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Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA  
RIVERSIDE

Synthesis and Characterization of Two-Dimensional Transition Metal Dichalcogenides,  
Alloys, and Heterojunctions Over Various Substrates via Chemical Vapor Deposition

A Dissertation submitted in partial satisfaction  
of the requirements for the degree of

Doctor of Philosophy

in

Materials Science and Engineering

by

David Barroso

December 2017

Dissertation Committee:

Dr. Ludwig Bartels, Chairperson

Dr. Boniface Fokwa

Dr. Phillip Christopher



The Dissertation of David Barroso is approved:

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Committee Chairperson

University of California, Riverside

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My thanks for all the people mentioned above is insurmountable. The time and sacrifices I have received from all of you has allowed me to accomplish everything which has brought me to the person who I am today. Thank you.

## ABSTRACT OF THE DISSERTATION

Synthesis and Characterization of Two-Dimensional Transition Metal Dichalcogenides, Alloys, and Heterojunctions Over Various Substrates via Chemical Vapor Deposition

by

David Barroso

Doctor of Philosophy, Materials Science and Engineering  
University of California, Riverside, December 2017  
Dr. Ludwig Bartels, Chairperson

Interest in two-dimensional (2D) electronic materials has exploded in the past decade, starting with the isolation of single layer graphene in 2004 by Novoselov.<sup>1, 2</sup> Similar to graphene, as a stable material in the single-layer, transition metal dichalcogenides (TMDs) further the advancement of 2D materials, but also provide an intrinsic transition to a direct bandgap in the single layer,<sup>3, 4</sup> thus giving these materials an advantage over graphene. Furthermore, TMDs have some of the highest notable  $I_{on}/I_{off}$  ratios of other 2D materials, making them extremely favorable.<sup>5, 6</sup> However, none of these 2D materials can be used as a standalone for modern electronic applications, therefore, heterostructures of these materials must be created.<sup>7-11</sup> An understanding of the way these materials are synthesized and ways to manipulate the synthesis is necessary to achieve such structures. Chemical vapor deposition (CVD) is a commonly used method to create single-layer TMDs<sup>12-18</sup> among others such as mechanical exfoliation<sup>19, 20</sup> and metal sulfurization/selenization.<sup>21, 22</sup> Here I present facile methods by which to synthesize pristine, pure, 2D TMDs via CVD process manipulation.<sup>19</sup> Additionally, in-situ operation of the CVD furnaces leads to the

ability to alloy these materials and create heterostructures, leading to a study of tunable optical and physical properties.<sup>12, 22, 23</sup> Last, I show the use of various/nanofabricated features on growth substrates in order to lead to a deeper understanding of the growth mechanisms for TMDs.<sup>14, 24-26</sup>

# Table of Contents

|                                                                                                                                                                |             |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| <b>ACKNOWLEDGEMENTS .....</b>                                                                                                                                  | <b>IV</b>   |
| <b>ABSTRACT OF THE DISSERTATION .....</b>                                                                                                                      | <b>VI</b>   |
| <b>TABLE OF CONTENTS .....</b>                                                                                                                                 | <b>VIII</b> |
| <b>LIST OF FIGURES .....</b>                                                                                                                                   | <b>X</b>    |
| <b>LIST OF TABLES .....</b>                                                                                                                                    | <b>XII</b>  |
| <b>LIST OF PUBLICATIONS .....</b>                                                                                                                              | <b>XIII</b> |
| <b>CHAPTER 1: INTRODUCTION.....</b>                                                                                                                            | <b>1</b>    |
| BACKGROUND.....                                                                                                                                                | 1           |
| TWO-DIMENSIONAL MATERIAL .....                                                                                                                                 | 1           |
| TRANSITION METAL DICHALCOGENIDES .....                                                                                                                         | 2           |
| CHALLENGES .....                                                                                                                                               | 2           |
| <b>CHAPTER 2: INSTRUMENTATION .....</b>                                                                                                                        | <b>4</b>    |
| RAMAN SPECTROSCOPY .....                                                                                                                                       | 4           |
| PHOTOLUMINESCENCE SPECTROSCOPY .....                                                                                                                           | 7           |
| ATOMIC FORCE MICROSCOPY .....                                                                                                                                  | 10          |
| PHOTOLITHOGRAPHY .....                                                                                                                                         | 11          |
| ATOMIC LAYER DEPOSITION.....                                                                                                                                   | 13          |
| ELECTRON-BEAM LITHOGRAPHY.....                                                                                                                                 | 14          |
| CHEMICAL VAPOR DEPOSITION .....                                                                                                                                | 16          |
| <b>CHAPTER 3: TRANSITION METAL DICHALCOGENIDES.....</b>                                                                                                        | <b>19</b>   |
| MOLYBDENUM DISULFIDE .....                                                                                                                                     | 21          |
| MOLYBDENUM DISELENIDE .....                                                                                                                                    | 23          |
| TUNGSTEN DISULFIDE.....                                                                                                                                        | 26          |
| TUNGSTEN DISELENIDE .....                                                                                                                                      | 29          |
| <b>CHAPTER 4: ALLOYS &amp; HETEROJUNCTIONS.....</b>                                                                                                            | <b>33</b>   |
| CHALCOGEN ALLOYING.....                                                                                                                                        | 33          |
| LATERAL HETEROJUNCTIONS .....                                                                                                                                  | 34          |
| <b>CHAPTER 5: MOS2-XSEX TRANSITION METAL DICHALCOGENIDE<br/>ALLOYS: IS THE PICTURE OF CONTINUOUS VARIATION OF MATERIAL<br/>PROPERTIES COMPREHENSIVE? .....</b> | <b>38</b>   |
| ABSTRACT: .....                                                                                                                                                | 38          |
| RESULTS .....                                                                                                                                                  | 40          |
| ACKNOWLEDGEMENTS: .....                                                                                                                                        | 48          |

|                                                                                                                                                     |           |
|-----------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| <b>CHAPTER 6: TWO-DIMENSIONAL MOS<sub>2(1-x)</sub>SE<sub>2x</sub> ALLOYS WITH TUNABLE BANDGAPS.....</b>                                             | <b>49</b> |
| INTRODUCTION .....                                                                                                                                  | 49        |
| METHODS .....                                                                                                                                       | 49        |
| RESULTS AND DISCUSSION.....                                                                                                                         | 50        |
| CONCLUSION.....                                                                                                                                     | 53        |
| <b>CHAPTER 7: LITHOGRAPHICALLY-ENCODED SINGLE-STEP DEPOSITION OF HYBRID 2-/3-DIMENSIONAL WSE<sub>2</sub> TRANSISTORS FOR ENHANCED MOBILITY.....</b> | <b>55</b> |
| ABSTRACT .....                                                                                                                                      | 55        |
| INTRODUCTION .....                                                                                                                                  | 56        |
| RESULTS AND DISCUSSION.....                                                                                                                         | 57        |
| CONCLUSION.....                                                                                                                                     | 64        |
| METHODS .....                                                                                                                                       | 64        |
| <i>Substrate Preparation</i> .....                                                                                                                  | 64        |
| <i>CVD Growth Method</i> .....                                                                                                                      | 65        |
| <i>Sample Characterization and Device Fabrication</i> .....                                                                                         | 65        |
| <b>CONCLUSION .....</b>                                                                                                                             | <b>67</b> |
| FINAL REMARKS .....                                                                                                                                 | 67        |
| OUTLOOK.....                                                                                                                                        | 67        |
| <b>REFERENCES.....</b>                                                                                                                              | <b>69</b> |

# List of Figures

|                 |    |
|-----------------|----|
| Figure 1 .....  | 6  |
| Figure 2 .....  | 7  |
| Figure 3 .....  | 9  |
| Figure 4 .....  | 10 |
| Figure 5 .....  | 11 |
| Figure 6 .....  | 13 |
| Figure 7 .....  | 14 |
| Figure 8 .....  | 15 |
| Figure 9 .....  | 18 |
| Figure 10 ..... | 20 |
| Figure 11 ..... | 22 |
| Figure 12 ..... | 25 |
| Figure 13 ..... | 27 |
| Figure 14 ..... | 28 |
| Figure 15 ..... | 30 |
| Figure 16 ..... | 31 |
| Figure 17 ..... | 32 |
| Figure 18 ..... | 34 |
| Figure 19 ..... | 35 |
| Figure 20 ..... | 36 |
| Figure 21 ..... | 37 |

|                        |           |
|------------------------|-----------|
| <b>Figure 22 .....</b> | <b>41</b> |
| <b>Figure 23 .....</b> | <b>44</b> |
| <b>Figure 24 .....</b> | <b>45</b> |
| <b>Figure 25 .....</b> | <b>47</b> |
| <b>Figure 26 .....</b> | <b>51</b> |
| <b>Figure 27 .....</b> | <b>52</b> |
| <b>Figure 28 .....</b> | <b>53</b> |
| <b>Figure 29 .....</b> | <b>59</b> |
| <b>Figure 30 .....</b> | <b>60</b> |
| <b>Figure 31 .....</b> | <b>61</b> |
| <b>Figure 32 .....</b> | <b>63</b> |

# List of Tables

**Table 1 .....5**

**Table 2 .....8**

**Table 3 .....17**

**Table 4 .....21**

**Table 5 .....24**

**Table 6 .....26**

**Table 7 .....29**

# List of Publications

## **MoS<sub>2-x</sub>Se<sub>x</sub> Transition Metal Dichalcogenide Alloys: Is the Picture of Continuous Variation of Material Properties Comprehensive?**

D. Barroso,<sup>a</sup> E. Preciado,<sup>a</sup> M. Isarraraz,<sup>a</sup> D. Le,<sup>b</sup> A. Barinov,<sup>c</sup> I. Tanabe,<sup>d</sup> M. Micklich,<sup>a</sup> V. Klee,<sup>a</sup> I. Liao,<sup>a</sup> S. Bobek,<sup>a</sup> T. S. Rahman,<sup>b</sup> P. A. Dowben,<sup>d</sup> and L. Bartels<sup>a</sup> (In progress)

## **Facile High-Vacuum Particulate-Free Deposition of Wafer-Scale Monolayer Transition Metal Dichalcogenides**

K. Almeida, M. Valentin, K. Yamaguchi, A. Berges, D. Barroso, M. Wurch, C. Huang, M. Gomez, I. Lu, A. Guan, Q. B. Yurek, A. Nguyen, A. E. Nguyen, V. Klee, J. Martinez, L. Bartels (In Progress)

## **Lithographically-Encoded Single-Step Deposition of Hybrid 2-/3-Dimensional WSe<sub>2</sub> Transistors**

I. Liao<sup>1</sup>, D. Barroso<sup>1</sup>, A. E. Nguyen, Q. B. Yurek, N. Duong, I. Lu, M. D. Valentin, M. H. Tahersima. Ma, A. J. Sorger, and L. Bartels (In Progress)

## **Strong Electron-Hole Symmetric Rashba Spin-Orbit Coupling in Graphene/**

## **Monolayer Transition Metal Dichalcogenide Heterostructures**

B. Yang, M. Lohmann, D. Barroso, I. Liao, Z. Lin, Y. Liu, L. Bartels, K. Watanabe, T. Taniguchi, and J. Shi. *Physical Review B* 96(4) 041409 (26 July 2017)

## **Band Structure Characterization of WS<sub>2</sub> Grown by Chemical Vapor Deposition**

I. Tanabe, M. Gomez, W. Coley, D. Le, E. Echeverria, G. Stecklein, V. Kandyba, S. Balijepalli, V. Klee, A. Nguyen, E. Preciado, I. Lu, S. Bobek, D. Barroso, D. Martinez-Ta, A. Barinov, T. Rahman, P. Dowben, P. Crowell, and Ludwig. Bartels, *App. Phys. Lett* **108**, 252103 (20 June 2016)

## **Chemical Vapor Deposition Growth of a Periodic Array of Single-Layer MoS<sub>2</sub>**

## **Islands via Lithographic Patterning of an SiO<sub>2</sub>/Si Substrate**

D. Sun, A. Nguyen, D. Barroso, X. Zhang, E. Preciado, S. Bobek, V. Klee, J. Mann, and Ludwig Bartels, *2D Mater.* **2** 045014 (12 Dec. 2015)

## Scalable Fabrication of a Hybrid Field-Effect and Acousto-Electric Device by Direct Growth of Monolayer MoS<sub>2</sub>/LiNbO<sub>3</sub>

E. Preciado, F. Schüle, A. Nguyen, D. Barroso, M. Isarraraz, G. von Son, I. Lu, W. Michailow, B. Möller, V. Klee, J. Mann, A. Wixforth, L. Bartels, and Hubert Krenner, *Nature Com.* **6** 8593 (8 Sept. 2015)

## Toward Ferroelectric Control of Monolayer MoS<sub>2</sub>

A. Nguyen, P. Sharma, T. Scott, E. Preciado, V. Klee, D. Sun, I. Lu, D. Barroso, S. Kim, V. Shur, A. Akhmatkhanov, A. Gruverman, L. Bartels and Peter Dowben, *Nano Lett.* **15**(5) 3364-3369 (30 April 2015)

## Superlinear Composition-Dependent Photocurrent in CVD-Grown Monolayer

## MoS<sub>2</sub>(1-x)Se<sub>2x</sub> Alloy Devices

V. Klee, E. Preciado, D. Barroso, A. Nguyen, C. Lee, K. Erickson, M. Triplett, B. Davis, I. Lu, S. Bobek, J. McKinley, J. Martinez, J. Mann, A. Talin, L. Bartels and François Léonard, *Nano Lett.* **15**(4) 2612-2619 (4 March 2015)

## A Direct Comparison of CVD-Grown and Exfoliated MoS<sub>2</sub> Using Optical

## Spectroscopy

G. Plechinger, J. Mann, E. Preciado, D. Barroso, A. Nguyen, J. Eroms, C. Schuller, L. Bartels and Tobias Korn, *Semicond. Sci. Technol.* **29** 064008 (6 May 2014)

## Postgrowth Tuning of the Bandgap of Single-Layer Molybdenum Disulfide Films by

## Sulfur/Selenium Exchange

Q. Ma, M. Isarraraz, C. Wang, E. Preciado, V. Klee, S. Bobek, K. Yamaguchi, E. Li, P. Odenthal, A. Nguyen, D. Barroso, D. Sun, G. Palacio, M. Gomez, A. Nguyen, D. Le, G. Pawin, J. Mann, T. Heinz, T. Rahman and Ludwig Bartels, *ACS Nano*. **8**(5) 4672-4677 (22 April 2014)

## 2-Dimensional Transition Metal Dichalcogenides with Tunable Direct Band Gaps:

## MoS<sub>2</sub>(1-x)Se<sub>2x</sub> Monolayers

J. Mann, Q. Ma, P. Odenthal, M. Isarraraz, D. Lee, E. Preciado, D. Barroso, K. Yamaguchi, G. Palacio, A. Nguyen, T. Tran, M. Wurch, A. Nguyen, V. Klee, S. Bobek, D. Sun, T. Heinz, T. Rahman, R. Kawakami and Ludwig Bartels, *Adv. Mater.* **26** 1399-1404 (12 Dec. 2013)

# Chapter 1: Introduction

## Background

The first application of semiconductors in electronics in the past century has been the basis of transistors, modern-day electronics, and the technological advances which lead to our modern world and the modern technological companies with it. In 1965, Gordon Moore, co-founder of Intel, stated an observation known to the world as Moore's Law, in which the number of transistors in an integrated chip would double approximately every two years. Since then, the observation has been modified to be doubling every 18 months, and for the most part has been true. To follow this trend, nodes, or transistor channels, have progressively been shrinking down, to the modern commercially available chip by Apple, the A10X, with a 10nm node, while IBM has revealed a 5nm silicon chip, the limits of current research publications. As we approach even smaller nodes in the next one or two decades, we approach the end of Moore's Law. One way to continue the advancements of electronics in this direction is to reevaluate the materials used in these transistors.

## Two-Dimensional Material

In 2004, Novoselov of the University of Manchester successfully isolated a single atomic thickness of carbon now known as graphene.<sup>1, 2</sup> Since this discovery, graphene has been a promising candidate for electrical applications due to its high mobility, high thermal conductivity, and most apparent, it's low volume.<sup>27-29</sup> However, graphene lacks a

traditional bandgap, thus giving rise to the need to explore other two-dimensional (2D) materials with unique properties.<sup>30</sup> Thus, the field of 2D materials has grown to include materials such as hexagonal boron nitride, phosphorene, germanene, silicene, and an ever-growing multitude of materials in a single-layer state, including transition metal dichalcogenides (TMDs).<sup>2, 17, 27, 31-34</sup>

## Transition Metal Dichalcogenides

TMDs are layered materials with weak interlayer Van der Waals forces in the form  $\text{MX}_2$  ( $\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{Se}$ ), where each combination provides a unique set of physical, optical, and electrical properties.<sup>33, 35-41</sup> TMDs raise interest for a wide range of applications from high-performance transistors to lasers.<sup>25, 42</sup> Unlike conventional 2D films, TMDs possess a transition from an indirect bandgap in the bulk to a direct bandgap in the single layer, allowing for expansion beyond electronics, into optoelectronics. The transition from an indirect bandgap at the  $\Gamma$ -point to a direct bandgap at the K-point as layers decrease can be attributed to a quantum confinement effect between layers.<sup>3, 35, 43</sup> TMDs also come in various phases. The work in this thesis focuses on molybdenum and tungsten based TMDs in the 2H, trigonal prismatic, semiconducting phase.

## Challenges

There are many challenges which must be overcome before TMDs and other 2D materials may be used in an industrial way for modern electronics. A simple search for articles with “MoS<sub>2</sub>” so far in 2017 brings up results over 10,000, indicating that TMDs are being studied intensely. TMDs can be found in various fields of engineering (mechanical,

chemical, biological, materials, electrical), physics, chemistry, biology, and numerous other fields. Each field and application bring with it a new set of challenges which must be overcome in one way or another. The challenges which are addressed in this thesis include: material growth, characterization, alloying, heterojunction synthesis, substrate selection, and device resistance.

## Chapter 2: Instrumentation

While atomic force microscopy can give a definitive layer number, 2D material layers can also be determined through optical contrast<sup>44</sup>. For TMDs, we can also use Raman and photoluminescence spectroscopy to determine layer number. There is a transition of the band structure being dominated in the bulk by the transition metal (Mo/W) at the  $\Gamma$ -point by a combination of  $d_{xy}$ ,  $d_{x^2-y^2}$ , and  $d_{z^2}$  orbitals to prominent K-point by the  $d_{z^2}$  in single layer<sup>4</sup>, leading to band alignment and a direct bandgap. This transition allows verification of single layer material through the presence of a strong optical response using photoluminescence spectroscopy<sup>45</sup>. Raman and photoluminescence spectroscopy was performed using a 532nm laser on a Horriba LabRam microscope equipped with a 100x objective, focusing 0.1mW power to a 1  $\mu$ m laser spot.

