition of a trimer (ReS$_2$) to the edge of the structure and its consequence on geometry in terms of energy. The energy comparison was done by obtaining the energy of a previous structure plus an unattached ReS$_2$ trimer with the new on with the new trimer attached to the edge. We considered the addition of the new trimer in the same edge as its previous trimer, giving rise to a 2D in-plane growth process. For the structure with periodicity in the y-direction, we added up to four trimers (in order to fully complete a column, due to the supercell size). We placed the additional trimer in a way to respect the symmetry of the system and from this initial configuration the geometry of the whole system was optimized. Calculations show that the addition of the first trimer makes the structure 4.5 eV more stable. The additions of the second and third trimers were done in the neighborhood of the first
one, and yields structures 6.4 and 4.2 eV more stable, respectively. With the addition of the fourth and last trimer we obtained a structure 8.5 eV more stable. The highest gain in the system stability, with the addition of the fourth trimer, is due to the complete filling of a column. In the end, the successive addition of the trimer renders a structure that poses an edge similar to the original. The same procedure described above was repeated to the system periodic in the x-direction. However, due to the strong atomic rearrangement in the edge where the rhenium atoms were exposed, there are many different possibilities to attach the trimer in order to align it to its neighbor. We presented two different possible initial configurations for the placement of the first trimer (Figure 2-18). The included trimer has its atoms highlighted in blue and red (blue for rhenium and red for sulfur). In the first case, the geometry optimization yields a configuration with one of the sulfur atoms out of the ReS$_2$ slab plane; in the second (Figure 2-19), the optimized structure is within the slab plane. The structure with the sulfur out of plane is 1.63 eV more stable than the configuration where all atoms remain in the slab plane. This out of plane sulfur atom can be an anchor point to the growth of a second layer above the first one. The migration of the edge sulfur atoms creates sites with atoms oriented in different directions in comparison with the atoms belonging to the central part of the slab, and acts as a nucleation site for the growth of a secondary layer on top of the existing layer. Hence, we observe a S rich nucleation of the second layer. Depending on the initial nucleation site, we observe the complex growth and dendritic morphology of the ReS$_2$. 
Figure 2-15 Energy comparison due to the addition of ReS$_2$ trimers (one up to four) in the edge of a ReS$_2$ slab.
Figure 2-16 Geometry optimization of a ReS$_2$ slab with periodic boundary conditions in the x-direction. In one of the edges, the rhenium atoms are initially exposed. An energetically stable geometry is found after the migration of some sulfur atoms on the edge where the rhenium atoms were exposed.
Figure 2-17 When the slab is periodic in the y-direction, the same effect of sulfur migration occurs in the edge where the rhenium atoms are more exposed. However, in this case the migration is less marked than in the previous case.
Figure 2-18 Addition of a ReS$_2$ trimer in the edge which presented the highest sulfur distortion. After geometry optimization, two energetic stable configurations were found. The most stable configuration presented one sulfur out of slab plane.
Figure 2-19 Addition of a ReS$_2$ trimer in the edge which presented the highest sulfur distortion. After geometry optimization, two energetic stable configurations were found. The most second stable configuration is when the added trimer remains in plane for the other configuration. In both cases, the obtained geometry presents defects, which can be the origin of the dendritic shape in the ReS$_2$ growth.
2.3.6. Photoluminescence

Photoluminescence (PL) is an important characterization technique for TMDs and was measured for a 40 µm hexagonal monolayer and a 100 nm thick quasi-bulk platelet. The PL spectrum shows a weak peak corresponding to a band gap of 1.65 eV, while a 100 nm thick quasi-bulk platelet shows a peak corresponding to a band gap of 1.47 eV (Figure 2-20). The values for the monolayer indicate a slightly shifted band-gap than in prior exfoliation work which is likely due to defects present in the crystals.\textsuperscript{83,84}

![Figure 2-20 Normalized PL Spectra with black corresponding to quasi bulk ReS\textsubscript{2} and blue corresponding to monolayer ReS\textsubscript{2}.]
2.3.7. Field Effect Transistor Performance

Investigating electronic properties is often a useful tool in understanding crystal quality. FET devices were fabricated using photolithography where the contacts were made across a series of randomly oriented monolayer ReS$_2$ hexagons to evaluate the electrical performance. The fabricated devices have a channel length of 2 µm and an approximate width of 5 µm (Figure 2-21). A transfer curve (drain current ($I_{ds}$) vs. Gate voltage ($V_g$)) and output characteristics (Drain current vs. $V_{ds}$) highlights an increased drain current with positive gate voltage indicating the n-type behavior of the ReS$_2$ flakes (Figure 2-22). The devices have an average mobility of 7.2e-2 cm$^2$/V and a threshold voltage of 35 V and an on/off ratio of 10$^3$. The low mobility of the ReS$_2$ transistors compared to the previously reported exfoliated ReS$_2$ transistors can potentially be attributed to defects and the limitations of device fabrication. Grains, random orientations, potential multiple layers could not be avoided which can heavily impact the electronic transport properties of ReS$_2$.$^{85}$ However, it is important to note that early reports of MoS$_2$ CVD growth also exhibited relatively low mobilities, but with further study and optimization of growth, annealing, and contact resistance investigations mobilities improved.$^{27,43}$ Future effort will be put to improve growth and the device fabrication and performance.
Figure 2-21 SEM image of a fabricated device.
Figure 2-22 Gating voltage vs. source/drain current with the I-V curves of various gating voltages as an inset.
2.3.8. Hydrogen Evolution Reaction Performance

HER catalyst performance was studied by using the PMMA transfer technique to transfer thick platelets of ReS2 onto a glassy carbon electrode. Linear sweep voltammetry was performed in a typical 3-electrode setup and polarization curves and Tafel slopes were plotted and compared to platinum (Figure 2-23, Figure 2-24). After initial cycling and reaching steady-state performance, we measure ~0.18V to reach 10mA/cm2 and a Tafel slope of 101mV/dec, which is comparable to prior work on exfoliated nanosheets of ReS2 and MoS2 nanosheets. Post SEM analysis highlights the active catalytic edge sites on the surface of the thick hexagonal domains (SI). This can be attributed to the edge steps seen under low magnification STEM. Further in-depth study of hydrogen evolution will pursued with an analysis of catalytic sites on dendritic monolayer hexagons in future works.
Figure 2-23 Polarization curve for ReS$_2$ to highlight HER catalyst performance with the Pt as a comparison.
Figure 2-24 Tafel slope for ReS$_2$ compared with Pt
Figure 2-25 Post SEM of ReS$_2$ after cycling highlights active catalytic edge sites on thick platelets.
2.4. Concluding Remarks

In summary, this study represents the report of the first CVD growth of ReS$_2$ monolayers, which is easily scalable and more efficient due to its low growth temperature (450°C). ReS$_2$ synthesized using this CVD technique exhibits an interesting morphology that is different from traditional monolayer CVD of TMDs which further explained with the help of different possibilities using DFT calculations. The as grown ReS$_2$ has also been shown to behave as an n-type semiconductor. Overall, this CVD growth method provides a fast and relatively simple method of synthesizing monolayer and multilayer ReS$_2$ for prototyping future complex electronic and optoelectronic devices.
Chapter 3

Photoemission Electron Microscopy of Molybdenum Disulfide

3.1. Motivation

The design and implementation of semiconductor homo- and heterojunctions are cornerstones of today’s growing electronic and optoelectronic industries. In addition to a tunable band gap and carrier control via spin and valley degrees of freedom heterojunctions based on atomic layers of transition metal dichalcogenides (TMDs) have displayed a wide range of favorable properties in laboratory devices, well-suited to electronic and optoelectronic applications. Layered TMDs exhibit high on-off ratios in field effect devices, high photoluminescence quantum efficiency, high percentages of light absorption, high photogain and photoresponse.\textsuperscript{26,29,99–105}

In high-performance devices, efficient injection of charge (or energy) across contacts and control of carrier transport across heterojunctions require accurate determination of band alignment, including offsets of the work function, valence band maximum, and conduction band minimum. While there has been tremendous
progress in the growth of TMD-based heterostructures for charge transport and optical measurements, information about their band alignment is not readily available. This is due in part to their electronic structures being sensitive to the number of layers and the stacking orientation. Measurement of the band alignment has been further complicated by poor screening of interactions with the supporting substrate and physisorbed or chemisorbed gas molecules, obscuring the electronic properties intrinsic to TMD layers. For MoS₂, a prototypical TMD, alignment of the electronic states at the junctions between layers of different thickness have been reported in studies of surface potentials typically using scanning Kelvin probe microscopy (SKPM) and electrostatic force microscopy (EFM). However, SKPM and EFM studies have yet to quantify the surface potential offsets at the junctions, or even just to achieve a clear consensus on whether the work function rises or falls as layer number is increased. Authors have ascribed incongruous results from SKPM and EFM, often performed in ambient conditions, to hydrophilicity of the MoS₂ surface. In this context, an accurate measurement of the electronic band alignment on a technologically relevant substrate, without any influence from the environment is a vital parameter for developing TMD heterostructures for novel optoelectronic devices. The requirement for quantitative determination of the electronic band alignment intrinsic to few-layer TMDs also necessitates that measurements be performed on TMD specimens supported by a substrate that interacts minimally with the overlying TMDs, preferably an insulator. This condition precludes the use of
electron-based spectroscopy tools, such as photoemission spectroscopy, due to the limitations imposed by sample charging. We overcome this restriction by using photoemission electron microscopy (PEEM) with deep-ultraviolet (DUV) illumination as an excitation source.

