

CHEMICAL VAPOR DEPOSITION GROWTH OF MOLYBDENUM DISULFIDE  
AND ITS NANOSCALE TRIBOLOGICAL CORRELATION WITH RAMAN  
SPECTROSCOPY

By  
SOL TORREL

A dissertation submitted to the  
Graduate School-New Brunswick  
Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Doctor of Philosophy

Graduate Program in Materials Science & Engineering

Written under the direction of

Manish Chhowalla, Ph.D.

And approved by

---

---

---

---

New Brunswick, New Jersey

October 2017

## ABSTRACT OF THE DISSERTATION

Chemical vapor deposition growth of molybdenum disulfide and its nanoscale tribological correlation with Raman spectroscopy

By

SOL TORREL

Dissertation Director:

Manish Chhowalla, Ph.D.

In this doctoral thesis work, two-dimensional (2D) molybdenum disulfide ( $\text{MoS}_2$ ) single crystals have been synthesized, characterized, and tribologically studied. Specifically, detailed analyses of processes that occur during chemical vapor deposition (CVD) of atomically thin  $\text{MoS}_2$  have been performed to understand key mechanisms responsible for reproducible growth of high quality materials. To this end, literature survey of growth parameters was performed and compared with original experiments performed here. The methods and mechanisms of nucleation and growth of large-area, single- and few-layer  $\text{MoS}_2$  are described with emphasis on variable control and repeatability. The synthesis work performed here provides new insights into the challenges of reproducible  $\text{MoS}_2$  growth using CVD.

Following the CVD work, the thesis research included phase transformation of  $\text{MoS}_2$  – building on ongoing research in our group. The aim of this part of the research was to understand how chemistry can change the structural phase of 2D  $\text{MoS}_2$ . More specifically, this work was performed to determine the root cause of challenges that are

encountered during phase transformation. Finally, my primary focus and most of my efforts were devoted to study of the tribological properties of 2D MoS<sub>2</sub> to further develop fundamental understanding of friction on the atomic level. Atomic force microscopy (AFM) was used to measure nanoscale tribological properties of semiconducting and metallic monolayer MoS<sub>2</sub> to study the influence of electronic structure on friction behavior. Furthermore, various multilayer semiconducting polytypes of MoS<sub>2</sub> were studied to elucidate the phononic contribution to friction. Electronic and phononic properties of this nanomaterial were probed, analyzed, and correlated through AFM and Raman spectroscopy. As a result, a preliminary methodology for remote prediction of friction behavior via laser excitation has been developed.

## Table of Contents

|                                                                    |     |
|--------------------------------------------------------------------|-----|
| Abstract .....                                                     | ii  |
| List of Figures .....                                              | vii |
| List of Tables .....                                               | x   |
| 1. Introduction .....                                              | 1   |
| 1.1 Objectives .....                                               | 2   |
| 1.2 Organization of Thesis .....                                   | 3   |
| 2. Motivation and Background .....                                 | 5   |
| 2.1 Motivation .....                                               | 5   |
| 2.1.1 Miniaturization of components .....                          | 5   |
| 2.1.2 Miniaturization of devices .....                             | 8   |
| 2.1.3 Enhancement of friction forces at small scales .....         | 8   |
| 2.1.4 Fundamental understanding of friction .....                  | 9   |
| 2.1.5 Challenges .....                                             | 10  |
| 2.2 Solution .....                                                 | 11  |
| 2.2.1 Transition metal dichalcogenides .....                       | 12  |
| 2.2.3 MoS <sub>2</sub> .....                                       | 13  |
| 2.2.4 Applications .....                                           | 14  |
| 2.2.5 Structure and Properties .....                               | 21  |
| 2.3 Synthesis and Growth .....                                     | 26  |
| 2.3.1 Top-down: mechanical exfoliation, chemical exfoliation ..... | 27  |

|                                                |    |
|------------------------------------------------|----|
| 2.3.2 Bottom-up: MBE, PLD, ALD, PVD, CVD ..... | 30 |
| 2.4 Phase transformations .....                | 35 |
| 3. Characterization .....                      | 37 |
| 3.1 Optical microscopy .....                   | 37 |
| 3.2 Raman microscopy .....                     | 39 |
| 3.3 Scanning Electron Microscopy .....         | 44 |
| 3.4 Transmission electron spectroscopy.....    | 48 |
| 3.5 X-ray photoelectron spectroscopy.....      | 50 |
| 3.6 Atomic force microscopy .....              | 53 |
| 3.6.1 Modes of Operation .....                 | 54 |
| 3.6.2 Friction.....                            | 56 |
| 4 Experimental Methods and Results .....       | 64 |
| 4.1 Synthesis.....                             | 64 |
| 4.2 Chemical vapor deposition.....             | 65 |
| 4.2.1 Stoichiometry.....                       | 70 |
| 4.2.2 Experimental variability .....           | 83 |
| 4.3 Phase transformations .....                | 84 |
| 4.4 Atomic force microscopy .....              | 87 |
| 4.4.1 Friction and Phase .....                 | 88 |
| 4.4.2 Friction and polytype.....               | 92 |

|                                                         |     |
|---------------------------------------------------------|-----|
| 4.4.3 Friction and Electrostatic Force.....             | 96  |
| 4.4.4 Tribology on a TEM grid.....                      | 98  |
| 4.4.5 Friction: Raman correlation.....                  | 100 |
| 5. Discussion and Conclusions .....                     | 114 |
| 5.1 Controllable CVD growth .....                       | 114 |
| 5.2 Friction vs. Phase .....                            | 116 |
| 5.3 Friction vs Polytype .....                          | 119 |
| 5.4 Predicting Friction Behavior Remotely.....          | 121 |
| 6. Future Work .....                                    | 122 |
| Appendix A: Python Scripts .....                        | 125 |
| Appendix B: Raman generated prediction of friction..... | 164 |
| References.....                                         | 166 |

## List of Figures

|                                                                                             |    |
|---------------------------------------------------------------------------------------------|----|
| Figure 1 Representation of a single layer of graphene. ....                                 | 1  |
| Figure 2 Transistors on a single chip. ....                                                 | 7  |
| Figure 3 Transistor constructed from a single layer of MoS <sub>2</sub> . ....              | 15 |
| Figure 4 Energy density vs power density of novel power storage devices. ....               | 17 |
| Figure 5 Schematic of MoS <sub>2</sub> /black phosphorus heterojunction and IV curves. .... | 18 |
| Figure 6 Various crystal structures of MoS <sub>2</sub> . ....                              | 22 |
| Figure 7 Coordination models. ....                                                          | 23 |
| Figure 8 Electronic band structure of MoS <sub>2</sub> for high symmetry points. ....       | 24 |
| Figure 9 Spin orbit coupling band splitting. ....                                           | 25 |
| Figure 10 Mechanical exfoliation ....                                                       | 28 |
| Figure 11 Chemical exfoliation. ....                                                        | 30 |
| Figure 12 Energy diagram for Raleigh and Raman scattering. ....                             | 39 |
| Figure 13 Principle Raman modes for MoS <sub>2</sub> . ....                                 | 42 |
| Figure 14 Photoluminescence (PL) of 2H MoS <sub>2</sub> as grown by CVD ....                | 44 |
| Figure 15 Penetration profile of a sample irradiated with an electron beam. ....            | 46 |
| Figure 16 Schematic of EBSD. ....                                                           | 47 |
| Figure 17 Transmission electron microscopy of MoS <sub>2</sub> . ....                       | 50 |
| Figure 18 Diagram of x-ray photoelectron spectroscopy (XPS) analysis. ....                  | 51 |
| Figure 19 XPS spectra from MoS <sub>2</sub> . ....                                          | 52 |
| Figure 20 Atomic force microscopy (AFM). ....                                               | 54 |
| Figure 21 Idealized diagram of probe/substrate contact area. ....                           | 57 |
| Figure 22 JKR and DMT models for contact area and friction vs load. ....                    | 60 |

|                                                                                                           |    |
|-----------------------------------------------------------------------------------------------------------|----|
| Figure 23 Two dielectric slabs and in relative motion. Left: .....                                        | 61 |
| Figure 24 Finite element analysis (FEM) of friction on 2D materials.....                                  | 62 |
| Figure 25 Photo of clamshell type furnace. ....                                                           | 65 |
| Figure 26 Diagram of early CVD MoS <sub>2</sub> growth setup. ....                                        | 66 |
| Figure 27 Optical image of CVD MoS <sub>2</sub> growth where SiO <sub>2</sub> contacted alumina boat..... | 68 |
| Figure 28 SiO <sub>2</sub> substrates positioned in alumina boat. ....                                    | 70 |
| Figure 29 XPS survey spectra.....                                                                         | 71 |
| Figure 30 Mo3d and S2p XPS scans.....                                                                     | 71 |
| Figure 31 Photograph of CVD experiment with isolated Mo source. ....                                      | 75 |
| Figure 32 Optical images of growth using 3 temperature zones and isolated reactants..                     | 75 |
| Figure 33 Diagram of CVD setup with isolated reactants. ....                                              | 77 |
| Figure 34 Optical images of CVD MoS <sub>2</sub> .....                                                    | 78 |
| Figure 35 SEM micrograph of 3-layer MoS <sub>2</sub> .....                                                | 80 |
| Figure 36 Contrast images from EBSD peripheral photodetectors. ....                                       | 81 |
| Figure 37 Raman spectra for 1, 2, and 3 layer MoS <sub>2</sub> .....                                      | 82 |
| Figure 38 1T MoS <sub>2</sub> from butyllithium intercalation. ....                                       | 85 |
| Figure 39 AFM topography of graphene sheet after annealing. ....                                          | 87 |
| Figure 40 1T MoS <sub>2</sub> topography. Left:.....                                                      | 88 |
| Figure 41 Friction of 1T and 1H MoS <sub>2</sub> .....                                                    | 89 |
| Figure 42 Friction of a multilayered MoS <sub>2</sub> pyramid.....                                        | 91 |
| Figure 43 AFM data from Park NX-10 of a MoS <sub>2</sub> pyramid. ....                                    | 93 |
| Figure 44 Friction of MoS <sub>2</sub> with 0-degree twist between 1st and 2nd layer. ....                | 95 |
| Figure 45 Scatter plot of friction vs layer number.....                                                   | 96 |

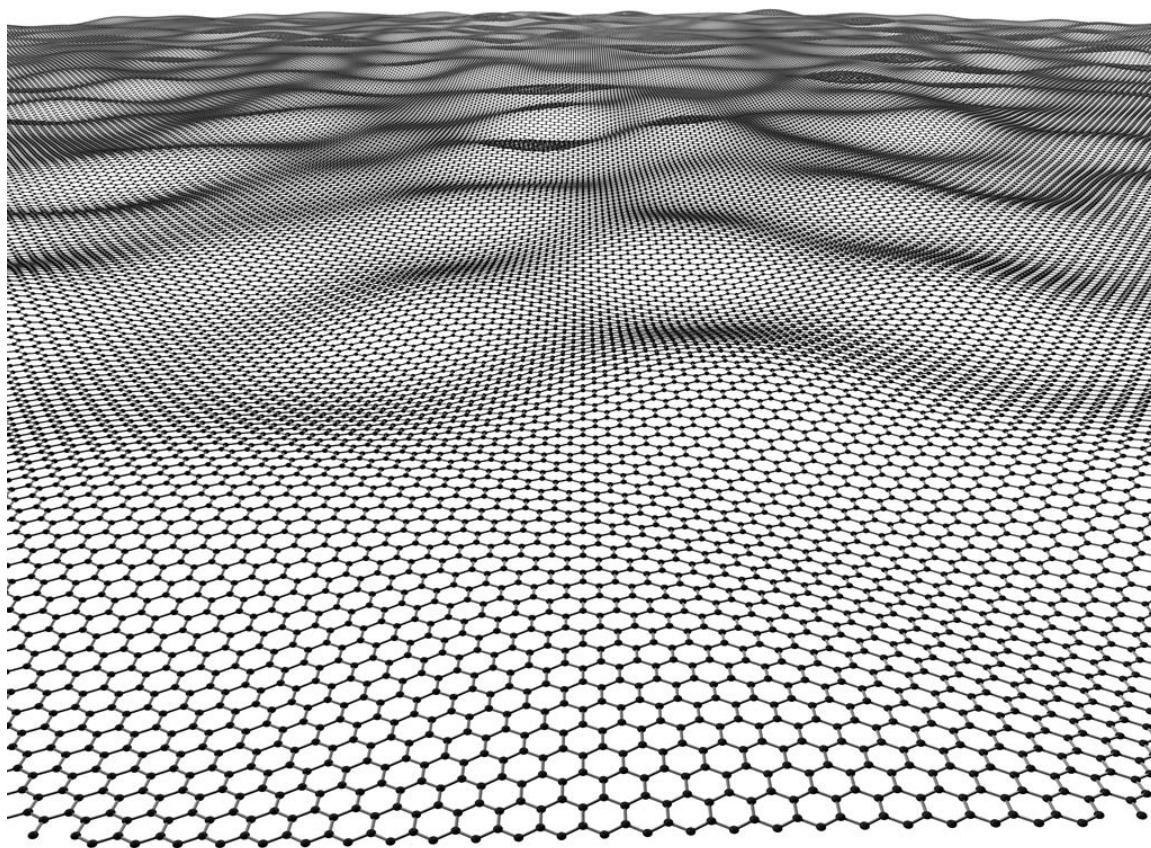
|                                                                                            |     |
|--------------------------------------------------------------------------------------------|-----|
| Figure 46 Electrostatic potential of trilayer MoS <sub>2</sub> flakes.....                 | 98  |
| Figure 47 MoS <sub>2</sub> flakes wet transferred onto TEM grid. ....                      | 99  |
| Figure 48 MoS <sub>2</sub> on continuous SiO <sub>2</sub> window TEM grid. ....            | 100 |
| Figure 49 Raman mapping and friction. ....                                                 | 101 |
| Figure 50 Mean square error vs structural similarity.....                                  | 103 |
| Figure 51 MSE and SSIM of 1024 <sup>2</sup> -pixel vs 100 <sup>2</sup> -pixel images. .... | 104 |
| Figure 52 Raman generated friction map.....                                                | 105 |
| Figure 53 Composite Raman map for predicting friction behavior.....                        | 106 |
| Figure 54 Friction predicted by Raman. ....                                                | 109 |
| Figure 55 Coefficient values vs wavenumber.....                                            | 110 |
| Figure 56 Coefficient values vs wavenumber detail.....                                     | 111 |
| Figure 57 Stacking of MoS <sub>2</sub> layers. ....                                        | 120 |

## List of Tables

|                                                                           |    |
|---------------------------------------------------------------------------|----|
| Table 1 Band gap energies of bulk and single-layer for several TMDs. .... | 13 |
| Table 2 Sample of parameters used in the literature for CVD.....          | 33 |

## 1. Introduction

Research conducted in recent decades demonstrates that the properties of materials are determined not only by their atomic and molecular composition but also by their dimensionality.<sup>16</sup> The reduction of one dimension to atomic limits has illuminated a panoply of novel properties and potential applications for two-dimensional materials. The Nobel prize-winning characterization of graphene, a single layer of carbon atoms, led the way to the development of other materials of one reduced dimensionality, giving rise to a 2D-materials revolution. These dimensionally reduced substances exhibit unique and enhanced properties that differentiate them from their bulk forms.



*Figure 1 Representation of a single layer of graphene. The ripples in graphene stabilize its single layer nature and represent unique features of atomically thin sheets.*

Graphene was first discovered in 1962, but it was not until it was isolated and characterized in 2004 using the simple mechanical exfoliation (or the Scotch tape) method that research on the material accelerated.<sup>17</sup> Fueled by an interest in commercializing its many mechanical and electronic advantages, research quickly spread to realization of and integration with other 2D materials; in particular, transition metal dichalcogenides (TMDs) have received significant attention.<sup>18-21</sup> While TMDs have layered structures similar to that of graphene, several of them, unlike graphene, are intrinsic semiconductors with band-gaps suitable for electronic devices capable of switching between on and off states.<sup>5,22,23</sup> Their low dimensionality and range of electronic properties has prompted further exploration for technological applications in catalysis,<sup>18,24,25</sup> energy storage,<sup>22,23</sup> sensing,<sup>26-29</sup> and nanoscale electronic switching devices including but not limited to field-effect transistors.<sup>30</sup> In order for any of these exciting potential applications to be realized, however, much work remains to be done in better understanding their structure, properties, and developing methods for realizing large scale synthesis of high quality atomically thin materials.

## 1.1 Objectives

The two primary objectives of this study were: elucidation of the parameters and conditions for synthesis of high quality and reproducible single-layer molybdenum disulfide ( $\text{MoS}_2$ ) by chemical vapor deposition (CVD), and exploration of motion-inhibiting tribological behavior and dependencies on a 2D nano-surface. There have been numerous reports on the growth of  $\text{MoS}_2$  by CVD,<sup>31-38</sup> but reproducibility from growth cycle to growth cycle remains a critical issue. In addition, inconsistencies exist amongst the different reports, making it difficult to make uniform conclusions. Thus, a simple aim

of this work is to understand the key synthesis parameters involved in realizing reproducible single layer MoS<sub>2</sub> by CVD. To elucidate this, I sought to rationally study key variables to investigate their role in determining the structure of the synthesized materials.

In parallel, I sought to understand how the electronic structure and layered arrangement of MoS<sub>2</sub> influence the friction encountered by a sliding probe of an atomic force microscope on its surface. MoS<sub>2</sub> is a well-known solid state lubricant, but the nanoscale tribological properties have been sparsely studied by only a few investigators. I wanted to understand these properties at the nanoscale to provide new insight into the fundamental mechanisms of frictional energy dissipation.