### Raman Spectroscopy

Raman Spectroscopy is a form of inelastic light scattering resulting from a ground state energy molecule being temporarily excited to a higher energy state via a photon source, or laser. This results in an inelastically scattered photon which is emitted at a lower or higher energy than the excitation photon, labeled Stokes and anti-Stokes respectively. These Stokes and anti-Stokes shifts are a direct result of the difference in the vibrational states of the material at rest and the excited states.

Through Raman spectroscopy we can see number of layers by the separation between the characteristic anti-Stokes  $A_{1g}$  out of plane and  $E_{2g}^1$  in plane vibrational mode of the TMD<sup>46</sup>.

Table 1 is a table of the characteristic  $A_{1g}$  and  $E_{2g}^1$  vibrational modes for their respective single layer TMDs<sup>47-49</sup> measured via raman spectroscopy on my as-grown TMD samples.

**Table 1:**

| <b>TMD</b>                                 | <b><math>A_{1g}</math> (cm<sup>-1</sup>)</b> | <b><math>E_{2g}^1</math> (cm<sup>-1</sup>)</b> |
|--------------------------------------------|----------------------------------------------|------------------------------------------------|
| Molybdenum Disulfide (MoS <sub>2</sub> )   | 400                                          | 380                                            |
| Molybdenum Diselenide (MoSe <sub>2</sub> ) | 250                                          | 238                                            |
| Tungsten Disulfide (WS <sub>2</sub> )      | 417                                          | 352                                            |
| Tungsten Diselenide(Wse <sub>2</sub> )     | 260                                          | 250                                            |

**Table 1  $A_{1g}$  and  $E_{2g}^1$  raman modes for MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub>.**

Specific differences in the  $A_{1g}$  and  $E_{2g}^1$  peaks can be used as an indication of layer number. For certain TMDs, as layer increases, the peaks will shift, or new peaks will arise, such as in WSe<sub>2</sub> in multilayer and bulk, a  $B_{2g}$  peak arises at 308cm<sup>-1</sup>.<sup>48</sup> Figure 1 shows the typical spectrum of each of these materials in a single layer. Relative intensities in addition to peak separation are clear indicators for layer number.

Figure 1: Raman Spectroscopy

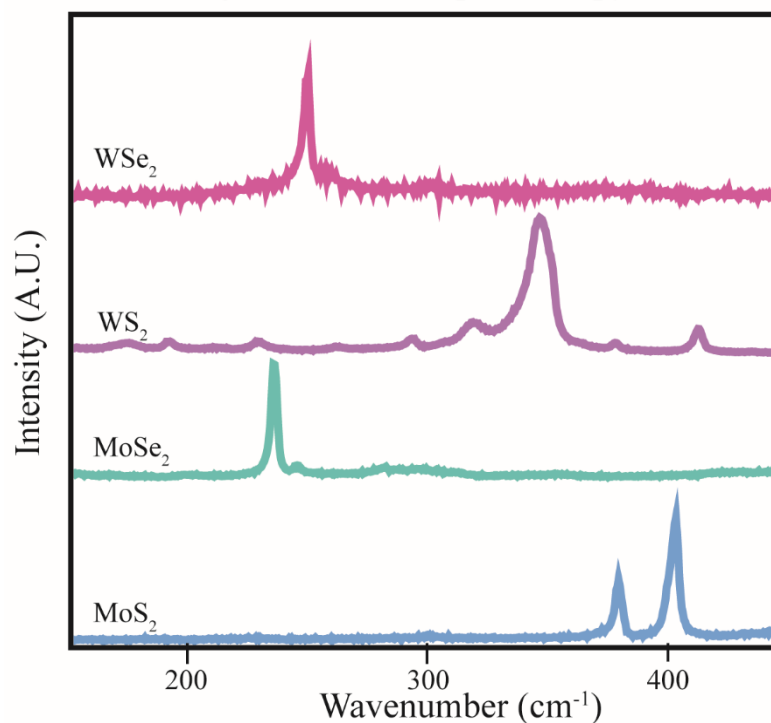


**Figure 1 Raman spectrum of MoS<sub>2</sub> (bottom), MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> (top) single layer films.**

Additionally, these pure materials may be alloyed with each other, which present familiar combinations of these spectra. Alloys of materials display characteristic  $A_{1g}$  and  $E_{2g}^1$  Raman modes of pure sulfur and selenium rich compounds, shown in figure 2.

Figure 2: Alloy Raman Spectroscopy

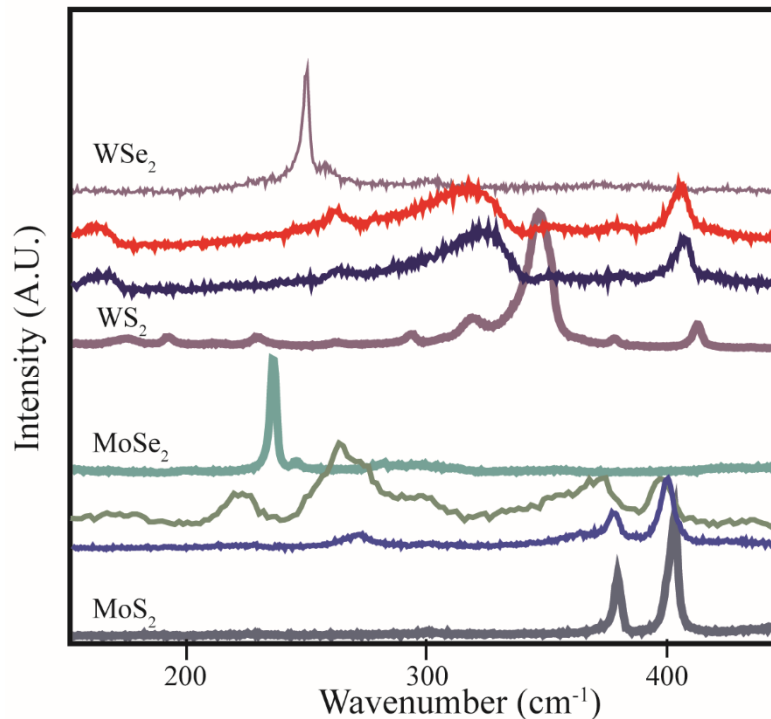


**Figure 2 Tungsten and molybdenum based alloy Raman spectrum, compared to the pure tungsten and molybdenum based TMDs on top and bottom respectively.**

When alloying the various TMDs, the active Raman peaks seen seem to be a combination of the pure material peaks. These peaks are shifted which can be attributed to strain of the material when compared to their pure counterparts as well as interactions between the differently weighted atoms.

## Photoluminescence Spectroscopy

Photoluminescence (PL) is light emission as the result of photon absorption in a material. An electron is excited to a higher energy state via a photon (laser) and then is allowed to relax back to its ground state via emission of a photon, PL. For TMDs, PL is made possible by the transition from an indirect bandgap in the bulk to a direct bandgap in the

monolayer, as previously explained. The energy of the photon which is emitted is directly related to the energy of the direct bandgap of the TMD. Table 2 is a table indicating the experimentally measured optical bandgaps of my as-grown single-layer TMD films.

**Table 2:**

| <b>TMD</b>                                | <b>Experimental (eV)</b> |
|-------------------------------------------|--------------------------|
| Molybdenum Disulfide ( $\text{MoS}_2$ )   | 1.85                     |
| Molybdenum Diselenide ( $\text{MoSe}_2$ ) | 1.55                     |
| Tungsten Disulfide ( $\text{WS}_2$ )      | 1.95                     |
| Tungsten Diselenide( $\text{WSe}_2$ )     | 1.60                     |

**Table 2 Optical bandgap for  $\text{MoS}_2$ ,  $\text{MoSe}_2$ ,  $\text{WS}_2$ , and  $\text{WSe}_2$ .**

Typically, PL intensity response for sulfur based TMDs is higher than for the selenium based, and tungsten based TMDs are also higher than the molybdenum based. Figure 3 below shows the normalized PL spectra for single layer TMD films.

**Figure 3: Photoluminescence Spectrum**

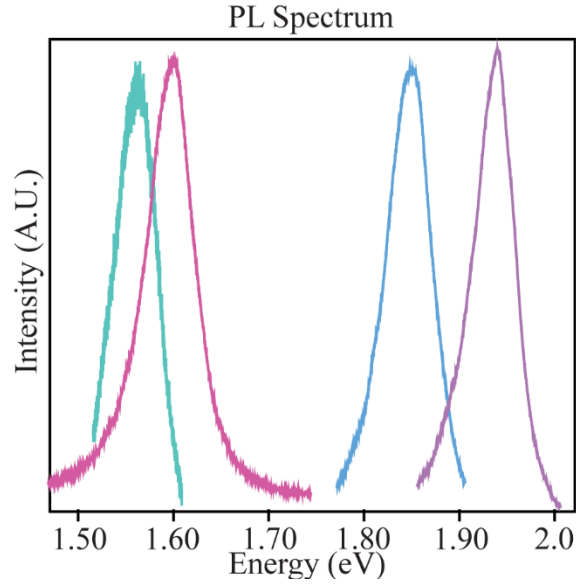


**Figure 3 PL spectrum of MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> (1.85, 1.55, 1.95, 1.60 eV respectively) single layers.**

TMD alloys ( $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  and  $\text{WS}_{2(1-x)}\text{Se}_{2x}$ ) show tunable bandgaps by composition of S:Se ratio. These alloys allow for band engineering anywhere between pure MoS<sub>2</sub>/WS<sub>2</sub> and pure MoSe<sub>2</sub>/WSe<sub>2</sub>. The range of these alloys is shown plotted against pure films in Figure 4.

**Figure 4: Alloy Photoluminescence Spectrum**

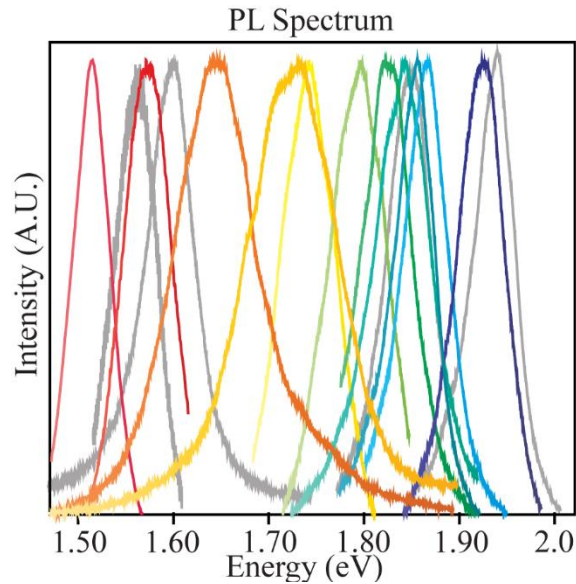


**Figure 4 Some of the possible optical bandgaps as measured through photoluminescence spectroscopy of alloys (colored) with respect to pure TMD materials (grey).**

Through engineering of the chalcogen composition present in the alloy, the observed optical bandgap can be shifted, allowing for an infinite spectrum and a much wider excitation range when in combination.

## Atomic Force Microscopy

Atomic force microscopy (AFM) is a method by which to tell the height profile of a surface. By maintaining a constant bias between a tip and a surface, the cantilever moves up and down. While the cantilever moves up and down, a laser which is deflected from that tip is then tracked on a photodetector. The movements of this laser are then manipulated to draw out the surface of the sample. Using AFM allows for a more precise determination of layer numbers, further combining with other characterization techniques to verify single-layer

films. Resolution required for a single layer of TMD would be greater than  $6\text{\AA}$ , which the AFM can resolve clearly. AFM was performed using an Asylum MFP-3D system in noncontact mode. Figure 5 below shows a typical setup of the cantilever passing over a surface.

**Figure 5: AFM**

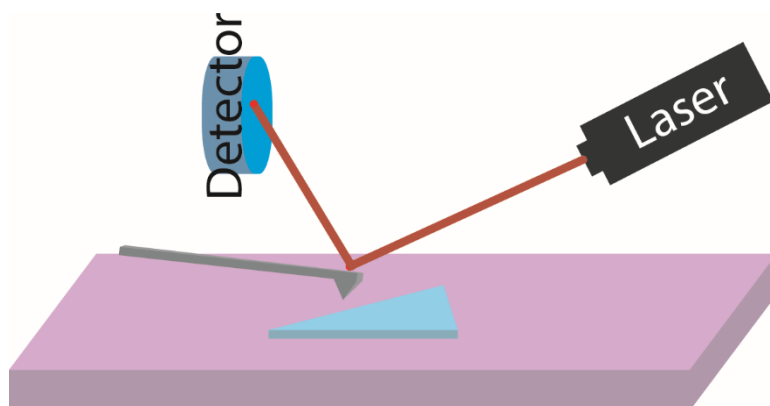


**Figure 5 Cartoon depiction of the basic principles of AFM.**

Some issues with performing AFM is resolving small surface features if the substrate is not even or if there are large clusters of oxide nearby the island of interest. Attempts to achieve resolution for large (micron) scale features and smaller (nano) scale features at the same time is very difficult in analyzing noise and signal, as well as limitations due to the tip dimensions. Additionally, AFM is also a more time-costly method, and was not ideal for every sample because we did not wish to expose samples to ambient conditions for too long due to oxidation.

## Photolithography

Photolithography, or optical lithography, is a microfabrication technique to pattern substrates/films. Light is used to activate a light-sensitive photoresist which is then

chemically treated to remove certain exposed or unexposed parts, called positive or negative lithography respectively. Patterns are determined by use of a photomask which protects regions and exposes regions according to how the mask is patterned. The machine which aligns the mask to substrate and exposes using a UV light source is called a mask aligner. The mask aligner I used for my processes is a Karl Suss Model MA-6 mask aligner. Substrates were prepared via a dehydration step at 110°C for 1 minute which was applied prior to spin coating with S1813 photoresist at 4000rpm for 45 seconds. Resist was then hardened by baking at 110°C for 60 seconds. The substrates are then aligned according to their feature sizes and needs. Longer exposure times will tend to end in larger regions of exposure and a slight undercut in the resist while a shorter time may end up in slightly smaller features than the mask. For my purposes, I used a 7.5s exposure time. Once patterns were exposed, a rinse in AZ300MIF developer was applied for 60 seconds with slight perturbation after 30 seconds to allow for resist which was exposed to be freely removed. The resist which was not exposed stayed on the substrate. Figure 6 shows a schematic diagram of this process as well as deposition of HfO<sub>2</sub> for patterning, as explained in chapter 8.

**Figure 6: Photolithography**

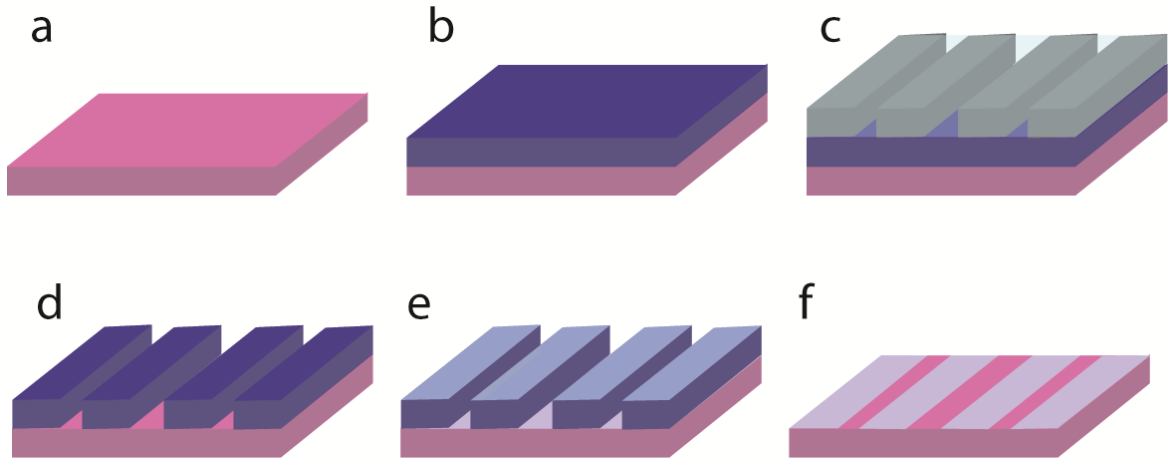


**Figure 6 (a) bare substrate. (b) resist on substrate. (c) chromium mask placed above. (d) exposed/developed regions lifted away. (e) ALD processing done over resist mask. (f) resist stripped to leave protected regions unchanged.**

## Atomic Layer Deposition

Atomic layer deposition (ALD) is a method in which precursors are adsorbed onto a substrate and then water is used to remove R-groups of the precursor and replace with oxygen, leaving an oxide in its stead. ALD works by terminating after a single layer by use of R-groups, allowing for extreme precision in deposition rates. Figure 7 shows a typical ALD reaction for  $\text{HfO}_2$  as used in my work.

**Figure 7: HfO<sub>2</sub> ALD**

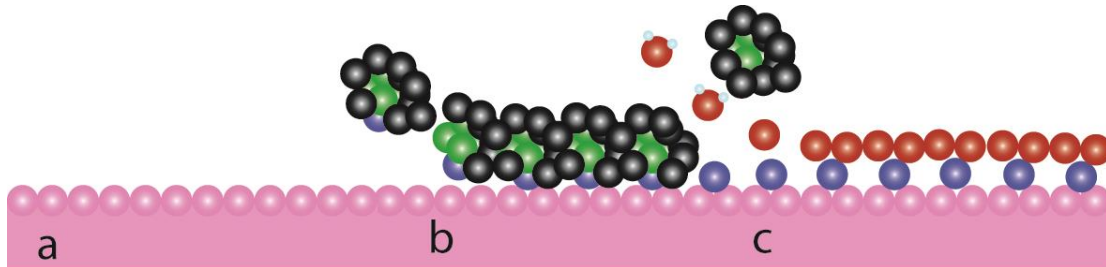


**Figure 7 Region (a) bare SiO<sub>2</sub>. (b) HfO<sub>2</sub> precursors being deposited and adsorbed onto the surface. (c) DI water replacing R groups from the HfO<sub>2</sub> precursor.**

Tetrakis(diethylamido)hafnium(IV) is deposited onto the substrate as shown in figure 7 region a and then region b depicts DI water vapor being pulsed to form a passivation layer with the precursor gas. Region c shows a completed HfO<sub>2</sub> layer on an SiO<sub>2</sub> surface. This is repeated for each cycle until the desired thickness is reached.

Figure 6e and 6f show ALD deposition over a patterned substrate and then resist being stripped, leaving a pattern of ALD HfO<sub>2</sub>. ALD was performed on the patterned substrate using a Cambridge Nanotech ALD system at 80°C for 12 cycles, giving 1.2nm.