In the work reported here, we studied the band alignment of a model TMD system, few-layer MoS$_2$ supported on 285-nm-thick SiO$_2$ grown on a Si wafer in an ultra-high vacuum environment using PEEM. Local determination of the vacuum level, valence band edge at the Brillouin zone (BZ) center, and ionization energy of monolayer (1ML), bilayer (2ML), and tri-layer (3ML) MoS$_2$ were obtained from the local photoemission spectra (PES) and the photon-energy-dependent photoemission yield (PEY). We observed the vacuum level and, hence, the work function to increase relative to 1ML MoS$_2$ with the addition of layers. The valence band edge also advanced toward the vacuum level with increasing layer number. Based on these results, we constructed a band diagram of 1ML, 2ML, and 3ML MoS$_2$, which shows type-I band alignment across monolayer-to-bilayer and bilayer-to-trilayer lateral junctions. We also determined that few-layer MoS$_2$ on 285-nm-thick SiO$_2$ is n-type. Our successful application of PEEM using deep-ultraviolet (DUV) light to measure the band alignment of semiconducting TMD crystals on a nominally insulating substrate, all the while encountering minimal charging of the sample, presents new insight into their electronic properties.
3.2. Experimental Procedure

3.2.1. Synthesis of MoS$_2$

All MoS$_2$ flakes were synthesized using a slightly modified version of a well-established chemical vapor deposition (CVD) technique that proceeds via sulfurization of a MoO$_2$ precursor.$^{118}$ The more common CVD technique using MoO$_3$ was not chosen because of its tendency to grow large-area 1ML with very scant 2ML nucleation.$^{43}$ Synthesis of MoS$_2$ with MoO$_2$ precursors and higher growth temperatures produced larger multilayer regions ideal for a layer-dependent PEEM study of MoS$_2$. 285-nm-thick SiO$_2$ thermally grown on a highly-doped silicon wafer (p-type, 12.0-16.0 $\Omega \cdot \text{cm}$) was chosen as a substrate material to produce optical contrast for as-grown structures.$^{119,120}$ Multilayer MoS$_2$ was synthesized at 850°C in a 1-inch diameter quartz tube furnace at atmospheric pressure. Argon was used as the carrier gas for sulfur during the deposition process. 10 mg MoO$_2$ powder (99% Sigma Aldrich) was placed in a quartz boat at the center the furnace with a 1 x 2 cm$^2$, 285-nm-thick SiO$_2$/Si wafer on top of the boat polished side down. The SiO$_2$/Si wafer was approximately 1 cm above the MoO$_2$ powder. 60 mg of sulfur powder (99.5%-100% Sigma Aldrich puriss) was placed in an alumina boat upstream approximately at the edge of the furnace hot zone. The upstream location for the sulfur was specifically positioned so the sulfur begins to visually melt ($\sim$115-200°C) when the hot zone of the furnace is approximately 800°C. Prior to ramping, Argon gas was purged through the quartz tube at 100 sccm for 15 minutes. The furnace
was then ramped to 850°C in 15 min and maintained at that temperature for 20 min with a constant argon flow rate of 100 sccm. The furnace was then turned off and allowed to cool to 35°C.

The layer number of each MoS\(_2\) region was verified using Raman spectroscopy. To remove adsorbed water from the sample surface, samples were annealed for ~12 hours at ~300°C in ultrahigh vacuum (UHV) prior to PEEM measurement.

### 3.2.2. Photoemission Electron Microscopy Setup

PEEM measurements were conducted in a LEEM-III system (Elmitec Elektronenmikroskopie GmbH) coupled to a tunable DUV light source comprised of a pressurized Xe lamp (Energetiq, EQ-1500 LDLS), a Czerny–Turner monochromator (Acton research, SP2150), and refocusing optics (fused silica and calcium fluoride/silica achromat lenses)\(^6\). The spectral width of the DUV light was set to 50-100 meV throughout the wavelength range used for the measurement (\(\lambda = 175-350\) nm).

During acquisition of photoemission spectra, we used an electron filter on the LEEM-III instrument to sweep through the kinetic energies of the photoemitted electrons. No aperture restricted the emission angle of the photoelectrons. Thus, the data presented here correspond to emission-angle integrated spectra. We set the energy resolution of the electron energy filter to 0.5 eV. The leading (left) and
trailing (right) edges of PES spectra yield information about the location of the vacuum level and the valence band edge at the center of the BZ, respectively. Maps of the vacuum level and the highest occupied states were obtained by fitting the PES spectra at each pixel (obtained at a fixed photon energy) and by correcting for the dispersion of the electron energy filter using a known surface (in this case, the SiO₂ background). Local variation in the vacuum level yields the work function variation.

Ionization energy maps were obtained from PEY curves recorded at each pixel as a function of photon energy using a monochromator in tandem with our DUV light source. The electron energy filter was not used for PEY measurements. We determined ionization energy pixel-by-pixel from the minimum photon energy above which photoemission is observed (photoemission threshold) in the photon-energy scan. The standard deviation of the signal acquired with lower energy photons (below the photoemission threshold) was used as a criterion to define the photoemission threshold at each pixel.¹²²

### 3.3. Results and Discussion

#### 3.3.1. Optical Microscopy and Raman Microscopy

As a result of growth, 40-60 µm MoS₂ monolayer triangles and truncated triangles with multilayer regions (primarily bi- and tri-layer) on top were crystallized on the wafer as shown in the optical image presented (Figure 3-1). The change in optical contrast as shown is attributed to a mono-, bi-, tri-layer region of a
MoS$_2$ crystal marked with a green, yellow, and orange dot, respectively. The same region was imaged with photoemission electron microscopy.

We performed Raman spectroscopy to determine the layer number of few-layer MoS$_2$ as grown. Raman spectra was obtained for the sample region imaged via optical microscopy and photoemission electron microscopy (Figure 3-1). Layer determination of as-grown MoS$_2$ was conducted using a WiTec Alpha 300R with 100x objective and a 532 nm laser, and is related to the optical contrast produced by the MoS$_2$ crystallites supported on a 285 nm SiO$_2$/Si substrate. Spectra were collected at various locations on multilayer MoS$_2$ crystals while taking note of the optical contrast exhibited. There is a tendency for the in-plane vibration ($E^{1_{2g}}$, $\sim$385 cm$^{-1}$) to upshift while the out of plane vibration ($A^{1_{g}}$, $\sim$401 cm$^{-1}$) to downshift from multilayer to monolayer MoS$_2$. By using the peak frequency difference between the $A^{1_{g}}$ and $E^{1_{2g}}$ modes the layer number of MoS$_2$ can be determined. It has been reported and is commonly accepted that for monolayer regions the peak difference is approximately 18 cm$^{-1}$, while bilayer and tri-layer is approximately 22 cm$^{-1}$ and 23.5 cm$^{-1}$, respectively, for mechanically exfoliated MoS$_2$. The as-grown sample exhibit regions where there is a 15.2 cm$^{-1}$, 20.4 cm$^{-1}$, and 22.8 cm$^{-1}$ peak difference that we attribute to mono-, bi-, and tri-layer, respectively. The slight deviation from the reported peak frequency difference could be due to strain between the substrate and the crystallites introduced during growth. The trend however is consistent with the reported exfoliated MoS$_2$ Raman study.
Figure 3-1 (a) Optical image of the exact MoS$_2$ flake PEEM measurements and Raman spectra was collected (b) Raman spectra at various points on the MoS$_2$ flake indicating the number of layers as portrayed by color dots in (a)
3.3.2. Band Alignment Determination

The PEEM measurements and an optical image of 1ML, 2ML, and 3ML MoS$_2$ grown on 285-nm-thick SiO$_2$ are shown in (Figure 3-2). The data in (Figure 3-2) were acquired using photons with $\lambda = 185$ nm (6.70 eV). (Figure 3-2) shows the vacuum level map, where the relative vacuum levels, $E_{\text{vac}}$, of 1ML, 2ML, 3ML, and multilayer MoS$_2$ as well as that of the SiO$_2$ substrate are clearly distinguishable. The vacuum level of the SiO$_2$ substrate lies $\sim$0.5 eV lower in energy than that of 1ML MoS$_2$. The thickness of the MoS$_2$ flakes is verified from the optical contrast shown in (Figure 3-2), and is further confirmed from the Raman spectra at the locations highlighted by the green, yellow, and orange dots corresponding to 1ML, 2ML, and 3ML. The crystallographic alignment between layers can be inferred from the relative orientations of the triangular edges$^{38}$. Most flakes display 2H or 3R stacking with random stacking orientation for thicker parts of the flakes$^{123}$.

(Figure 3-2) shows representative PES spectra for 1ML, 2ML, and 3ML regions indicated by the black dotted line in the (Figure 3-2). The leading (left) edge and trailing (right) edge of PES spectra, which yield information about the location of $E_{\text{vac}}$ and valence band edge at the center of the BZ, are indicated by tick marks in (Figure 3-2). With increasing layer number, $E_{\text{vac}}$ (left edge of the PES peak) and the valence band edge (right edge of the PES peak) are shifted higher in kinetic energy for MoS$_2$. The variation of the local $E_{\text{vac}}$ shown in (Figure 3-2) establishes a layer-dependent surface potential in MoS$_2$. In (Figure 3-2) the PES
intensity from 1ML MoS$_2$ appears higher than that of 2ML and 3ML MoS$_2$. Note that the relative intensities between MoS$_2$ regions with different thicknesses varied as a function of photon energy. We postulate that this enhancement of the photoemission intensity results from the difference of the photoemission cross section for different thicknesses of MoS$_2$ at the particular photon energy used in the measurement.
Figure 3-2 The (a) vacuum level, $E_{\text{vac}}$, map, (b) the optical image, (c) the representative photoemission spectra, and (d) the alignment of the electronic states of MoS$_2$ flakes grown on SiO$_2$. (a), (c), and (d) were acquired using photons with $\lambda = 185$ nm (6.70 eV). The color scale bar for (a) is in eV. The black dotted line and the white solid line in (a) illustrate the locations where the photoemission spectra shown in (c) and (d) were obtained. In (c) the leading edges of $E_{\text{vac}}$ (left edge) and the valence band edge (right edge) are indicated by tick marks. In (d), the alignments of $E_{\text{vac}}$ and the valence band edges of 1ML, 2ML, and 3ML MoS$_2$ are indicated by the red and green dots. Superimposed images are the photoemission intensity map. The black dash dot lines illustrate the energy of the Fermi level deduced from the work function of 1ML MoS$_2$ reported in ref. Error! Bookmark not defined..
Combining information concerning $E_{\text{vac}}$, the valence band edge, and the photon energy enables us to examine the alignment of the electronic states across 1ML, 2ML, and 3ML MoS$_2$. PES spectra at each pixel along the white line in (Figure 3-2) were extracted and are presented as surface band alignment. Higher PES intensities appear darker in color. The green photoemission intensity map represents the initial filled state, which is inferred by offsetting the black PES spectra by the photon energy used for the PES measurement ($\lambda = 185$ nm). The energy of the valence band edge is thereby expressed in terms of the electron binding energy with respect to the vacuum level of 1ML MoS$_2$. Because we use low-energy photons in our measurement, the highest occupied states measured reflect the valence band edge near the $\Gamma$-point.