## 1.2 Organization of Thesis

This work is divided into three parts that seek to answer the questions: why, how, and what. Why is this research important? The first section describes why this research is fundamentally and technologically relevant, and explains the motivation for the study of two-dimensional materials in general, and MoS<sub>2</sub> in particular. Once the reason for this exploration is established, a detailed description follows of *how* the research was conducted. The answer to this question is divided into two sections from the bottom up: from synthesis to characterization. The methods of growing molybdenum disulfide are compared, contrasted, and detailed. Once the materials are built, their properties are probed and understood through the utilization of tools such as Raman spectroscopy, electron spectroscopy, atomic force microscopy, and others. These will be described in detail, with special emphasis on the tools integral to the goals of this thesis. What did this

research reveal? With the why and how developed in the first three chapters, Chapter Four describes what work was performed and what implications follow. Lastly, a discussion of the findings and what conclusions were drawn is provided in Chapter Five.

## 2. Motivation and Background

### 2.1 Motivation

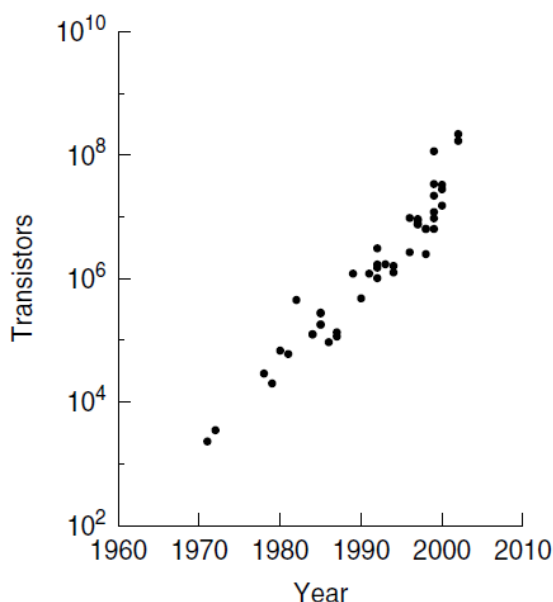
The motivation for this research is two-fold: to improve techniques for synthesizing high-quality two-dimensional nanomaterial with high potential for applications in future electronic and other devices; and to investigate tribological dependencies at the nanoscale. Tribology is the study of all things relating to bodies in contact and relative motion namely, friction, wear, adhesion, and lubrication. With technology design continually being refined to smaller and smaller scales, these two motivations coalesce into one: nanoscale design for macroscale benefit.

#### 2.1.1 Miniaturization of components

With the growing need for more computational power in our electronic devices, the number of transistors on integrated circuits has approximately doubled every two years since the beginning of the silicon-transistor computing paradigm over 40 years ago.<sup>39</sup> This paradigm is built on the complementary metal-oxide semiconductor (CMOS) transistor-comprised architecture of logic gates. Used to perform computations on input signals, they are constructed from complementary n- and p-type metal-oxide semiconductor field effect transistors (MOSFETs). MOSFETs rely on the bending of conduction and valence bands of a semiconductor in the presence of an electric field that changes the material from insulating to conducting and allows a current to flow through the semiconductor. Virtually all portions of microprocessors have continually been miniaturized over the decades to allow more and more transistors to be contained within

integrated circuits. This miniaturization will continue until the electronic and materials limits for this architecture are reached.

For the entirety of the CMOS computer paradigm, we have relied on silicon as our semiconductor material. An intrinsic band-gap of 1.1 eV.<sup>40</sup> and relatively simple fabrication techniques have made silicon a godsend for technological advancement. It is not without its limits, though: channel widths have a lower limit of 5-10nm, below which quantum tunneling results in current leakage, causing excess heat and decreased efficiency. Feature lengths of silicon transistors have steadily decreased from the order of a millimeter to tens of nanometers.<sup>1</sup> Advances in fabrication techniques such as electron beam lithography, chemical vapor deposition (CVD), and molecular beam epitaxy (MBE) have enabled transistors to decrease in size continually. With these and other fabrication advances, the transistors per integrated circuit have thus far followed Gordon Moore's 1975 prediction that every two years there will be a doubling of the number of transistors on a dense integrated circuit (See Figure 2).



*Figure 2 Transistors on a single chip. The number of transistors on a microchip has approximately doubled every year since 1970 as shown by the linearity on logarithmic scale.<sup>1</sup>*

To date, silicon has met the structural and electronic demands necessary for production electronics to follow this trend, but it is nearing its limit. Quantum tunneling allows electrons to jump the gap between source and drain, with channel widths that approach the electron de Broglie wavelength, resulting in current leakage and lower on/off ratios as silicon MOSFETs are miniaturized further.<sup>41-44</sup> Future semiconductor devices will need to employ materials that can be reduced in at least one dimension for continued densification of MOSFET-based microprocessors. In order for Moore's Law to hold in the coming years and before a paradigm shift away from transistor computing can take place, a new material must replace silicon as the transistor semiconductor material. As discussed below in sections 2.2.4 *Applications* (pg. 14) and 2.2.5 *Structure and Properties* (pg. 21), MoS<sub>2</sub> is one of the potential 2D materials that may be utilized as the switching material in future electronic components by taking advantage of its electronic properties.

### 2.1.2 Miniaturization of devices

Downsizing and improvement of transistors over the past 40 years has resulted in a size reduction of consumer devices by a factor of more than 200 and an increase in processor speed of 1,000 times. The first commercially available portable computer (IBM 5100) had a 1.9 MHz processor and weighed 24 kilograms.<sup>45</sup> Current cell phones have clock speeds of greater than 2 GHz<sup>46</sup> and weigh approximately 100 grams. Extending these trends of size reduction and increasing processing power forward, we should soon see electronic devices on the millimeter scale and below that possess innumerable capabilities.

### 2.1.3 Enhancement of friction forces at small scales

Both now and in the future, we need to understand and mitigate friction forces: parasitic friction hinders the performance of all tribological systems (automotive, manufacturing, aerospace, etc.) and accounts for 22-33%<sup>47,48</sup> decrease in the efficiency of automobiles.

Furthermore, in the future we will need to tune friction forces on a small scale to enable micro- and nano-electromechanical systems (MEMS/NEMS), as frictional forces are largely scale-dependent and will inhibit the motion of in-vivo MEMS/NEMS.

At the macroscopic level, translation inhibiting forces scale approximately with mass:  $F=ma$ , and frictional drag forces for biologically achievable motion are only minimally dependent on surface area or contact area. In contrast, at the micro-scale and below, the parasitic drag forces are sensitively dependent on surface area, contact area, and electromagnetic interactions between medium and media.

#### 2.1.4 Fundamental understanding of friction

In order to accommodate mobility of future electronics (e.g. micro-scale in-vivo medical devices), frictional forces will need to be tuned and/or mitigated. Relative to other forces acting on an object, friction acts more intensely on small scales due to van der Waals surface forces and electronic and phononic excitations. Adhesive and motion-inhibiting forces acting on micro-scale devices pose a major challenge to their ability to detach from or traverse arbitrary surfaces. While the factors contributing to friction (excluding material wear) at the nano- and micro-scale (namely electronic and phononic) are known, general models and methods for tuning them have yet to be described.

The behavior of macro-scale tribological systems has been described with reasonable accuracy using two laws described by Guillaume Amontons in the 17<sup>th</sup> century.

Amontons found that friction force is directly proportional to applied load and that the friction force is independent of contact area. While these laws are suitable to predict friction in certain engineering applications, they break down on small scales and to this day, accurate models for predicting the interplay between electronic and phononic contributions and the resultant friction on an atomic- or nano-scale have not yet been developed.

Atomic force microscopy (AFM) and lateral force microscopy (LFM) have enabled a more intimate investigation of friction phenomena at sub-micron scales. More recently, the invigorated study of graphene and its 2D relatives has enabled experimentation to probe the components of friction deeper, with the goal of resolving models for prediction and mitigation or tuning of frictional forces.

### 2.1.5 Challenges

The most significant barrier to realization of the potential benefits of MoS<sub>2</sub> is the difficulty of producing large-area, uniform, single-layer sheets in a scalable, energy-efficient manner. Research groups all over the world are able to create single-layer uniform MoS<sub>2</sub> by CVD,<sup>31,34,49-51</sup> but on the macro-scale these samples are greatly inhomogeneous with varying film thickness and small (<100 μm), anisotropic grains. Once uniform single-layer CVD MoS<sub>2</sub> growth methods emerge, the next challenge will be growth of directionally oriented grains. Presently, as regions of MoS<sub>2</sub> merge together to form a large single layer sheet, grain boundaries form and often present sites for further growth. Grain boundaries reduce or inhibit electronic applicability as charge-carrier mobility values diminish as a result of scattering at the mismatched grains.<sup>52-54</sup> Microwave impedance microscopy (MIM) suggests that conductivity at a grain boundary may be one order of magnitude lower than within a single crystal.<sup>55</sup> Thus the challenge is to develop methods, through elucidating fundamental growth parameters, for producing MoS<sub>2</sub> in a manner that allows grains to merge seamlessly or grow in single, monolithically large sheets. Given the isotropic alignment of all seeds and subsequent grains grown from vapor phase, merging should occur naturally. Growth on a (0001) sapphire substrate produces grains predominantly aligned in one of two directions differing by 30 degrees.<sup>56</sup> This finding opens the potential for large-area, single-crystal epitaxial MoS<sub>2</sub> growth based on substrate material and crystallinity. Another potential means of controlling grain orientation is with applied electric fields. Electric fields have been used to aid preferential growth direction for carbon nanotubes.<sup>57</sup> Titanium dioxide thin films grown by aerosol-assisted chemical vapor deposition show thickness,

roughness, and preferred crystallographic orientation dependence on an applied DC electric field.<sup>58</sup> One such approach, or another yet unexplored, must be developed if the many potential applications of MoS<sub>2</sub> are to be realized.

## 2.2 Solution

Several novel materials and morphologies have emerged in recent decades that show promise for future transistor devices. Reducing one dimension to its limit enables heterostructuring and layering to substantially increase transistor density in microprocessors. The minimum limit for compounds is one atom or unit cell thick. Several materials have ordered, repeating arrangements in two lateral dimensions but are held together in the third dimension by only weak van der Waals forces with vertical thickness ranging between one angstrom and one nanometer.<sup>52,59,60</sup> While commonly referred to as 2D, these layered materials are quasi two-dimensional as they possess a finite thickness. Many interesting and tunable properties of these materials depend on their thickness, strain, and environment.<sup>61-65</sup> Some of the most researched 2D materials for transistor applications are graphene/hexagonal boron nitride,<sup>66</sup> MoS<sub>2</sub>,<sup>67</sup> WS<sub>2</sub>,<sup>68</sup> silicene,<sup>69</sup> and combinations of these.<sup>70</sup> In addition to their potential applications for future electronic applications, 2D materials provide a unique and insightful means of exploring friction on the nanoscale. Their atomically smooth surfaces allow the study of electronic and phononic friction in the absence of wear and anisotropic multi-asperity contact. The phononic friction can be reduced or eliminated by testing at low temperatures and the electronic friction can be suppressed by choice of material.

### 2.2.1 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) are quasi-2D, van der Waals-bonded solids. These are layered structures of the form  $\text{MX}_2$  where M is a transition metal and X is a chalcogen atom. Single layer TMDs can exist in one of two phases (or polymorphs): either the trigonal prismatic phase (1H) or the octahedral phase (1T). When multiple layers of a polymorph are present, several polytypes can be produced that exhibit different properties based on how the layers are arranged and will be discussed further in 2.2.5 *Structure* on page 21. Unlike graphene, the single layer of TMDs consists of three atomic layers (rather than one) with the transition metal sandwiched between the chalcogens.

Many TMD compounds are intrinsic semiconductors in the bulk form. However, most layered TMDs in bulk form tend to be indirect band-gap semiconductors. For example,  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{MoSe}_2$ , and  $\text{WSe}_2$  possess sizable band-gaps so that field-effect transistors can be readily realized from them.<sup>9,67,68,70-73</sup> Table 1 Shows the band-gaps of TMDs which range from metallic (zero band-gap) for those with transition metals niobium and tantalum to band-gaps of approx. 2 eV for  $\text{MoS}_2$ ,  $\text{WS}_2$ , and  $\text{PtS}_2$ .

| Bandgap (eV) |           | Mo      | W       | Ti    | Zr    | Hf    | V     | Nb    | Ta    | Ni    | Pd   | Pt   |
|--------------|-----------|---------|---------|-------|-------|-------|-------|-------|-------|-------|------|------|
| S            | monolayer | 1.8-2.1 | 1.8-2.1 | ~0.65 | ~1.2  | ~1.3  | ~1.1  | metal | metal | ~0.6  | ~1.2 | ~1.9 |
|              | Bulk      | 1.0-1.3 | 1.3-1.4 | ~0.3  | ~1.6  | ~1.6  | metal | metal | metal | ~0.3  | ~1.1 | ~1.8 |
| Se           | monolayer | 1.4-1.7 | 1.5-1.7 | ~0.51 | ~0.7  | ~0.7  | metal | metal | metal | ~0.12 | ~1.1 | ~1.5 |
|              | Bulk      | 1.1-1.4 | 1.2-1.5 | metal | ~0.8  | ~0.6  | metal | metal | metal | metal | ~1.3 | ~1.4 |
| Te           | monolayer | 1.1-1.3 | ~1.03   | ~0.1  | ~0.4  | ~0.3  | metal | metal | metal | metal | ~0.3 | ~0.8 |
|              | Bulk      | 1.0-1.2 | metal   | metal | metal | metal | metal | metal | metal | metal | ~0.2 | ~0.8 |

*Table 1 Band gap energies of bulk and single-layer for several TMDs. First row, first column of the table shows MoS<sub>2</sub> with monolayer band-gap just below 2 eV and bulk slightly over 1 eV. All values are in electron volts (eV) ranging from metallic (zero band gap) to over 2 eV.<sup>8</sup>*

An interesting fact about TMDs is that they undergo a dramatic change in the electronic structure when their dimensions are reduced from 3D to 2D.<sup>74,75</sup> Specifically, the absence of electronic interactions among the layers due to quantum confinement leads to a transformation from indirect to direct band-gap semiconductor.<sup>18,59,60,76</sup> This is significant because direct band-gap semiconductors, in principle, can possess quantum efficiency of 100% (due to Fermi's Golden Rule<sup>77,78</sup>) for light emission. In practice, the presence of defects reduces this value,<sup>74,75,79</sup> but the possibility of achieving high quantum yield makes these materials promising for opto-electronics. A large body of research has been completed regarding the synthesis, electronic properties, and electronic applications of MoS<sub>2</sub> in particular.

### 2.2.3 MoS<sub>2</sub>

Molybdenum disulfide (MoS<sub>2</sub>) is currently the most widely studied TMD. With its desirable electronic and mechanical properties, MoS<sub>2</sub> has a broad range of applications, most of which are currently emerging. In the following, I briefly outline recent progress

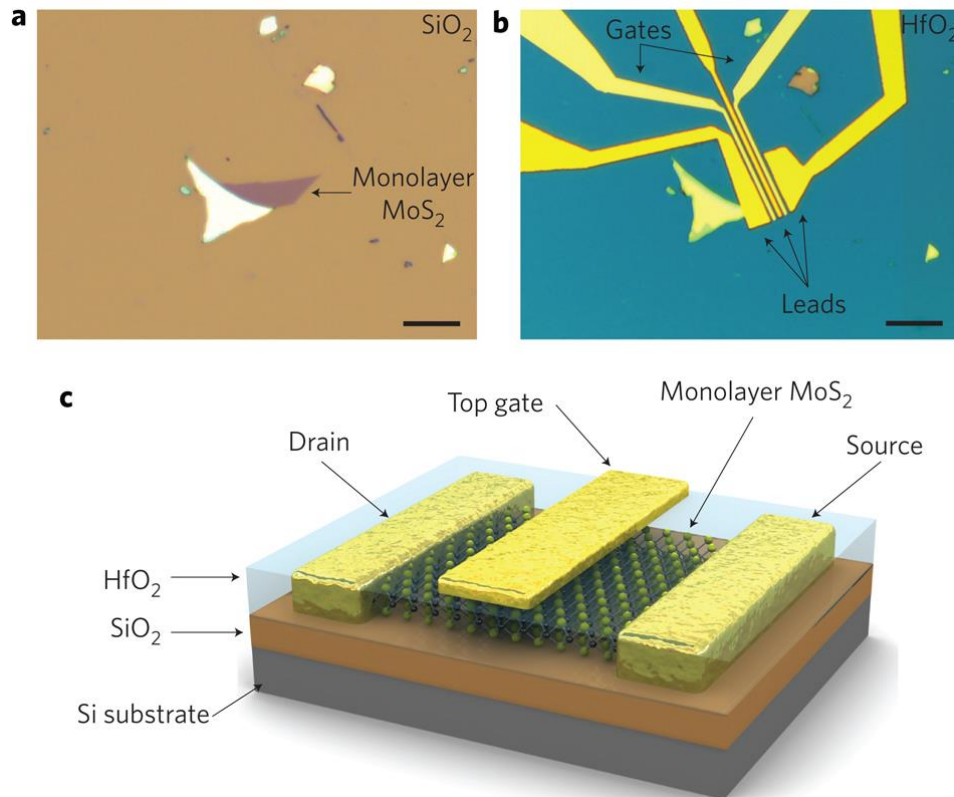
on devices implementing MoS<sub>2</sub> as the channel material in transistors, as a catalyst for the hydrogen evolution reaction, and as an energy storage material supercapacitors.