Deposited substrates were then stripped of resist using an acetone wash for 30 seconds.

Substrates were then annealed at 900°C under an N<sub>2</sub> rich environment.

## Electron-Beam Lithography

Electron-beam, “e-beam”, lithography is another type of lithography in which materials are processed with nanofabricated features. E-beam lithography has the benefit of unique designs which are not restricted to a mask design, as well as theoretically being limited to

the size of an electron, as opposed to the size of UV light, as per optical lithography. The current limit of e-beam lithography is 10nm feature sizes.

Similar to optical lithography, substrates are covered by resist, this one which is activated by exposure to an electron beam. Negative sides of e-beam lithography is the low throughput where each design must be drawn manually and takes much longer than the large scale optical lithography exposure. Figure 8 shows a schematic diagram of typical e-beam lithography.

**Figure 8: e-beam lithography**



**Figure 8 (a) shows electron beam patterning of resist on an SiO<sub>2</sub> substrate. (b) development of exposed resist, exposing bare SiO<sub>2</sub> under exposed regions. (c) e-beam evaporated gold over entire substrate. (d) lift-off of resist, leaving gold only where the resist was developed and washed away.**

Using e-beam lithography and electron beam evaporation allows for fabrication of nanoscale features, particularly, nanoscale devices for transport characteristics. Substrates are prepared by rinsing with Acetone, IPA and water, followed by a 115°C dehydration baked. Once cleaned of organics, the sample is spun with polymethyl methacrylate (PMMA) C5 (5% chlorobenzene) at 4000 RPM for 45 seconds to reach a thickness of 500nm. The spun sample is then baked at 115°C for a minute and then follow patterning as shown in figure 8. Development is done using 1:3 methyl isobutyl ketone (MIBK):IPA for 30s followed by 30s of an IPA rinse.

## Chemical Vapor Deposition

All CVD processes were performed using a 1" quartz tube in a single-zone furnace (Lindberg 55031-S) with a maximum temperature of 1473K. Furnaces were heated via controlled programming using Honewell controller UDC3300. Alumina crucibles (CoorsTek 65560 Combustion Boat 1mL) were used to hold powder precursors. 300nm SiO<sub>2</sub>/Si substrates are treated with an Acetone rinse, an IPA rinse, a water cleaning rinse, and then a Piranha treatment. Piranha is an industry standard process to remove impurities from surfaces of silicon based substrates by mixing 1part (10mL) hydrogen peroxide and 3 parts (30 mL) sulfuric acid for 1 hour.

**Table 3:**

| Chemical Name                  | Formula                                                                                            | Supplier           | Purity  | CAS No.    |
|--------------------------------|----------------------------------------------------------------------------------------------------|--------------------|---------|------------|
| Molybdenum (VI) Oxide          | MoO <sub>3</sub>                                                                                   | Alfa-Aesar         | ≥99.95% | 1313-27-5  |
| Diphenyl Diselenide            | C <sub>12</sub> H <sub>10</sub> Se <sub>2</sub>                                                    | Sigma-Aldrich      | 98%     | 1666-13-3  |
| Carbon Disulfide               | CS <sub>2</sub>                                                                                    | Sigma-Aldrich      | ≥99%    | 75-15-0    |
| Benzenethiol                   | C <sub>6</sub> H <sub>5</sub> SH                                                                   | Sigma-Aldrich      | ≥99%    | 108-98-5   |
| Tungsten hexacarbonyl          | W(CO) <sub>6</sub>                                                                                 | Sigma-Aldrich      | 99.99%  | 14040-11-0 |
| Selenium (100mesh)             | Se                                                                                                 | Sigma-Aldrich      | ≥99.95% | 7782-49-2  |
| Sulfur (powder)                | S                                                                                                  | Sigma-Aldrich      | 99.98%  | 7704-34-9  |
| Ammonium Metatungstate Hydrate | (NH <sub>4</sub> ) <sub>6</sub> H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> • xH <sub>2</sub> O | Sigma-Aldrich      | 99.99%  | 12333-11-8 |
| Tetrahydrofuran                | C <sub>4</sub> H <sub>8</sub> O                                                                    | Fischer Scientific | ≥99.9%  | 109-99-9   |
| Ethanol                        | C <sub>2</sub> H <sub>6</sub> O                                                                    | Koptec             | 100%    | 64-17-5    |
| Nitrogen Gas                   | N <sub>2</sub>                                                                                     | AirGas             | 99.999% | 7727-37-9  |
| Argon Gas                      | Ar                                                                                                 | AirGas             | 99%     | 7440-37-1  |
| Hydrogen Gas                   | H <sub>2</sub>                                                                                     | AirGas             | 99.999% | 1333-74-0  |

**Table 3 Reagent list for all processes detailed in this work**

Once tube furnaces are appropriately loaded (detailed in Chapter 3) and then generally follow this CVD process for TMD growth:

1. Purge: High Purity N<sub>2</sub> flows through the tube at a rate of 5 Standard Cubic Feet per Hour (SCFH) in order to create an oxygen-free, inert environment. This flow is typically held at room temperature for 20 minutes.
2. Ramp: N<sub>2</sub> flow is decreased to a rate of 0.5 SCFH. The furnace is programmed to ramp from room temperature to the appropriate growth temperature

3. Inject: (If using an organic liquid precursor)  $N_2$  flow stays at 0.5 SCFH and the temperature is still at the growth temperature while the precursor is injected at a rate of 0.1 mL/s.
4. Hold:  $N_2$  flow stays at 0.5 SCFH and the temperature is still at the growth temperature for 10 minutes in order to allow the reaction to happen and for TMD films to grow.
5. Cool:  $N_2$  flow stays at 0.5 SCFH and the temperature is allowed to drop naturally below 473K, at which point the furnace is opened to remove the sample. This natural cooling is so as to not disturb the natural growth of the TMD.

Tube furnace set-ups are similar to what is shown below in figure 9, with some minor deviation for some different styles.

**Figure 9: CVD Furnace**

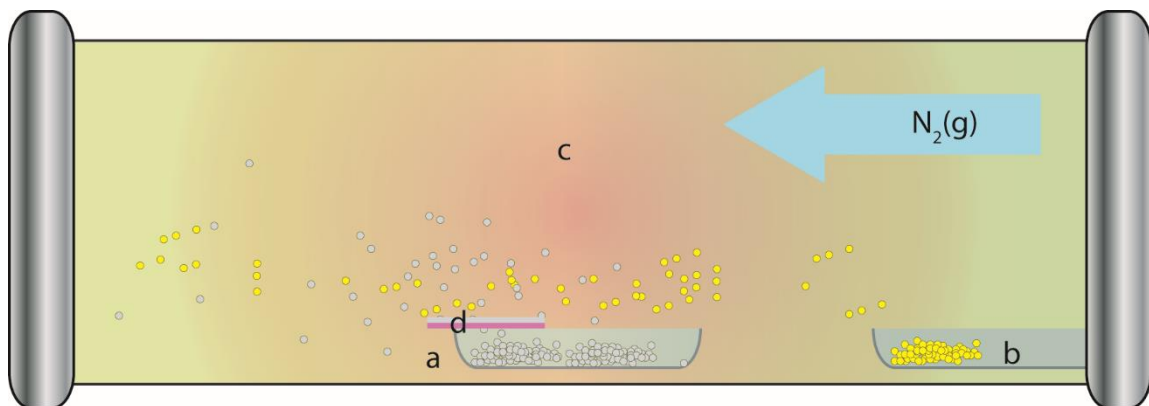


**Figure 9 CVD furnace set up for TMDs. Region a is the crucible placed in center of the furnace. Region b is the chalcogen placed upstream, offset from the hot zone of the furnace. Region c is the center, hot zone of the furnace where temperature is measured using a thermocouple. Region d indicates the substrate being placed directly over crucible of a, face down.**

# Chapter 3: Transition Metal

## Dichalcogenides

Typical studies of TMDs involve mechanical exfoliation, resulting in lowered optical response when compared to as-grown 2D films<sup>19</sup>. Using chemical vapor deposition (CVD), I am able to produce alloyed materials by adding variation to the typical CVD technique<sup>50</sup> such as introduction of organic precursors via a syringe injection<sup>12</sup> and drop casting or spin coating of the transition metal,<sup>51</sup> both giving control of alloy composition in resultant material. When grown via CVD on SiO<sub>2</sub>, these materials result in large single-crystal “islands” in the shape of triangles, visible optically over SiO<sub>2</sub> substrates.

**Figure 10: TMD CVD Optical Images**

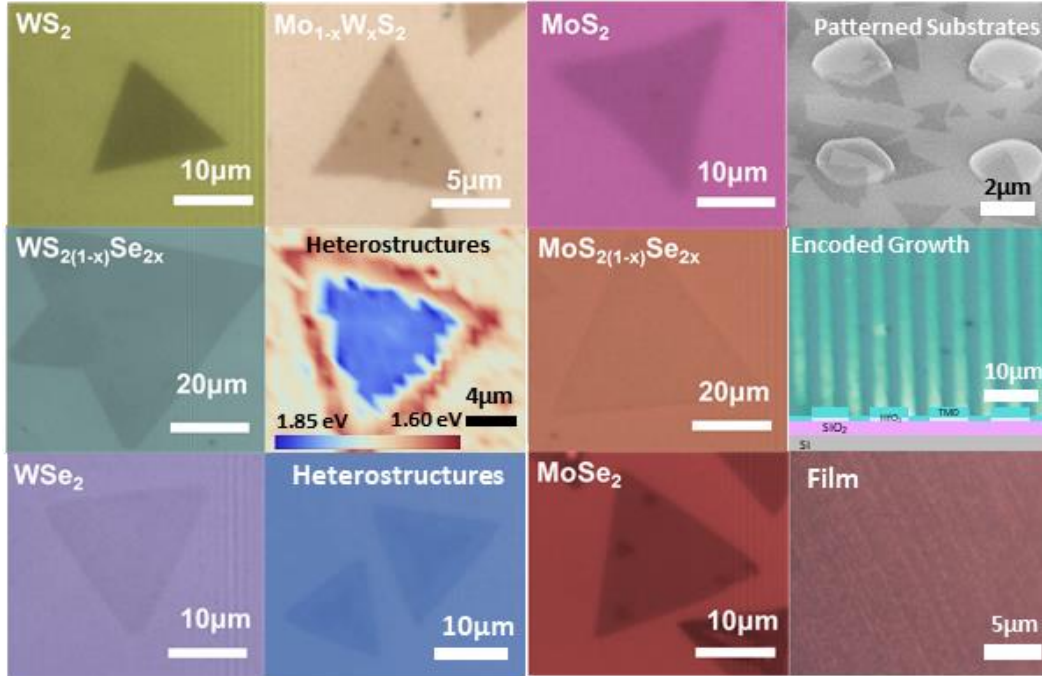


**Figure 10: Results of CVD grown TMDs**

While the array of TMDs all optically look similar, there are vast differences in the properties of each. Additionally, the CVD process for each of them are similar, but have slight distinctions beyond reagent which had to be optimized over hundreds of attempted CVD trials in order to maximize the desired properties of each growth.

This chapter details the properties of each individual material and how to optimize the growth for desired properties. Typically, the optical response (PL) is the figure of merit used to compare quality of samples. This is for the most part true, with the exception of a desired resulting structure or a substrate other than 300nm SiO<sub>2</sub>.

## Molybdenum Disulfide

Molybdenum Disulfide ( $\text{MoS}_2$ ) is the most studied of the TMD pure materials both in my studies and for other research groups.  $\text{MoS}_2$  is desired for numerous properties as detailed in table 4.

**Table 4: Properties of  $\text{MoS}_2$  and Growth Process**

| Property               | Detail                                                                                                                |
|------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Optical Bandgap        | 1.85eV                                                                                                                |
| Active Raman Modes     | $380\text{ cm}^{-1}$ , $400\text{ cm}^{-1}$                                                                           |
| CVD Growth Temperature | 660-670°C                                                                                                             |
| Ease of Growth         | Very Easy                                                                                                             |
| Stability              | Highly stable; few weeks ambient, few months in vacuum                                                                |
| Reagents               | $\text{MoO}_3(\text{g})$ , $\text{S}(\text{s})$ , $\text{CS}_2(\text{l})$ , $\text{C}_6\text{H}_5\text{SH}(\text{l})$ |

**Table 4 shows the typical properties and growth parameters for  $\text{MoS}_2$  CVD growth.** The growth of  $\text{MoS}_2$  via CVD is typically done with  $\text{MoO}_3$  in a crucible with a substrate laying on top, face down, placed in the center of a furnace at temperature near 670°C.

$\text{MoS}_2$  has an indirect bandgap in the bulk at 1.29eV in the  $\Gamma$ -point which transitions to a direct bangap at 1.90eV in the K-point.<sup>45</sup> The active Raman modes for  $\text{MoS}_2$  single layer materials are the  $A_{1g}$  and  $E_{2g}^1$  peak at 400 and  $380\text{ cm}^{-1}$  respectively. These observations allow for determining layer number through optical spectroscopy. However, CVD grown material may be strained from substrate interactions, causing Raman peaks to shift, making the  $20\text{ cm}^{-1}$  difference between peaks not an accurate depiction of the material thickness,

thus we use a combination of PL and Raman spectra as well as optical imaging as shown in figure 11.

**Figure 11: MoS<sub>2</sub>**

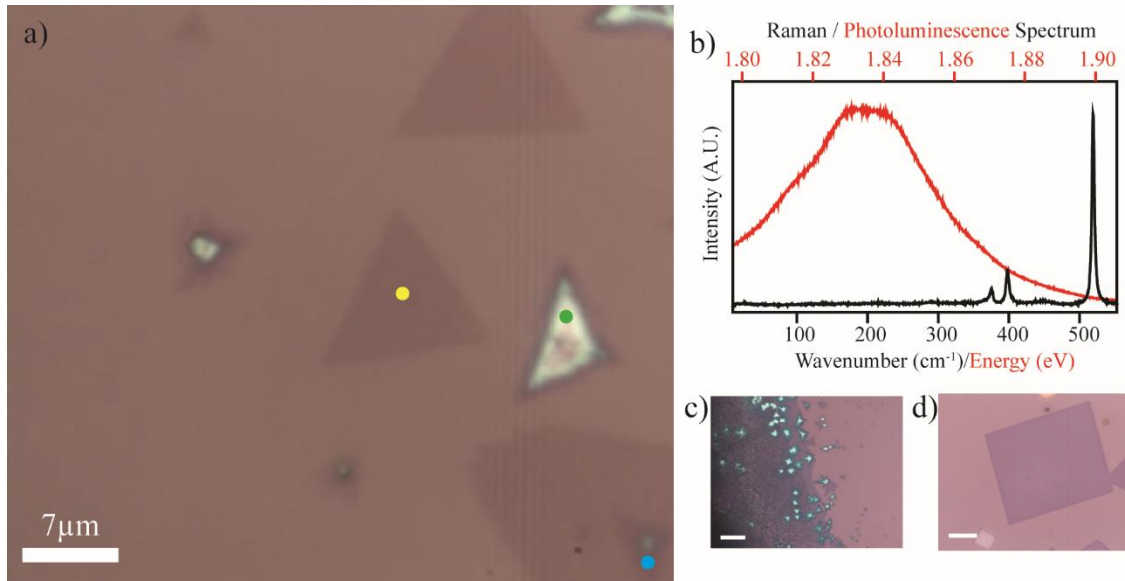


**Figure 11 (a) optical image of various layer counts. (b) Raman and Photoluminescence of typical single layer MoS<sub>2</sub> on 300nm SiO<sub>2</sub>/Si. (c) 10x optical image of a sample with single layer material, scale bar 10 μm. (d) 100x optical image of MoO<sub>3-x</sub>S<sub>2-x</sub>, scale bar 5μm.**

In figure 11a I show an optical image of MoS<sub>2</sub> grown on 300nm SiO<sub>2</sub>/Si substrate. The lighter regions are the substrate while the darker pink shapes are MoS<sub>2</sub>. White spots are thick regions of MoS<sub>2</sub> and possibly oxide growth. The region with a yellow dot shows a single layer “island” of MoS<sub>2</sub>, the blue dot shows bi-/tri-layer material, and the green dot shows a region of bulk MoS<sub>2</sub> growth. Figure 11b shows Raman and PL of a typical island as shown in 11a yellow, indicating Raman and PL as expected and described previously. Figure 11c shows a 10x optical image of a region outside of the thick crucible oxidized region. The purple film is single layer material with bulk (white/blue) growth in some spots which teeters out to islands; pink region is bare substrate. Figure 11d shows a typical region

which lacks sulfur and is oxidized. The growth parameters to achieve consistent single-layer islands requires tuning of the temperature and reagent content. Typical amounts of  $\text{MoO}_3$  range around 0.100g while amounts of sulfur powder should be about 7 times as much, near 0.700g. If samples are grown at too hot temperature, there is typically a “burned” look as shown in 11d where regions of growth are highly oxidized and not pure  $\text{MoS}_2$ . Lack of sulfur partial pressure also can lead to partially sulfurized oxides, but will typically end in an abrupt end from bulk material to bare substrate, leaving very little single layer material. Additionally, a lack of chalcogen may result in holes appearing in the islands and a much lower stability which will further oxidize at a faster rate than more chalcogen rich material.

## Molybdenum Diselenide

Molybdenum diselenide ( $\text{MoSe}_2$ ), like  $\text{MoS}_2$  has a direct bandgap and is in the 2H phase stable at ambient conditions. A list of properties can be found below in table 5 for the typical properties of  $\text{MoSe}_2$  grown on 300nm  $\text{SiO}_2/\text{Si}$ .

**Table 5: Properties and Growth Parameters of MoSe<sub>2</sub>**

| Property               | Detail                                      |
|------------------------|---------------------------------------------|
| Optical Bandgap        | 1.55eV                                      |
| Active Raman Modes     | 250 cm <sup>-1</sup> , 238 cm <sup>-1</sup> |
| CVD Growth Temperature | 700-720°C                                   |
| Ease of Growth         | More difficult                              |
| Stability              | Very unstable, few hours; Many defects      |
| Reagents               | MoO <sub>3(g)</sub> , Se <sub>(s)</sub>     |

**Table 5 properties and growth parameters for MoSe<sub>2</sub> CVD growth.**

MoSe<sub>2</sub> has an indirect bandgap in the bulk at 1.41eV in the  $\Gamma$ -point which transitions to a direct bangap at 1.55eV in the K-point.<sup>43</sup> The active Raman modes for MoSe<sub>2</sub> single layer materials are the A<sub>1g</sub> and E<sub>2g</sub><sup>1</sup> peak at 250 and 238 cm<sup>-1</sup> respectively. These observations allow for determining layer number through optical spectroscopy. We use a combination of PL and Raman spectra as well as optical imaging as shown in figure 12. We deem MoSe<sub>2</sub> as more difficult to synthesize because it is far less stable than MoS<sub>2</sub>.