The vacuum level alignment is presented via red dots in (Figure 3-2). These values were extracted from the leading edge of the PES spectra (the left edge in (Figure 3-2) shifted 0.25 eV higher in electron kinetic energy (i.e. toward the right edge) to account for energy broadening due to the moderate electron energy resolution of the measurement ($\sim$0.5 eV). The alignment of the valence band edge at BZ center is presented in green dots, whose values were extracted from the trailing edge of the PES spectra (the right edge in (Figure 3-2)). Again, the trailing edge of the PES spectra was shifted to lower kinetic energy by 0.25 eV to account for energy broadening. The magnitude of the ionization energies for 1ML, 2ML, and 3ML MoS$_2$ that were determined from the PEY map shown in (Figure 3-3) are represented by red arrows in (Figure 3-2).
Assuming a 4.52 eV work function for monolayer MoS\(_2\), and that the Fermi level is aligned between 1ML, 2ML, and 3ML MoS\(_2\) within a single crystalline flake, the location of the Fermi level is shown by the black dash-dot lines illustrated in (Figure 3-2).\(^{124,125}\) The latter assumption is reasonable given a lack of chemical bonding between MoS\(_2\) and the underlying SiO\(_2\) and the van der Waals interlayer coupling between MoS\(_2\) layers.\(^{27,126}\) Further assuming that the band gap values of 1ML, 2ML and 3ML MoS\(_2\) are \(\sim\)1.9 eV, \(\sim\)1.6 eV, and \(\sim\)1.4 eV, our experimental data suggest that the Fermi-level of the MoS\(_2\) flake is above mid-gap, indicating n-type character. This result is consistent with the n-type conductivity commonly found in monolayer MoS\(_2\) on SiO\(_2\) and bulk 2H-MoS\(_2\).\(^{28,106,127}\) Another important aspect of (Figure 3-2) is the abrupt transitions of both \(E_{\text{vac}}\) and the valence band edge at the junctions between MoS\(_2\) regions of different thicknesses. Band bending at the heterojunctions between TMDs with different layer numbers has been observed, but at the nanometer scale. (Figure 3-2) confirms that such band bending is absent at the larger length scale probed in the PEEM experiment. Further details of the band alignment are discussed in the following.

From (Figure 3-2) it appears that the ionization energy we measured from PEY (red arrow) and the ionization energy we deduced from the PES spectra (green dots) do not agree for 1ML and 2ML MoS\(_2\), deviating significantly (\(\sim\)0.9 eV) for 1ML MoS\(_2\). In contrast, they show reasonable agreement for 3ML MoS\(_2\). These discrepancies in 1ML and 2ML MoS\(_2\), we believe, are largely due to the photoemission signal of the underlying SiO\(_2\) substrate. (Figure 3-2) shows that the
measured ionization energy of SiO$_2$ is lower than that of MoS$_2$. Therefore, we expect the PEY intensity of the MoS$_2$ flakes at the lower photon energy (longer wavelength) range would be overwhelmed by the photoelectrons from SiO$_2$. Furthermore, a general trend of a longer probing depth with longer wavelength photons could increase the relative contribution of the underlying SiO$_2$ in the photoemission intensity.$^{128}$ This scenario is supported by PES spectra acquired for photons with $\lambda = 200$ nm where additional spectral weight from the SiO$_2$ substrate is visible in the PES spectra, beyond that of MoS$_2$. We note that 1ML and 2ML MoS$_2$ show larger additional spectral weights than does 3ML, in which the SiO$_2$ signal is mostly attenuated. Overall, reasonable agreement of the ionization energy of 3ML MoS$_2$ evaluated from the PES and PEY measurements supports the validity of the energy scale used in our analysis. Because results from PES spectra for MoS$_2$ are reliable regardless of the MoS$_2$ thickness, we continue our discussion of the band alignment based on the PES data taken with higher-energy photons ($\lambda = 185$ nm).

Clear distinction between 1ML, 2ML, and 3ML regions in the $E_{\text{vac}}$ map in (Figure 3-2) allows for quantifying variation in the local work function. The histogram of the extracted $E_{\text{vac}}$ values and the plot of relative work function are presented in (Figure 3-3). We fit the $E_{\text{vac}}$ distribution with Voigt functions. The FWHM of each fit component corresponds to the error in relative work function values plotted in (Figure 3-3). We note that, because our PES measurements using PEEM do not have an absolute energy scale, the $E_{\text{vac}}$ measurements are reported relative to that of 1ML MoS$_2$. 

Figure 3-3 Determination of the work function variation in a MoS$_2$ flake. (a) Histogram of $E_{\text{vac}}$ obtained for the imaged MoS$_2$ island shown in the inset. (b) The relative work function of 1ML, 2ML, and 3ML MoS$_2$. The error bars in the relative work function are the widths of the fitted peaks in (a).
We found that the relative work function increases by \( \sim 70 \text{ meV} \) with each additional \( \text{MoS}_2 \) layer. Thus, if the work function of 1ML \( \text{MoS}_2 \) is 4.52eV, our results suggest that those of 2ML and 3ML \( \text{MoS}_2 \) are 4.58 eV and 4.66 eV, respectively. The trend of work function increase with increasing number of layers has not been established amongst SKPM and EFM studies of \( \text{MoS}_2 \). Both increasing and decreasing work function with increasing layer number have been reported. One may surmise that hydrophilicity of \( \text{MoS}_2 \) and the effects of ambient conditions account for this inconsistency. We also note that to arrive at surface potentials, SKPM uses the capacitive difference between a conducting AFM probe and a charge layer thickness in the sample. For semiconducting crystals suspended on substrates it is not clear to what extent charge layers in the substrate may contribute to stray fields, and whether the substrate and sample have reached thermodynamic equilibrium. Both can influence SKPM results. To our knowledge, the only SKPM study to observe work function variation similar to what we observed in the present work was conducted in UHV (the work function increases by \( \sim 50 \text{ meV} \) with each additional \( \text{MoS}_2 \) layer). This appears to confirm that the work function increase as a function of the layer number we observed reflects the electronic properties of \( \text{MoS}_2 \) flakes supported on an insulating substrate, minimally perturbed by environmental effects (thanks to UHV conditions).

Based on the measured variations of the relative work function and valence band edge at the \( \Gamma \)-point of \( \text{MoS}_2 \), we determine the band alignments across 1ML, 2ML, and 3ML. \( \textbf{(Figure 3-4)} \) shows a simplified schematic of the band alignment.
between MoS$_2$ and SiO$_2$. The schematic includes reported band gap values for 1ML, 2ML, and 3ML MoS$_2$ as well as the energy differences of the valence band edges at the $\Gamma$-point versus the $K$-point ($\Delta E_{\Gamma-K}$) based on theoretical calculations$^{130,131}$. Also shown in **(Figure 3-4)** is the position of the Fermi level deduced from the 4.52 eV work function for monolayer MoS$_2$ reported.$^{130,131}$
Figure 3-4 A simplified band diagram of 1ML, 2ML, and 3ML MoS$_2$ and SiO$_2$, which includes quantities measured with PEEM in boldfaced, italicized type. The ionization energies were calculated from PES, and are represented with red arrows and fonts. Other numbers are based on the reported values as described in the main text.
As a whole, (Figure 3-4) points to some important aspects of the junctions between 1ML, 2ML, and 3ML MoS₂. First, the Fermi-levels of the MoS₂ lie a few 100 meV above mid-gap in all three thicknesses, as described earlier. Because of the similar effective electron and hole masses for 1ML MoS₂ (\(m^e = 0.54\) and \(m^h = 0.44\)) we can expect that the Fermi level of the intrinsic 1ML MoS₂ would lie close to the mid gap.\(^{132}\) This scenario suggests the n-type character of 1ML MoS₂ grown on SiO₂.

As the effective electron and hole masses are similar for 2ML and 3ML, they are expected to be n-type as well. The band diagram also suggests type-I band alignment across the 1ML-2ML and 2ML-3ML heterojunctions. This result is in a qualitative agreement with the theoretical calculations by Padilha et al. and Kang et al., and contradicts a scanning photocurrent microscopy study, which suggests a type-II heterojunction between 1ML and multilayer MoS₂ on SiO₂.\(^{133,134}\)

One uncertainty in the band diagram (Figure 3-4) is the difference in energy of the valence band edges at the \(\Gamma\)-point versus the \(K\)-point (\(\Delta E_{\Gamma,K}\)) in 1ML MoS₂. While we use \(\Delta E_{\Gamma,K} = 0.1\) eV based on a theoretical work, an angle resolved photoemission spectroscopy (ARPES) measurement of 1ML MoS₂ on Au(111) suggests \(\Delta E_{\Gamma,K}\) as large as 0.3 eV.\(^{135,136}\) Were this so, it would imply that band alignment across the 1ML-2ML MoS₂ heterojunction is type-II. Because ARPES measurements of 1ML MoS₂ on less interacting substrates (thin SiO₂/Si and graphene/SiC) suggest \(\Delta E_{\Gamma,K} = 0.1\) eV, we presume \(\Delta E_{\Gamma,K} = 0.1\) eV for 1ML MoS₂ on thick SiO₂. Accordingly, a type-I heterojunction is expected at the 1ML-2ML MoS₂ interface formed on SiO₂.\(^{73,137}\) We speculate that the type-II heterojunction found in
the scanning photocurrent microscopy study may be the result of trapped charges at the surface of SiO$_2$ influencing the band alignment of MoS$_2$. Further study is needed to gain a comprehensive understanding of the influence of trapped charge. We also note that even $\Delta E_{r-K} = 0.3$ eV does not alter our assessment of n-type character for 1ML MoS$_2$.

(Figure 3-4) provides electronic structure information for SiO$_2$ in addition to that for MoS$_2$. $E_{\text{vac}}$ of SiO$_2$ is located at 0.5 eV below that of 1ML MoS$_2$, while the highest occupied state in SiO$_2$ lies at -4.8 eV binding energy (with respect to the $E_{\text{vac}}$ of 1ML MoS$_2$). (Figure 3-4) also shows an 8.0 eV bandgap and 8.6 eV ionization energy for SiO$_2$, and a Fermi level that sits above mid-gap (4.8 eV above the valence band of SiO$_2$) based on previous reports$^{138,139}$. There is type-I band alignment across the lateral MoS$_2$-SiO$_2$ heterojunction for which we expect minimal band bending owing to Van der Waals interactions between MoS$_2$ and the substrate. We note that the 4.3 eV energy difference between $E_{\text{vac}}$ and the highest occupied state in SiO$_2$ is significantly smaller than the expected ionization energy of SiO$_2$ (8.6 eV).