#### 2.2.4 Applications

##### *Transistors*

Transistors are becoming smaller and smaller to enable the production of more powerful devices by fitting more transistors into current microprocessors than were contained in historical devices. While Moore's law has held up in recent years, the downsizing of silicon transistors will reach a limit in the near future (<10 years) and thus in order to continue using the current computing architecture of logic gates via field effect transistors (FETs), new materials must therefore be employed to make transistors smaller. Two-dimensional materials such as graphene, MoS<sub>2</sub> and the like are particularly appealing for their potential application in future microprocessors.<sup>9,80</sup> With layer thicknesses of less than one nanometer, it may be possible to improve upon the lower limit of silicon transistors. A key problem with state of the art electronics is power dissipation in the off state.<sup>81-83</sup> That is, in the very small channel devices, the electric field coupling between the gate electrode and the semiconducting channel is not sufficiently good so that carriers can conduct even in the off state.<sup>84-86</sup> The main reason for this is because in 3D semiconductor channels, there a distribution of electron concentration over thickness of few nanometers. In contrast, electrons in 2D materials are confined to thickness of the material, which is less than 1 nm.<sup>84,87-89</sup> Therefore, gate voltage is able to influence all carriers in the 2D material channel equally, giving rise to excellent gate electrostatics. With more efficient switching, larger band-gap materials can be used which increases the tunneling barrier. It is believed that this should lead to low off state current and much

lower energy dissipation in the off state. Figure 3 depicts the first high performance field effect transistor constructed from single-layer of MoS<sub>2</sub> as the channel between source and drain electrodes on an oxidized silicon substrate, and top gate insulated by hafnium dioxide.



*Figure 3 Transistor constructed from a single layer of MoS<sub>2</sub>. (a) Monolayer MoS<sub>2</sub> seen by optical microscopy. (b) actual device with patterned electrodes on single layer region. (c) schematic of device architecture showing top gate with source and drain electrodes encapsulated in insulated HfO<sub>2</sub>. Scale bars in **a**, **b** are 10  $\mu\text{m}$ .<sup>9</sup>*

Single-layer MoS<sub>2</sub> transistors have been constructed with an on/off current ratio (i.e. the difference in current in the off and on states of the device) of  $10^8$ .<sup>9</sup> Another important factor in determining the applicability of MoS<sub>2</sub> for FETs in future microprocessors is its ability to function at high-frequency switching. Top-gated MoS<sub>2</sub> transistors have been shown to operate in the gigahertz range with cutoff frequency of 6 GHz.<sup>72</sup> The data and

research conducted to date satisfactorily demonstrate the feasibility of 2D materials to potentially extend Moore's law beyond silicon.

### *Hydrogen evolution*

2D MoS<sub>2</sub> is widely being studied for generation of hydrogen using electro- or photo-catalysis.<sup>90-93</sup> With an annual global usage of over 60 million tonnes<sup>94</sup>, hydrogen and its production are the subject of significant economic and environmental concern. Currently used predominantly as a reactant in the production of ammonia and as a catalyst for fossil-fuel hydrocracking, hydrogen is produced through steam reforming of methane in natural gas.<sup>94</sup> As the supply of natural gas is limited, it is of environmental importance that novel methods of producing hydrogen be discovered and implemented. The best catalyst for evolving hydrogen is platinum.<sup>95</sup> However, its prohibitive cost has limited its use as practical catalyst for making hydrogen. To this end, MoS<sub>2</sub> has been shown to be an effective catalyst for hydrogen evolution. The use of MoS<sub>2</sub> as a catalyst is particularly attractive because its elements are earth abundant and therefore inexpensive. Electrodes made from 2D TMDs have been shown to evolve hydrogen in acidic electrolyte.<sup>24</sup> With an applied overpotential of ~100 mV, 1T-MoS<sub>2</sub> on glassy carbon electrodes evolves hydrogen from 0.5 M sulfuric acid.<sup>25</sup> This can be further improved through advanced nanostructuring to increase surface area per unit mass.<sup>96-98</sup> Since hydrogen currently comes from a non-renewable resource and energy costs of extraction are relatively low,<sup>99</sup> electrochemical production has not been significantly investigated, but as supplies run out or environmental regulations curb fossil-fuel usage, more research will be devoted to novel methods of hydrogen production, including the use of MoS<sub>2</sub> catalysts.

### Supercapacitors

Another promising application of MoS<sub>2</sub> and other TMDs is for energy storage in the form of supercapacitors and batteries.<sup>5,100-102</sup> Supercapacitors store electrical energy through the polarization of a dielectric material by the application of an external electric field. Due to the large surface area per unit mass of 2D nanostructured materials, there is great potential for TMDs as supercapacitor materials. 1T-MoS<sub>2</sub> has been shown to perform well as a supercapacitor electrode material with specific capacitance of several hundred farads per cubic centimeter. For comparison, traditional electrolytic capacitors typically yield micro- or milli-farads per cm<sup>3</sup>. Figure 4 shows some common and novel charge storage devices as energy density vs power density.

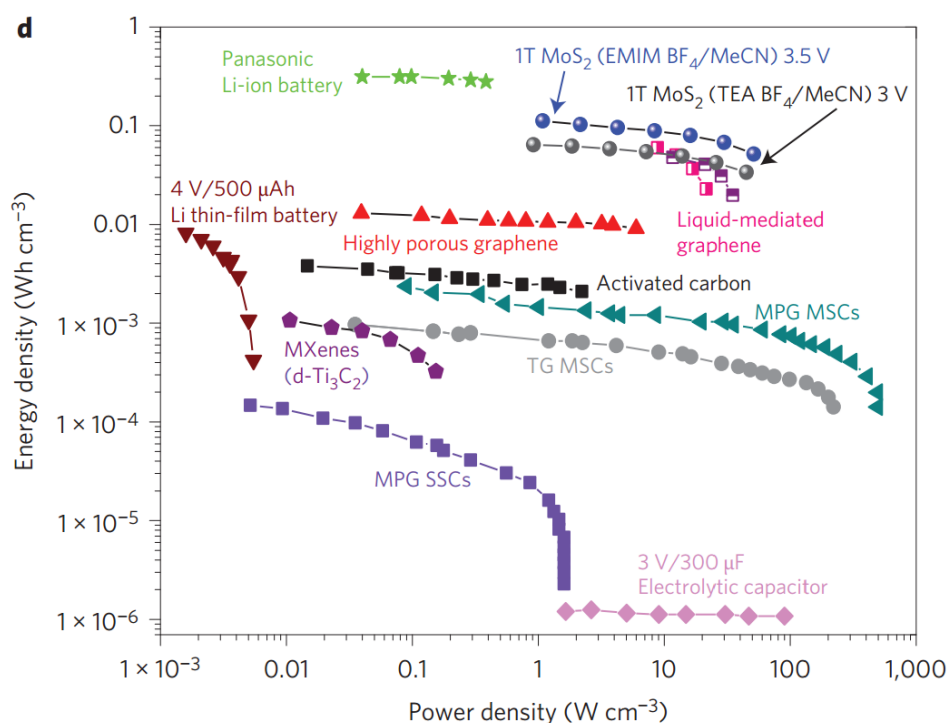


Figure 4 Energy density vs power density of novel power storage devices. Compare high power density of 1T MoS<sub>2</sub> supercapacitor on top right in blue with lower power density but slightly higher energy density Panasonic Li-ion battery.<sup>5</sup>

The ideal device has both high energy density and power density. Laboratory MoS<sub>2</sub>

electrodes exhibit higher power density than state-of-the-art lithium ion batteries but slightly lower energy density.

### Photodetection and photovoltaics

As an optically active material, MoS<sub>2</sub> shows much potential for optoelectronics such as photodetectors and photovoltaics. MoS<sub>2</sub> in its as synthesized form is always n-type.<sup>73,103,104</sup> The reason for this is not well established, but it is typically attributed to presence of impurities or doping effect from presence of sulfur vacancies. Thus, coupling MoS<sub>2</sub> with a p-type 2D material such as black phosphorus provides opportunities for realizing atomically thin interfaces and p-n junctions. A device incorporating single layer of n-type MoS<sub>2</sub> and an overlapping layer of p-type black phosphorus (BP) forming a heterojunction is shown in Figure 5.

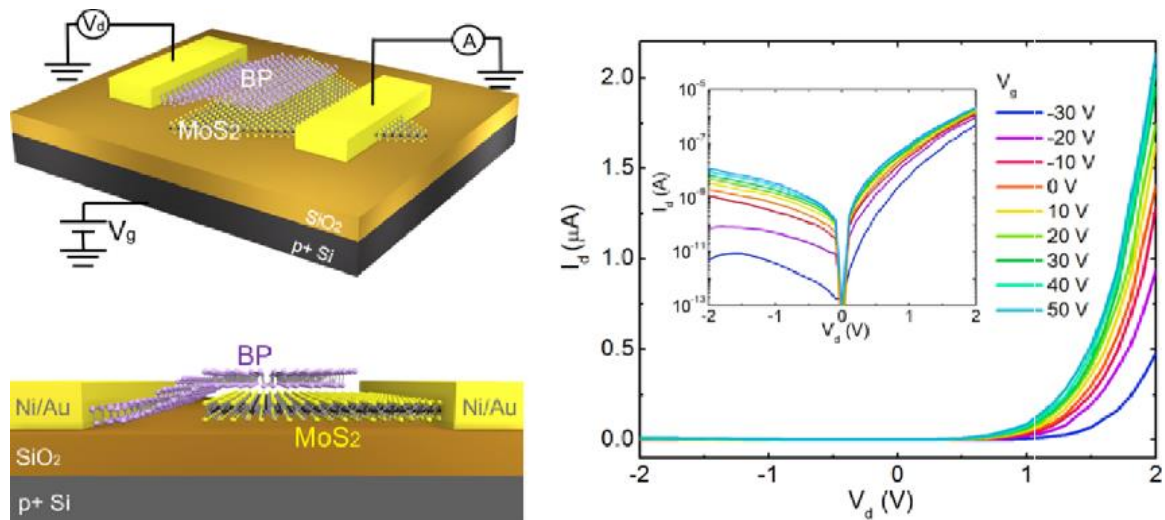


Figure 5 Schematic of MoS<sub>2</sub>/black phosphorus heterojunction and IV curves. Due to the disparity in work functions of BP and MoS<sub>2</sub>, this junction the application of a potential to the p-doped bottom gate allows current to flow from the source (labeled A) to drain (labeled V<sub>d</sub>) as shown on the right in the characteristic IV plot for various gate voltages with semi-log inset.<sup>11</sup>

The heterojunction shows diode-like current versus voltage output characteristics as

shown in the figure. Further, it can be seen that the diode output can be modulated with a gate voltage. The p-n junction can be used to generate power in the form of a photovoltaic device in which incoming photons are absorbed by the 2D layers and excitons are generated in both. At the interface of the 2D layers, there is a built-in voltage which dissociates the excitons into free electrons and holes that are transported via the n-type and p-type materials, respectively – generating power. This small device is able to generate power conversion efficiency of 0.3% with ~11 nm thick BP, but is predicted to reach 18% upon reduction to bilayer BP. This type of device can also be used as a photodetector in which the photons over a broad range of wavelengths are absorbed and the photo-generated current is measured. The responsivity of this photodetector is on the order of 418 mA/W,<sup>11</sup> which compares well with the state of the art photodetectors based on silicon devices.<sup>105</sup>

#### *Lubricant additive/friction modifier*

Used for many decades predominantly as a lubricant additive for its friction- and wear-resisting properties, MoS<sub>2</sub> is found in most formulated automotive oils and dry, oxygen-free vacuum environments. Molybdenum-sulfur compounds used as lubricant additives are not strictly MoS<sub>2</sub> nanosheets; molybdenum dialkyldithiocarbamate (MoDTC) nanoparticles have been found to greatly improve tribological behavior in formulated oils. While MoDTC contains other atomic species, the improved friction is attributed to sliding planes of MoS<sub>2</sub> in the presence of zinc dialkyldithiophosphate (ZDTP).<sup>106</sup> As a standalone lubricant, MoS<sub>2</sub> sheets do not perform well tribologically in oxygen- or water-containing environments because oxidation of unterminated bonds on the edges of MoS<sub>2</sub> sheets create asperities and destroy the layered structure so as to reduce the efficacy of

MoS<sub>2</sub>'s desirable interplanar sliding behavior. Fullerene-like MoS<sub>2</sub> nanoparticles – with no edges due to their closed structure – have been found to greatly decrease friction in humid environments due to reduction of exposed edges and thus their oxidation.<sup>23</sup> Thin films of MoS<sub>2</sub> deposited using physical vapor deposition techniques such as sputtering can be incorporated directly onto tribological components.<sup>107-109</sup> Thin films of MoS<sub>2</sub> are useful in systems where liquid lubrication is undesirable or unfeasible. – for example in space or dry machining in applications. Micro- and nano-electromechanical systems (N/MEMS) could also utilize atomically thin coatings of MoS<sub>2</sub> or similar friction-reducing material to facilitate surface locomotion that would otherwise be impossible due to the substantial impact of friction on micro and nanoscale systems. Friction behavior of bulk layered materials is reasonably well understood, but only limited information is available on the tribological properties of 2D materials. Thus, understanding the behavior of very thin layers is required for implementation of such materials to reduce friction.

#### *Tribological model*

The prevalence of layered MoS<sub>2</sub> as a solid-state lubricant and friction modifiers combined with the ability of change phases makes it an ideal material for studying the nanoscale and atomic scale friction to obtain fundamental insights. MoS<sub>2</sub> has a large Raman cross section, and thus it is possible to obtain information about phonons within and between layers. Furthermore, the vibrational density of states changes dramatically for different phases. It is thus possible to monitor the phase and phononic changes with treatments and before and after tribological measurements. Further, vibrational interactions between layers and with the substrate can also be monitored since they can also influence the tribological properties due to available phonon modes. Surface charge of substrate and

over sample topology influence the resultant tribological behavior, and their contributions can be elucidated through experimental testing of select sample, substrate, thickness, and layer stacking orientation.

#### 2.2.5 Structure and Properties

MoS<sub>2</sub> belongs to the P6<sub>3</sub>/mmc crystal symmetry group with lattice constants  $a = b = 3.15$  Å and  $c = 12.27$  Å.<sup>14,15</sup> Unless otherwise specified, MoS<sub>2</sub> typically refers to the multilayer, thermodynamically stable 2H polytype, but other phases and polytypes exist, such as the 1T and 3R. The 2H polytype is shown in Figure 6(a), which shows layers of (1H) MoS<sub>2</sub> stacked in the ABA sequence. The unit cell of the bulk 2H phase consists of two layers of MoS<sub>2</sub>, thus the prefix 2 is added for the trigonal prismatic phase, H. Based on the trigonal prismatic polymorph (1H), 3R MoS<sub>2</sub> contains 3 layers in a unit cell with

each layer shifted by laterally by 1/3 of the unit cell (Figure 6b).