**Figure 12: MoSe<sub>2</sub>**

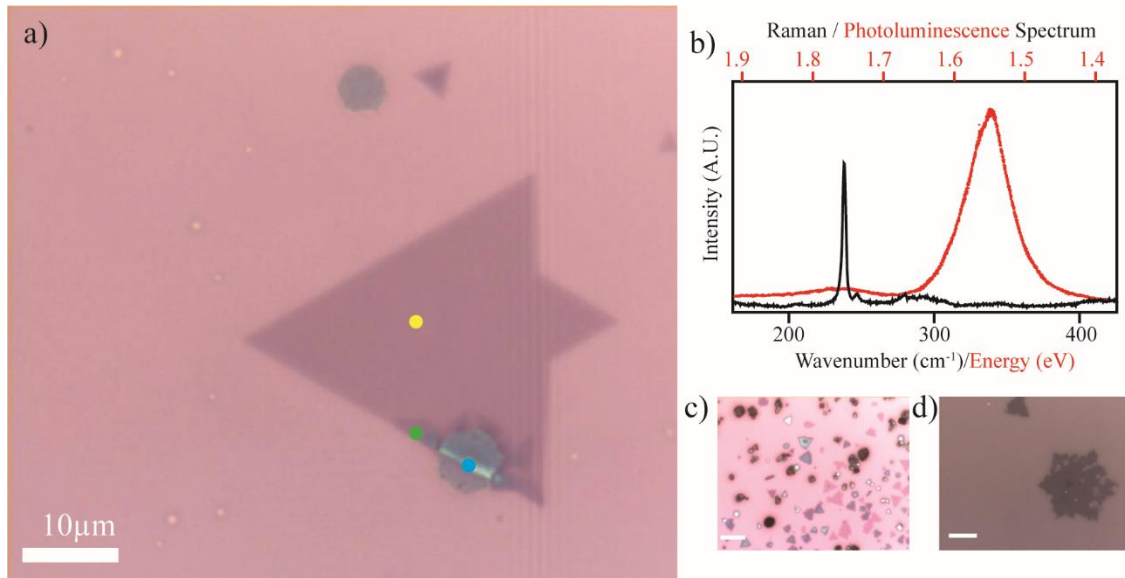


**Figure 12 (a) optical image of MoSe<sub>2</sub> island grown via CVD. (b) Raman and PL spectra for single layer MoSe<sub>2</sub>. (c) MoSe<sub>2</sub> growth at too high temperature (750°C). (d) MoSe<sub>2</sub> growth done with too little selenium, degrading.**

In that sense, most selenium based TMDs have low stability and oxidize quickly, as shown in the WSe<sub>2</sub> subject of this chapter. Similar to MoS<sub>2</sub>, MoSe<sub>2</sub> is also grown in CVD method using selenium instead of sulfur. Typical reagent quantities are about 0.100g of MoO<sub>3</sub> and about 1.00g of selenium. Higher amounts of selenium are used in order to ensure less vacancies which lead to a faster degradation rate. Figure 12 shows a typical CVD grown MoSe<sub>2</sub> island with single layer marked as yellow, bi-/tri-layer as green, and bulk as blue. Additionally, figure 12c shows the growth when the temperature is too high. Similar to the MoS<sub>2</sub> growths, we see a higher amount of oxide particles and a dirtier region of interest. Figure 12d indicates a growth which had too little selenium and can be seen with “holes” or degradation regions in the islands. A pristine sample of MoSe<sub>2</sub> would have high PL and the proper Raman signature as described above, which can be seen in figure 12b.

## Tungsten Disulfide

Tungsten disulfide ( $\text{WS}_2$ ) is an exciting material because it has more pronounced spin splitting than the molybdenum-based TMDs, as well as having the highest photoluminescence response. When measuring  $\text{WS}_2$ , we see that the PL response tends to be at least an order of magnitude higher than  $\text{MoS}_2$ . Table 6 below shows properties of  $\text{WS}_2$  and its growth parameters.

**Table 6: Properties and Growth Parameters of  $\text{WS}_2$**

| Property               | Detail                                                                                                                                                                    |
|------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Optical Bandgap        | 1.90eV                                                                                                                                                                    |
| Active Raman Modes     | $417\text{ cm}^{-1}$ , $352\text{ cm}^{-1}$                                                                                                                               |
| CVD Growth Temperature | 850-900°C                                                                                                                                                                 |
| Ease of Growth         | Very easy                                                                                                                                                                 |
| Stability              | Very stable.                                                                                                                                                              |
| Reagents               | $\text{WO}_3(\text{g})$ , $\text{S}(\text{s})$ , $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}(\text{s})$ [AMT], $\text{CS}_2(\text{l})$ |

**Table 6 Detailed properties of typical  $\text{WS}_2$  grown on 300nm  $\text{SiO}_2/\text{Si}$**

$\text{WS}_2$  transitions to a direct bandgap at 1.90eV, the largest bandgap of the pure TMDs. With this,  $\text{WS}_2$  has the highest PL response, making it a prime candidate for optical applications. However, the electrical characterization of  $\text{WS}_2$  is perhaps the lowest of the four TMDs described in this thesis. Additionally,  $\text{WS}_2$  has some spin splitting in the valence band, as shown in previously published work in collaboration with Tanabe et al.<sup>52</sup> While  $\text{WS}_2$  does not have as high spin splitting as  $\text{WSe}_2$ , it is still a possibly desirable material for its optical response.

**Figure 13: WS<sub>2</sub>**

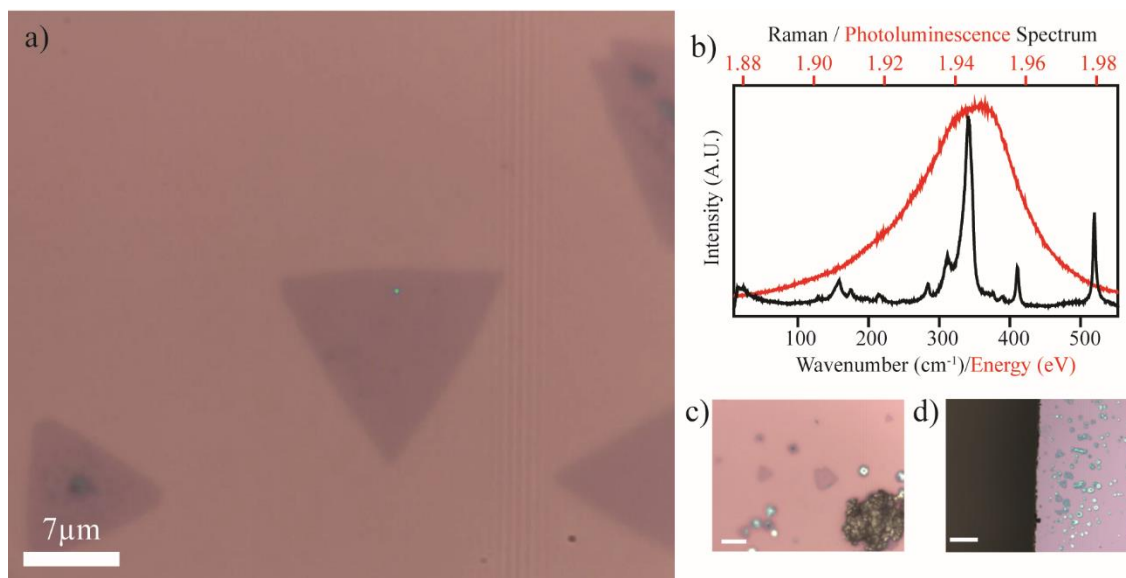


**Figure 13 (a) WS<sub>2</sub> optical image. (b) Raman and PL spectrum for WS<sub>2</sub> single layer. (c) Optical image of low reagent WS<sub>2</sub> growth. (d) Optical image of thick WS<sub>2</sub> growth.**

WS<sub>2</sub> has A<sub>1g</sub> and E<sub>2g</sub><sup>1</sup> Raman modes at 417 and 352 cm<sup>-1</sup>, however, as can be seen in figure 13b, there are also many other active peaks, even in the single layer. This makes Raman a poor figure of merit for determining single layer material. Additionally, few layer WS<sub>2</sub> also exhibits a high PL response, making PL relative intensity a poor figure of merit as well. However, when combining the optical image, as shown in 13a with a combination of PL and Raman, it is possible to gauge an educated guess of the thickness of the material. For that reason, it is a bit difficult to determine single layer material WS<sub>2</sub> as compared to the other materials which are a bit easier. Figure 13c and 13d show that the resulting thickness of the WS<sub>2</sub> growth is highly dependent on the concentration of the reagents. 14c shows a CVD growth with low concentration of AMT while 14d shows high concentration and a longer hold period. The CVD method for WS<sub>2</sub> varies a little from the molybdenum based

TMDs in that instead of having a crucible and a substrate in the center of the furnace, two substrates are stacked, with AMT (3.1mM) spun on the substrate twice at a speed of 4000RPM. By spinning multiple times, or less times, you can vary the concentration and quality of growth. Additionally, instead of using sulfur powder, I transitioned to using CS<sub>2</sub> because it is a liquid. CS<sub>2</sub> is heated in a bubbler to 90C and then bubbled into the carrier gas at optimal temperature. Figure 14 below shows a typical CVD set up for WS<sub>2</sub>.

**Figure 14: WS<sub>2</sub> CVD**

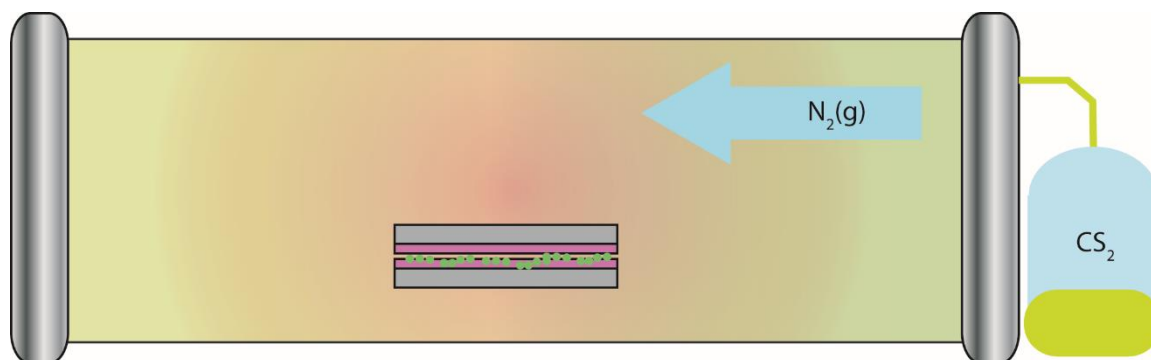


**Figure 14 shows a typical CVD furnace set up for WS<sub>2</sub> growth.**

The benefits of using AMT as a precursor instead of WO<sub>3</sub> is that AMT has a much lower melting point, thus raising the partial pressure for a lower growth temperature. WS<sub>2</sub> CVD with AMT requires a temperature near 850°C while CVD with WO<sub>3</sub> requires nearly 950°C. Also, you increase your yield by having a bottom sample which is where the AMT is spun on which will tend to have higher concentration of growth and a top sample which tends to be a bit cleaner than the bottom sample. This allows for specific substrate targeting during growth, as well as making it possible to have a much cleaner substrate after growth. Use of CS<sub>2</sub> provides benefit over using a solid powder in that you can control the moment you introduce the sulfur source, as well as making it a much cleaner growth. Overall, the

use of AMT and CS<sub>2</sub> are steps towards making these CVD processes more applicable in industry.

## Tungsten Diselenide

Tungsten diselenide (WSe<sub>2</sub>) is a very exciting material in that it has the highest spin splitting of the pure TMDs. WSe<sub>2</sub> also has a unique B<sub>2g</sub> peak which is only present in multilayer samples. This makes raman the optimal characterization technique for WSe<sub>2</sub> single layer. The table below has some properties of WSe<sub>2</sub>.

**Table 7: Properties and Growth Parameters of WSe<sub>2</sub>**

| Property               | Detail                                                                                                                                                          |
|------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Optical Bandgap        | 1.60eV                                                                                                                                                          |
| Active Raman Modes     | 360 cm <sup>-1</sup> , 350 cm <sup>-1</sup>                                                                                                                     |
| CVD Growth Temperature | 900-910°C                                                                                                                                                       |
| Ease of Growth         | Relatively easy                                                                                                                                                 |
| Stability              | Not very stable                                                                                                                                                 |
| Reagents               | WO <sub>3(g)</sub> , Se <sub>(s)</sub> , (NH <sub>4</sub> ) <sub>6</sub> H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> •xH <sub>2</sub> O <sub>(s)</sub> [AMT] |

**Table 7 shows detailed properties of typical WSe<sub>2</sub> grown on 300nm SiO<sub>2</sub>/Si**

Similar to WS<sub>2</sub> growth, WSe<sub>2</sub> uses AMT for lower temperature CVD and cleaner growth. Unlike WS<sub>2</sub>, we still utilize powder chalcogen precursors for safety and cost reasons. Selenium based chemicals are much more toxic than any of the sulfur based chemicals, making safety an extremely important aspect of CVD growth of WSe<sub>2</sub>. Figure 16 below shows typical CVD results of WSe<sub>2</sub>.

**Figure 15: WSe<sub>2</sub>**

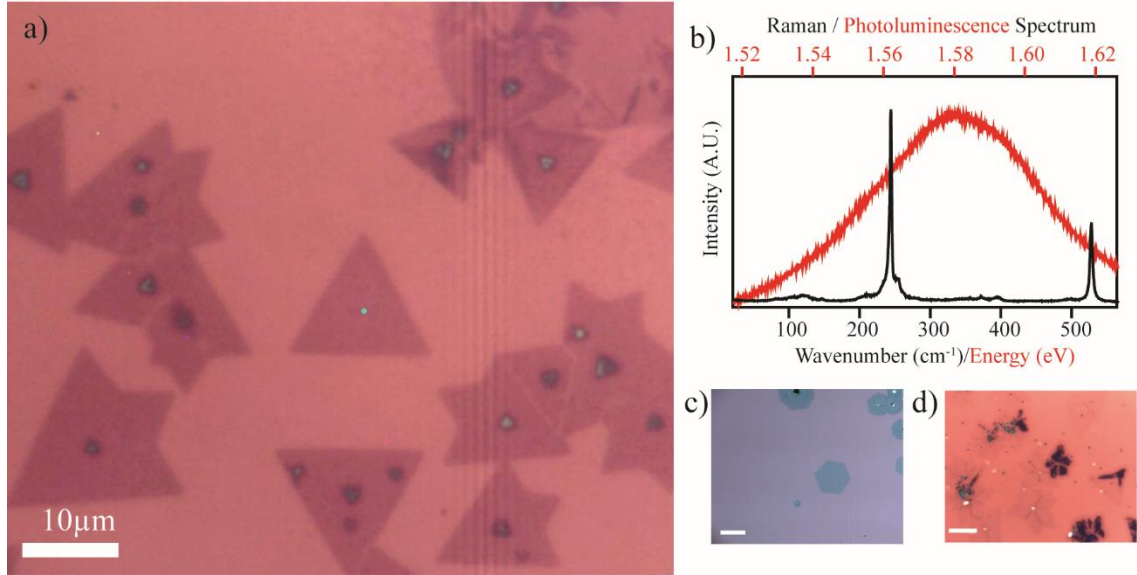


**Figure 15 (a) shows WSe<sub>2</sub> optical image. (b) Raman and PL spectrum for WSe<sub>2</sub> single layer. (c) large scale WSe<sub>2</sub> image with 50μm scale bar. (d) oxidized WSe<sub>2</sub> image.**

As shown in figure 15a, WSe<sub>2</sub> tends to grow in clusters, according to where AMT could be found. Islands which congregate together tend to have many defects in the interfaces and it is also visible that there are large seeds in the centers of islands. Figure 15b shows the typical PL and raman for a single layer of WSe<sub>2</sub>; there is no B<sub>2g</sub> peak present at 308cm<sup>-1</sup> which indicates a single layer. Figure 15c shows that WSe<sub>2</sub> can also grow as hexagons, and in very large scales; scale bar is 50μm. Finally, figure 16d shows that WSe<sub>2</sub> is very unstable where this sample was taken out 1 day before and left in ambient atmosphere. The presence of thick material persists, but grain boundaries become increasingly apparent.

**Figure 16: Raman and PL study of WSe<sub>2</sub> multi-layers.**

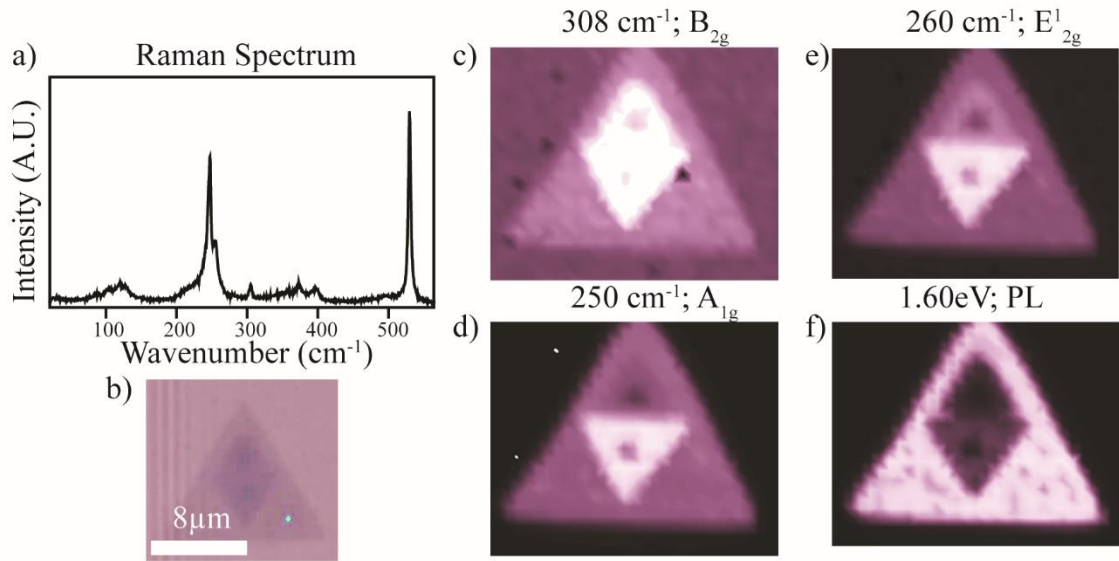


**Figure 16 (a) Raman spectrum of tri-layer WSe<sub>2</sub>. (b) optical image of WSe<sub>2</sub> island of 1-/2-/3-layers. (c-d) 308 cm<sup>-1</sup>, 260 cm<sup>-1</sup>, 250 cm<sup>-1</sup>, and 1.60 eV Raman/PL mapping of island shown in (b) with lighter color meaning higher intensity.**

Figure 16 shows a study of Raman between 1-/2-/3-layer WSe<sub>2</sub>. By Raman and PL mapping, it is apparent that the peak intensities for the 3 active raman peaks increase as layer numbers increase. Through this study we see that the optical image is showing 3 unique layer numbers, with the largest triangle being 1-layer, the top triangle facing the same way being bi-layer, and the concentric, flipped triangle being tri-layer.