We postulate the highest occupied state shown in the PES spectra from SiO$_2$ corresponds to defects in SiO$_2$. From photoluminescence studies, oxygen deficiency centers (ODCs) have been shown to produce emission bands 4.3 eV above the valence band of SiO$_2$$^{140-144}$. Defects in SiO$_2$ are also observed in the DUV photoemission spectra of glassy SiO$_2$ and quartz implanted with metals ions$^{145,146}$. The highest occupied state probed in our experiment is located at 4.3 eV below the
vacuum level of \( \text{SiO}_2 \), and coincides well with an energy level of ODCs. Over the course of our PES measurements we observed the photoemission intensity from the SiO\(_2\) substrate to vary in a manner consistent with the photoemission intensity variation reported.

Photoemission experiments on insulating materials are generally not reported because of sample charging, which obscures the interpretation of the spectra or image. In this regard, this report presents a unique case where photoemission microscopy and spectroscopy can be performed on MoS\(_2\) flakes supported on nominally-insulating 285-nm-thick SiO\(_2\). Similar PEEM measurements of 2D crystals on thick SiO\(_2\) are reported, but they were conducted with the aid of additional grounding or alkali metal doping to alleviate charging\(^{74,147,148}\). Furthermore, PEEM imaging of an insulator surface free of image distortion or charging was once demonstrated on a SiO\(_2\) film using a supplemental electron source in addition to the UV illumination\(^{149}\). These works suggest that PEEM of 2D semiconducting layers supported by insulating substrates is possible, provided there are means to compensate for charge accumulation at the sample surface.

To verify that the PES spectra presented here are minimally influenced by charging, we recorded PES spectra as a function of photon energy, and confirmed that the spectral width increases linearly with a slope close to unity. This result confirms that there is no additional elongation of the spectral width as a function of the photon energy, which is one signature of sample charging. We attribute the
apparent absence of charging to two factors: the low photoelectron current of our measurement technique, and the dissipation of photoholes responsible for surface charging by photoactive defects in SiO$_2$ moving charges to and from the MoS$_2$ flakes. We note that illumination of a similar sample using a He discharge lamp ($h\nu = 21.2$ eV) resulted in instant charging, likely because of the higher photoelectron current produced at the higher excitation energy. Further experimental verification of the charging behavior of MoS$_2$ flakes on SiO$_2$ using a He lamp is provided in Supporting Information.

Electron spectroscopy is a powerful tool for studying electronic properties of materials, but it is generally limited to conductive materials. This limitation has hampered the study of electronic properties intrinsic to 2D crystals supported on insulating substrates in order to minimize electronic perturbation. The work presented here resolves this quandary for 2D crystals research, and suggests that a new approach based on PEEM and DUV illumination may be used to study the electronic properties intrinsic to other 2D crystals supported on SiO$_2$.

### 3.3.3. Photoemission Yield Map to Evaluate the Ionization Energy

An example of a map of the local ionization energy extracted from the photon-energy dependence of the photoemission yield (PEY) is given in (Figure 3-4). Ionization energy maps are constructed from PEY data at each pixel. 1ML, 2ML, and 3ML MoS$_2$ are clearly discernible in the ionization energy map. In contrast with the small shift of the vacuum levels within the MoS$_2$ islands (< 200 meV), the
ionization energy of MoS$_2$ varied significantly more for different layer number (> 400 meV). A cross section of the ionization map in (Figure 3-5) shows the ionization energy illustrated by the red arrows in (Figure 3-2).

Figure 3-5 The (a) ionization energy map of MoS$_2$ islands grown on SiO$_2$. The scale bar is in eV. (b) The cross section of the ionization energy map along the white line in (a) illustrates the ionization energy of 1ML, 2ML, and 3ML MoS$_2$. 
3.3.4. Evaluation of Sample Charging Behavior for MoS$_2$ flakes on SiO$_2$

In order to verify the lack of additional elongation of the photoemission spectral width due to sample charging, we plotted the PES spectral width from a 3ML MoS$_2$ region as a function of photon energy. Because the PES spectra acquired using our PEEM instrument does not have an absolute energy reference, each spectra in (Figure 3-6) was shifted such that the leading edge of the vacuum level (left edge) coincides. The valence band onset was determined and plotted as a function of photon energy. A slope near unity suggests minimal elongation of the PES spectra due to charging effects within this photon energy range. We note that the PES spectra for 3ML MoS$_2$ was convolved with additional peaks from the substrate for $\lambda \geq 200$ nm (where the PES intensity of the substrate is higher), which complicate extraction of the vacuum level and valence band edge. We assumed the line-shape of the PES spectra of 3ML MoS$_2$ for $\lambda = 200$ nm is similar to spectra acquired at $\lambda < 200$ nm to estimate the valence band edge onset for that photon energy. To minimize the need to account for substrate effects for the PES spectra discussed in the results section of the main text, we used PES spectra for 1ML, 2ML and 3ML MoS$_2$ acquired with photons of wavelength, $\lambda = 185$ nm.
Figure 3-6 The photon-energy dependent (a) photoemission spectra and (b) plot of valence band edge onset values of 3ML MoS2 on 285nm-thick silicon oxide. The solid red line in (b) is the linear fit to the plot of the valence band edge onset, and the equation describing the linear fit is displayed.
We postulate that the lack of sample charging we encountered during photoemission measurements is attributed to the low photoelectron current using the DUV light source and charge dissipation via photoactive defects in the SiO$_2$ substrate. Given the low energy of our DUV light source ($\lambda = 175 - 350$ nm, or $h\nu \sim 4 - 7$ eV), the photoemission spectra have a relatively narrow energy width, which resulted in a low total photoelectron current. We note that illumination of a similar sample using a He discharge lamp ($h\nu = 21.2$ eV) resulted in instant charging, likely because of the higher photoelectron current produced by the photons with higher excitation energy.

To verify the possibility of dissipating photoemission-induced charging using PEEM, we observed a MoS$_2$ flake on SiO$_2$ illuminated using a He discharge lamp and a DUV light source simultaneously. After the illumination with a He lamp was discontinued, PEEM image contrast was recovered in a few seconds to a minute, indicating the dissipation of photoholes during the DUV illumination. Carrier transport through defects could facilitate removal of the photoemission-induced charge in a manner similar to balancing charge accumulation at the surface of SiO$_2$ using a supplemental electron source. We also found that after prolonged annealing in UHV (~300 °C, > 20 hrs.), samples exhibited mild charging (< 1 V) when imaged with PEEM using the DUV light source. This seems to indicate that prolonged annealing impacts charge dissipation, perhaps by passivating defects in the SiO$_2$. Further study is necessary to better identify photoactive defects in SiO$_2$ and understand
their influence on PEEM images and the local photoemission spectra of layered TMDs supported on SiO$_2$.

### 3.4. PEEM Measurement of Transferred MoS$_2$ on Native Silicon Oxide

To compare the electronic properties of transferred MoS$_2$ to our results for as-grown MoS$_2$, we measured MoS$_2$ structures grown via the same CVD technique and transferred to a silicon wafer with a full native oxide layer. Few-layer MoS$_2$ regions were identified by optical contrast prior to transfer, which was carried out using a PMMA membrane as the transfer medium. Afterward, the PMMA membrane was removed by cleaning the sample with acetone.

A PEEM image of the surface of transferred MoS$_2$ crystallites is shown in (Figure 3-7). We found large-scale variations in the photoemission contrast across SiO$_2$ regions that suggest that the electronic properties vary on a size scale (> $10^3$ μm$^2$) larger than the individual MoS$_2$ crystallites (< $10^3$ μm$^2$).

We proceed to use information regarding the local vacuum level, the valence band edge, and the ionization energy of few-layer MoS$_2$ enables us to construct the band alignment of MoS$_2$ layers transferred to native oxide. We obtained PES spectra and ionization energy (PEY) measurements at each pixel along the white line trace in (Figure 3-7), which includes monolayer and tri-layer regions of MoS$_2$. To determine the layer number of the MoS$_2$ crystallite in the trace region, we used
morphology as a guide, comparing the trace region with other regions nearby. The PES spectra are presented in (Figure 3-7), with higher PES intensity appearing darker in color. Again, the PES spectra are reproduced and shifted downward by the photon energy of illumination (purple unidirectional arrow) and illustrated as dark green false-color spectra for clarity. Ionization energy measurements are indicated by red bidirectional arrows.

We find that there is no clear variation of the work function cutoff and the valence band edge on the scale of the layered regions within the MoS$_2$ island, therefore, we were unable to construct a trace of the vacuum level and highest occupied state in a manner similar to what is shown for as-grown MoS$_2$. Importantly, the highest occupied states determined from the PES spectra (green false color image) and those inferred from the ionization energy (red bidirectional arrow) do not coincide for 1ML or for 3ML MoS$_2$. Assuming an intrinsic work function of ~4.5 eV for monolayer MoS$_2$ (illustrated by the black dot and dash line), the results show slightly p-type character for 1ML MoS$_2$ and slightly n-type character for 3ML MoS$_2$. Interestingly, the highest occupied state as deduced from PEY measurements is in close proximity to the Fermi level (the black dot and dash line) suggesting the metallic character of the surface. The irreconcilability of results for the highest occupied state throughout the MoS$_2$ region along with the smearing of PES spectra obscuring the vacuum level and valence band edge in MoS$_2$ may imply that the surface is covered by residues remaining after the transfer process.
Measurement of the substrate revealed that the energy difference between the highest occupied state and the vacuum level in SiO$_2$ is $\sim$4.3 eV, similar to the as-grown sample. In (Figure 3-7) we present a band diagram of thin SiO$_2$ on p-type Si (111) constructed from x-ray and ultraviolet photoemission spectroscopy measurements.
Figure 3-7 PEEM measurement of transferred MoS2. (a) A PEEM image of few-layer MoS2 crystallites with a white line trace bisecting 1ML (darker) and 3ML (lighter) regions. (b) Alignment of the electronic states between 1ML and 3ML MoS2 determined from PES spectra and a PEY photon energy scan (not shown). PES spectra are shown as a black false color image. The green false color image represents the initial state obtained by shifting the black false
3.5. Dispersion Correction and its Effect on Relative Work Function Determination

An electron energy filter is a dispersion element that affects the PES spectra we obtain with PEEM. We use data processing to remove the contribution of the analyzer dispersion from our data after it has been collected. This dispersion correction could affect or skew the information we extract from PES spectra. To test the effect of dispersion correction on our relative work function measurement, we analyzed $E_{\text{vac}}$ distributions obtained at the same sample location with $\lambda = 185 \text{ nm}$ (6.7 eV) and $\lambda = 190 \text{ nm}$ (6.5 eV) for comparison.