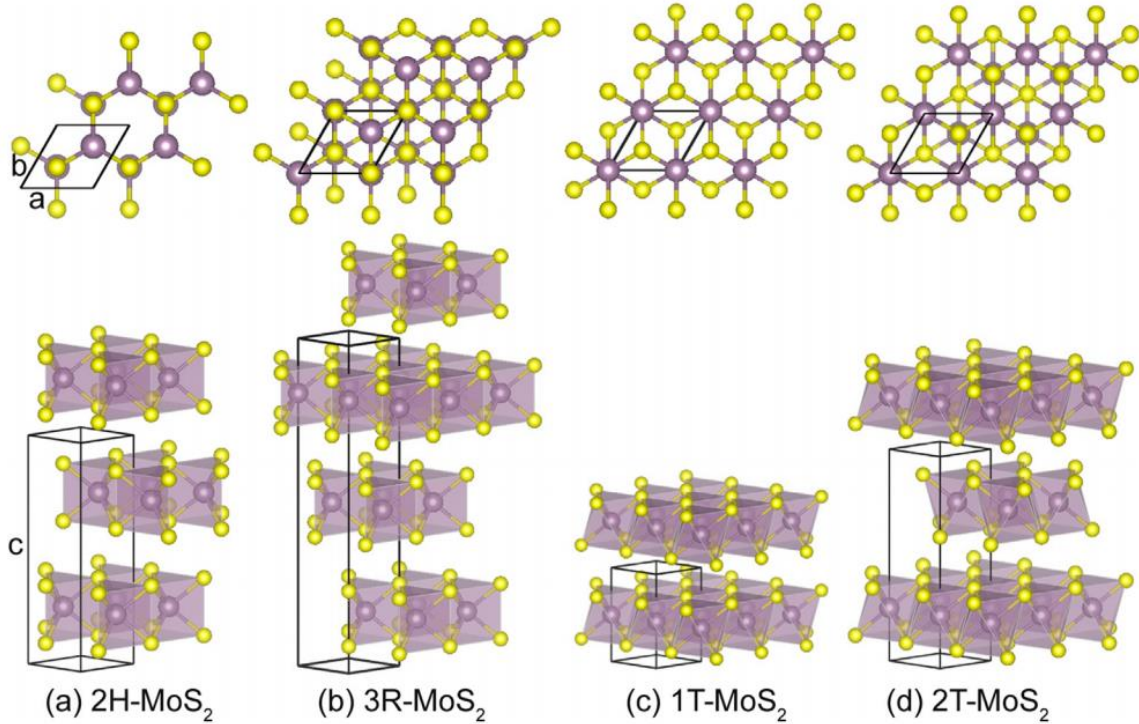


Figure 6 Various crystal structures of MoS<sub>2</sub>. Yellow (smaller) and purple (larger) spheres represent sulfur and molybdenum atoms respectively. (a) Trigonal prismatic 2H polytype (of 1H MoS<sub>2</sub>) with ABA stacking, lateral unit cell dimensions of *a* and *b* (top, as viewed from above), and vertical unit cell length of *c*. L2 rotated  $\pi/6$  about vertical axis through hexagon center so that S atoms are above Mo of L1 and vice versa. (b) 3R rhombohedral polytype with ABC stacking. L2 and L3 each shifted  $-(\mathbf{a} + \mathbf{b})/3$  relative to L1 and L2 respectively. (c) Octahedral 1T polymorph. Unit cell S atoms in this phase do not share a vertical axis; second layer of sulfur is rotated  $\pi/6$  about vertical axis through Mo. (d) 2T polytype. L2 rotated  $\pi/6$  about a vertical axis through a sulfur atom.<sup>14,15</sup>

The octahedral 1T phase in MoS<sub>2</sub> (Figure 6c) is non-centrosymmetric meaning that the

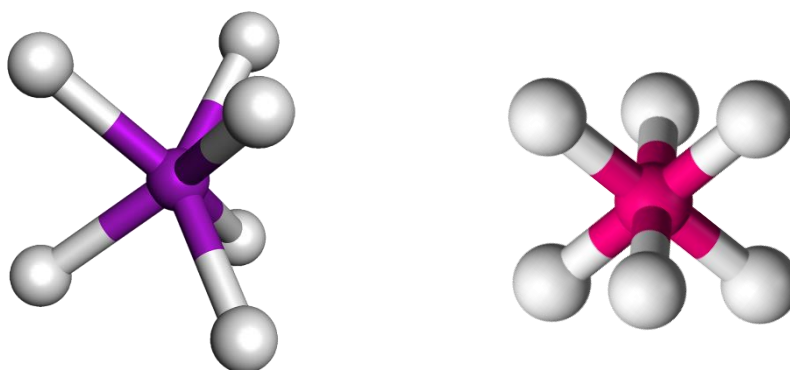
Mo atoms are not located in the center of the unit cell, in contrast to the 1H phase.

Because of its inversion center of symmetry, 1T MoS<sub>2</sub> cannot exhibit piezoelectric

response, but it has been observed in 1H MoS<sub>2</sub>.<sup>110 111</sup>

It should be noted that while 1T MoS<sub>2</sub> can refer to multiple layers of this polytype, 1H can only be 1 layer thick because multiple layers of 1H stacked MoS<sub>2</sub> are thermodynamically unstable.

The naturally occurring, stable, trigonal prismatic 2H phase of MoS<sub>2</sub> can be transformed into the metastable octahedral 1T phase via lithium intercalation. During the intercalation, lithium ions donate electrons to the MoS<sub>2</sub> lattice and this excess charge makes the trigonal prismatic phase unstable. With excess charges located in the sulfur orbitals, the repulsive force experienced by sulfur atoms results in their shifting to maximize the mean separation between the sulfur atoms. Sulphur atoms sharing a z-axis in charge neutral MoS<sub>2</sub> have S-Mo-S bond angles of less than 90° (as shown in Figure 7) because the Mo z orbitals push them radially.



*Figure 7 Coordination models. Left: trigonal prismatic with bond angles of 90° for in plane ligands and 82° for out of plane ligands. Right: octahedral with 90° bond angles.*

As electrons are added, the repulsive force among S atoms overcomes the influence of non-bonding Mo orbitals to maximize sulfur separation and results in the octahedral coordination with 90° for all S-Mo-S angles. DFT calculations for MoS<sub>2</sub> show that the 1T phase becomes more thermodynamically stable upon injection of greater than 1 electron per MoS<sub>2</sub> unit.<sup>112</sup>

Single layer 1H MoS<sub>2</sub> is semiconducting with a direct bandgap of  $\sim 1.7$  eV while in the bulk form, 2H MoS<sub>2</sub> has an indirect band-gap of 1.29 eV<sup>17</sup>. This can be seen in Figure 8 where the valence band maximum at the  $\Gamma$  point and the conduction band minimum between the K and  $\Gamma$  points possess the lowest energy gap for MoS<sub>2</sub> consisting of more than one layer.

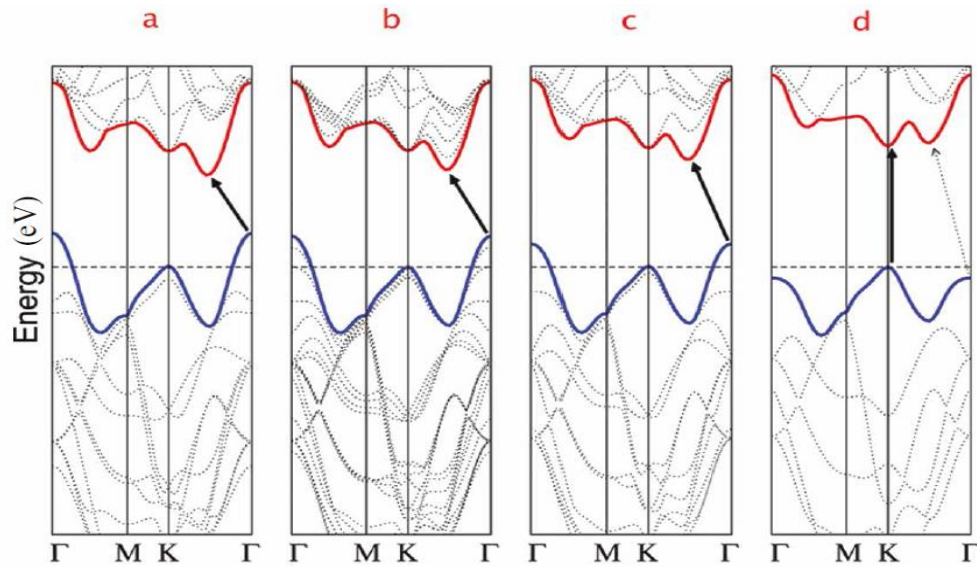
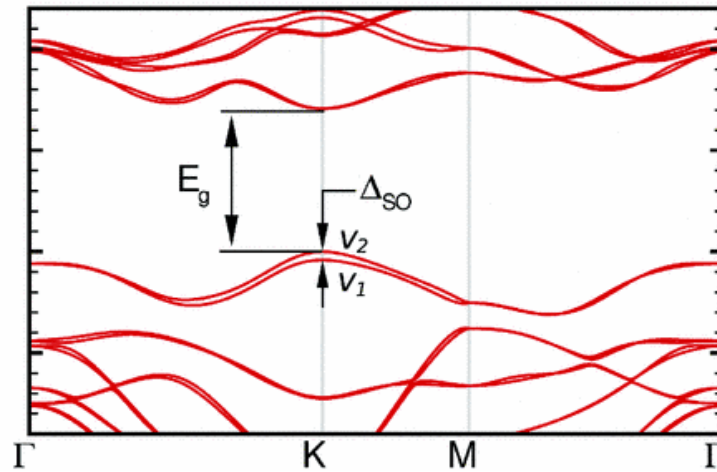


Figure 8 Electronic band structure of MoS<sub>2</sub> for high symmetry points in momentum space. a) Bulk, b) four, c) two, and d) single layer MoS<sub>2</sub> show transition from indirect band gap from the  $\Gamma$  point (center of Brillouin zone) for bulk MoS<sub>2</sub> to direct band gap at the K point for single layer MoS<sub>2</sub>.<sup>16</sup>

This is attributed to weak interactions between the layers. MoS<sub>2</sub> with more than one layer is indirect band-gap because in order for an electron in the valence band to be excited into the conduction band, it must be given not only energy equal to or greater than the gap but also momentum. In contrast, it can be seen from Figure 8 that for single layer MoS<sub>2</sub>, the conduction band minimum and valence band maximum are both located at the K point and thus only energy is needed for electrons to be excited from valence band to conduction band.

In addition to the transition from indirect to direct band-gap, the electronic structure of the single layer differs from multilayer or bulk in one other significant way. In MoS<sub>2</sub>, there is a large spin-orbit coupling which gives rise to splitting of the valence band.<sup>113,114</sup> That is, there is a sizable (tens to hundreds of meV) separation between the split energy levels of the valence band.<sup>115,116</sup> (See Figure 9) These split energy levels are referred to as different “valley” states and there is a huge amount of research being conducted to probe the valley states, excite them using circularly polarized light, and manipulate them electronically to realize valleytronics based devices.<sup>115</sup>



*Figure 9 Spin orbit coupling band splitting. Valence band maxima splits at the K point due to spin orbit coupling which produces a secondary transition with energy equal to  $E_g + E_{SO}$*

For single layer MoS<sub>2</sub> the spin orbit coupling of electrons in the valence band result in a splitting of the band at the K point. This results in two potential transitions to the conduction band minima. Excitons (electron-hole pairs) thus form from two different energies: the smaller A-type corresponding to  $V_2$  and the larger B-type corresponding to  $V_1$  in Figure 9. These transitions are discussed further in the Raman spectroscopy section on page 39.

## 2.3 Synthesis and Growth

Since the isolation of single layer graphene in 2004 by mechanical exfoliation and its subsequent realization on copper substrates by chemical vapor deposition, there has been tremendous work and progress on synthesis of 2D materials. The scientific community has learned a tremendous amount about synthesis and fabrication of 2D materials from the graphene research. Many of the techniques used to realize high quality graphene have also been utilized from obtaining high quality MoS<sub>2</sub> and other 2D TMDs. I will briefly summarize these methods below.

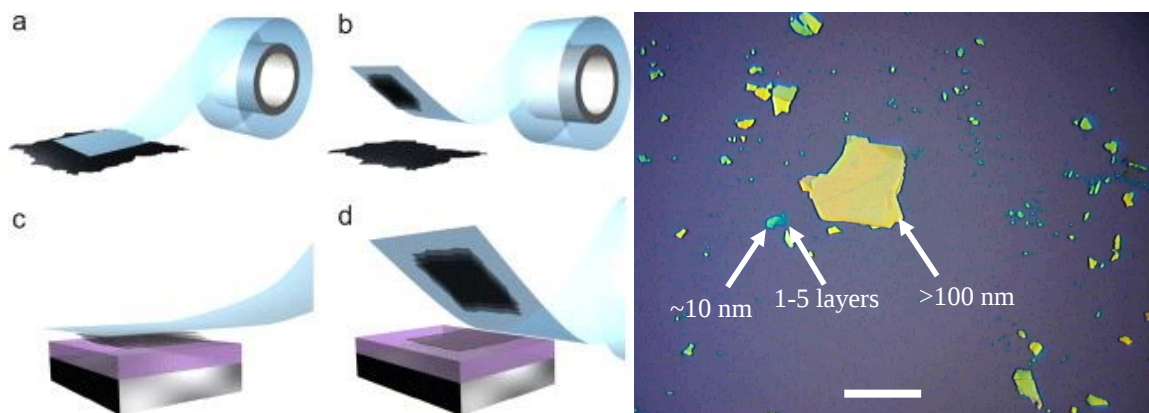
Various techniques have been employed for the synthesis of MoS<sub>2</sub>. Most prevalent are mechanical exfoliation,<sup>117-119</sup> chemical exfoliation,<sup>4,97,118,120</sup> and chemical vapor deposition (CVD).<sup>31-38,58,67,121,122</sup> The simplest but relatively impractical method for realizing large samples is mechanical exfoliation which separates weakly bonded layers of bulk MoS<sub>2</sub> by placing it between two faces of a suitable adhesive and subsequent separation. Repeated many times until semi-transparent few- and single-layered regions develop. From the adhesive the MoS<sub>2</sub> can be transferred to arbitrary substrates. This method is ideal for obtaining high quality single- or few-layered samples that can be isolated through optical microscopy and then probed for fundamental condensed matter effects.<sup>119</sup> Chemical exfoliation uses liquid infiltration of an intercalant between layers of MoS<sub>2</sub> nanosheets, sonication to separate and disperse layers, and subsequent separation and isolation of unexfoliated material via centrifuging.<sup>123,124</sup> Typically, the intercalant is butyl lithium (BuLi), which transfers charge to the MoS<sub>2</sub> layers resulting in a phase change to the 1T polymorph.<sup>96,97</sup> Since the 1T phase is metastable, it can be transformed into the semiconducting 2H phase by mild annealing in controlled environment. Thus,

unlike mechanical exfoliation and CVD, it is possible to obtain both the 1T and the 2H phases of MoS<sub>2</sub>. The solution of butyl lithium, hexane, and MoS<sub>2</sub> produced can then be filtered and transferred to arbitrary substrates. The disadvantages of chemically exfoliated MoS<sub>2</sub> are irregular, randomly oriented nanosheets, and small lateral dimensions.

### 2.3.1 Top-down: mechanical exfoliation, chemical exfoliation

#### *Mechanical exfoliation*

In this method, bulk MoS<sub>2</sub> can be exfoliated into thin films by mechanical means with the use of an adhesive tape. Millimeter-scale pieces of bulk MoS<sub>2</sub> are placed on blue adhesive tape, brought into contact with a pristine region of tape, and then pulled apart. These steps are repeated until the film thickness is reduced to the desired range. By pressing the tape against arbitrary substrates such as SiO<sub>2</sub> the MoS<sub>2</sub> films are transferred. These basic steps are shown graphically in Figure 10.



*Figure 10 Mechanical exfoliation (Scotch tape method). (a) Adhesive tape is pressed against bulk MoS<sub>2</sub>. (b) Tape is lifted and removes top layers of bulk sample. (c) Tape + MoS<sub>2</sub> are pressed against target substrate and then lifted again leaving bottom layers of MoS<sub>2</sub> on substrate surface (d).<sup>6</sup> Right: optical micrograph showing exfoliated flakes. When viewed on 300 nm SiO<sub>2</sub> substrates, gold-colored flakes are typically >100 nm thick, bright blue are typically ~10 layers thick, and single or few layer flakes appear faint, light blue. Scale bar is 30  $\mu$ m.*

The key benefit of this approach is its simplicity, but the drawbacks are that thickness is not well controlled and flake size is highly non-uniform. The flakes of desired thickness are typically identified by optical microscopy (Figure 10 Right) and used primarily for electronic devices.

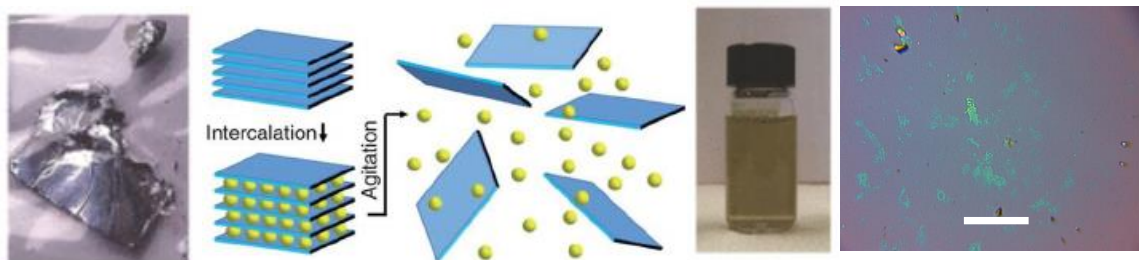
### *Chemical exfoliation*

Chemical exfoliation of bulk MoS<sub>2</sub> powder has been known for decades.<sup>120,125</sup> The original work on chemically exfoliated MoS<sub>2</sub> resulted from study of intercalation compounds.<sup>125-128</sup> In particular, there was substantial interest in using MoS<sub>2</sub> as an electrode for lithium ion batteries. Indeed, the first results on Li intercalation showed that it was possible to intercalate very large quantities of Li in MoS<sub>2</sub>. In fact, so much so that the MoS<sub>2</sub> electrodes became unstable. Examination of the destroyed electrode material revealed that the presence of single layer sheets. The intercalation of MoS<sub>2</sub> is typically done with butyl lithium (BuLi) – a liquid containing organic chain with a Li atom

attached at one end.<sup>129-131</sup> Bulk MoS<sub>2</sub> powder is mixed with butyl lithium and the intercalation reaction is allowed to occur over several hours or a few days. Intercalation leads to expansion of interlayer spacing to the point where the van der Waals forces are not strong enough to hold the layers together to maintain a cohesive solid. This allows the individual layers to separate and exfoliation to occur. During the intercalation reaction, the butyl donates an electron to the MoS<sub>2</sub> to induce phase transformation as described above, while Li ion compensates this additional charge on the lattice to maintain charge neutrality. Thus, the exfoliated products contain mostly 1T phase MoS<sub>2</sub>.<sup>71,131-</sup>

<sup>133</sup> Additional purification steps are required to achieve a uniform dispersion and removal of any non-exfoliated flakes. This is done by sonication and centrifugation. Once a uniform suspension is achieved, the samples are cleaned by washing with hexane to remove the butyl residue and then with de-ionized water to remove the lithium ions. A detailed description of the preparation of chemically exfoliated MoS<sub>2</sub> along with the purification and deposition steps are described in reference <sup>118</sup>.