In addition to having a relatively facile, successful growth process, WSe<sub>2</sub> is also able to be grown on multiple substrates. Figure 17 a-d show WSe<sub>2</sub> being grown on 300nm SiO<sub>2</sub>/Si, HfO<sub>2</sub> fortified substrates, native oxide SiO<sub>2</sub>, and XY-128 Black LiNbO<sub>3</sub> respectively.

### **Figure 17: WSe<sub>2</sub> Growths**

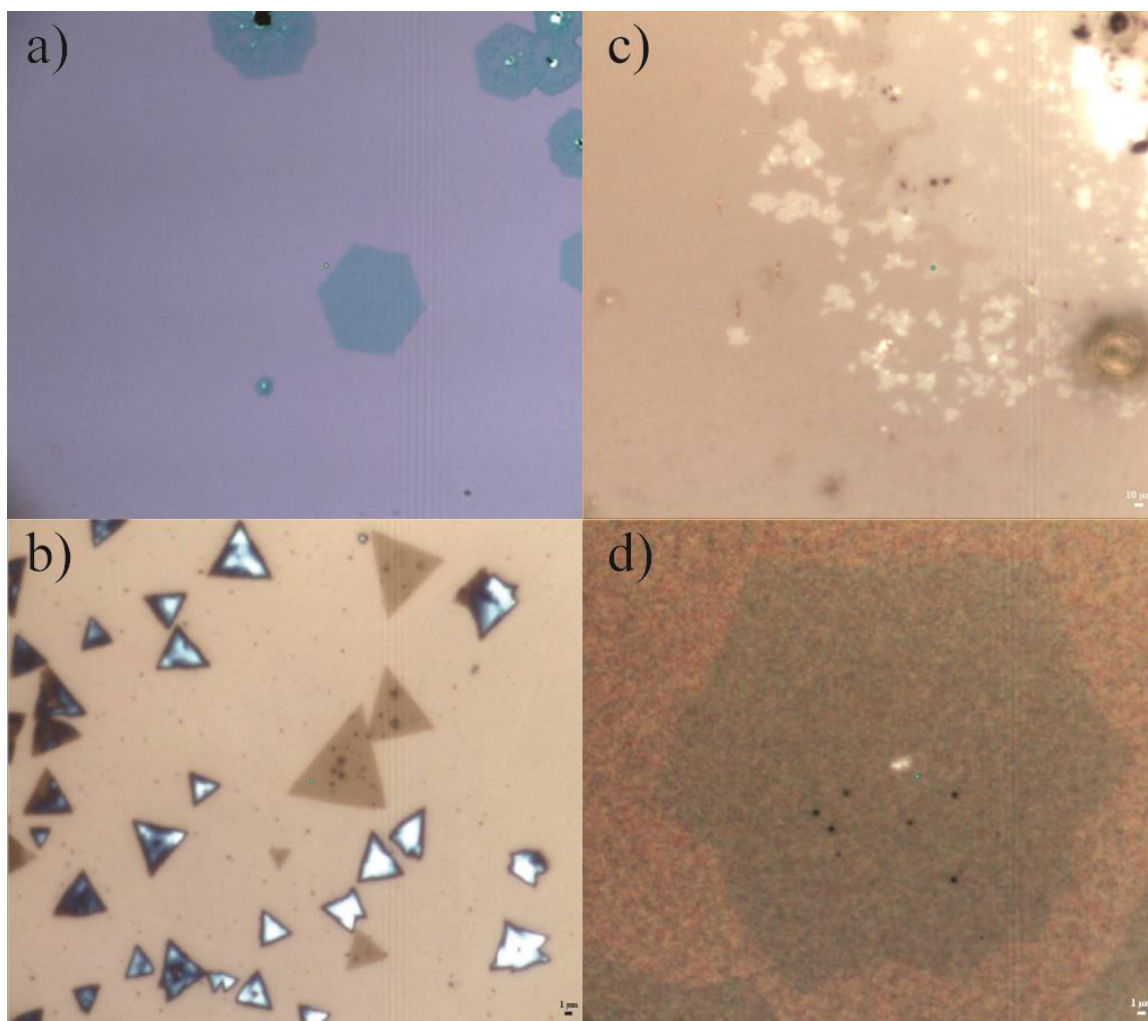


**Figure 17 shows CVD growth of WSe<sub>2</sub> over (a) 300nm SiO<sub>2</sub>, (b) HfO<sub>2</sub> fortified SiO<sub>2</sub>, (c) Native oxide Si, and (d) XY-128 Black LiNbO<sub>3</sub>.**

# Chapter 4: Alloys & Heterojunctions

Expanding beyond a binary system towards a ternary system through alloying ( $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ), we see that optical properties of the materials are tunable in a near-linear fashion.<sup>12, 13, 40, 53-55</sup> This chalcogen alloying has been studied extensively to show that raman modes show traces of pure materials, bandgap engineering is linearly dependent on composition, and electronic properties behave similarly.<sup>23</sup> Alternatively, Transition metal based alloying shows a superlinear bowing of the optical properties of the material.<sup>56, 57</sup>

These non-periodic alloys maintain an effective bandgap while having no defined band structure<sup>55</sup>. One benefit of alloying is that we may be able to overcome the problem of instability<sup>40</sup> and ready oxidation as seen with heavier chalcogen based TMDs<sup>20</sup>, while maintaining a wide range of optical excitation and electrical response.

## Chalcogen Alloying

Alloying of the chalcogen atoms can be made possible through the use of solution or powder based combinations of reagents. Solution based combinations tended to be injected solutions of  $\text{CS}_2$ /Benzenethiol and  $\text{Ph}_2\text{Se}_2$  in THF while powder based mixes tended to be powdered selenium and sulfur. The use of these carbon-based solutions ended up with a resulting carbon film present in on the film, noticeable by amorphous carbon Raman modes present. In order to remove this excess carbon, the use of  $\text{H}_2$  gas was employed during the

reaction time to cause some chains of  $H_{2x+2}C_x$  or some cyclic carbon rings to be removed during the growth.

**Figure 18: Alloy PL Spectra**

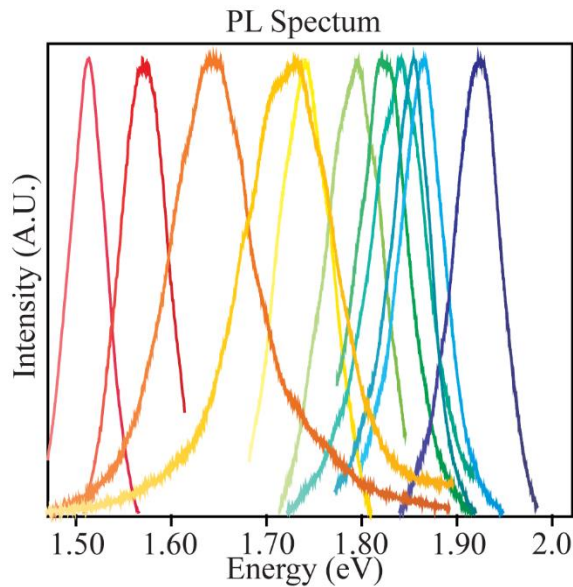


**Figure 18 the range of PL for pure and chalcogen alloyed materials,  $MoS_{2(1-x)}Se_{2x}$ ,  $WS_{2(1-x)}Se_{2x}$ .**

Through control of the chalcogen ratios, alloys were able to be created, resulting in PL spectra ranging anywhere from 1.55eV (Pure  $MoSe_2$ ) to 1.95 (pure  $WS_2$ ) as shown above in figure 18.

## Lateral Heterojunctions

Injection and bubbling growth methods has also introduced a control of when chalcogens are presented, allowing for specific alloys or materials to be produced or stopped, relatively quickly. The first method by which heterojunctions have been made is by sequential injection of the various chalcogen precursors. Figure 20 below shows a heterojunction with an abrupt transition from a selenium rich alloy in a sulfur rich alloy. Optically, there is no

separation between the two different semiconducting materials (20a), but through PL mapping, we can see that there is a clear shift in the optical bandgap, with red representing 1.71eV and the blue representing 1.83eV (20b). 20c shows that there is also a distinct step height difference at this junction with the selenium based TMD edge being 0.71nm thick and the center sulfur rich TMD being 0.06nm thinner, as would be expected.

**Figure 19: Alloy Heterojunction**

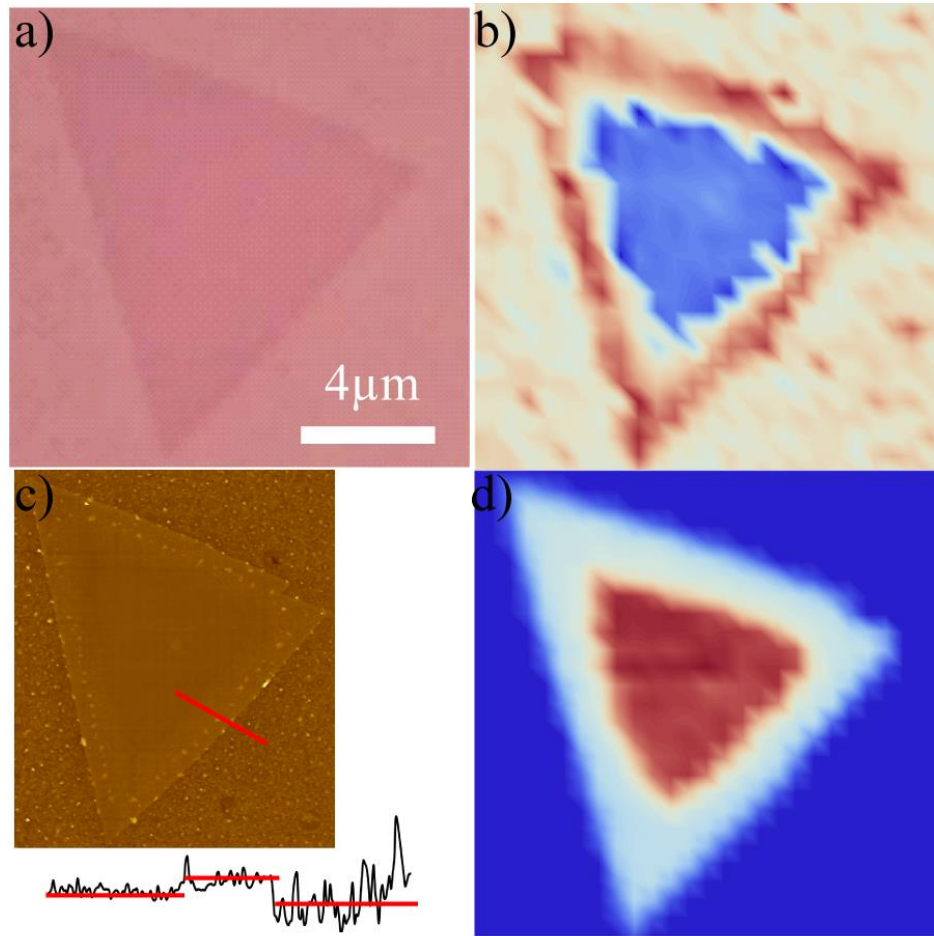


**Figure 19 (a) optical image of heterojunction. (b) PL band position map. (c) AFM. (d) PL intensity map.**

Figure 19d shows an intensity map of the PL for the island which further agrees with previous findings that the more selenium content in an alloy, the lower the PL response. Additionally, by using the temperature gradient of the furnace and moving the tube, I can activate the different transition metal precursor. Figure 20a shows an optical image of a growth in which MoSe<sub>2</sub> was grown (center) and then the tube was shifted to a hotter area to allow for WSe<sub>2</sub> to grow surrounding that island. Raman mapping in 20b shows mapping of the 238cm<sup>-1</sup> peak, the the E<sub>2g</sub><sup>1</sup> peak for MoSe<sub>2</sub> with a higher response in the center and then 20c shows Raman mapping of the 250cm<sup>-1</sup> E<sub>2g</sub><sup>1</sup> peak for WSe<sub>2</sub>, showing higher intensity on the outside part. This raman mapping confirms a sharp transition from one material to the other.

**Figure 20: Mo/WSe<sub>2</sub> lateral heterojunction**

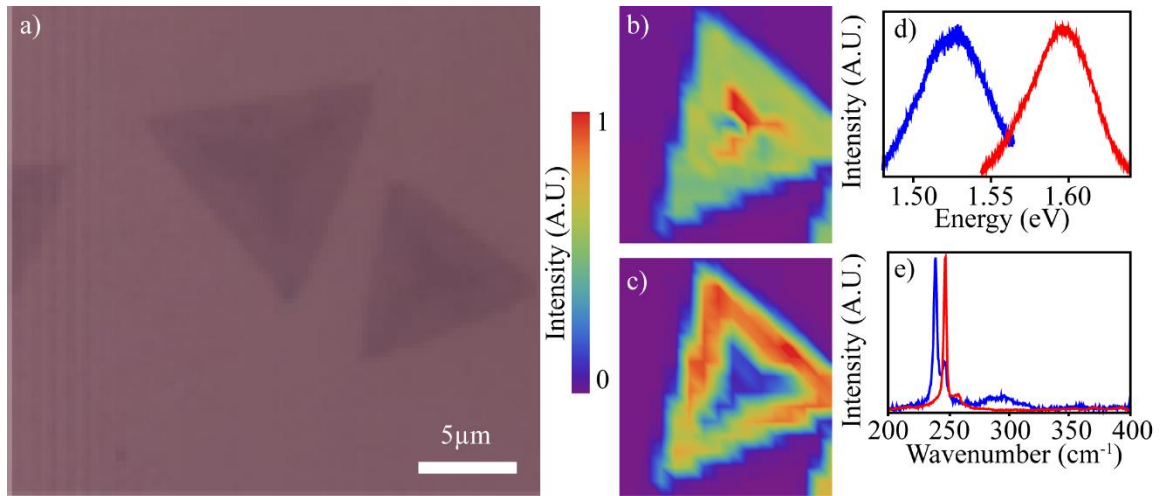


**Figure 20 (a) optical image of heterojunction. (b) Raman mapping at 238cm<sup>-1</sup>. (c) Raman mapping at 250cm<sup>-1</sup>. (d) PL spectra of inside and outside region (blue and red respectively). (e) Raman spectra of inside and outside region (blue and red respectively).**

Figure 20d shows PL spectra for the inside (blue) to be about 1.53eV, pure MoSe<sub>2</sub>, and the outside (red) being about 2.60eV, pure WSe<sub>2</sub>. This with the corresponding Raman spectra shown in figure 20e further prove that these materials are pure in form and not alloys.

Through a slow introduction of the various reagents, multiple transitions are able to be made as a heterostructure rather than a single heterojunction. Figure 21 shows PL mapping of a film area which transitions from a selenium rich 1.68eV bandgap material to a 1.76eV, sulfur rich material.

**Figure 21: Photoluminescence Mapping of Gradient**

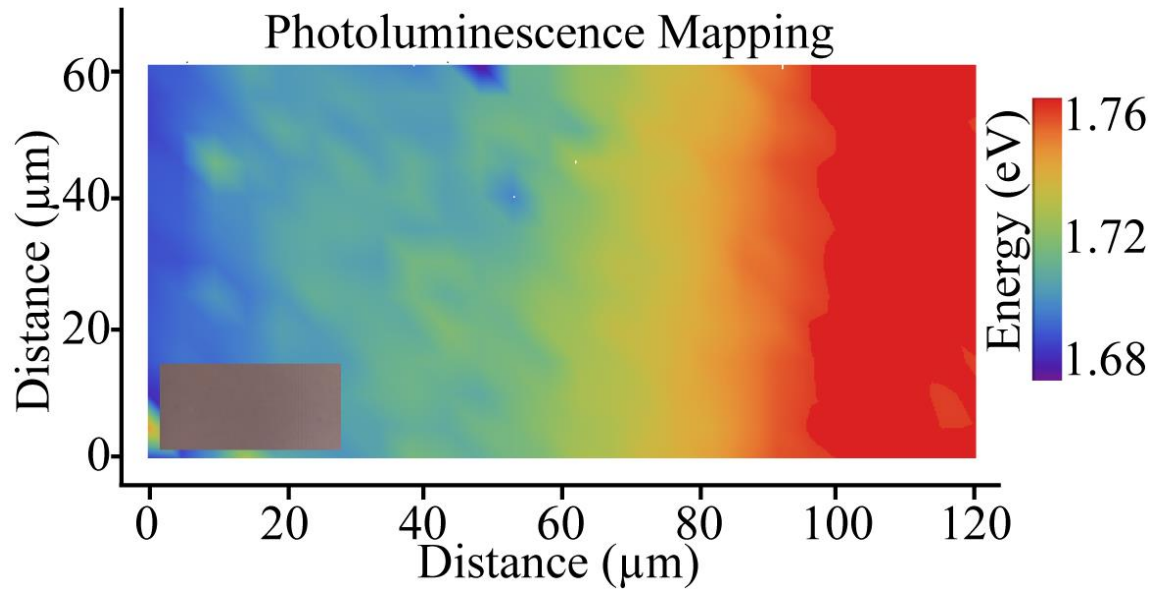


**Figure 21 photoluminescence mapping of a film of 60x120 μm with a gradient going from 1.68eV to 1.76eV. Inset of optical image with no discernable features.**

By slowly injecting more and more selenium, I was able to achieve a slow gradient shift of the alloy Se:S ratio over at least 100μm region. The PL mapping shows that this film is not a single sharp transition as shown in the previous figures, but instead a heterostructure with gradual transition over space.

# Chapter 5: $\text{MoS}_{2-x}\text{Se}_x$ Transition Metal Dichalcogenide Alloys: Is the Picture of Continuous Variation of Material Properties Comprehensive?

The following is taken from an article being written in collaboration between myself, and other students of Ludwig Bartels, Talat Rahman, and Peter Dowben.