The results are presented in (Figure 3-8) along with Voigt functions to fit the line shapes. The regions of the distribution that can unambiguously be associated with 1ML, 2ML, and 3ML MoS$_2$ are displayed with black lines. Additional components highlighted as green curves, lying between the leftmost and central peaks in black, were needed to obtain a reasonable fit. Overall, the locations of the black curves relative to one another and their respective FWHM vary minimally between the two photon-energy data. We attribute the additional component (green curve) to the incomplete correction of the dispersion of the electron energy filter within the images. This correction error is also apparent in the $E_{\text{vac}}$ image obtained at $\lambda = 185 \text{ nm}$ showing noticeable variation in the relative intensity in the 1ML MoS$_2$ region when compared to the $E_{\text{vac}}$ image obtained at $\lambda = 190 \text{ nm}$. We note that the
relative work function data shown in (Figure 3-8) of the main text is representative based on the similar data acquired using several photon energies.

Figure 3-8 Histograms of the vacuum levels obtained for (a) $\lambda = 185$ nm (6.7 eV) and (b) $\lambda = 190$ nm (6.5 eV) from the imaged MoS$_2$ island shown in the inset.
3.6. **Concluding Remarks**

In summary, a study of the electronic state alignment in monolayer, bilayer and tri-layer MoS$_2$ on a 285-nm-thick SiO$_2$ substrate have been presented. The layer dependence of the photoemission spectra showed a trend of increasing work function and shifting of the valence band edge at Brillouin zone center toward the vacuum level with increasing layer thickness. Based on our measurements, we proposed the band alignment between MoS$_2$ layers. We deduced that MoS$_2$ is n-type, and showed type-I band alignment across monolayer-to-bilayer and bilayer-to-trilayer lateral junctions. Our results demonstrate that photoemission electron microscopy coupled to a deep ultraviolet light source is a powerful tool to evaluate the electronic properties of MoS$_2$ with minimal environmental influence, and can be employed to study other 2D layered semiconductors and metals. The band alignment derived in the present work is essential information for building electronic and optoelectronic devices based on atomically thin MoS$_2$. 
4.1. Motivation

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to build semiconductor heterojunctions. These absolute band positions dictate how the band gaps of semiconductors would line up with respect to each other, and determine the charge transfer when one semiconductor is brought in contact with another material.\textsuperscript{150–152} Defined as an energy separation between the vacuum level and the highest occupied electronic states, the ionization energy is of particular importance for atomically-thin TMDs to predict their performance in their sought-after applications in semiconductor heterojunctions for high performance electronics and optoelectronics and as catalysts for photochemical reactions.\textsuperscript{153–157}
The ionization energy can be, in general, determined using photoemission spectroscopy or a photoemission threshold measurement. These approaches are, however, not applicable to TMDs in most cases because the specimens are typically micron-size flakes supported on silicon wafer with particular thicknesses of silicon oxide (SiO$_2$) films (typically ~100 or ~300 nm thick). This configuration allows the flakes to be located under optical microscopes but can lead to sample charging when photoemission spectroscopy is conducted due to the insulating nature of SiO$_2$. Conductive supports can alleviate the charging issue, but they introduce doping in TMDs due to the sizable electronic interaction (the charge transfer) with the supports. The ionization energies for a series of TMDs have been investigated based on theoretical calculations, but to the best of our knowledge, no experimental confirmation is reported despite their importance.

We present here a systematic determination of the ionization energies of the TMD flakes: MoSe$_2$, WS$_2$, and MoS$_2$, using a newly-developed photoemission electron microscopy (PEEM) combined with deep ultraviolet (DUV) illumination. Here we extract the ionization energy from the energy positions of the vacuum level cut-off and the highest occupied states near the Brillouin zone center in the local photoemission spectra. In qualitative agreement with the reported values calculated via density functional theory based on the GW approximation, the measured ionization energy decreases from MoS$_2$, to WS$_2$, to MoSe$_2$. In the PEEM micrographs, we found a sizable downward shift of the vacuum level at the edges of the MoSe$_2$ and WS$_2$ flakes due to the edge band bending induced by defects possibly due to
aging. This study reveals a new metrology to systematically determine ionization energies intrinsic to 2D crystals owing to the absence of gas absorption in ultrahigh vacuum (UHV) and the insulating SiO$_2$ support minimally interacting with the overlying 2D crystals.

### 4.2. Experimental Procedure

#### 4.2.1. Chemical Vapor Deposition

TMD flakes were synthesized using a chemical vapor deposition (CVD) technique based on previously reported procedures.$^{37,38,118,162}$ A 285 nm-thick SiO$_2$ thermally grown on a highly-doped silicon wafer (p-type, 12.0-16.0 Ω·cm) was chosen as a substrate material to produce optical contrast for as-grown flakes. The layer number of each TMD flake was verified using Raman spectroscopy, photoluminescence mapping, atomic force microscopy and optical contrast. To remove adsorbed water and unwanted hydrocarbons from their surfaces, samples were annealed for 4 to 12 hours at ~300°C in ultrahigh vacuum (UHV) prior to PEEM measurements.

#### 4.2.2. Photoemission Electron Microscopy

PEEM measurements were conducted in a LEEM-III system (Elmitec Elektronenmikroskopie GmbH) coupled to a tunable DUV light source. The spectral width of the DUV light was set to 50-100 meV throughout the wavelength range
used for the measurement. Photoemission spectra were acquired by sweeping through the kinetic energies of the photoemitted electrons with an electron filter. No aperture restricted the emission angle of the photoelectrons. Thus, the data presented here correspond to emission-angle integrated spectra. The energy resolution of the electron energy filter was set to 0.5 eV.

The leading (lower electron kinetic energy side) and trailing (higher electron kinetic energy side) edges of photoemission spectra yield information about the energies of the vacuum level and the highest occupied states near \( \Gamma \)-point (the center of the BZ), respectively.\textsuperscript{153,154} Maps of the vacuum level and the highest occupied states were obtained by fitting the photoemission spectra at each pixel and by correcting for the dispersion of the electron energy filter using the SiO\textsubscript{2} background. Because the vacuum level and the highest occupied states are extracted via fitting, we can determine the spatially-varying energy differences better than 0.05 eV despite a large energy resolution of the measurements (0.5 eV). The fitting procedures to extract the vacuum level and the valence band edge near the BZ center are identical to those cited. The origin of the energy scale is referenced to the vacuum level of one monolayer (1ML) TMDs.

4.3. Results and Discussion
4.3.1. PEEM Measurements of As Grown TMDs on Si/SiO$_2$

We measured three TMDs, MoSe$_2$, WS$_2$, and MoS$_2$, using photoemission electron microscopy (PEEM) to examine the influence of isoelectronic metals, Mo and W, and the chalcogen family (group 16), S and Se, to their ionization energies. Typical PEEM images of the TMD flakes are shown in (Figure 4-1). The images are acquired with the electron kinetic energy 0.1eV below the vacuum level ($E_{\text{vac}}$) of the 1ML area. Each flake consists of areas with varying thicknesses displayed in different image intensities. Higher photoemission intensity is shown as darker grey. The TMD thicknesses are verified using Raman spectroscopy, photoluminescence mapping, or optical contrast, and labeled in each image. The crystallographic alignment between layers can be inferred from the relative orientations of the edges of triangular flakes.$^{38}$ Most flakes display 2H or 3R stacking with random stacking orientation for thicker parts of the flakes.$^{123}$
Figure 4-1 1PEEM images of MoSe$_2$, WS$_2$, and MoS$_2$ acquired at 0.1 eV below E$_{\text{vac}}$ of the 1ML area. Photon energy used is 6.53 eV ($\lambda = 190$ nm).
Note that PEEM intensity does not change monotonically as a function of the local thicknesses. For instance, 1ML displays the strongest photoemission intensity among different thicknesses for MoSe$_2$ and MoS$_2$. While for WS$_2$, 1ML shows the least photoemission intensity. We postulate that this variation of the photoemission intensity is due to the photoemission cross section for different thicknesses of TMDs at the particular photon energy used in the measurement.$^{163}$

The information of the vacuum level and the highest occupied states near $\Gamma$-point (BZ center) is reflected on the leading (lower electron kinetic energy side) and trailing (higher electron kinetic energy side) edges of the photoemission spectra. (Figure 4-1) shows the false color representations of the series of photoemission spectra along the dash lines in (Figure 4-1) acquired using photons with various wavelengths. For all three TMDs, photoemission intensity varies significantly as a function of photon energy. One common feature throughout (a) to (c) in (Figure 4-1), is the higher relative intensities of the bare SiO$_2$ area with respect to the TMD flakes at larger photon wavelengths (lower photon energy). The relative intensity of the bare SiO$_2$ maximizes at 260-280 nm ($h\nu = 4.43–4.77$ eV, data not shown) consistent with the previous reports on the low photon energy photoemission of glassy SiO$_2$ and quartz implanted with metals ions.$^{145,146}$
Figure 4-2 Photoemission spectra of MoSe$_2$, WS$_2$, and MoS$_2$ in false color images acquired using selected photon wavelengths. Blue and red dots illustrate the fitted positions of the vacuum level and the highest occupied states near $\Gamma$-point (BZ center). The photon wavelength and the TMD thicknesses are indicated in each image.
Fitting the leading and trailing edges of the photoemission spectra visualizes the variations of the vacuum level ($E_{\text{vac}}$) and the highest occupied states (near $\Gamma$-point). The energies of the fitted edges are shown in (Figure 4-1) by red dots for $E_{\text{vac}}$ and by blue dots for the highest occupied states. The photoemission data acquired using photons with $\lambda = 185$ nm and 190 nm show the clearest contrast of $E_{\text{vac}}$ and the highest occupied states. We believe that the lack of photoemission intensity of the underlying SiO$_2$ at lower photon wavelength helps extract the $E_{\text{vac}}$ and the highest occupied states in the fitting process. For MoS$_2$, both $E_{\text{vac}}$ (red dots) and the highest occupied states (blue dots) increase as a function of the layer thickness. A similar trend is seen for MoSe$_2$ except that $E_{\text{vac}}$ and the highest occupied states of its monolayers are slightly smaller than those of bilayers. For WS$_2$, the highest occupied states near $\Gamma$-point (blue dots) moves closer to $E_{\text{vac}}$ with additional layers, similar to the cases of MoS$_2$ and MoSe$_2$. In contrast, $E_{\text{vac}}$ (red dots) becomes lower for larger thicknesses.