Prepared solutions of exfoliated MoS<sub>2</sub> are then diluted with deionized water to the desired concentrations. The chemically exfoliated MoS<sub>2</sub> nanosheets are stored in suspensions since they can be readily deposited on any substrate using solution based techniques. (Figure 11) For example, thin films can be achieved by spraying,<sup>134</sup> inkjet printing,<sup>135</sup> spin coating<sup>136</sup> or by vacuum filtration<sup>118,137,138</sup>. The latter typically involves filtering the solution through 25nm pore methyl ester cellulose filter in which the liquid (water) passes through the filter pores but the nanosheets become trapped. After deposition, the films are transferred by slowly submerging in deionized water, beginning at one edge of the filter.



*Figure 11 Chemical exfoliation. Bulk MoS<sub>2</sub> is intercalated with super base solvent such as butyllithium followed by sonication to separate layers. Prepared solutions (middle right) can then be transferred to arbitrary substrates (Right: MoS<sub>2</sub> on SiO<sub>2</sub>. Scale bar is 30  $\mu$ m)*

Low adhesion between the MoS<sub>2</sub> layer and filter allows water to delaminate the film, which then floats on the surface of the water. It is possible to precisely control the thickness and the number of layers with vacuum filtration and relatively uniform films over large areas can be realized on variety of substrates. The films can then be used in applications such as photodetectors,<sup>139</sup> supercapacitors,<sup>5,101</sup> and optoelectronics.<sup>140</sup> This method produces much larger and more uniform films than mechanical exfoliation, but single- and few-layer films are difficult to produce in large areas with any uniformity. There is also the challenge of locating films on the water surface when MoS<sub>2</sub> solutions are of suitable concentration to produce single or few-layered flakes. Another issue with this method is the inevitable wrinkling and folding of films as they are transferred and dried.

### 2.3.2 Bottom-up: MBE, PLD, ALD, PVD, CVD

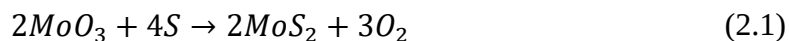
In contrast to working from naturally occurring bulk samples of MoS<sub>2</sub> and deconstructing them in to ultrathin films, there are several bottom-up approaches that instead build the material synthetically from the atomic or molecular level. Thin films of TMDS have been successfully synthesized via molecular beam epitaxy (MBE),<sup>141</sup> atomic layer deposition

(ALD),<sup>142</sup> physical vapor deposition (PVD),<sup>143</sup> pulsed laser deposition (PLD),<sup>144,145</sup> hydrothermal synthesis,<sup>146</sup> and chemical vapor deposition (CVD).<sup>31-38,67</sup>

### *Chemical vapor deposition*

Of the MoS<sub>2</sub> film synthesis techniques available, chemical vapor deposition (CVD) shows the most potential for producing scalable, uniform, large-area, single or few-layer MoS<sub>2</sub>.<sup>31</sup> CVD crystals are grown by vaporizing reactants in an environmentally isolated chamber that allows their diffusion to a substrate for nucleation and growth.

Many variables are involved in the CVD reaction. The temperature for realizing monolayer MoS<sub>2</sub> of the substrates and each reactant determine the nucleation and growth kinetics for crystal formation. The melting points of the molybdenum and sulfur sources also determine the activity of the synthesis reaction. In addition, the growth reactants are carried to the growth surface via inert carrier gas. Thus, the flow rate and chamber pressure of the inert gas provide an oxygen-free environment, allowing reaction products to condense on the substrate and unreacted species to leave the furnace. The inert gas flow also moderate partial pressures and diffusion of all vapor-phase species. In order for a crystal to grow, there must be a driving force for it to do so. The driving forces are temperature below the melting point of the desired crystal structure and energy liberated when adding an atom or molecule to the crystal. In order for crystal growth to be favorable, the energy to create a new bond must be less than the energy of the unbonded state. For the case of MoS<sub>2</sub> growth in an oxygen-free, sulfur environment, sulfur atoms reduce MoO<sub>3</sub> and liberate oxygen according to the following chemical equation:



A 1 cm<sup>2</sup> single layer of MoS<sub>2</sub> is composed of a mere 0.07 µg and 0.1 µg elemental sulfur and molybdenum, respectively, given a lattice constant of 3.15 Å.<sup>28</sup> (3 Mo and 6 S atoms per hexagon of area  $2(1 + \sqrt{2})(3.15 \text{ Å})^2 \approx 48 \text{ Å}^2$ ). Thus, the mass of reactants and vaporization rate need not be excessive for growth of a single layer. MoO<sub>3</sub> has a melting temperature of 795°C while sulfur powder melts at only 115°C. This large difference in melting points (and thus activities) necessitates two different temperature zones in the furnace for reactants.

The obvious consequence of flow rate is delivery of reactants from their respective locations to the intended growth area; another significant contribution is moderation of reactant partial pressures. Assuming ideal gas behavior and a flow rate of 100 standard cubic centimeters per second (SCCM), the drift velocity of particles in a 2.5 cm (1-inch) tube at 850° C and 1 atm is 2.6 cm/s. But a reduction in the flow rate to 50 SCCM will result in a doubling of reactant partial pressures. With lower flow rates, reactant partial pressures are allowed to build up substantially, resulting in more nucleation and growth.

Most experimental setups for CVD growth of MoS<sub>2</sub> in the literature place substrates in the same temperature zone as the molybdenum source powder, (typically MoO<sub>3</sub> powder<sup>33,34,36,50,55,121,147</sup>) with sulfur powder located upstream somewhere in the temperature gradient between the furnace hot zone and room temperature.<sup>36,55,121,148</sup> A few recent publications<sup>50,56,149</sup> have also utilized a cooler region for vaporization of the molybdenum source. Growth (substrate) temperatures ranging from 650-1000 °C, MoO<sub>3</sub> temperatures ranging from 300-1000 °C, and S temperatures ranging from 100-600 °C have been

published.<sup>5,29-46</sup> Table 2 highlights some growth methods as reported in recent publications.

*Table 2 Sample of parameters used in the literature for CVD growth of MoS<sub>2</sub> chosen to highlight the broad range of experimental conditions resulting in single layer growth of large area (>10  $\mu$ m) single-layer MoS<sub>2</sub> Cells were left empty when information was not provided.*

| Growth Temp (°C) | MoO <sub>3</sub> Temp (°C) | MoO <sub>3</sub> Mass (g) | S Temp (°C) | S Mass (g) | Flow Rate (SCCM) | Growth Time (minutes) | Source |
|------------------|----------------------------|---------------------------|-------------|------------|------------------|-----------------------|--------|
| 700              | 700                        | 550                       | 200         | 700        | 236              | 10                    | 121    |
| 800              | 300                        | 20                        | 180         | 600        |                  |                       | 32     |
| 715              | 715                        | 10                        |             | 1000       | 50               | 15                    | 37     |
| 750              |                            | 10                        |             | 20         | 200              | 15                    | 38     |
| 700              | 700                        | 20                        |             | 7          | 15               | 10                    | 55     |
| 700              | 700                        | 14                        |             | 120        | 10               | 5                     | 148    |
| 800              | 800                        |                           | 150         |            | 20               |                       | 36     |
| 840              | 530                        |                           | 100         |            | 50               | 45                    | 149    |
| 750              | 750                        |                           | 113         | 1500       | 175              | 10                    | 49     |
| 700              | 700                        | 5                         |             | 350        | 10               | 10                    | 51     |
| 850              | 850                        | 15                        | 350         | 1000       | 10               | 5                     | 55     |
| 750              | 750                        | 20                        |             | 100        |                  | 15                    | 71     |
| 650              | 650                        | 18                        |             | 16         | 5                |                       | 35     |
| 750              | 540                        | 35                        | 130         | 600        | 130              | 30                    | 50     |
| 1000             | 1000                       | 13                        | 130         | 1000       | 200              | 10                    | 33     |
| 650              | 650                        |                           |             |            | 1                | 15                    | 31     |
| 850              | 850                        |                           | 600         | 1000       | 200              | 15                    | 122    |

There are several possible reasons for this large range of experimental parameters producing similar results: Single-layer growth may not be occurring at maximum temperature since reactants are not isolated during heating and cooling ramps, thus growth (dwell) time may be irrelevant; Most experiments in the literature are conducted in single-zone furnaces, so the reported sulfur temperatures are unreliable due to the steep temperature gradient at the furnace edge; Descriptions of prior cleaning or oxidation procedure for CVD tube are not typically provided, and so it cannot be assumed that

residue from previous experiments was not present in subsequent experiments; Surface areas of reactants were not measured/controlled despite the fact that vaporization rate depends on temperature, the reactant's activity, and its surface area.

Neglecting nucleation, we can simplify the growth rate ( $Gr$ ) to depend on the substrate temperature, the partial pressure of molybdenum reactant, and the partial pressure of sulfur reactant as follows:

$$Gr = f(T_{GS}, P_s, P_{Mo}) \quad (2.2)$$

where  $T_{GS}$  is the temperature at the growth surface

$$P_s = f(T_s, SA_s, FR) \quad (2.3)$$

is the partial pressure of sulfur source, and

$$P_{Mo} = f(T_{Mo}, SA_{Mo}, FR) \quad (2.4)$$

is the partial pressure of molybdenum source where the partial pressures of each reactant depend on their temperatures ( $T_{S/Mo}$ ), surface areas ( $SA_{S/Mo}$ ), and the flow rate (FR) of inert gas. Considering that less than one microgram of each reactant is needed to cover a substrate with a monolayer of  $MoS_2$ , it is apparent that growth sensitively depends on all three of these variables.

Methods described in the literature where the molybdenum reactant temperature differs from the substrate temperature often involve one reactant held at steady state temperature before the other is ramped up. This and the huge variation in all experimental parameters

provided in the literature may indicate that single-layer growth occurs not during the dwell time, but while one of the reactant temperatures is changing, and for a brief period both partial pressures are appropriate for single-layer growth. Current experiments are designed to increase control where possible and uncover optimal growth parameters.

## 2.4 Phase transformations

Our group utilized butyl lithium to intercalate lithium ions between bulk MoS<sub>2</sub> layers to exfoliate into single sheets.<sup>20,118,134</sup> The intercalation process alters the electronic structure of the MoS<sub>2</sub> due to a transfer of electrons from butyl groups to the MoS<sub>2</sub>. This change of structure is from the 2H trigonal prismatic to the hexagonal 1T and can be reversed by heating above 300° C.<sup>47</sup> Treatment with BuLi solution was found to transform CVD grown single layer samples of MoS<sub>2</sub> as well, indicated by quenching of the photoluminescence (PL) observed in the 2H phase.<sup>67,71</sup> That is, it is possible to grow single layer of MoS<sub>2</sub> by CVD and treat it with butyl lithium to transform it to the 1T phase. I will discuss how this is done and how the transformation impacts the photoluminescence and Raman characteristics later in the thesis in Chapter 3, Section 2. However, this transformation of CVD grown samples is not straightforward because AFM analysis reveal that the samples tend to be lifted from the substrate due to intercalation of the liquid between the substrate and the monolayer flake. This leads to distortion of the flake. A way to mitigate this is to anchor the flake via deposition of metal thin film electrodes to prevent detachment of the CVD grown flake from the substrate. Studies that go beyond what is reported in this thesis will need to overcome this limitation if friction measurements from phase converted CVD grown samples are to be studied in detail. Experiments are ongoing to improve the transformation process by

varying the concentration of BuLi, time in solution, and the washing/drying methods used. Other group-one ionic intercalants such as sodium and potassium are also being explored for phase transformation. The advantage of these intercalants is that they can be directly deposited in solid or atomic form and therefore penetration of liquid between substrate and the CVD flake is not an issue.

### 3. Characterization

A plethora of analytical tools and techniques are commonly used to characterize research materials. In my research, I mostly utilized the following techniques: optical microscopy, Raman microscopy, transmission electron microscopy, and atomic force microscopy. These are particularly useful for understanding the structure of the nanosheets such as number of layers, atomic structure, morphology, molecular structure, stoichiometry, and electronic behavior. In order to interpret the experimental results obtained during my research, I describe some of the key fundamental aspects of analytical tools I utilized throughout my research.

#### 3.1 Optical microscopy

The first mode of analysis following CVD synthesis is optical microscopy. Lateral features of 2D nanosheets are readily observed with a modest 500 X optical magnification as these are on the micron scale: typical MoS<sub>2</sub> triangles grown by CVD have lateral dimensions of 5-100 microns.<sup>31,49,51,150</sup> In 1873 Ernst Abbe discovered the diffraction limited resolvable size of features viewed using an optical microscope:

$$d_{xy} = \frac{\lambda}{2n \sin \theta} \quad (3.1)$$

where  $d_{xy}$  is the lateral width of a spot in the focal plan formed by light of wavelength  $\lambda$  travelling in medium with refractive index  $n$  converging with angle  $\theta$ .<sup>151</sup> Since that time, several methods have evolved from efforts to circumvent this limit by using structured illumination,<sup>152</sup> fluorescence microscopy,<sup>153</sup> metamaterials,<sup>154</sup> and near field techniques.<sup>155</sup> But for standard visible-light, far-field optical microscopes the limit

remains with figure of merit being the numerical aperture (NA) which is product of the sine of the convergence angle and refractive index and has a practical upper limit of less than 1 in air and about 1.4 for oil immersion systems. Thus, with visible light centered at 550 nm, the minimum resolvable spot size is 300 nm. While the vertical dimensions of single- and few-layer MoS<sub>2</sub> (7 angstroms per layer) are far below the resolvable optical limit, individual layers can be differentiated due to optical interference.

Specifically, interference results from the fact that MoS<sub>2</sub> films are typically deposited on thermally grown 300 nm SiO<sub>2</sub> on silicon wafers. Since the optical cross section of single layer MoS<sub>2</sub> is very low, most of the photons from the white light source of the optical microscope are transmitted through the MoS<sub>2</sub> and the underlying SiO<sub>2</sub>. However, it is reflected back by the buried silicon and thus the incoming light is doubly transmitted through the thin film of MoS<sub>2</sub> after reflection from the substrate combines with photons reflected from the MoS<sub>2</sub> surface. Because the photon that is transmitted twice through the MoS<sub>2</sub> travels a distance equal to twice the film thickness, its phase is shifted relative to the reflected photon. Thus, dependent on the film thickness, the optical microscope will reveal contrast due to the difference in complex refraction indices between air and MoS<sub>2</sub>. Optical contrast has been used to determine accurately the number of layers present through empirically derived models.<sup>156</sup> However, other characterization tools are needed and have been used to provide validation of the thickness.<sup>60,157</sup>

### 3.2 Raman microscopy

Raman microscopy is a particularly useful tool for characterizing MoS<sub>2</sub>: it can differentiate the phases of MoS<sub>2</sub>, quantify its band-gap, and corroborate the number of layers. Raman scattering occurs when monochromatic light inelastically scatters from a crystal due to absorption of a portion of incident photon energy. The energy absorbed from the photon transforms via excitation of a quantized rotation or vibration (phonon). As the excited modes relax, they emit light that is either shifted to lower frequencies (Stokes scattering) or combine with another scattered photon resulting in emittance of higher frequencies (anti-Stokes scattering) as depicted graphically in Figure 12.

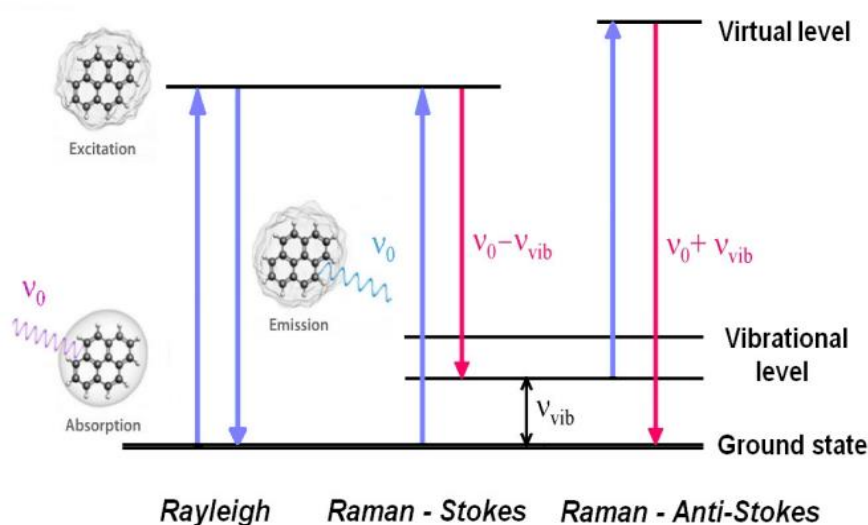


Figure 12 Energy diagram for Rayleigh and Raman scattering. Lower energy emitted photon than incident photon (Stokes shift) or emitted light is more energetic by taking energy from a vibrational mode.<sup>3</sup>

While all materials participate in Rayleigh scattering – elastic scattering in which the incoming and emitted photons have the same energy, only those with certain crystal symmetries produce Stokes or anti-Stokes shifted reemission. Excitation of a vibrational state is equivalent to the induction of a dipole moment such that:<sup>158</sup>

$$\mu_{in} = \alpha E \quad (3.2)$$

where  $\alpha$  is the polarizability of a molecule and  $E$  is the electric field of an incident photon. Larger atoms have strong polarizability because electron clouds are farther from the nucleus. At the molecular equilibrium geometry, the polarizability is some value  $\alpha_0$ ; at some distance  $dr$  away from the molecular equilibrium geometry, the instantaneous polarization is given by

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial r} \right) dr \quad (3.3)$$

where the derivative represents the change in polarization with change of position. Since the molecule is vibrating in sinusoidal fashion, we can write

$$dr = r_{max} \cos(2\pi\omega t) \quad (3.4)$$

Given a photon of energy

$$E = E_{max} \cos(2\pi\omega_{in} t) \quad (3.5)$$

the induced dipole moment can be described by

$$\mu_{in} = \left( \alpha_0 + \left( \frac{\partial \alpha}{\partial r} \right) r_{max} \cos(2\pi\omega t) \right) E_{max} \cos(2\pi\omega_{in} t) \quad (3.6)$$

$$\mu_{in} = \alpha_0 E_{max} \cos(2\pi\omega_{in} t) + E_{max} r_{max} \left( \frac{\partial \alpha}{\partial r} \right) \cos(2\pi\omega t) \cos(2\pi\omega_{in} t) \quad (3.7)$$

$$\begin{aligned}
\mu_{in} = & \alpha_0 E_{max} \cos(2\pi\omega_{in}t) \\
& + \frac{E_{max}r_{max}}{2} \left( \frac{\partial\alpha}{\partial r} \right) [\cos(2\pi t(\omega_{in} + \omega)) \\
& + \cos(2\pi t(\omega_{in} - \omega))]
\end{aligned} \tag{3.8}$$

Thus, if there is no change in polarization with change in atomic position  $\left(\frac{\partial\alpha}{\partial r} = 0\right)$  then there will be no Raman signal. These conditions define whether the vibration state is Raman active or not.