## Abstract:

We explore the impact of substitutional alloying on the band structure of single-layer transition metal dichalcogenides (TMD) by utilizing a combination of angle-resolved photoemission spectroscopy (ARPES) at the Elettra synchrotron facility, Raman and photoluminescence spectroscopy, and density function theory calculations. The formation of TMD alloys such as  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  offers the exciting opportunity of tuning their bandgap almost at will. Yet our measurements highlight that the random occupation of the chalcogen sites in such alloys either by Se or S represents sufficient perturbation of the periodic potential of the substrate that already at small  $x$  the band structure appears broadened and modified. At larger  $x$  no band structure can be found anymore; an

observation that may have far reaching implications for fundamental alloy TMD properties including the direct nature of the bandgap, spin splitting at the K-point of the Brillouin zone, valleytronics, and the correlation between effective mass and mobility.

**Keywords:** MoS<sub>2</sub>, band structure, metal dichalcogenide alloys, short range order parameters, photoemission, DFT

PACS numbers: 73.20.-r, 73.20.At, 63.20.kd, 73.61.At

## Results

Transition metal dichalcogenides (TMD) have attracted an enormous amount of attention as the semiconducting cousins of graphene; their direct and sizeable native bandgap at the single-layer limit provides device engineering opportunities not offered by the (semi-)metallic graphene: the direct nature of the TMD bandgap holds potential for photonic application, the size of the bandgap enables on off ratios as high as  $\sim 10^8$  and the spin-split nature of the valence and, to a lesser degree, conduction band give rise to valleytronics physics<sup>5, 36, 58</sup>. Application of TMD materials utilizing each of these properties could conceptually benefit from an ability to tune the size of the bandgap of the TMD material by compositional variation and, in particular, alloying. Indeed alloying has been found to shift the optical bandgap of TMD materials such as  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  (Fig. 22a) and  $\text{Mo}_x\text{W}_{(1-x)}\text{S}_2$  continuously and practically linearly with  $x$ <sup>12, 13, 53</sup>. Yet in order to regard alloy TMD semiconductors just as bandgap-tuned stoichiometric ones, more aspects of their properties need to vary continuously with composition than just their optical bandgap. In particular, it would be desirable, if the spin-splitting, effective mass, and mean free path were to behave likewise so as to understand the variation of the material's transport properties (Fig. 22b) during alloying. The latter are all properties of the bandstructure of the material, posing the question how the single-layer TMD bandgap is affected by the introduction of alloying species. The bandstructure is a reciprocal space phenomenon whose existence depends on the periodicity and spatial invariance of the material. Thus, the question whether properties of the bandstructure of single-layer TMD materials scale with composition during alloying requires answering the question whether the alloy TMD

films have a bandstructure *per se* at all, or whether the random variation between S and Se ( $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ) or W and Mo ( $\text{Mo}_x\text{W}_{(1-x)}\text{S}_2$ ) prevent the establishment of a bandstructure in the first place.

In this manuscript we describe bandmapping performed on a  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  films grown by chemical vapor deposition (CVD). As we and others reported earlier, these materials grow as disordered substitutional alloys. The periodicity of the  $\text{MoX}_2$  lattice is, however, not affected very much by the alloying process.  $\text{MoSe}_2$  has a lateral lattice spacing just  $\sim 3\%$  larger than  $\text{MoS}_2$ . The similarity between these materials is also highlighted by the ability of sputtering out one species from a  $\text{MoX}_2$  lattice and replacing it with another, a process which also proceeds upon straightforward thermal excitation in the  $\text{Se} \rightarrow \text{S}$  direction.<sup>22</sup>

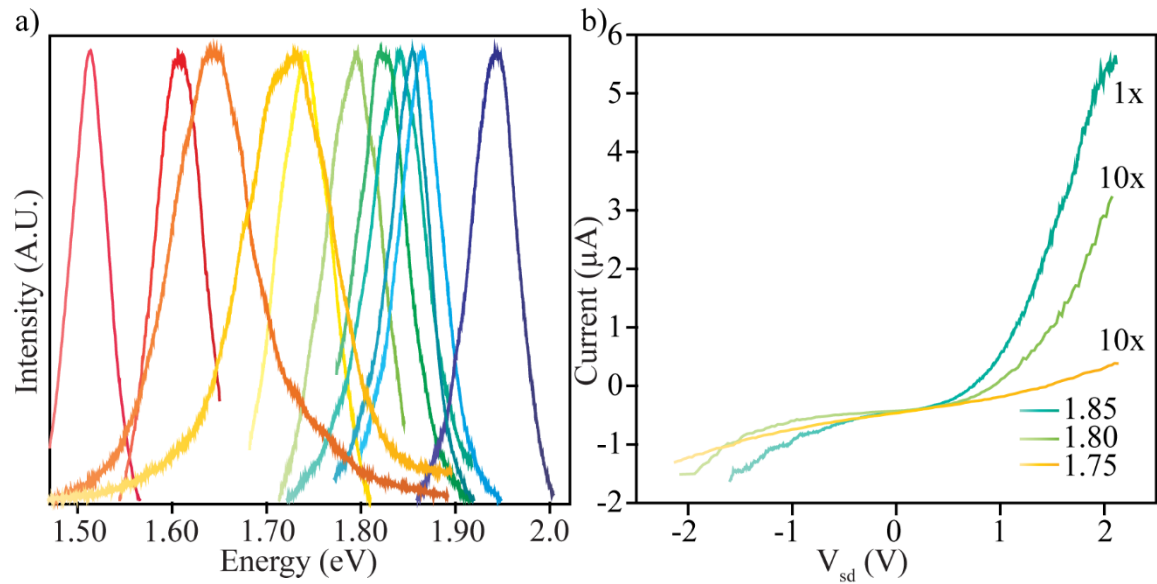


**Fig. 22 a) Normalized photoluminescence (PL) spectra of  $\text{WS}_2$ ,  $\text{WSe}_2$ ,  $\text{MoSe}_2$ ,  $\text{MoS}_2$ ,  $\text{Mo}_x\text{W}_{(1-x)}\text{S}_2$  and  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  ranging from 1.55eV to 1.98eV. b) Electrical transport of laser excited  $\text{MoS}_2$  (1.85eV) and alloys with increasing Se content at 1.80 and 1.75eV optical bandgap. As Se content increases, current decreases and becomes more ohmic. [This figure was directly taken from an article in preparation]**

In the context of bulk alloys the question about the impact on the bandstructure has been answered a long time ago: the variation of the chemical composition associated with alloying disturbs the lateral periodicity, invalidates the translational invariance of the solid, and – thus - alters the electronic structure of the solid, which facilitates, for instance, optical transitions in otherwise indirect semiconductors<sup>55, 59</sup>. *Ad extremum*: if there is no strict periodicity or translational invariance in the lattice, there is no k-space and, hence, momentum matching stops being a concern; considerations typically applied to molecules such as allowed transitions and Fermi’s Golden Rule are rather to be applied.

The experimental band structure mapping of single layer  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  was performed using a photon energy of 74 eV at the 3.2L spectromicroscopy undulator beamline of the Elettra light source. The incident radiation was linearly polarized (along the  $k_x$  direction) and focused to a  $\sim 0.6 \mu\text{m}$  spot by means of a Schwarzschild objective<sup>60</sup>. An incident angle of  $45^\circ$  with respect to the sample surface was used to optimize surface sensitivity. The ARPES data were acquired using a hemispherical electron energy analyzer with a combined energy resolution of  $\sim 50$  meV and angular resolution of  $\pm 0.33^\circ$ . The sample was mounted onto a scanning stage, which enables positioning and raster imaging with respect to the fixed photon beam. Photoelectron intensity distribution maps  $I(k_x, k_y, E)$ , from microscopic areas of the  $\text{WSe}_2$  monolayer flakes, were taken by rotating the electron energy analyzer with respect to the sample using a two-axis goniometer.

To provide a theoretical perspective for comparison, we performed density functional theory (DFT) calculations of  $\text{MoS}_2$  using the super-cell method with a plane-wave basis set and the projector-augmented wave (PAW)<sup>61, 62</sup> technique, as implemented in the Vienna

*ab-initio* Simulation Package (VASP)<sup>63, 64</sup>. We set the cut-off energy for the plane-wave expansion at 500 eV. Here, we utilize results obtained using the Generalized Gradient Approximation (GGA), in the form of the Perdew-Burke-Ernzerhof (PBE)<sup>65</sup> functional. We sampled the Brillouin Zone with a  $(15 \times 15 \times 1)$  k-point mesh for single layer MoS<sub>2</sub>. Our computational super-cells include 20 Å of vacuum, which separates the MoS<sub>2</sub> layers from one another thereby rendering inter-layer interactions negligible. The above functionals resulted in optimized lattice parameters for of 3.182 Å, a little bit larger than experimental value of 3.16 Å<sup>66</sup>. For evaluating the embedding of selenium we choose supercells of (6×6) TMD units (large enough to vary the S:Se ratio) that are vertically separated by 15 Å of vacuum.

The single layer MoS<sub>2-x</sub>Se<sub>x</sub> samples were prepared by ambient pressure chemical vapour deposition (CVD) utilizing liquid organic chalcogen precursors as described by Mann et al<sup>12</sup> as well as the supporting information section. In order to allow for ARPES measurements, the samples were directly grown onto very thin SiO<sub>2</sub> (<3 nm) films on Si. The proximity of the underlying semiconductor and the associate charge density reduces the photoluminescence (PL) yield and broadens the Raman peaks in such samples. Fig. 23a shows the PL spectra of the films used in this study in reference to prior preparative work from our lab spanning the entire composition space. Fig. 23b indicates the Raman spectrum of the two films: the typical A<sub>1g</sub> and E<sup>1</sup><sub>2g</sub> modes of MoS<sub>2</sub>, as well as the Si optical mode of the underlying substrate, are readily discernible. In addition, there is evidence of weaker vibronic modes associated with the insertion of selenium in the lattice. Unlike Mo<sub>x</sub>W<sub>(1-x)</sub>S<sub>2</sub>, which follows a one-mode behavior leading to continuous shifting of the Raman spectrum

with composition, the modes of  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  follow a two-mode behavior in which a range of combination modes is found during alloying but little shifting of the respective fundamental ones.

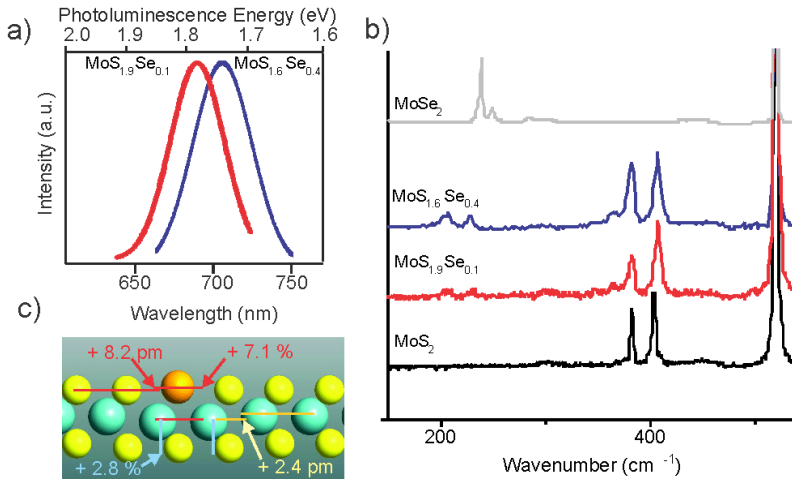


**Fig. 23 a) Photoluminescence (PL) spectra of the two films investigated in this work. The photoluminescence of the material shifts continuously with composition as seen in Fig. 1. b) Raman spectra of the films; for reference, also the Raman spectra of pure  $\text{MoS}_2$  and  $\text{MoSe}_2$  are indicated. The modes of  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  follow a two-mode behavior and do not shift continuously. The prominent mode on the right originates from the Si substrate. c) schematic representation (not to scale) of the upward shift of a Se atom in an  $\text{MoS}_2$  lattice and accompanying downward shift of the adjacent Mo atoms. The percentage values are based on the lateral Mo spacing and the Mo-S interlayer separation. [This figure was directly taken from an article in preparation]**

The scanning XPS mode of the synchrotron instrument was used to zoom in onto the TMD alloy islands/film initially investigated by PL and Raman spectroscopy. Fig. 24a shows optical and scanning XPS images at different magnification of an  $\text{MoS}_{1.9}\text{Se}_{0.1}$  sample. On the left hand side the sample edge is visible. The majority of the imperfections on the substrate are particulates that originate from cutting of the substrate so as to optimally fit into the sample holder. A direct correspondence between some of the defects in the optical and XPS images is apparent.

The XPS survey spectrum of Fig.24b validates the alignment in our measurements: on and off the  $\text{MoS}_{1.9}\text{Se}_{0.1}$  islands we find the presence and absence of selenium and molybdenum binding energy peaks. The relative intensity of the peaks affirm the stated composition, which is based originally on the correlation between PL shift and composition found experimentally in Ma et al<sup>22</sup>. As sulphur does not exhibit any XPS signature within the photon energy range of the beamline (74 eV), no direct evaluation of the S/Se XPS intensity is feasible. The presence of additional density of states in the band gap of the substrate is readily discernible. The dispersion in this regime is investigated in the following.

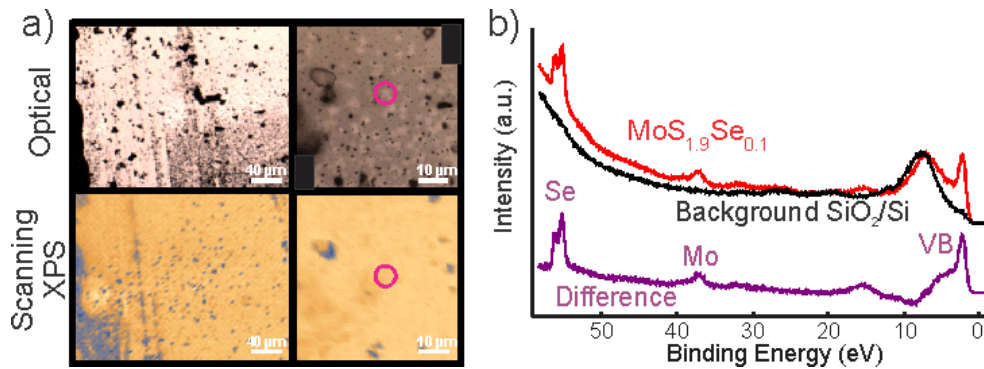


**Fig. 24 a) optical and scanning XPS imaging of the sample areas for  $\text{MoS}_{1.9}\text{Se}_{0.1}$  alloy. Edge of substrate is shown on left. Particulates on substrate are caused by cutting of sample to  $1\text{cm}^2$  dimension to fit into sample holder. b) XPS data showing measurement on and off of alloy island, red and black respectively. Purple line shows XPS data of material with background subtracted, indicating presence of molybdenum and selenium. [This figure was directly taken from an article in preparation]**

With a low concentration level of selenium,  $\text{MoS}_{1.9}\text{Se}_{0.1}$ , with a photoluminescence at 1.77 eV, a band structure with evidence dispersion is retained. Fig. 25a shows the experimental single-layer  $\text{MoS}_{1.9}\text{Se}_{0.1}$  band structure as obtained from angle-resolved photoemission spectroscopy (ARPES). As expected, there is superficial agreement with the calculated

band structure for single layer  $\text{MoS}_2$  (Figure 25b), although it is quite clear that the experimental band structure does not have as well-defined bands as prior ARPES studies of metal dichalcogenide monolayers<sup>67-72</sup>. The experimental band mapping of single-layer  $\text{MoS}_{1.9}\text{Se}_{0.1}$  is best defined at the Brillouin Zone boundary, and most diffuse near the center of the Brillouin zone,  $\bar{\Gamma}$ . This is to be expected if the Se substitutions into the sulphur sites are random. Small wave vectors  $k$  corresponds to long range order, while the Brillouin zone edge corresponds to short range order, and thus is dominated by the preponderance of S-S and S-Mo-S local ordering. Increasing the Se substitutional doping was found to degrade the experimental band structure, that no bands with dispersion could be observed in our experimental geometry. Increasing the level of selenium substitutions to  $\text{MoS}_{1.6}\text{Se}_{0.4}$ , with a photoluminescence at 1.72 eV, leads to a much greater loss of wave vector dependence as seen in Figure 25c. Little of the dominant  $\text{MoS}_2$  single layer band structure is evident.

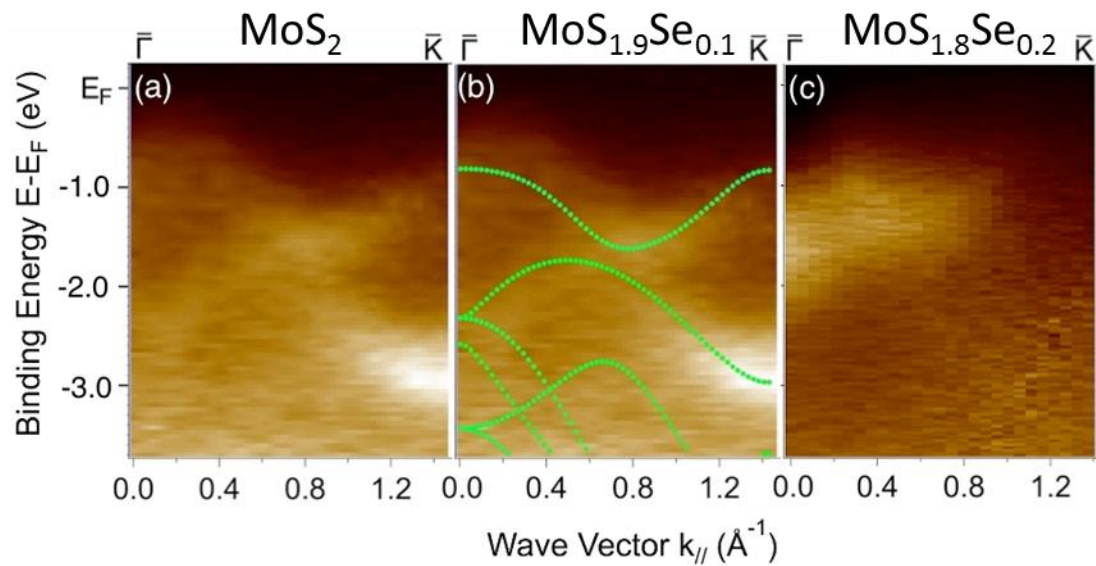


**Fig. 25 XPS bandstructure of single layer a)  $\text{MoS}_{1.9}\text{Se}_{0.1}$ , b)  $\text{MoS}_{1.9}\text{Se}_{0.1}$  with DFT calculation overlaid aligned with band structure and c)  $\text{MoS}_{1.8}\text{Se}_{0.2}$  with no**

**discernible bandstructure is present. [This figure was directly taken from an article in preparation]**

This destruction of the band structure, beginning at the smaller wave vectors, and leading to broader bands generally, is hardly unexpected having been predicted more than  $\frac{1}{2}$  a century ago<sup>72</sup>. Yet it has fundamental implications for the suitability of single-layer TMD alloys for spintronic and valleytronics applications, which fundamentally rely on the presence of spin-split bands/valleys at a particular location of the Brillouine zone. It is also noticeable, that ARPES does not reveal any evidence of a direct bandgap at K for this material; rather the top of the remnants of the valence band is located at G. As ARPES does not provide us with information about the unoccupied states, we can only speculate about the location of the transition in reciprocal space, that gives rise to the strong PL signal observed in this sample. If there were effectively no reciprocal space at all anymore, then all states would permit transitions free of translational momentum consideration, yet be subject to considerations of angular momentum (allowed/disallowed transitions) and state overlap (Fermi's Golden Rule).