We note that TMD flakes with thicknesses that exhibit a lower $E_{\text{vac}}$ tend to be located at the edges of flakes. For example, 2ML and 3ML WS$_2$ display lower $E_{\text{vac}}$ than 1ML, and have a tendency to cover the edges of flakes preferentially as is shown in (Figure 4-1) (b). On the contrary, most edges of the MoS$_2$ flakes are terminated by 1ML. Although it is tempting to draw a simple conclusion, numerous studies suggest that the growth of TMDs via CVD or vapor transport processes is
highly anisotropic and far from thermodynamic equilibrium. It has been shown that
the relative positions of the precursor materials and the growth substrate can play
important roles. Establishing an explicit correlation between the growth
morphology and the work function variation would require further understanding
of the kinetic process during the growth.

4.3.2. Construction of Absolute Band Diagrams for TMDs

The absolute band diagrams of MoSe₂, WS₂, and MoS₂ are constructed based
on the average of the energy positions of E_{vac} and the highest occupied states near Γ-
point using the photoemission spectra of λ = 185 nm and 190 nm (Fig. 2). They are
shown in (Figure 4-1) (a), (b), and (c), respectively. The energy scale is referenced
to E_{vac} of 1ML TMDs. The predicted energy difference of the valence band edges at Γ-
point versus K-point (ΔE_{Γ-K}) and the reported optical band gap were used to
evaluate the positions of the highest occupied states at K-point and the conduction
band minimum, respectively. Additionally, for MoS₂, we assumed the work function
for monolayer to be 4.52 eV reported for a chemically exfoliated and assembled
large area monolayer MoS₂ on silicon support determined using photoemission
spectroscopy. The expected position of the Fermi level is shown as a blue
dash-dot line in (Figure 4-1) (c).
Figure 4-3 Absolute band diagrams of MoSe$_2$ (a), WS$_2$ (b), and MoS$_2$ (c) as a function of their thicknesses, constructed based on the photoemission spectra shown in Fig. 2. The blue dash-dot line in (c) indicates the Fermi level of MoS$_2$ reported in ref. Error! Bookmark not defined. The highest occupied state at K-point for WS$_2$ is not specified due to the lack of a reported value.
In (Figure 4-1), there are clear tendencies that both the valence band maximum and the conduction band minimum shift away from the vacuum level ($E_{\text{vac}}$) as the thickness of the TMDs increases. This trend is consistent with what is predicted for monolayer vs. bulk absolute band positions of TMDs.\textsuperscript{150–152} Also, the types of the band alignment at the lateral (in-plane) junctions of the same TMD with different thicknesses can be evaluated from the absolute band diagrams. WS\textsubscript{2} and MoS\textsubscript{2} are expected to display type-I heterojunctions between 1ML, 2M, and 3ML based on (Figure 4-1) (b) and (c). On the contrary, homojunctions made of MoSe\textsubscript{2} are likely to exhibit type-II staggered band alignment.

4.3.3. Absolute Band Diagram Comparison with Theory

We now compare the influence of isoelectronic metals (Mo and W) and the chalcogen family (S and Se) to their band positions. It is apparent in (Figure 4-1) that the valence band maximum and the conduction band minimum shift toward the $E_{\text{vac}}$ from MoS\textsubscript{2}, WS\textsubscript{2}, to MoSe\textsubscript{2}. In other words, ionization energy (i.e. the energy separations between the vacuum level and the valence band maximum) decrease monotonically from MoS\textsubscript{2}, WS\textsubscript{2}, to MoSe\textsubscript{2}, anticipated from the electro-negativities of the constituent atoms. To make this point clearer, the absolute band energies of monolayer MoSe\textsubscript{2}, WS\textsubscript{2}, and MoS\textsubscript{2} determined from our photoemission spectra are compared to those predicted using the density functional theory (DFT) calculations based on the GW approximation as shown in (Figure 4-1).\textsuperscript{150–152} Again, the experimental results are in qualitative agreement with the DFT predicted values.
The experimental and theoretical ionization energies are tabulated in (Table 2). The ionization energies of 2ML and 3ML TMDs determined experimentally also follow the expected decrease from MoS$_2$, WS$_2$, to MoSe$_2$ shown in (Table 2). We note that the decrease in ionization energies from MoS$_2$, WS$_2$, to MoSe$_2$ is also shown in multilayer flakes by the photoemission threshold measurements obtained by recoding the photoemission intensity as a function of the photon wavelength (Figure 4-1).\textsuperscript{153} We emphasize that this systematic trend of the ionization energies is experimentally verified for the first time to the best of our knowledge.
Figure 4-4 Absolute band diagrams of monolayer MoSe$_2$, WS$_2$, and MoS$_2$. The experimentally determined diagrams (blue bars) are compared to the reported ones predicted using density functional theory calculations (black bars). The red dash-dot and dash lines in (d) are the redox potentials for the reduction ($\text{H}^+/\text{H}_2$) and oxidation ($\text{H}_2\text{O}/\text{O}_2$) of water, respectively.
Table 2 Ionization energies of MoSe$_2$, WS$_2$, and MoS$_2$ in electron volts, determined from the photoemission spectra and predicted based on the reported density functional theory calculations.

<table>
<thead>
<tr>
<th></th>
<th>1ML</th>
<th>2ML</th>
<th>3ML</th>
<th>Bulk</th>
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<tr>
<td></td>
<td>PEEM</td>
<td>Theory</td>
<td>PEEM</td>
<td>PEEM</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>5.77</td>
<td>5.86</td>
<td>5.66</td>
<td>5.61</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>5.74</td>
<td>5.50</td>
<td>5.42</td>
<td>5.34</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>5.34</td>
<td>5.23</td>
<td>5.29</td>
<td>5.30</td>
</tr>
</tbody>
</table>
Figure 4-5 Comparison of the ionization energies acquired using photoemission spectroscopy and photoemission threshold measurements in MoSe$_2$, WS$_2$, and MoS$_2$. Blue and red dots illustrate the fitted positions of the vacuum level and the highest occupied states near $\Gamma$-point (BZ center) shifted by the excitation photon energy (190 nm or 6.525 eV). The red arrows with the energies indicate the ionization energies determined using photoelectron threshold measurement. The ionization energies determined from photoemission spectroscopy and photoemission threshold agree well for the area with a few layers, and display the systematic decrease from MoSe$_2$, WS$_2$, to MoS$_2$ as predicted by density functional theory calculations.
The valence band maximum and conduction band minimum align between different TMDs is one of the most important criteria to assess their usefulness in the technological applications. We suggest that the vertical heterojunction or heterobilayer comprised of any of the three TMD monolayers based on (Figure 4-1). Assuming that the interlayer coupling due to the Van der Waals is not significant, heterojunctions comprised of any of the monolayers MoSe$_2$, WS$_2$, and MoS$_2$ are likely to form a staggered (type-II) band alignment. Type-II band alignment is advantageous for hosting interlayer or indirect excitons expected to display a long lifetime, and for efficient charge separation in photovoltaic applications.

We anticipate that the spin-orbit coupling and the interlayer interaction could have some influence on the conclusion drawn here. The splitting of the highest occupied state at the $K$-point originates from the spin-orbit, and can be affected in the vertical heterojunctions. The interlayer interaction splits the highest occupied state at the $\Gamma$-point, and could make this state the valence band maximum. A type-II band alignment has recently been verified for the similar hetero-bilayer comprised of WSe$_2$ and MoSe$_2$ based on the angle resolved photoemission spectroscopy of such a heterostructure formed between a sheet of graphene and a graphite support.$^{168}$ Their result suggests a non-negligible interlayer splitting in such hetero-bilayer at $\Gamma$-point. As such, we expect that the resulting band alignment depends on the interplay between the two as well as the charge transfer from the supporting substrate and
the interface structure, for example interlayer distance and azimuthal misalignment (or twist), between TMD layers. PEEM coupled to DUV illumination can alleviate the possible impact of the conductive support by examining electrically isolated heterojunctions formed on SiO$_2$.

4.3.4. Using Ionization Energies to Determine Electrochemical activities of TMDs

Systematic verification of the ionization energies also allows us to access the electrochemical activities of TMDs, including the photocatalytic water splitting reaction.$^{150,151,160}$ The red dash-dot and dash lines in (Figure 4-1) indicate the redox potentials of the reduction (H$^+$/H$_2$) and oxidation (H$_2$O/O$_2$) of water, respectively. The data shown in (Figure 4-1) suggest that the 1ML MoS$_2$ can, in principle, be used as an anode as well as a cathode. On the contrary, WS$_2$ and MoSe$_2$ can be used only as cathode materials to produce hydrogen. It has been reported that the calculated conduction band minimum of MoS$_2$ based on density functional theory differs significantly between the local density approximation (LDA) and GW approximation (GWA).$^{161}$ As a result, the LDA result suggested that 1ML MoS$_2$ is not suitable as a cathode, yet the GWA predicts contrary. Our experimental result is in favor for the prediction based on the GWA, and contradicts with the LDA prediction.
4.3.5. PEEM Measurement Effects with TMD Aging

A closer inspection of the PEEM micrographs and the photoemission spectra allows us to examine the spatial variation of the electronic properties in TMDs. In (Figure 4-1) (a) and (b), we found a sizable shift of the electronic bands at the edges of the MoSe$_2$ and WS$_2$ flakes, extending a few microns toward the interior of the flakes as highlighted by the ovals with black dotted lines. The shift is as large as 0.5 eV as is shown in the $E_{\text{vac}}$ and the highest occupied states displayed by the red and blue dots in (Figure 4-1) (a) and (b). We speculate that the electrical transport of MoSe$_2$, WS$_2$, and their alloys as well as their junctions with metal contacts could be significantly influenced by the conductance through the edges.$^{158}$

We presume that this edge band bending results from the aging of MoSe$_2$ and WS$_2$ flakes. Recently, it has been reported by several groups that aging is initiated by the local oxidation of the edges.$^{156}$ In this context, the downward band bending in TMDs can be explained due to the Fermi level pinning by defects at edges, and not by the charge transfer between the TMDs and transition metal oxides. Tungsten oxidizes into semiconducting WO$_3$ with the large ionization energy of 9.8 eV.$^{157}$ Molybdenum forms stable oxides, which have the stoichiometry of MoO$_2$ and MoO$_3$ with a large work function and the ionization energies of 6.0 and 9.4 eV, respectively. When WO$_3$ (or MoO$_2$/MoO$_3$) comes into contact with WS$_2$ with the ionization energy of 5.74 eV (or MoSe$_2$ with 5.34 eV), we anticipate that the electrons would transfer from TMDs to oxides, forming the electron depletion
region. Such a depletion region is expected to develop an upward band bending extending into the interior of TMDs contrary to the downward bending shown in (Figure 4-1) (a) and (b). We note that MoSe$_2$ flakes exposed to air for a few weeks shows the increased ionization energy of 5.6-5.9 eV presumably due to the partial oxidation of the flakes. This observation further supports the notion of edge band bending due to the Fermi level pinning.