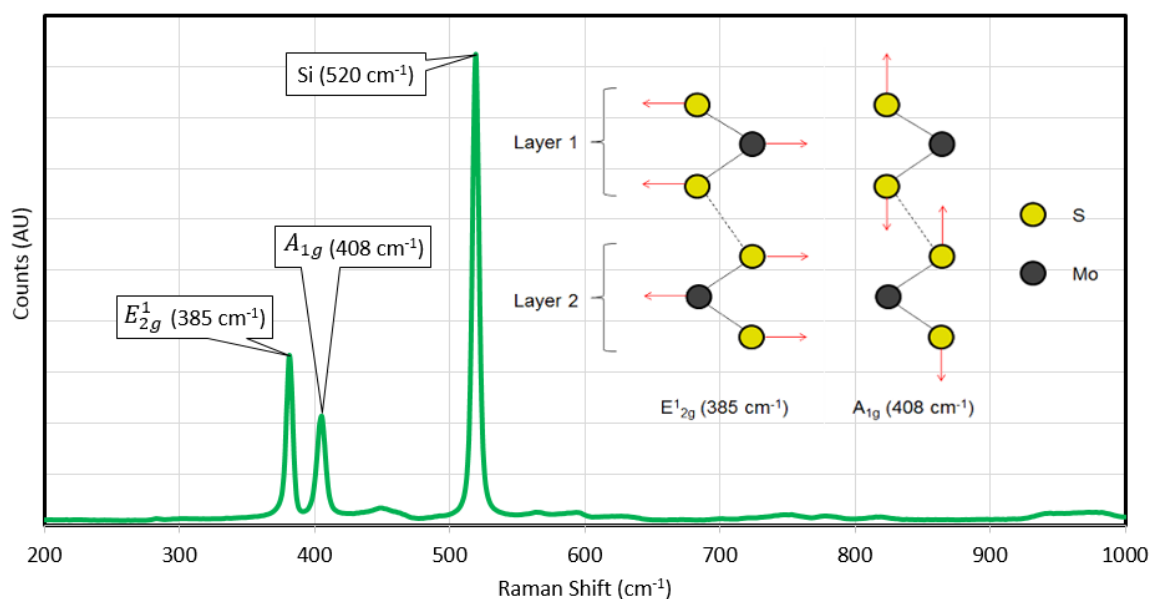
Materials which have vibrational modes that affect the polarizability of molecules and with energy less than incident photon energy are Raman active. Infrared spectroscopy is considered complementary to Raman because IR absorption occurs in molecules that exhibit no change in polarization with change in atomic position, but whose atomic vibrations result in the formation of permanent dipole moments.

The majority of a monochromatic beam impinged on a Raman active substance will be elastically (Rayleigh) scattered at the same wavelength, but if a spectrum of photons vs energy above laser energy is collected, peaks will indicate the energies of vibrational resonances. In order to express Raman shifts in a manner independent of the excitation wavelength, the energy shift is expressed as a wavenumber shift:

$$\Delta w = \frac{1}{\lambda_0} - \frac{1}{\lambda_1} \tag{3.9}$$

where  $\lambda_0$  is the excitation wavelength and  $\lambda_1$  is the emitted wavelength. The difference in wavenumbers ( $\lambda^{-1}$ ) between the incident light and emitted light is the Raman shift,

typically given in  $\text{cm}^{-1}$  for convenience. Both phases of  $\text{MoS}_2$  have two prominent Raman active vibrational modes that produce the two peaks called  $A_{1g}$  and  $E_{2g}^1$  (see Figure 13), but the spacing of these peaks depends on the number of layers present.<sup>159</sup>



*Figure 13 Principle Raman modes for  $\text{MoS}_2$ . In-plane oscillation of sulfur atoms (yellow) relative to molybdenum atoms (black) corresponding to  $385 \text{ cm}^{-1}$  shift called the  $E_{2g}^1$  mode (left) and out-of-plane oscillation of sulfur atoms 180 degrees out of phase corresponding to  $385 \text{ cm}^{-1}$  shift called the  $A_{1g}$  mode.*

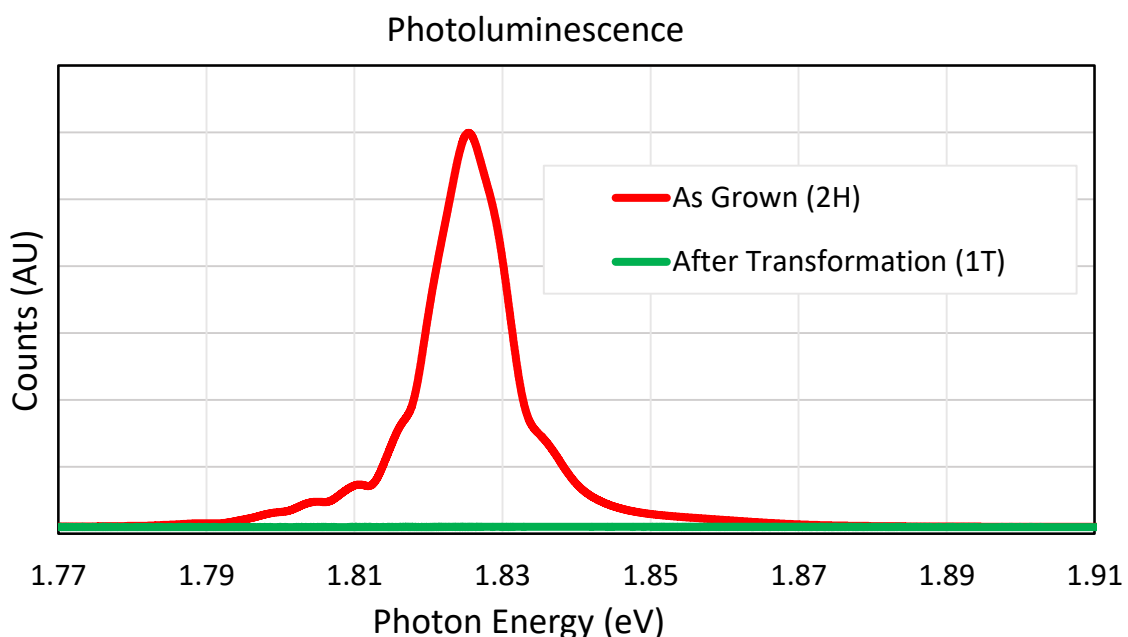
As the number of layers decreases, the separation of these peaks decreases due to less interlayer coupling.<sup>160</sup>

In addition to detection of specific vibrational modes in a crystal, Raman microscopy can also be used in photoluminescence (PL) mode to identify the phases and quality of  $\text{MoS}_2$  samples. That is, upon excitation with green Raman laser (532 nm), electronic transitions also occur. Since single layer  $\text{MoS}_2$  is a direct band-gap semiconductor, the probability of electron-holes pairs (excitons) recombining radiatively is high.<sup>115,161</sup> This radiative recombination can be measured by the Raman detector. Thus, it is possible to measure both the Raman and PL simultaneously. The appearance of a strong PL signal centered

around the band-gap of MoS<sub>2</sub> is clear indication that the sample is single layer. The presence of a weak PL signal at around 1.4 eV (from indirect band-gap transition) is a clear indication of the presence of multi-layers. The absence of PL is an indication of 1T phase since metallic materials do not emit PL.<sup>115,118,162,163</sup>

More specifically, when a semiconductor is subjected to electromagnetic radiation with energy larger than the semiconductor's band-gap, an electron-hole pair is created and the pair's excess energy is shed through phonon interactions and coulomb scattering until they reach their respective minima and maxima in conduction and valence bands. In addition to excitation of Raman modes in a crystal, a Raman microscope can also be used to identify the phases and quality of a MoS<sub>2</sub> sample by its photoluminescence. When a semiconductor is subjected to electromagnetic radiation with energy larger than the semiconductors band-gap, an electron-hole pair is created and the pair's excess energy is shed through phonon interactions and coulomb scattering until they reach their respective minima and maxima in conduction and valence bands. After a short time, the exciton decays via recombination at defect or edge sites and a photon is emitted with energy equal to the band-gap. Thus if a semiconductor is irradiated with laser light in Raman microscope higher than the band-gap, it will produce a photoluminescence peak centered at the band-gap energy. Single layer MoS<sub>2</sub> has a band-gap of 1.7 eV<sup>18</sup> so a laser with wavelength shorter than 730 nm will result in photoluminescence. Examination of the spectra at 1.7 eV (equivalent to 4500 cm<sup>-1</sup> Raman shift using a 514 nm green laser) thus provides a good measure for the presence and quality of single layer 2H MoS<sub>2</sub>. Upon transformation to the metallic 1T phase, photoluminescence is quenched and no peak is observed in at or near 1.7eV for a fully transformed MoS<sub>2</sub> sample. This makes the Raman

microscope a great tool for identifying 2H vs 1T MoS<sub>2</sub>. Figure 14 shows strong PL of the 2H MoS<sub>2</sub> at 1.82 eV (4500 cm<sup>-1</sup>) and quenched PL for 1T MoS<sub>2</sub> in the same figure.



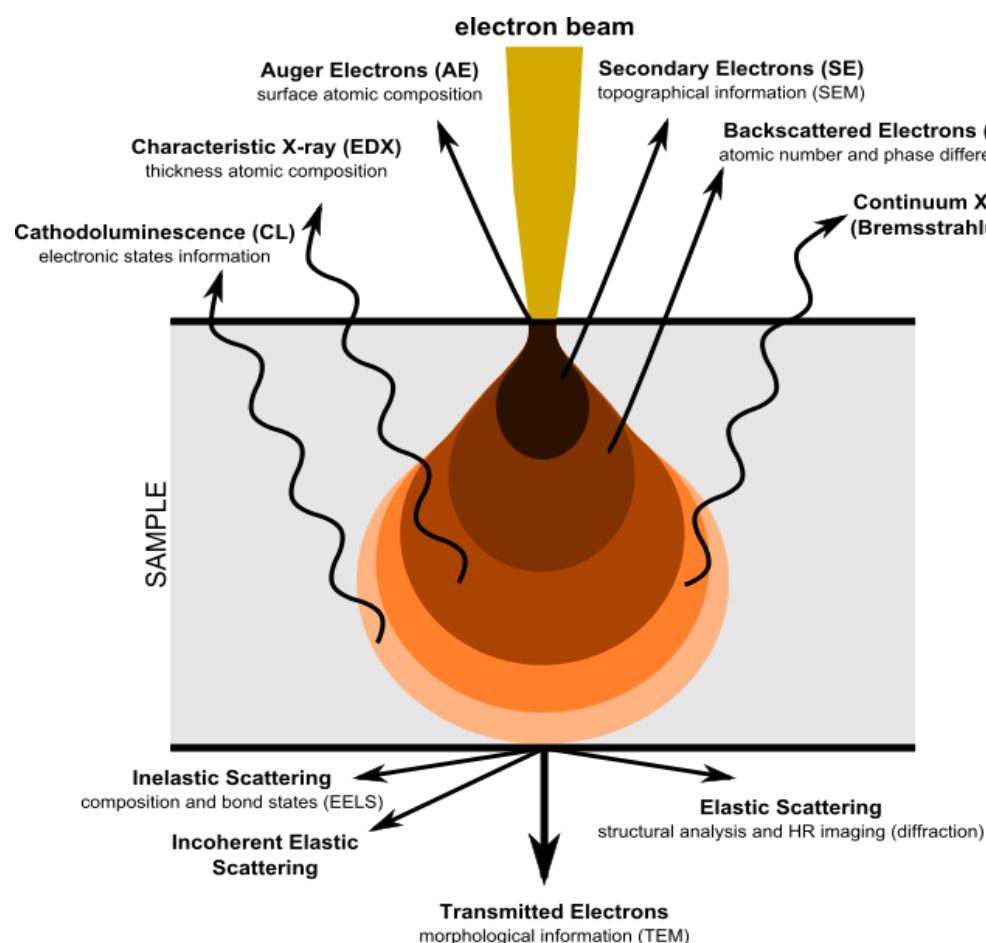
*Figure 14 Photoluminescence (PL) of 2H MoS<sub>2</sub> as grown by CVD (red) and quenched PL of 1T MoS<sub>2</sub> transformed by butyllithium intercalation. (green)*

Given that the Raman microscope provides information regarding vibrational states and electronic behavior of MoS<sub>2</sub>, it thus serves as a unique means of exploring the two components of friction at nanoscale: electronic and phononic.

### 3.3 Scanning Electron Microscopy

Electron microscopy is able to resolve smaller physical features than diffraction-limited optical microscopy, and can thus reveal the sub-micron level. When struck with a beam of electrons emitted thermionically from a tungsten filament or via field emission from a cold cathode, a material will either absorb, transmit, or reflect the impinging energy, resulting in current, charging, back-scattered electrons, production of secondary electrons, or production of photons. The Scanning Electron Microscope (SEM) utilizes

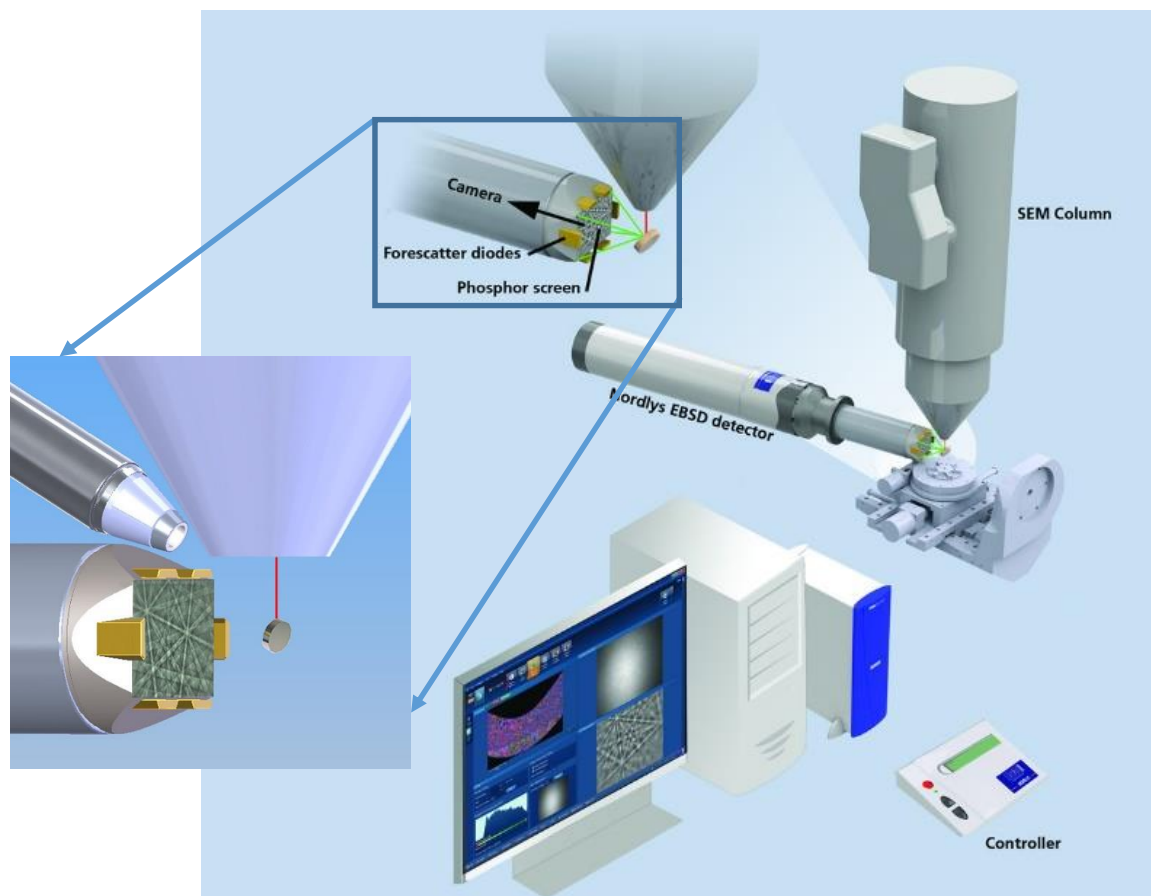
several detectors to collect scattered particles from a target material. A detector to collect secondary electrons (those ejected from a material due to incident electrons) provides the means of imaging sample surfaces with contrast generated from the relative energy of scattered electrons. SEM obtains high-resolution contrast topography maps of a sample surface by recording the energy of electrons scattered from the sample as the focused beam of electrons scans over the surface. By collecting the reflected electrons scattered diffusely in a back-scatter detector, an SEM acquires information about the target composition (atomic number). As electrons penetrate into the target sample, multiple interactions rapidly decrease their energy as they spread into a teardrop-shaped interaction volume as shown in Figure 15.