### **Conclusion:**

While the band gap engineering of the transition metal dichalcogenides is certainly possible through alloying<sup>12, 22, 53, 54, 57, 73, 74</sup>, the loss of a band structure representative of light hole and electron states would indicate the potential for a much, reduced mobility, possibly offsetting any value as a tunable narrow semiconductor.

## Acknowledgements:

This work was supported by C-SPIN, part of STARnet, a Semiconductor Research Corporation program sponsored by MARCO and DARPA (SRC 2381.002 and 2381.003). Further funding was provided through the NSF funded Nebraska MRSEC DMR-1420645, DMR-1449601 (UCR) and from DOE grants DE-FG02-07ER15842 (UCR and UCF) and DE-FG02-07ER46354 (UCF). Access to XPS at Nanoscale Characterization Facility of IU Nanoscience Center was provided by NSF Award DMR MRI-1126394. DFT calculations were performed using resource from the Extreme Science and Engineering Discovery Environment (XSEDE) and the Advanced Research Computing Center at UCF.

# Chapter 6: Two-Dimensional $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ Alloys with Tunable Bandgaps

The following is taken from an article published in Advanced Materials, in collaboration between myself, John Mann, and other students of Ludwig Bartels, Rowland Kawakami, Talat Rahman and Tony Heinz<sup>12</sup>. It has been rewritten in a form appropriate for the dissertation.

## Introduction

This chapter shows that through control of the chalcogen composition, a wider tuning range of the bandgap is accessible. Using the capabilities for alloy growth presented below, the formation of both vertical and lateral heterostructures of monolayers of  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  of differing composition are made possible as previously shown.

## Methods

In this synthesis process, organic precursors for both sulfur (Thiophenol) and selenium (diphenyl-diselenide in tetrahydrofuran) are used, combined with the  $\text{MoO}_3$  as a source for molybdenum. Furnace is set up as explained for figure 9 with the use of a syringe filled with the precursors for injection at optimal temperature.

## Results and Discussion

Fig 26a shows the method by which these alloy TMDs were grown with chalcogens being injected via syringe at optimal temperatures near 670C. Fig 27b c show the respective growths using a mesh to suspend and by the typical laying a substrate over the crucible. Fig. 26 d,e shows optical and atomic force microscopy (AFM) images of the resultant films, which resemble those found in prior CVD growth of MoS<sub>2</sub>.<sup>75-79</sup>

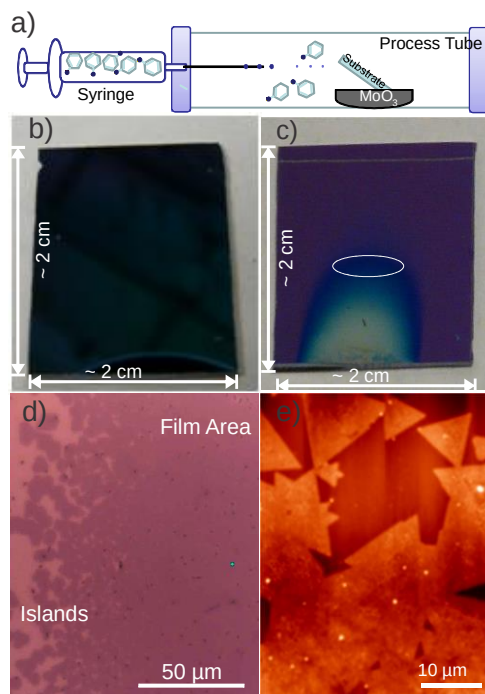


**Figure 26:** a) Schematic representation of the growth process. A substrate is suspended above  $\text{MoO}_3$  powder in a tube furnace heated to  $650\text{-}700^\circ\text{C}$  in nitrogen, at which point the liquid chalcogen precursors are injected. b,c) Optical images of  $\text{MoS}_2$  and  $\text{MoSe}_2$  films, respectively. A single-layer  $\text{MoS}_2$  film covers the entire substrate, except the dark area at the bottom. Homogeneous single-layer growth of  $\text{MoSe}_2$  is found in the circled area of the substrate, with the purple area being empty and the bright area carrying a thick film. d) optical micrograph of the area near an edge of a  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  film with 1.8 eV optical bandgap. On the left, individual (mostly triangular) islands are visible. On the right, the film becomes continuous and presumably contains many rotational domains. e) representative AFM image of the area near the edge of an alloy film showing triangular single-layer islands (top,  $\sim 0.8$  nm in height) that merge into a continuous film (bottom). [This figure was directly taken from DOI: 10.1002/adma.201304389]

Fig. 27a shows room-temperature (RT) PL spectra for a series of  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  films of different composition. The samples range from pure  $\text{MoS}_2$ , with a PL emission peak at 1.87 eV, to pure  $\text{MoSe}_2$ , with a PL peak at 1.54 eV. The chemical composition of the samples is obtained from the relative intensity of the S 2p and Se 3p features measured using X-ray

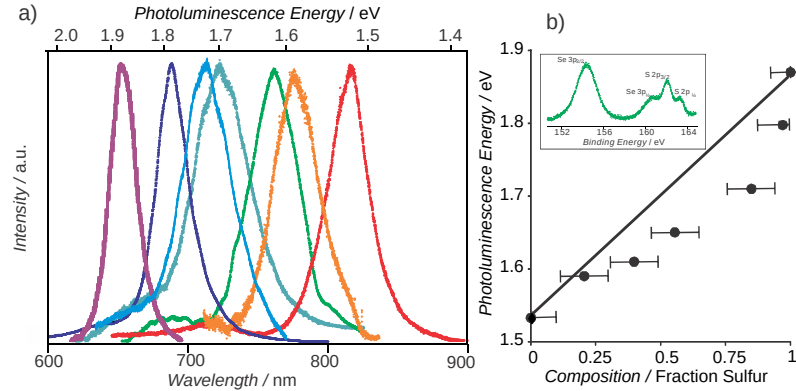


**Figure 27. (a) Normalized RT PL spectra for  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  films of different composition. (b) Variation of the photon energy of the PL emission peak as a function of sample composition, as determined by XPS. (The inset shows a representative XPS spectrum of the Se 3p and S 2p peaks). The black line indicates a linear variation between the values of the stoichiometric compounds as found in the DFT calculations. [This figure was directly taken from DOI: 10.1002/adma.201304389]**

photoelectron spectroscopy (XPS). The variation of the optical gap with the composition of the  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  alloy monolayers is presented in Fig 27b. The results are based on the A exciton emission energy in PL spectra like those in Fig. 27a showing a monotonic increase of the optical gap with the fraction of sulfur in the film.

The experimental Raman spectra of the  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  monolayer films show two distinct sets of features, with one set related to  $\text{MoS}_2$ -like  $E_{2g}$  and  $A_{1g}$  modes at around  $400\text{ cm}^{-1}$  and the other set related to the corresponding  $\text{MoSe}_2$ -like features near  $240\text{ cm}^{-1}$ .

Unlike the bandgap, which is expected to vary smoothly with composition, the vibrational behavior of alloys is seen to be more complex than that of the stoichiometric compounds. The spectra represent typical “two-mode behavior” (2MB)<sup>80</sup> and do not imply phase separation. Similar behavior is observed in the S/Se alloy of  $\text{CdS}_x\text{Se}_{1-x}$ ,<sup>81, 82</sup> as well as in well-studied alloys such as  $\text{AlInAs}$ ,<sup>83</sup>  $\text{InGaP}$ ,<sup>84</sup>  $\text{Si-Ge}$ <sup>85</sup> and  $\text{Al}_x\text{In}_{(1-x)}\text{N}$ <sup>86</sup>. 2MB occurs when the frequencies of phonon modes in the pure AB and AC compounds differ sufficiently in

frequency from one another. For the present case of  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ , the strong phonon features are shifted from one another by  $\sim 200 \text{ cm}^{-1}$  in the two pure compounds, which is sufficient for 2MB. For the case of  $\text{Mo}_{(1-x)}\text{W}_x\text{S}_2$  alloys, for which the corresponding difference is less than  $50 \text{ cm}^{-1}$ , one observes “one-mode behavior” with a continuous shift of phonon frequencies with composition.<sup>87</sup> This is seen in figure 28 below.

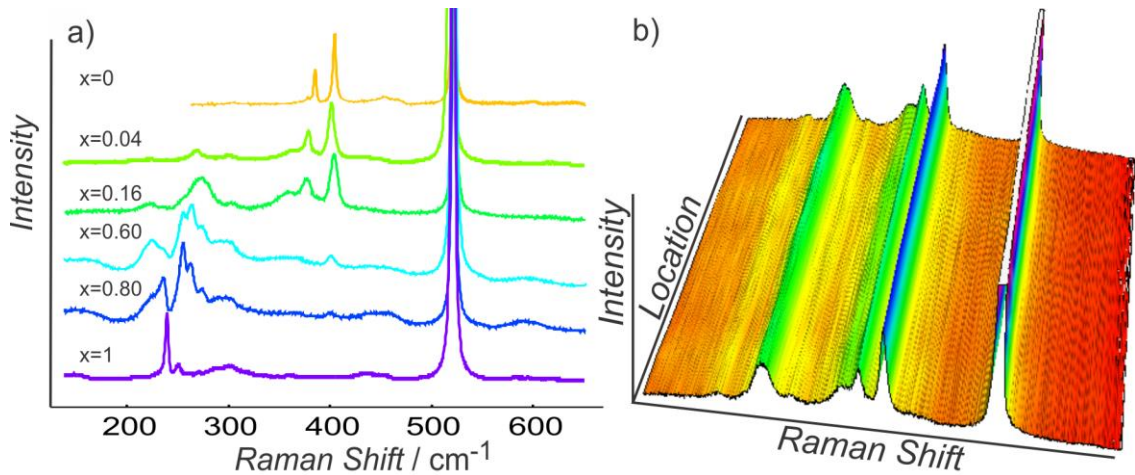


**Figure 28: a) Raman spectra measured for  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  films of different selenium content  $x$ . The pronounced feature near  $520 \text{ cm}^{-1}$  arises from the  $\text{SiO}_2$  substrate vibrations. While the peak patterns for the pure materials are simple and sharp, the patterns for alloy films are broader and more complex. The evolution is understood in terms of two-mode behavior, as discussed in the text. b) Three-dimensional representation of the Raman spectra as a function of location on a  $0.5 \mu\text{m}$  grid covering the same location as the bottom part of 27c. [This figure was directly taken from DOI: 10.1002/adma.201304389]**

## Conclusion

In conclusion, the ability to grow alloy monolayer films of  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  of arbitrary composition is made possible through control of the S/Se ratio of the organic precursors used in the growth process. The band structure of the alloy films can be tuned continuously with composition. Another important fundamental property of the alloys is the variation of

the spin-orbit splitting of the bands, which is predicted to increase continuously with increasing Se content, and the implications of this variation for spin manipulation.

# Chapter 7: Lithographically-Encoded Single-Step Deposition of Hybrid 2-/3- Dimensional WSe<sub>2</sub> Transistors for Enhanced Mobility

The following is taken from an article published in Progress, in collaboration between myself, Ingrid Liao, and other students of Ludwig Bartels.

## **Abstract**

The effective mobility of field effect transistors (FET) based on two-dimensional (2D) single-layer transition metal dichalcogenide (TMD) films is frequently limited by barriers at the contacts rather than by the native properties of the TMD material. Their thinness and resulting small total number of native charge carriers renders screening at contacts very inefficient, amplifying effect such as Schottky Barriers compared to the bulk. Here we demonstrate a scalable single-step deposition method for hybrid 2D/bulk (3D) TMD structures encoded by lithographic patterning prior to deposition. The resultant TMD features offer effective mobilities of nearly 100 cm<sup>2</sup>/V·s for bottom-gated devices (through 300nm of oxide) even for comparatively long channels (>5 microns) and absent of other

contact optimization, i.e. approximately an order of magnitude enhancement with respect to conventional 2D TMD devices, while not compromising on the exceptional on-off ratio in such films ( $>10^6$ ). The TMD structures of predetermined channel length and position were grown *in-situ* via a single-step chemical vapor deposition (CVD) process. Lithographic patterning of a hafnium (IV) dioxide film onto the  $\text{SiO}_2/\text{Si}$  substrate prior to TMD growth allows us to control the CVD TMD thickness so that the electrical contacts to the FET can utilize bulk-like material with enhanced screening of charge transfer and the FET channel single-layer material with exceptional on-off ratio.

## Introduction

Lowering power consumption while increasing the density of device architectures is a key objective of the semiconductor industry in its ongoing effort to extend Moore's law to ever smaller device dimensions. Layered, two-dimensional (2D) materials with native van der Waals (vdW) gaps such as graphene, hexagonal boron nitride, phosphorene, and transition metal dichalcogenides (TMDs) have particular appeal in this pursuit.<sup>26, 30, 33, 36, 42</sup> As device dimensions shrink, surfaces and interfaces between materials make up an increasingly larger volume fraction of the device.<sup>88-90</sup> If natively three-dimensional materials are used, their properties are generally degraded at these locations through dangling bonds or other crystallographic defects;<sup>91</sup> an effect avoided by the use of natively 2D materials. Even taking account for realistic defect densities and extrinsically induced carriers, the overall carrier density in TMD films is very low resulting in very long screening lengths and – important in the context of this work – pronounced deterioration

of transport properties at metal contacts through Schottky-like barriers (SBs).<sup>92, 93</sup> At the same time, these low carrier densities offer ultra-low leakage current in field effect transistor (FET) devices and high on-off ratios.<sup>94</sup> A broad array of methods have been proposed to mitigate the effects of SBs including edge contacts,<sup>28, 95-97</sup> metallic-phase contacts,<sup>98-100</sup> and carbon or graphene based contacts.<sup>95, 101, 102</sup> Here we describe an alternative approach to avoid the 2D SBs: hybrid 2-/3-dimensional (2D/3D) TMD features prepared by a scalable, single-step, lithographically-controlled deposition method.

## Results and Discussion

Fig. 30a shows this approach schematically: a  $\text{SiO}_2/\text{Si}$  substrate patterned by a few cycles of atomic layer deposition (ALD)  $\text{HfO}_2$  through a lithographically defined resist followed by lift-off encodes bulk-like (3D) TMD growth in a chemical vapor deposition (CVD) process at the hafnia locations and 2D growth elsewhere. In the following we show that adjacent 2D and 3D TMD material is electrically connected; using the bulk-like material for contact formation and the 2D material as transistor channel (Fig. 30c), the hybrid 2D/3D device combines the benefit of 3D screening of contact effects and the gate response of a 2D material. In this work we utilize as patterns a periodic array of parallel lines (Fig. 30b); the approach is not limited to such simplistic pattern, however, and may lend itself to nanoscale contact formation of any kind or shape (supplemental figure 1 offers a variation). Because of the layeredness of even the bulk-like material, concerns auspicated with high surface area or quantum confinement in bulk semiconductor material are avoided.

Substrate-encoded growth of 2D TMD films into predetermined 2D patterns has been achieved previously. A variety of approaches utilized substrate geometric features, polymer layers, or even organic patterning,<sup>9, 14-17, 24, 103</sup> to this end. Our work reaches beyond 2-dimensional encoding, because it not only controls the location but also the morphology of the resultant film. Fig. 30b shows the result where thicker regions of WSe<sub>2</sub> are grown at the location of the periodic array of HfO<sub>2</sub> –modified substrate while the bare SiO<sub>2</sub> region is covered by single-layer material only.

It is beneficial for modern transistors to maintain a 2D channel as shown here in order to reduce not only channel length, but also for minimized electrostatic screening effects.<sup>30, 104</sup> For these TMD devices, it is further important to maintain a single layer for the high on/off ratio (nearly 10<sup>10</sup> for MoS<sub>2</sub> and upwards of 10<sup>6</sup> for WSe<sub>2</sub>).<sup>30, 105</sup> in order to reach these, further optimization of contact barriers is required, as addressed here. Other attempts at contact optimization include selection of metals for contact formation such as the use of Indium, resulting in record high mobilities and on/off ratios for WSe<sub>2</sub> of 142 cm<sup>2</sup>/V·s and 10<sup>6</sup> respectively.<sup>106</sup> This work furthers this effort by offering another method by which to decrease barriers resistances, a known hurdle in TMD device application.

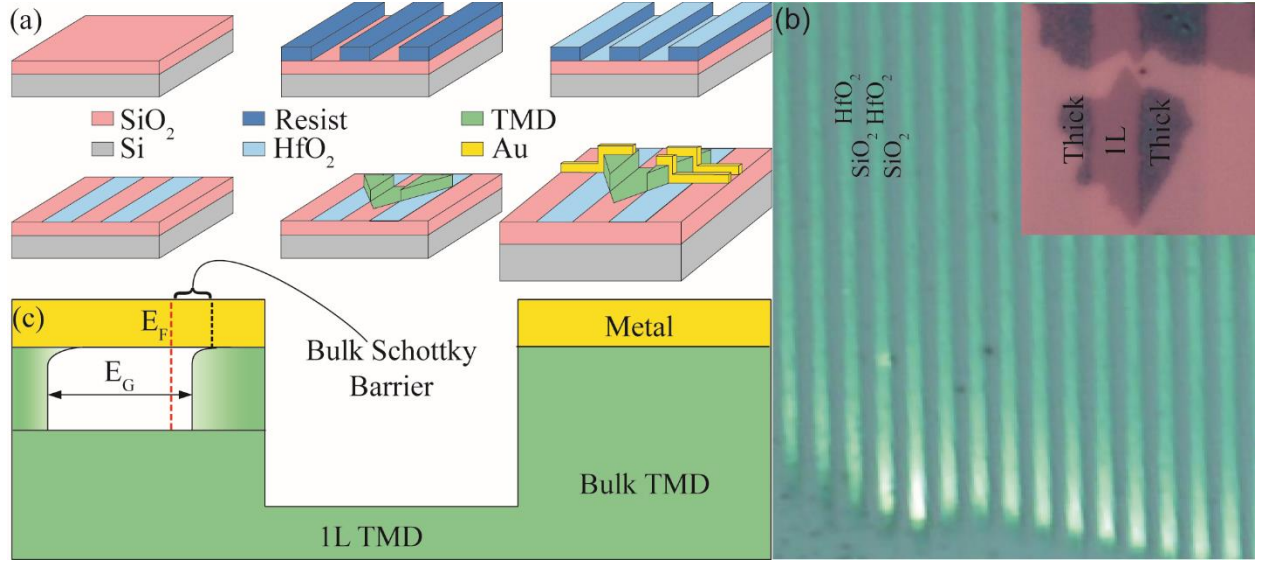


**Figure 29. (a) Schematic of process to lithographically pattern HfO<sub>2</sub>/SiO<sub>2</sub> strip substrate for bulk-TMD electrode devices. (b) Optical image at 10x magnification of SiO<sub>2</sub>/HfO<sub>2</sub> substrate with WSe<sub>2</sub> grown. Inset of a 100x objective image. (c) Cartoon of the Schottky Barrier created at a metal-bulk TMD interface for a 2D TMD channel device. [This figure was directly taken from an article in preparation]**

Initial patterning of the substrate involved photolithographic patterning of a resist layer on the 300nm SiO<sub>2</sub>/Si substrate followed by atomic layer deposition of HfO<sub>2</sub> and subsequent lit-off. CVD growth of WSe<sub>2</sub> proceeded in a 1" tube furnace at 900°C utilizing ammonium meta tungstate<sup>51</sup> and selenium powder as transition metal and chalcogen source, respectively. The methods section provides further detail. A large number of substrates have been patterned in several batches; using samples from different batches reliable deposition of patterned TMD films has been found.