The apparent lack of a band bending in MoS$_2$ at the limit of our lateral resolution, in turn, suggests a higher chemical stability of MoS$_2$. The emergence of metallic edge states and the associated edge band bending are reported for the MoS$_2$ flakes, which had never been exposed to air, using scanning tunneling microscopy.$^{169,170}$ This metallic edge state-induced band bending has a few nanometers length scale suggesting a different physical origin from the ones we observed in MoSe$_2$ and WS$_2$ flakes. We can also exclude the possible influence of the stray built-in field affecting the trajectory of photoemitted electrons,$^{165}$ because the edge band bending is absent in the MoS$_2$ flakes or thicker parts of MoSe$_2$ and WS$_2$ flakes.

4.4. Concluding Remarks

We report the ionization energies of three prototypical TMD, monolayers and a few layers MoSe$_2$, WS$_2$, and MoS$_2$ on SiO$_2$, using photoemission electron microscopy combined with deep ultraviolet illumination. Based on this imaging spectroscopy, we extracted the ionization energy from the absolute band positions.
The ionization energy displays a progressive decrease from MoS$_2$, WS$_2$, to MoSe$_2$ which are in qualitative agreement with the theoretical values based on density functional theory calculations. Combined with the measured energy position of the valence band edge at the Brillouin zone center, we deduce that a heterojunction comprised of any of the three TMD monolayers would form a staggered (type-II) band alignment. In the PEEM micrographs, we found a sizable downward shift of the vacuum level at the edges of the MoSe$_2$ and WS$_2$ flakes induced presumably by defects due to aging. This study reveals a new metrology to systematically determine ionization energies intrinsic to 2D crystals owing to the absence of gas absorption in ultrahigh vacuum (UHV) and the insulating SiO$_2$ support minimally interacting with the overlying 2D crystals.
Chapter 5

Other Work (ARL)

5.1. Motivation

Reducing the weight of micro-vehicles has always been a primary concern for the U.S. Army when trying to provide soldiers advanced capabilities on the battlefield. The current-state-of-the-art energy storage platforms for micro-vehicles are bulky standalone packs that account for the majority of the weight. Developing flexible energy storage platforms that can bear mechanical loads, and are in essence the structure of the vehicles, allow for reduced payloads and smaller, streamlined architectures. The reduced payloads would allow engineers to add extra sensors and electronics that could aid the soldier on the battlefield. The streamlined architecture provide soldiers a small, low weight micro-vehicle that can be easily carried onto battlefield.

Though current lithium ion batteries are lighter than the previous generation of nickel cadmium batteries, further mass reduction can be achieved. The Lithium ion batteries on the market primarily use graphite as their anode material. The
maximum theoretical capacity of graphite is 372 mAh/g, however due to irreversible reactions during the solid electrolyte film formation realistic capacities are as low as 290 mAh/g\textsuperscript{171}. Various natural and synthesized carbon based anodic materials have potential to increase the capacities for lithium ion batteries. Carbon nanotubes (CNT) present good electrical properties along with high activated surface areas for Lithium ion intercalation on the nanotube surfaces and inside the nanotubes via end caps or sidewall openings\textsuperscript{172}. Doping heteroatoms is also an effective method of tailoring the nature of carbon materials. For example, polymerized carbon nitride nanobells exhibited an improvement of lithium ion intercalation with a reversible capacity of 480 mAh/g\textsuperscript{173}.

Other anode materials such as silicon and zinc oxide have higher theoretical capacities, 4200 mAh/g and 988 mAh/g respectively\textsuperscript{174}. However, these anodic materials have poor cycle performance due to the large lattice expansion and shrinkage during lithiation and delithiation process (400%) and the low electronic conductivity\textsuperscript{175}. Mitigating the effects of volume expansion and improving conductivity by using different architectures provide some promising routes to improve the capacity of lithium ion batteries. One methodology for solving issues regarding volume expansion and electronic conductivity is to utilize nanowire arrays (SiNW) which can accommodate volume expansion, provide one dimensional electronic pathways to the current collector and be highly more resistant to fracture during lithiation\textsuperscript{176}. Other approaches that have been taken is to utilize the core shell design approach where high capacity materials such as silicon are
encapsulated with a conductive polymer in order to maintain electronic conductivity to the current collector\textsuperscript{177}.

For multifunctional structural applications all these electrodes must be flexible in nature so they can conform or be in the shape of any structural material for micro-vehicles. By infiltrating polymers that are based on separator materials (PVDF) silicon nanowire array electrodes has can be rolled up into various shapes\textsuperscript{178}. In this work flexible SiNW-CNT composite electrodes were fabricated and shown to achieve high specific capacities as well as maintain sufficient cycle life for use-and-throw micro-vehicles. The silicon nanowires provides a high capacity core which can accommodate volume expansion and reduce the chances of fracture. Meanwhile a conductive carbon nanotube shell framework around the silicon nanowires provides an electronic percolation network and improves capacity retention of these highly flexible anode electrodes

Secondary power sources such as supercapacitors are also important in micro-vehicles for high power applications. Supercapacitors store energy within a helmholtz layer or electric double layer between electrodes and electrolyte\textsuperscript{179}. Due to this behavior extensive research has been on high surface carbon based materials which include CNTs, porous carbon, carbon nanospheres, graphene, etc\textsuperscript{180–182}. These type of materials provide very large electrode/electrolyte interface for improved capacities at a relatively low weight penalty. Most supercapacitor research usually utilizes liquid electrolytes due to their inherent high ionic conductivity, however for
multifunctional structural applications liquid electrolytes are not conducive to structural integrity and flexibility of design since they must be sealed to prevent electrolyte from drying out\textsuperscript{179}. Although solid polymer electrolytes have lower ionic conductivity they exhibit great structural integrity and flexibility of design, since they are chemically stable and do not degrade due to drying out\textsuperscript{183}.

Extensive work has been done on utilizing various high surface area carbon materials like CNTs with various solid polymer electrolytes such as Polyvinyl Alcohol/Phosphoric Acid to achieve highly flexible supercapacitor cells that can be bent at various angles and yet maintain high capacities\textsuperscript{184–189}. By sandwiching two Nafion infiltrated CNT forests D.P. Cole was able to achieve constant capacities upon strains of up to 6\% using a microtensile stage\textsuperscript{190}. This work highlights the inherent flexibility and structural integrity of these supercapacitor. Building upon D.P. Coles work with Nafion infiltrated CNTs forests, branched CNTs are utilized for improved capacity performance due to improved electronic percolation and more isotropic mechanical behavior due to the branched nature of the CNTs.

Exploiting feasible and scalable materials for multifunctional structural/energy storage materials is crucial for actual immediate implementation in micro-vehicles. Nanocomp Technology inc. has developed a scalable process of synthesizing carbon nanotube yarns and mats. In this work Nanocomp yarns and mats were explored for use as supercapacitors.
5.2. Experimental Procedure

5.2.1. Silicon Nanowire Array Fabrication

To synthesize SiNW arrays, a metal assisted wet chemical etching procedure was carried out. N-type silicon wafers (1 cm² samples) with a crystal orientation of (100) was first washed for 15 minutes with Piranha solution which is 3:1 volume ratio of H₂SO₄ (95-98%) and H₂O₂ (30%). The sample were then rinsed Deionized water and then immediately immersed in dilute HF (10% by volume) for 20 minutes in order to remove the native oxide layer and hydrogen terminate the surface of the samples. The samples were then covered in Ag nanoparticles by immersing the samples in a solution of 0.005M AgNO₃ + 5M for 2 minutes at room temperature. The samples were then rinsed off with deionized water and was placed in an 8M HF + 0.2M H₂O₂ solution for etching for 15 minutes at room temperature. The samples after the etching were immediately rinsed with dilute HF (10% by volume) and then with deionized water and allowed to air dry. HF concentration, temperature of etching, and time of etching are various parameters that can be adjusted to change the length the spacing and the diameters of the nanowires. The mechanism behind the metal assisted wet chemical etching process consists of a simultaneous redox events. When the silicon is subjected to Ag+ ions there is an immediate redox event where the Ag+ captures an electron from the silicon substrate causing the nucleation of Ag metal on the substrate surface as shown in equation 1. This electron transfer occurs due to the underlying energy level of Ag+/Ag system being
below the silicon valance band edges. The silicon directly underneath the Ag metal is oxidized as shown in equation 2. The concentrated HF then immediately dissolves the oxide therefore causing puts in the surface of the silicon substrate as shown in equation 3.

\[ \text{Ag}^+ (\text{aq}) + e^- \rightarrow \text{Ag}^0 (\text{solid}) \]

**Equation 5-1**

\[ \text{Si (solid)} + 2\text{H}_2\text{O} - 4e^- \rightarrow \text{SiO}_2 (\text{solid}) + 4\text{H}^+ \]

**Equation 5-2**

\[ \text{SiO}_2 (\text{solid}) + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + \text{H}_2\text{O} \]

**Equation 5-3**

### 5.2.2. Multiwall Carbon Nanotube Growth

Multiwall carbon nanotubes were synthesized using a water-assisted chemical vapor deposition (CVD) technique\textsuperscript{194}. The Fe catalyst layer was deposited
in various ways such as soaking the silicon nanowire arrays in 1 wt% Ferrocene in xylene, electron-beam (e-beam) evaporation of 10nm Al and 1.5nm Fe, and 2.5 wt% of iron acetate in ethanol. Samples were made using each of the various Fe catalyst layer deposition techniques and then placed in a quartz tube and heated to 775°C with an Ar/H₂ carrier gas. By using a bubbler a controlled amount of water vapor was introduced meanwhile ethylene was supplied as the carbon source. The time of growth was varied based on the duration of ethylene being introduced in the quartz tube.

5.2.3. Li-Ion Battery Anode Electrode Fabrication and Cell Assembly

The silicon nanowire and SiNW-CNT composites were pulled off from the bare wafer by infiltrating a blend of 5 wt% PvDF-HFP (Kynar Flex 3801, Arkema Inc.) and 5-10 wt% fumed silica with respect to the PVDF-HFP amount) in acetone at 60°C on a hot plate. Once fully infiltrated using a razor blade against the wafer the polymer film along with the SiNW-CNT composite was peeled off. A suspended flexible film was formed and used as anode material with the polymer film as the separator. Half cells were then fabricated in a Nitrogen filled glove box using the flexible film pressed against a stainless steel current collector and a lithium foil used as the counter electrode. The polymer film on the silicon nanowire and SiNW-CNT composites were used as the separator material. The polymer film was then soaked with 1M solution of LiPF₆ in 1:1 (V/V) mixture of ethylene carbonate (EC) and
dimethyl carbonate (DMC). These cells were assembled in a coin cell and pressed and sealed together.