*Figure 15 Penetration profile of a sample irradiated with an electron beam. Many scattering mechanisms are possible, but those analyzed in scanning electron microscopy involve those closest to the sample surface: auger electrons and secondary electrons. Detectors may also be included to count characteristic x-rays, and backscattered electrons.*

This volume is dependent on the kinetic energy (accelerating voltage) of incident electrons, and the composition (primarily atomic number) of the target. The typical incident electron energies range from 5 keV to 30 keV and at these energies, the penetration depth of electrons ranges from several nanometers to a few microns. Thus, it is possible to obtain chemical and structural information about the sample from subsurface regions at these depths.

Another mode of operation called electron backscatter diffraction (EBSD) can be used on crystalline samples to explore lattice parameters, grain orientation, and differentiate phase. In this mode, (shown graphically in Figure 16) the sample is tilted approximately 70 degrees toward the EBSD detector that captures a diffraction pattern seen as Kikuchi bands on a phosphor screen to enhance the efficiency of the CCD.



*Figure 16 Schematic of EBSD. Sample is tilted by approx. 70 degrees towards the EBSD detector consisting of a phosphor screen and up to six peripheral forescatter diode detectors. Intersecting (Kikuchi) lines on phosphor screen result from Bragg refraction from lattice planes as backscattered electrons reflect back through the sample surface.*

These bands are formed in a similar manner as the diffraction patterns discussed below in Section 3.4 *Transmission electron spectroscopy*, but in this case the diffracted electrons originate from below the sample surface. As electrons penetrate into the sample, some are

backscattered back out of the sample. Regular lattice planes will then diffract the electrons and produce the Kikuchi lines collected by the EBSD detector. The EBSD detector also has up to six detectors surrounding it which can provide additional information about the orientation and type of grains present on the sample surface.

### 3.4 Transmission electron spectroscopy

Transmission electron microscopy (TEM) on the other hand gathers information from the electrons that pass through a thinly prepared electron transparent sample. Since the penetration depth for electrons is dependent on the electron energy and the atomic number(s) of atoms being bombarded, a thin sample will allow electrons with sufficiently high energy to pass through. Similar to SEM in that it also uses electrons to probe a material of interest, TEM offers different and complementary information. While both use an electron gun to ballistically fire electrons at a sample, the TEM acquires information from the scattering of the electrons that are transmitted through a thin sample rather than reflected. The electrons in a TEM are typically accelerated at energies ranging from 60 keV to 400 keV. At these energies, samples thinned to tens of nanometers become electron transparent so that the beam can easily travel through the sample. While the vast majority of the electrons pass through the sample without much interaction with the sample atoms (these are referred to as zero loss electrons), some are electrons encounter atoms in the sample material and are deflected based on their closest approach, the atomic number, and arrangement of target atoms. As with SEM, several methods are used to analyze the scattering for sample analysis in TEM.

Bright-field imaging in TEM projects a contrast image from the electrons passing through the sample resulting in lowest contrast from regions of higher thickness or atomic number (z contrast). With the smaller de Broglie wavelength of electrons compared to photons, TEM routinely resolves sub-nanometer features including individual atoms. (see Figure 17)

In addition to the bright field imaging, also allows for what is referred to as dark field imaging, which captures scattered electrons in the annulus surrounding the unscattered beam. At small angles (between incident beam, specimen and annular detector), the collected electrons result from Bragg scattering, while at larger angles high-angle annular dark field (HAADF) imaging captures incoherent scattering which is sensitive to atomic number.<sup>164</sup> It is possible to use small apertures in the TEM to pass electrons through small selected areas of the sample and observe the diffraction of electrons passing through. Since the de Broglie wavelength of electrons is much smaller than the spacing between atoms in a crystal, the electrons pass through, but are subject to diffraction similar to visible light passing through a grating. In selected area electron diffraction (SAED), a region of the sample is impinged with electrons and the diffracted beam is collected on a screen. A single crystal produces discrete points owing to its regular periodicity, which diffracts many electrons at the same angle. Figure 17 shows SAED diffraction patterns of an MoS<sub>2</sub> film at different sample tilt angles relative to incident beam showing a blurring of diffraction spots for when the electron beam impinges off normal.<sup>4</sup>

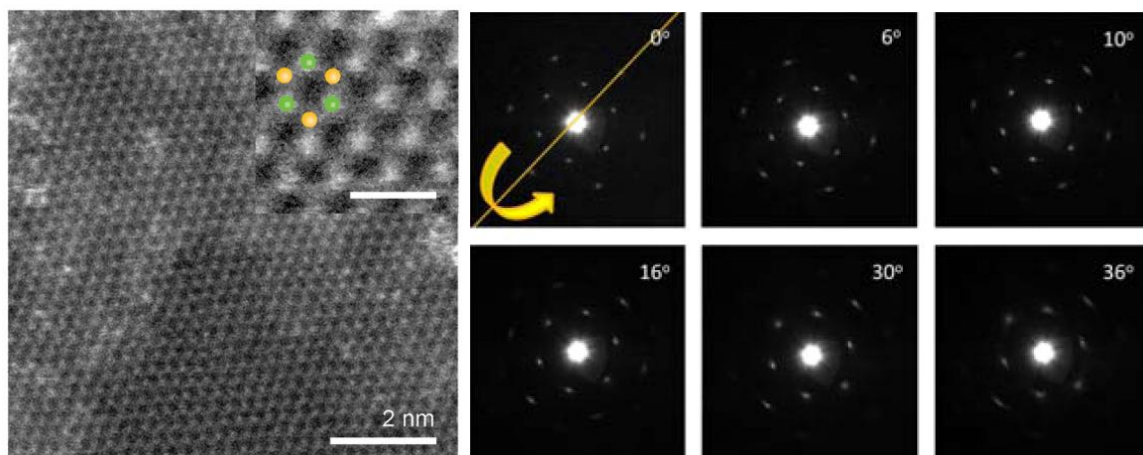


Figure 17 Transmission electron microscopy of MoS<sub>2</sub> captured via HAADF (left) and SAED pattern at various sample tilt angles (right).<sup>4</sup> The central spot shows the undeflected electrons while the dimmer spots result from electrons diffracted from the sample. As the sample is tilted the spots become blurred due to contribution from multiple atoms.

Each spot corresponds to a satisfied diffraction condition and the resulting arrangement and spacing of diffraction spots yields information about the crystal space group, orientation, and lattice constants.

### 3.5 X-ray photoelectron spectroscopy

As discussed above, Raman spectroscopy gives *qualitative* information about the structure (phases, number of MoS<sub>2</sub> layers) of the materials through measurement of the vibrational spectrum. Quantitative information about the chemical composition can be obtained by X-ray photoelectron spectroscopy (XPS). It also gives a much clearer picture of the relative quantities of each phase present in a given sample.<sup>165</sup> XPS is performed by irradiating a sample surface with a focused beam of X-rays and measuring the quantity and kinetic energy of electrons that are ejected from the sample and incident on an electron detector. Figure 18 shows a schematic of XPS working principle.

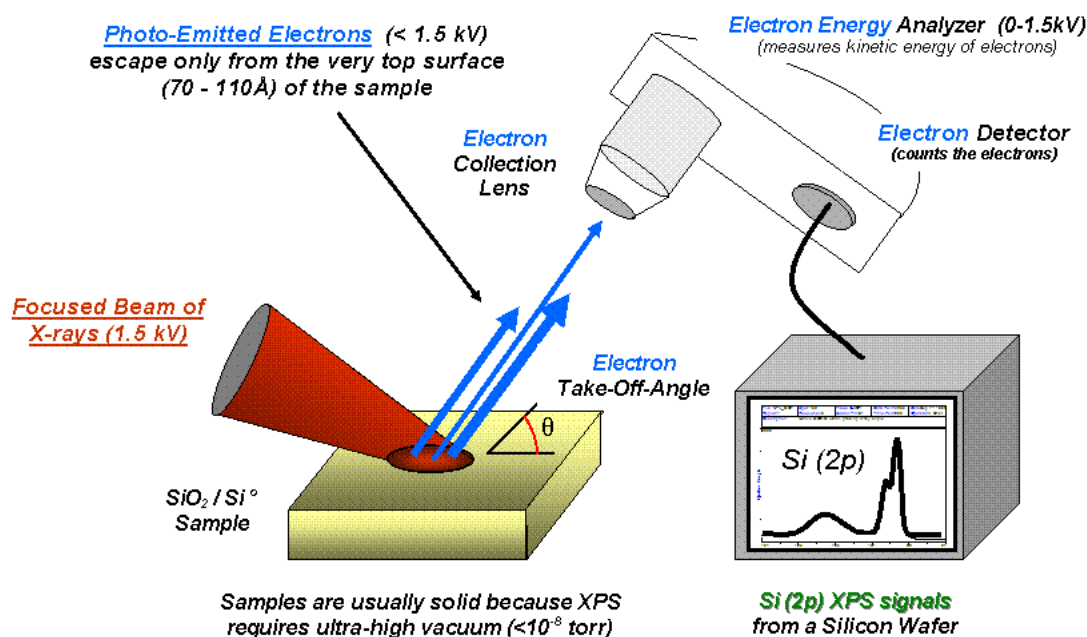


Figure 18 Diagram of x-ray photoelectron spectroscopy (XPS) analysis. Focused beam of monochromatic X-rays (red) are impinged upon sample surface (yellow) resulting in electrons being ejected from the sample (blue) are captured by an electron energy analyzer. Discrete peaks show the binding energies of outer electrons present at the sample surface which can identify elements, chemical bonds, and relative abundances.

In my work, I utilized the Thermo Scientific K-Alpha spectrometer. All spectra were taken using an Al K $\alpha$  microfocused monochromatized source (1486.7 eV) with a resolution of 0.6 eV and a spot size of 400  $\mu\text{m}$ . Since the energy of ejected electrons depends on their binding energy before ejection, the collected spectra give information not only about elemental composition but also about the chemical and electronic states of the elements present. The X-rays penetrate only a small distance (0-10nm) into the surface, so this technique suits 2D material analysis well in that it provides only surface information.

XPS for MoS<sub>2</sub> is particularly helpful because it provides quantitative information about the Mo:S ratio. Experimentally it has been found that MoS<sub>2</sub> rarely has Mo:S

stoichiometry of 1:2. Instead, vast majority of CVD grown and mechanically exfoliated samples are sub-stoichiometric with Mo:S ratio being close to 1:1.8. In addition, the treatment of MoS<sub>2</sub> powder with butyl lithium during chemical exfoliation can lead to formation of LiS<sub>2</sub> during the reaction. Thus, XPS is particularly useful for monitoring the chemical composition after the chemical exfoliation.

The concentration of the different phases of MoS<sub>2</sub> can also be resolved from XPS.<sup>20,71,118</sup>

This is done by examining the Mo and S peaks in XPS, similar to the ones shown in Figure 19 which shows the Mo 3d, S 2s, and S 2p peaks for a chemically exfoliated MoS<sub>2</sub> sample that contains a mixture of 1T and 2H phases.

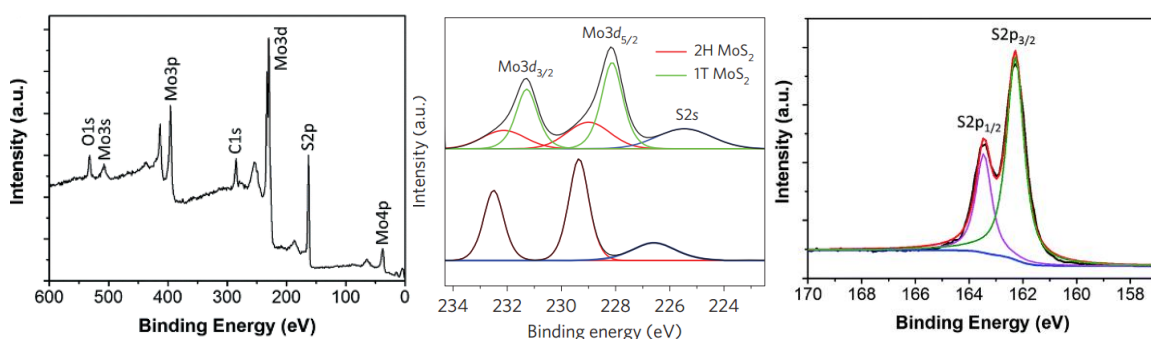


Figure 19 XPS spectra from MoS<sub>2</sub>. a) Survey spectra used to identify elements present. b) Higher resolution scan of the Mo3d and S2s photoexcited electron spectra. Black curve in upper is the measured spectra with fitted peaks for 1T and 2H phases in green and red respectively. The lower spectra results from 100% 2H MoS<sub>2</sub>. c) Sulfur scan with fitting for 2p<sub>1/2</sub> and 2p<sub>3/2</sub>.

The Mo3d XPS spectrum consists of two peaks located at 229 and 232 eV. These peaks correspond to Mo<sup>4+</sup>3d<sub>5/2</sub> and Mo<sup>4+</sup>3d<sub>3/2</sub> components of 2H phase MoS<sub>2</sub>, respectively.

However, closer examination of these peaks shows that they are down shifted by approximately 0.9 eV in comparison to the peaks for 100% 2H phase XPS spectra.

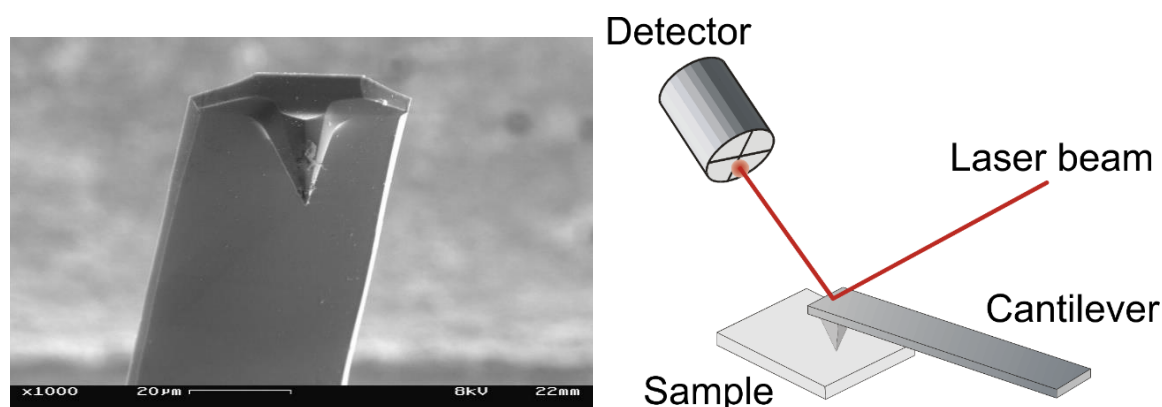
Similarly, the sulfur peaks can also be observed in XPS. The S 2s region of the XPS spectrum is also shown in Figure 18 which has well-known doublet peaks of 2H-MoS<sub>2</sub>: S

$2p_{1/2}$ , and S  $2p_{3/2}$ , which appear at 163 and 161.9 eV, respectively. The peak shift in the Mo peak along with the additional peaks in the sulfur spectrum relative to the pure 2H phase  $\text{MoS}_2$  arise from the 1T phase. It is thus possible to quantitatively determine the concentration of the 1T and 2H phases in chemically exfoliated samples by fitting the peaks and extracting the relative intensity ratios of the different phases.

### 3.6 Atomic force microscopy

Atomic force microscopy (AFM) produces a topological map of a surface by monitoring the deflection of a cantilever with an attached nanoscale tip that is scanned in a raster pattern across a sample surface. The invention of the AFM is attributed to Binnig, Quate, and Gerber in the 1980s when it was adapted from their earlier invention of the scanning tunneling microscope (STM) for which they earned the Nobel Prize for Physics in 1986.<sup>166</sup> Both AFM and STM are used to probe topography and surface properties, but AFM probes the sample surface with less influence from electronic properties and does not rely on a tunneling current to operate. As the tip encounters topographical changes in the surface, the cantilever deflection is registered via reflection of a laser beam off of the

cantilever onto a photodiode array as shown in Figure 20.



*Figure 20 Atomic force microscopy (AFM). Left: Scanning electron micrograph of an AFM cantilever and probe with adhered debris. Right: Simplified graphic of AFM operation showing cantilever on sample surface with laser light reflected into a four quadrant photodetector.*

### 3.6.1 Modes of Operation

Piezoelectric transducers under the sample stage control both lateral raster scanning motion and vertical height in coordination with feedback from the photodetectors. As the cantilever angle changes in response to vertical inhomogeneity on a sample surface, the laser position moves on the photodetector, providing sensitive feedback for the z (vertical) transducer.