In the following, we will show that these hybrid 2D/3D patterns provide appealing targets for field-effect transistor channels. The inset in fig. 29b shows a sample location, at which we fabricated a prototypical device. For reason of better defined channel width, we chose an isolated island as shown in the inset of Fig. 29b where Fig. 30c shows the completed device. Raman spectroscopy was performed in each of the bulk-like areas of the device of

Fig. 41c as well as in the channel region (Fig. 30b). The  $250\text{cm}^{-1}$   $A_{1g}$  and  $260\text{E}^2_g$  peak are present in all three locations; their relative intensity is higher in the single layer material, as expected. The bulk-like regions, additionally exhibit the  $B_{2g}$  mode at  $308\text{cm}^{-1}$  which is absent for single layer material.<sup>48</sup>

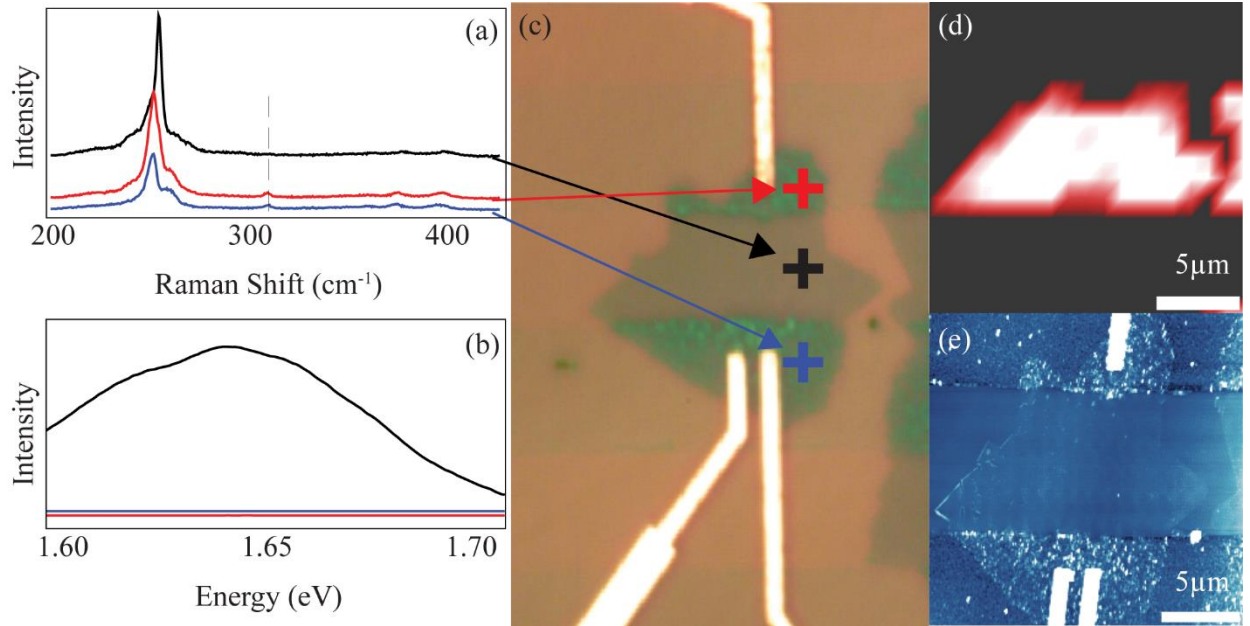


**Figure 30. (a) Optical image of WSe<sub>2</sub> device with contacts placed at bulk-like regions of WSe<sub>2</sub>. (b) Photoluminescence mapping indicating uniform high responsivity on single layer channel near  $1.65\text{eV}$  (c) AFM image of device in 2a verifying single layer material with a height  $<1\text{nm}$ . (d). Raman spectra of regions marked in 41c, showing single layer, bulk, and bulk (black, red, blue)  $A_{1g}$  and  $E^2_g$  modes.  $308\text{cm}^{-1}$  peak marked with dotted line not present in single layer material. (e) Photoluminescence spectra of single layer, bulk, and bulk (black, red, blue) indicating high intensity around  $1.65\text{eV}$  for single layer material and no intensity for bulk materials. [This figure was directly taken from an article in preparation]**

Similarly, Photoluminescence (PL) spectra were acquired in each of the bulk-like regions as well as in the channel (Fig. 30a). The characteristic single-layer PL of WSe<sub>2</sub> at  $1.65\text{eV}$  was detected only in the channel region. Spatial mapping of the PL intensity across the area of Fig. 31c highlights the single-layer channel region. (shown in Fig. 30d). Atomic force microscopy shown in Fig. 30e verifies the single-layer height of the material in the center

region with an edge height (to the SiO<sub>2</sub> substrate) of 9.1 Å, similar to reference heights for single layer WSe<sub>2</sub>.<sup>106</sup> The thickness of the bulk-like TMD material is found to be approximately 10.7 nm.

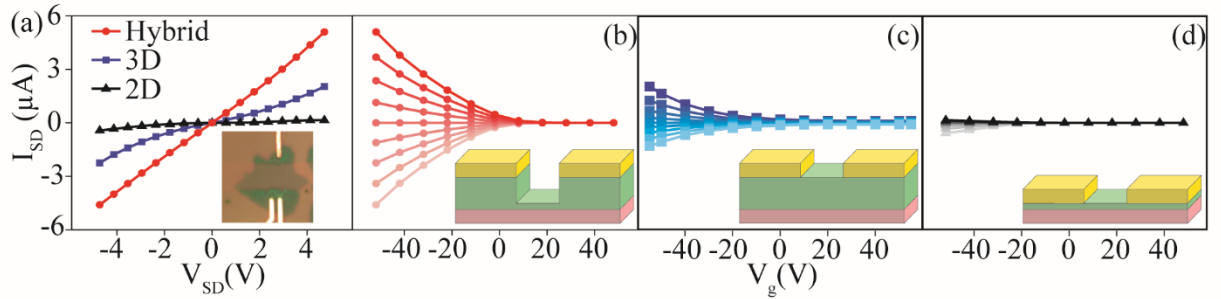


**Figure 31. (a)  $I_{sd}$  vs  $V_{sd}$  of single layer (black), bulk (blue), and hybrid (red) WSe<sub>2</sub> devices; inset of 3D and hybrid device. (b, c, d)  $I_{sd}$  vs  $V_g$  for hybrid (red, b), bulk (blue, c), and thin reference (black, d) devices with  $V_{sd} = -4V \rightarrow +4V$  (lighter to darker, 1V step). Insets indicate schematics of devices. [This figure was directly taken from an article in preparation]**

Fig. 31a compares the transfer characteristics measured across the hybrid 2D/3D device of Fig. 31 (red) to characteristics found between two contacts on bulk-like material (blue) and 2D material (black). The supporting information provides images and dimensions of the 2D reference device. The transfer characteristics measurements of Fig. 31a were obtained at a back-gate bias  $V_g = -50$  V. The hybrid 2D/3D device outperforms both the bulk-like and the 2D material device by a significant margin. Unsurprisingly, the bulk-like device exhibits increased conductivity compared to the single layer material.

We characterize this set of devices further by gate-dependent transport measurements. Figures 31b-d show output characteristics measured at 280K with  $V_g$  ranging from -60V to +60V and  $V_{sd}$  ranging from -4V to +4V. In each case, we observe a p-type response in agreement with previous studies on WSe<sub>2</sub>.<sup>107, 108</sup> The hybrid 2D/3D device is shown in fig

31b (red); it exhibits very high current response for a back-gated device across a  $7\mu\text{m}$  transistor channel. The device fabricated from bulk-like material (Fig. 31c) shows a lower gate response (3x) response. Moreover, we observe comparatively high leakage current. The device fabricated from 2D WSe<sub>2</sub> film shows the lowest performance in this set (10x less) and an asymmetric response on the source-drain voltage, as typically observed for devices suffering from imperfect contacts. The asymmetry in the single layer device could be due to a charge build-up, occurring at the contact site, causing further gating, explaining the higher current for negative V<sub>sd</sub> compared to positive. Our measurements of the on-off ratio ( $I_{\text{on}}/I_{\text{off}}$ ) are limited by a current noise of the Keithley 2400 source meter of a few pA. For the hybrid device, we observe a current swing from noise level to  $\sim 6\mu\text{A}$ , i.e. a minimum of  $\sim 10^6$ . This is 3 orders of magnitude better than for the 2D device; the bulk device suffers from significant leakage even at blocking bias resulting in a low on-off ratio.

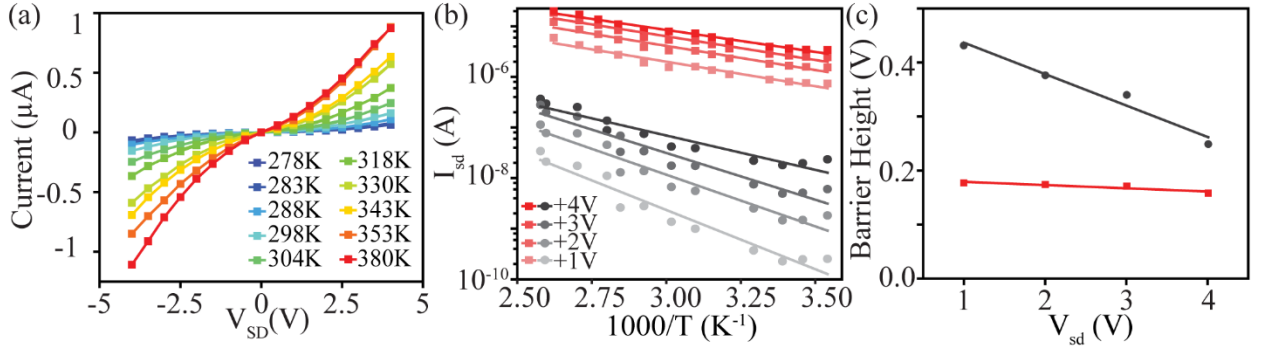


**Figure 32. (a) Temperature dependent transport of hybrid device from 278K  $\rightarrow$  380K shows an increase in current with temperature. (b) Arrhenius plot of  $I_{sd}$  vs  $1000/T$  with varying  $V_{sd}$ , comparing hybrid (red) and 2D (black) devices. (c) barrier height of hybrid (red) and 2D (black) devices. [This figure was directly taken from an article in preparation]**

Figure 32a shows transfer properties at varying temperature from 278K  $\rightarrow$  380K, indicating device performance increasing as temperature increases, which can be attributed to thermionic emission. Temperature dependent measurements of the transfer characteristics offer us insight into the barriers associated with the transport process. Transport properties were plotted in an Arrhenius plot in figure 32b as a function of temperature for the bulk-contacted device (black, top set) and for the 2D reference device (red, bottom set). The devices were measured from 276K to 380K at a  $V_g = +50V$  at source drain biases  $V_{sd}$  as indicated. SB heights are extracted for the hybrid and the 2D reference device from the linear fit to the model:  $\ln(I) = \left(-\frac{E_a 1000}{kT}\right) - \ln(A)$  to be  $\sim 0.19V$  and  $0.25-0.45V$  respectively. The activation energy is larger for the 2D device than that of the hybrid device for all  $V_{sd}$ , clearly indicating that the contacts in the hybrid device can support more current. Figure 33c shows the barrier height of hybrid (black) and 2D (red) devices indicating a barrier as a function of the source drain bias for 2D devices while the hybrid device maintains a barrier less effected by bias. This perhaps goes to say that the Arrhenius

activation energy model as described above is too simple and a more realistic model would include thermionic emission, thus giving a dependence on the bias. Such a model is proposed by Yu et al. such that as the effective mass of the junction increases, the effect of the bias becomes minimalized.<sup>109</sup> Mobility for hybrid and 2D devices is calculated to be 85.89 cm<sup>2</sup>/V·s and 12.76 cm<sup>2</sup>/V·s respectively, nearly 7x higher mobility in the hybrid device. This increase in mobility can be attributed to the lowered SBH and overall resistivity which the hybrid devices provide.

## Conclusion

In summary, we show that through modification of the substrate before growth, TMDs can be grown in-situ via single-step CVD synthesis in a method to create bulk-like contacts with substrate encoded channel length and location by oxide deposition and patterning. These bulk-like contacts allow for a reduced Schottky-barrier created at a metal-3D TMD interface instead of at a metal-2D interface, resulting in more ohmic contacts and higher mobility up to 85.89 cm<sup>2</sup>/V·s.

## Methods

### Substrate Preparation

300nm SiO<sub>2</sub>/Si substrates were cleaned using a standard piranha etch for one hour in 1:4 hydrogen peroxide, sulfuric acid mixture. Substrates were then patterned using photolithography on a Karl Suss Model MA-6 mask aligner. A dehydration step at 110°C for 1 minute was applied prior to spin coating with S1813 photoresist at 4000rpm for 45 seconds. Resist was then hardened by baking at 110°C for 60 seconds. ALD was

performed on the patterned substrate using a Cambridge Nanotech ALD system at 80C for 12 cycles, giving 1.2nm. Deposited substrates were then stripped of resist using an acetone wash for 30 seconds. Substrates were then annealed at 900C under an N<sub>2</sub> rich environment.

### **CVD Growth Method**

Samples were grown via chemical vapor deposition, using a 1” single zone tube furnace. Ammonium meta tungstate (3.1mM) was spin coat onto patterned HfO<sub>2</sub>/SiO<sub>2</sub> strip substrates at 4000rpm for 20 seconds, immediately before growth. The furnace was purged for 20 minutes with 2.0 SCFH N<sub>2</sub> (99.999%) gas at a temperature of 400°C and then ramped with a decreased N<sub>2</sub> flow rate of 0.5 SCFH and heating at a rate of 25°C/min until a final temperature of 900°C. Temperature and gas flow was maintained for 10 minutes to allow for growth of the WSe<sub>2</sub> films, after which, temperature was cooled naturally to 500°C and held for a total of 30 minutes with additional 0.05 SCFH H<sub>2</sub> (99.999%) flow rate. Finally, the furnace was allowed to cool to room temperature for 2 hours with 1.0 SCFH N<sub>2</sub> gas.

### **Sample Characterization and Device Fabrication**

Raman and photoluminescence spectroscopy were performed using a 532nm laser on a Horriba LabRam microscope equipped with a 100x objective. Raman was performed using an 1800 cm<sup>-1</sup> grating centered at 300cm<sup>-1</sup>. Photoluminescence was performed using a 600 cm<sup>-1</sup> grating centered near 1.60 eV, the expected optical bandgap for single layer WSe<sub>2</sub>.

Upon verification of WSe<sub>2</sub> grown in a thick-thin-thick pattern, Ti/Au metal contacts were placed for electrical characterization. Samples were spun twice using PMMA(A4) at a rate of 4000rpm for 45 seconds then hardened at 180C for 2 minutes, resulting in an approximately 500nm layer. Using electron beam lithography, electrodes were drawn to reach near edge of the thick material interface with the thin material. Channel length ranged from 5-7nm depending on the device and the oxide pattern while channel widths were 1nm for all devices. Devices were patterned using a Leo XB1540. After lithographic patterning, exposed resist was developed using a 1:3 mixture of MIBK/IPA. Patterned samples were then placed in a Temescal BJD 1800 E-beam evaporation system where 5nm Ti and 50nm Au were deposited. Remaining resist was lifted off using acetone, leaving behind device patterns. A schematic is shown in figure 1a. AFM was performed using an Asylum MFP-3D system. Transport properties were measured in a probe station housed in a glovebox utilizing a Keithley 2400 source meter.

# Conclusion

## Final Remarks

As this thesis outlines, there is much to learn about TMDs in their pure form, and even more to learn of alloys and heterojunctions of these materials. With a deeper understanding of how these materials are influenced during their growth process and ways which we can manipulate that growth to achieve desired traits, we become closer of realizing an applicable device using TMDs and other 2D materials. At the beginning of my research in TMDs, there was very little to be found of alloying these materials, and even less about WSe<sub>2</sub>. While my research conducted here has contributed to these two niches, there is far more research being done on a global scale of these materials. The materials which I have grown have been used by myself for the purposes of my own studies in growth, as well as by collaborators across the United States and even internationally in Germany. Much has been discovered in the past 5 years, but much more is needed to be understood. Only through collaborative efforts such as those which I have contributed to will we continue to push forward the forefront of 2D materials.

## Outlook

My work will be continued by my lab, specifically by my undergraduate students, Natalie Duong and Quinten Yurek. While I have mapped out the spectrum of molybdenum based alloys/heterojunctions, there is much to learn about tungsten based alloys/junctions, with the added promise of a possible lateral p-n single-layer junction created by incorporating

WSe<sub>2</sub>. Creative growth process steps have achieved desired materials, but can be further tuned to include more TMDs and a higher success rate. Through manipulation of substrates, it may be possible to create even more complex single-step processes to achieve device ready growth. One promise in this step is work done with my lab mate, Thomas Empante who is studying the growth of telluride TMD and the different phases which are stable in ambient conditions by growth processes. If a material with an effect such as the HfO<sub>2</sub> patterning can be found to assist in phase control, it would be possible to create a junction of 1T (metallic) and 2H (semiconducting) phase material in one-step in order to further decrease any device barriers, and have it be in a predetermined feature shape/size. Further research will develop in these directions to make a more feasible 2D material device.

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