5.2.4. Electrochemical Measurements for Li-Ion Cells

Galvanostatic charge-discharge measurements were the primary electrochemical measurements which were conducted using an Arbin BT 2000 Battery Analyzer. The cells were cycled at a slow rate of ~5µA/cm\(^2\) between 0.02V to 1.5V vs Li/Li\(^+\). Capacity retention for bare SiNW were compared with the SiNW-CNT composites.

5.2.5. Branched Multiwall Carbon Nanotube Growth

Branched multiwall carbon nanotubes were synthesized using a chemical vapor deposition (CVD) technique\(^{194,195}\). The Fe catalyst layer was deposited by electron-beam (e-beam) evaporation of 10nm Al and 1.5nm Fe on a bare silicon wafer. The samples were then placed in a quartz tube and heated to 790°C with an Ar/H\(_2\) carrier gas and a 1% (mg/ml) ferrocene/xylene solution (0.2ml/min).

5.2.6. Supercapacitor Fabrication

The branched CNT framework electrodes were processed by a polymer infiltration method\(^{190}\). The branched carbon nanotube framework attached to the silicon wafer was heated to 60°C on a hot plate and then slowly drop coated with
Nafion 115 solution (5wt% aliphatic alcohols). This was repeated until the electrolyte covered slightly over the branched carbon nanotube framework. The uniform polymer layer covering the top serves as the separator layer. Using a razor blade, the Nafion infiltrated branched carbon nanotube framework was peeled off the silicon wafer to form a free standing flexible electrode. A conductive polymer ink (Dupont silver conductor) was then applied to one back surface of the electrode using a doctor blade technique. The electrode was cut into two identical sized parts and pressed together to form a supercapacitor for electromechanical testing. A similar procedure was applied to the Nanocomp mats.

Nanocomp Technologies inc. carbon nanotube based yarn supercapacitors were fabricated by first aligning identically sized pieces of the yarn next to each other in parallel and then held down on a pre-coated predefined 3 cm section of Nafion 115 solution on a glass slide by a thin piece of scotch tape on the ends of the yarns (Figure 1-11). One of the edges of each of the yarns was taped onto aluminum foil to serve as current collectors. The yarns aligned next to each other were then coated with Nafion 115 solution to correspond to the 3 cm pre-coated section on the glass slide. The assembly was then heated for approximately 5 minutes at 60°C on a hot plate. Using a razor blade the Nafion coated yarns were removed from the glass slide. Other polymers were looked into to serve as binding agents. The coating was carried out similarly to the Nafion 115 solution coating. Baseline electrochemical performance was carried out on the freestanding flexible supercapacitors. For in-situ tensile and electrochemical testing the supercapacitor
fabrication was carried out in a similar fashion except with a transparency paper template tensile stage with 1 cm by 1 cm cutout.
Figure 5-1 Nanocomp yarn supercapacitor assembly
5.2.7. Electrochemical Measurements for Supercapacitors

Galvanostatic charge-discharge measurements were the primary electrochemical measurements which were conducted using an Arbin BT 2000 Battery Analyzer. Unless specifically specified all supercapacitors were charged and discharged at a consistent 5 µA. By clamping down the fabricated supercapacitors on a 200N load cell microtensile stage in-situ charge-discharge measurements were carried out upon various strains. The samples were mechanically loaded with an average strain rate of 0.01 min⁻¹ and held at various strains to run a series of charge-discharge cycles.

5.3. Results and Discussion

5.3.1. Scanning Electron Microscopy of Silicon Nanowires and Silicon Nanowire/Carbon Nanotube Hybrids

Scanning electron microscopy (SEM) was used to characterize the SiNW arrays (Figure 5-2). The length of SiNW are approximately 10µm with diameters ranging in the hundreds of nanometers. Ferrocene/xylene soaking followed by water assisted CVD resulted in carbon nanotube growth but with large amounts of amorphous carbon (Figure 5-2). Iron acetate soaking followed by water assisted
CVD resulted in conformal CNT coating around the SiNW (Figure 5-2). Al/Fe electron beam evaporation followed by water assisted resulted in carbon nanotube growth topographically grown on the tops of each of the SiNW.
Figure 5-2 SEM image of a side view of a SiNW array still attached on the silicon substrate.
Figure 5-3 (a) SEM image of the top view of a SiNW array with Fe/Xyl soaked WACVD CNT growth. (b) SEM image of the side view of a SiNW array with iron acetate soaked WACVD CNT growth. (c) SEM image of the side view of a SiNW array with Electron beam evaporation of Al/Fe followed by WACVD CNT growth.
5.3.2. Silicon Nanowires and Silicon Nanowire/Carbon Nanotube Hybrid Li-Ion Battery Performance

Galvanostatic charge-discharge measurements were conducted with Fe/Xyl soaked SiNW-CNT composite anodes and compared with bare SiNW anodes (Figure 5-2). Within 18 cycles the bare silicon nanowire anode’s capacity retention dropped to 2% of the original capacity of the anode. However, the composite anode maintains approximately 20% capacity retention and seems to stabilize after 20 cycles. The sudden drop in retention after the first cycle is primarily due to the solid electrolyte interface layer being developed over the anode material. The poor cycling performance of the bare SiNW anode is attributed to the pulverization of the nanowire upon cycling and disconnection from the current collector. The CNT framework provides an electronic percolation network to allow nanowires dismounted from the current collector to still be charged and discharged.
Figure 5-4 Capacity retention vs. cycle number of a bare silicon nanowire anode compared with Fe/Xyl soaked silicon nanowire/CNT composite anode.
5.3.3. Scanning Electron Microscopy of Branched Carbon Nanotubes

SEM was used to characterize the synthesized branched CNT frameworks (Figure 5-2). The framework is composed of multiwall carbon nanotubes with junctions.
Figure 5-5 SEM image of the branched CNT framework
5.3.4. Supercapacitor Performance of Branched Carbon Nanotubes and Commercial Nanocomp Carbon Nanotube Yarns

Branched Galvanostatic charge-discharge measurements were taken at various current densities for the branched carbon nanotube supercapacitors (Table 3). At very low current densities (0.1 mA/cm²) capacities were at approximately 12.57 F/g. However, at this low current density supercapacitor discharge times of approximately 7 minutes is not practical. The large dependence on current density on performance and average capacities could be attributed poor infiltration or lack of current collector interfaces. Since the branched CNT framework is random in growth tips of the CNTs may not be in contact with the current collector.

Galvanostatic charge-discharge measurements were conducted with Nanocomp CNT mats. Performance was poor at approximately 1.6 F/g. Since the mats are dense plies of CNTS pressed together infiltration of the polymer most likely did not penetrate the first ply. Therefore, the only one ply was active for each electrode. Galvanostatic charge-discharge measurements were also conducted with Nafion 115 solution coated Nanocomp CNT yarns and various other binding agents (Figure 5-2). Capacity performance was considerably high for Nanocomp yarns (Table 3). By the inclusion of binders performance increase but in doing so there is a large IR drop that occurs upon discharge. The supercapacitors with the inclusion of binding agents exhibited poor stability, within 48 hours the supercapacitors would not hold a charge.
Galvanostatic charge-discharge measurements were also taken upon various strains with the nafion coated Nanocomp yarn supercapacitors (Figure 5-2). Upon a large strain of 0.15 the supercapacitors were able to maintain a consistent capacity of approximately 70-75 F/g. It should be noted that it is difficult to de-convolute slipping from strain due to the fabrication limitations. Bare Nanocomp yarn only strains to about 0.07 before fracture. The charge-discharge curves proceeding the sudden in stress were very noisy which could signify loss in connection to the current collectors.
### Branched Carbon Nanotube

<table>
<thead>
<tr>
<th>Current Density (mA/cm²)</th>
<th>Capacity (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>12.57</td>
</tr>
<tr>
<td>0.2</td>
<td>6.85</td>
</tr>
<tr>
<td>0.5</td>
<td>2.69</td>
</tr>
<tr>
<td>1</td>
<td>0.98</td>
</tr>
<tr>
<td>2</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 3 Supercapacitor performance based on current density
Figure 5-6 Typical charge-discharge profile curves of Nanocomp yarn supercapacitors
<table>
<thead>
<tr>
<th>Polymer Electrolyte/Binder</th>
<th>Capacity (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>61.4</td>
</tr>
<tr>
<td>Nafion+PVDF+Silica</td>
<td>91.9</td>
</tr>
<tr>
<td>Nafion+ 80:20 wt. PMMA:PVDF</td>
<td>171.6</td>
</tr>
</tbody>
</table>

Table 4 Supercapacitor performance based on polymer electrolyte/binder
Figure 5-7 Stress strain plot with capacity in relation to various strains for Nafion coated Nanocomp yarn supercapacitors
5.4. Concluding Remarks

SiNW/CNT composite anodes presents a useful technique in mitigating the volume expansion effects for lithium ion batteries. By being able to utilize high theoretical capacity materials on a flexible electrode architecture, significant mass reduction is achieved along with being able to fabricated cells within the architecture of micro-vehicles. A significant amount of further work is necessary, such as comparing the various other techniques of CNT growth with one another. Also moving into solid electrolyte polymers is crucial for the end goal for micro-vehicle applications.

Branched CNTs supercapacitors performance was adequate compared to D.P. Cole’s previous work with CNT forest supercapacitors. Electromechanical performance must still be looked into and compared with the CNT forest supercapacitors. Due to a single unified frame work the mechanical properties could show a more isotropic behavior which is more suitable for micro-vehicles where strains could occur in various directions. Applying currently already scaled materials such as Nanocomp mats and yarns can serve as a more practical approach to developing multifunction structural/energy storage platforms for micro-vehicles. Nanocomp mats presented problems within infiltration due to the dense plies that exist in the structure. Looking into other polymer electrolytes and infiltration techniques could allow optimal performance with the Nanocomp mats.
yarns consistent performance upon various strain shows promise in multifunction structural/energy storage applications. Improving the experimental setup and supercapacitor fabrication techniques and designs is crucial for getting more meaningful and accurate stress-strain capacity relations. A solid polymer electrolyte comparison would be a useful study to determine the optimal polymer. The work performed this summer has just scratched the surface of multifunctional structural/energy storage platforms. Two avenues of energy storage were looked into and has shown potential in becoming useful for the future development of micro-vehicles.
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