As its name implies, the AFM responds to forces generated at an atomic level. Interactive forces between the tip and atoms in the sample create the bending motion of cantilever and resultant feedback via photodetector. These forces are the sum of van der Waals, dipole-dipole interactions, electrostatics, and chemical bonding. The first of two principal modes of AFM operation is contact mode. In this mode the tip is brought into contact with the sample and the deflection feedback keeps the cantilever angle constant via modulation of the z transducer. In ambient environments, surfaces tend to adsorb water

molecules which particularly interfere with contact mode AFM measurements.<sup>167-169</sup>

Additionally, when scanning in contact mode, the tip is subject to abrasion and may damage the sample surface. The second principal mode of AFM, tapping mode, avoids much of the unwanted tip-sample interaction by oscillating the cantilever at its resonant frequency given by  $f_0 = \frac{1}{2\pi} \sqrt{\frac{k_c}{m_0}}$  where  $k_c$  is the spring constant and  $m_0$  is the effective mass. As the tip approaches the sample topography, the oscillation amplitude decreases and provides feedback for the z transducer to maintain an amplitude set point which is less than the free oscillation amplitude. In this way the AFM senses the van der Waals and other factors acting at distances greater than a nanometer while avoiding those arising from contact, such as meniscus drag, solvation and chemical bonding.

Through use of conducting cantilevers (typically doped silicon or silicon nitride), the AFM can probe several other surface phenomena. The surface work function can be mapped in non-contact mode by supplying cantilever with an AC potential at the tip resonant frequency. Where a static potential difference exists between tip and sample, the tip will begin to oscillate. As the oscillations provide feedback, a DC bias is applied to the cantilever to dampen oscillations, and thus the applied bias is proportional to the work function at the sample surface. This can be understood by considering the tip and sample surface as a capacitor with energy

$$E = \frac{1}{2} CV^2 = \frac{1}{2} C(V_{DC} + V_{AC} \sin \omega_0 t)^2 \quad (3.10)$$

In the absence of an external electric potential, the time average voltage and thus the force on the cantilever is zero when the applied DC potential matches the potential at the

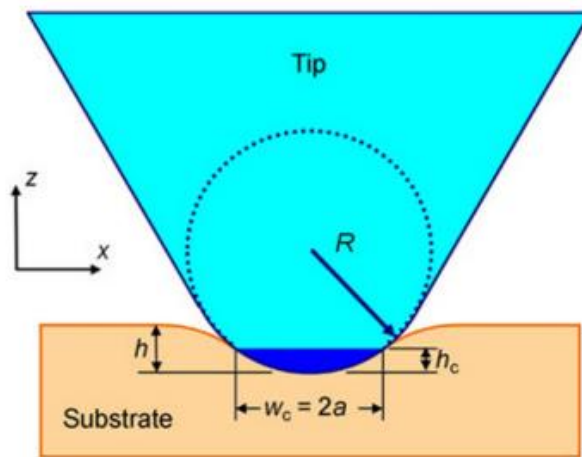
sample surface. This mode is commonly called scanning kelvin probe microscopy (SKPM) and is similar to electrostatic force microscopy (EFM) except that EFM measures the force on a charged tip rather than using a modulated nulling bias. A cantilever in contact mode scanned perpendicularly to its length experiences torque in proportion to the lateral force arising from friction between the tip and the sample surface. In this configuration, most AFMs are capable of lateral force microscopy (LFM) by utilizing photodiode array that has a lateral differentiation in addition to vertical. As the cantilever slides along the sample surface regions of greater friction twist the cantilever more shifting the laser laterally on the photodiode array. Lateral force measurements are proportional to frictional forces on the sample surface, which can be quantitatively determined through calibration of the cantilever.

### 3.6.2 Friction

Utilizing the capabilities of the AFM for lateral force measurements, the variation in friction due to number of layers, phase, and stacking can be probed in order to better understand the roles of screening, conductivity, and interlayer coupling. Screening occurs as a result of dielectric or semiconducting material separating the probe from the electromagnetic phenomena occurring beneath. This effect is most pronounced where mobile charge carriers are present but also occurs in semiconductors and dielectrics. Electric fields produced from a material create instantaneous dipoles on a nearby material, which has the effect of reducing or screening the electric field strength beyond the second material. It has been found that screening also depends on the interlayer coupling of MoS<sub>2</sub>.<sup>170</sup>

With regard to the potential future deployment of MEMS/NEMS, the effect of friction on their functionality warrants serious consideration. To date, no micro scale devices employ sliding interfaces due to enhanced friction forces at small scales.<sup>7,171</sup>

Friction on the macroscale is largely independent of contact area as described by Amontons' law, but for nanoscale systems, the friction force is proportional to the true contact area.<sup>172-174</sup> Thus in order to understand the mechanisms at work in nanoscale sliding systems, it is necessary to describe the dimensions of the contacting materials being investigated. The contact area of an AFM tip can be approximated by the contact area of a small solid-angle portion of a sphere as shown in Figure 21.



*Figure 21 Idealized diagram of probe/substrate contact area.  $R$  is the radius of curvature at end of tip,  $h$  is the depth of penetration into the substrate,  $h_c$  is the height of contact, and  $w_c$  is the width of the contact area as seen from a cross-section through the center of the tip.*

The dependence of this contact area on the normal force was developed in the late 19<sup>th</sup> by Heinrich Hertz. The Herztian model describes the contact area  $a$  of a sphere of radius  $R$  on a flat glass plane with applied normal load  $P$ .

$$a = \left( \frac{PR}{K} \right)^{1/3} \quad (3.11)$$

Where

$$K = \frac{4}{3} \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right)^{-1} \quad (3.12)$$

Where  $E_1$  and  $E_2$  are the Young's moduli and  $\nu_1$  and  $\nu_2$  are the Poisson ratios for sphere and plate respectively. This model is applicable to limited systems, fails at small scales due to the lack of consideration for adhesion. In 1971 Johnson, Kendall, and Roberts (JKR) modified the Hertz contact model to include adhesion between contacting materials with contact radius

$$a = \left( \frac{R}{K} \left( P + 3\pi\gamma R + \sqrt{6\pi RP + (3\pi\gamma R)^2} \right) \right)^{1/3} \quad (3.13)$$

Where  $\gamma$  is the Dupré adhesion energy which is an energy per unit area representing the work necessary to completely separate the contacting area.<sup>7</sup> This model correctly predicts the experimentally observed phenomena called the pull-off force necessary to overcome adhesion between the two bodies with no applied loading.

$$P_{c(JKR)} = -\frac{3}{2}\gamma\pi R \quad (3.14)$$

In 1975 Derjaguin, Muller, and Toporov (DMT) derived a different modification of the Hertz contact model to account for adhesion and the pull-off force  $P_c$ .

$$a = \left( \frac{R}{K} (P + 2\pi\gamma R) \right)^{1/3} \quad (3.15)$$

$$P_{c(DMT)} = -2\gamma\pi R \quad (3.16)$$

These two models have limited applicability for AFM measurements: with stiff, small-radii AFM cantilevers and weak adhesive forces the DMT model fits while soft, large-radii tips with strong adhesion can be better approximated by the JKR model.

Unfortunately, most sliding systems cannot be accurately modeled by either DMT or JKR but fall somewhere between the two models in a transition regime. In 1992, Maugis defined the transition parameter

$$\lambda = 2\sigma_0 \left( \frac{R}{\pi\gamma K^2} \right)^{\frac{1}{3}} \quad (3.17)$$

Where  $\sigma_0$  is the minimum adhesional stress for a Lennard-Jones potential.

The Maugis transition parameter  $\lambda$  which is specific to the contacting materials provides a means of determining which model applies. For  $\lambda < 0.1$  the DMT model applies and if  $\lambda > 5$  the JKR model applies. For  $\lambda$  between 0.1 and 5 the system is said to be in the transition regime. Friction vs normal force is plotted for a silicon AFM tip with native oxide termination on a silicon dioxide substrate with thin hydrocarbon monolayer film in Figure 22 with both DMT and JKR lines fitted. <sup>7</sup>

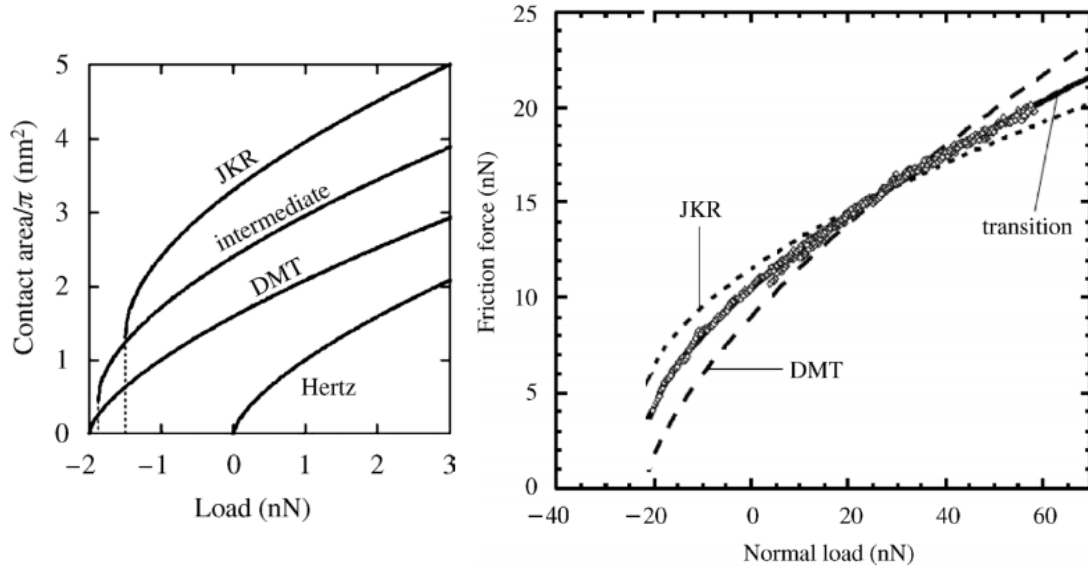


Figure 22 JKR and DMT models for contact area and friction vs load. Left: contact area vs normal load curves plotted from equations 6.11, 6.13, and 6.15 with  $K=1$  GPa,  $R=1$  nm and  $\pi\gamma=1$  J/m<sup>2</sup>. Right: Friction force vs normal load of silicon on silica with DMT and JKR model fits.<sup>7</sup> Circles are actual data points, DMT is the heavy dashed line, JKR is the lighter dotted line and the black line is the transition region where nearly all the experimental data lies.

Neither the DMT or JKR models fit the data very well as this tribological system lies in the transition regime. While models can be produced using the adaptations of DMT and JKR models with a transition parameter specific to the tribological system, this parameter relies on the equilibrium separation of the surfaces and the adhesion energy  $\gamma$  which must be determined empirically. These ad hoc transition models do not allow for accurate prediction of friction behavior and lack of general models severely inhibit the potential for intelligent design of tribological materials and systems. Further still, scientific conceptions regarding idealized limiting cases of non-contact friction remain unresolved as recently as 2010.

Controversy regarding the presence of quantum friction e.g., a frictional force between two insulating materials in close proximity and relative motion at zero degrees kelvin. In

2009 Philbin et al asserted that there should be no friction between uniformly moving plates and just one year later John Pendry refuted this assertion in the New Journal of Physics.<sup>2,13</sup> Pendry describes a model of two perfectly flat dielectric materials with localized surface charge density oscillations, called plasmons. Given relative shear velocity  $v$  between the surfaces, the phase velocity  $v_{\text{phase}}$  is equal and opposite for the surfaces as shown in Figure 23 Two dielectric slabs and in relative motion.

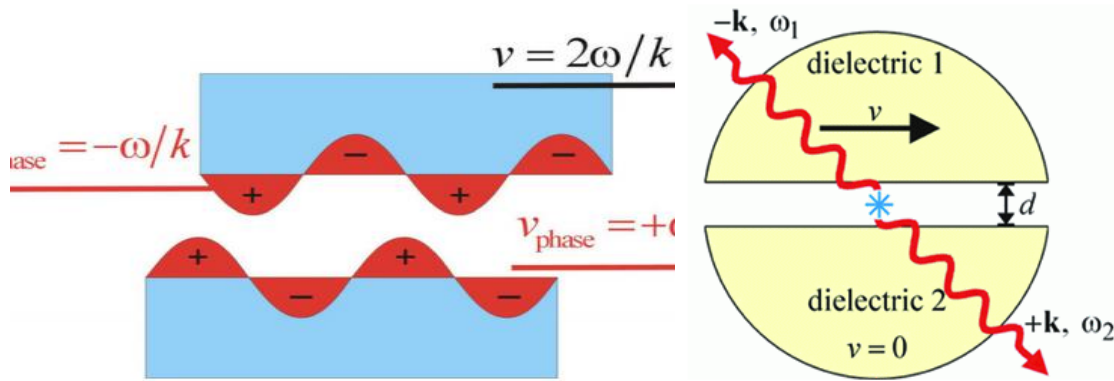


Figure 23 Two dielectric slabs and in relative motion. Left: Phase velocities for the surface plasmons are equal and opposite for the two planar materials.<sup>2</sup> Right: Creation of a photon  $-k$  with frequency  $\omega_1$  necessarily produces a complimentary photon  $+k$  with frequency  $\omega_2$  for energy conservation.<sup>13</sup>

Pendry states that the plasmons between dielectrics will interact when the shear velocity matches the difference in phase velocities,  $2\omega/k$ . The zero-point friction is then found by integrating the energy of interaction over all frequencies. The discrepancy between the two derivations is described by Pendry as a failure to account for the Doppler shifted transmission coefficient during the rotation of the integration contour.<sup>2</sup>

The debate continues with some authors claiming Pendry's result violates the first law of thermodynamics: that energy cannot be created in an isolated system.<sup>175</sup> Most authors

tend to argue for the case of zero-temperature friction response but in any case, the models they derive have yet to prove generally accurate.<sup>176-178</sup>

2D materials and the application of AFM allow researchers to explore special systems to isolate contributions to frictional response with the goal of forming cohesive general models that can be applied to any comprehensible tribological system.<sup>179,180</sup> Carpick et al. found that frictional force decreased monotonically as the number of layers of atomically thin sheets increased.<sup>10</sup> The mechanism for friction dependence was explained by higher adhesion of the tip to samples with fewer layers causing local deformity or “puckering” for thinner nanosheets confirmed by finite element modeling (FEM). The modeling was ostensibly done by considering a single layer of varying thickness rather than a varying number of layers, although thickness and number of layers seem to be used synonymously, see Figure 24.

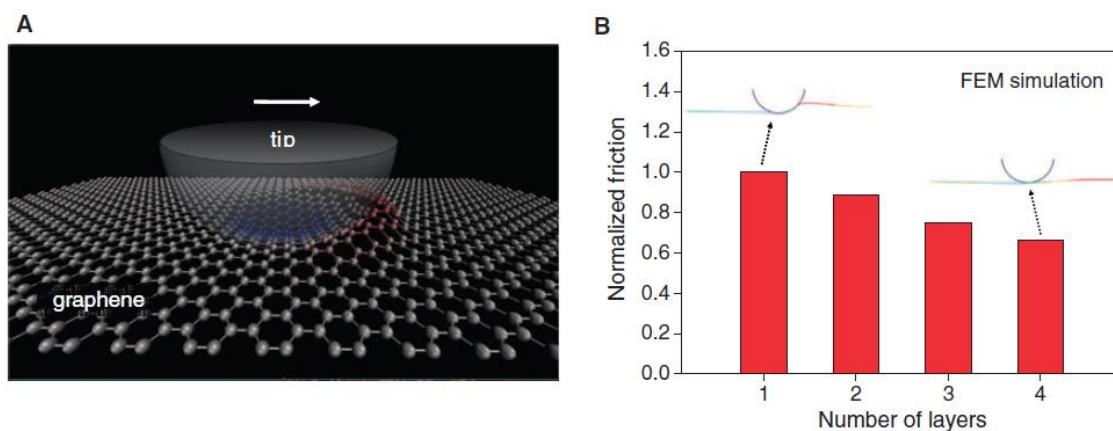


Figure 24 Finite element analysis (FEM) of friction on 2D materials. A) cartoon of depiction of finite element modeling (FEM) of the interaction between silicon AFM tip and graphene monolayer. B) Layer thickness dependent friction results from FEM showing monotonic decrease from normalized value of one layer as number of layers (thickness) increases.<sup>10</sup>

With the tools for synthesis and characterization of MoS<sub>2</sub> nanosheets understood, its unique electronic and mechanical properties provide an exceptional means of advancing electronic and fundamental physics.

## 4 Experimental Methods and Results

### 4.1 Synthesis

Working from the bottom up, the first step to nano-tribological experimentation and discovery is synthesis. During my doctoral research, I utilized various techniques for the synthesis of MoS<sub>2</sub>. I began with mechanical exfoliation of single crystal MoS<sub>2</sub>, but this proved challenging because the samples were highly non-uniform in thickness and lateral dimension, making it challenging to make measurements or achieve reproducible samples. I then pursued chemical exfoliation to obtain large area thin films. While our group has built a high level of expertise on this technique, which I exploited for achieving large-area, thin films, I found that the small later dimensions of the flakes led to surface roughness that made it challenging to carry out AFM measurements. Thus for the purpose of this research, I chose to pursue chemical vapor deposition (CVD) to produce single and few-layer MoS<sub>2</sub> with lateral dimensions in tens of microns. CVD grown samples are reproducible, have large later dimensions and for the most part are atomically smooth, allowing AFM studies to be carried out with ease. In particular, by using as-grown samples without transferring, the pristine monolayers remained smooth, with arithmetic mean roughness<sup>1</sup> of one angstrom or less.

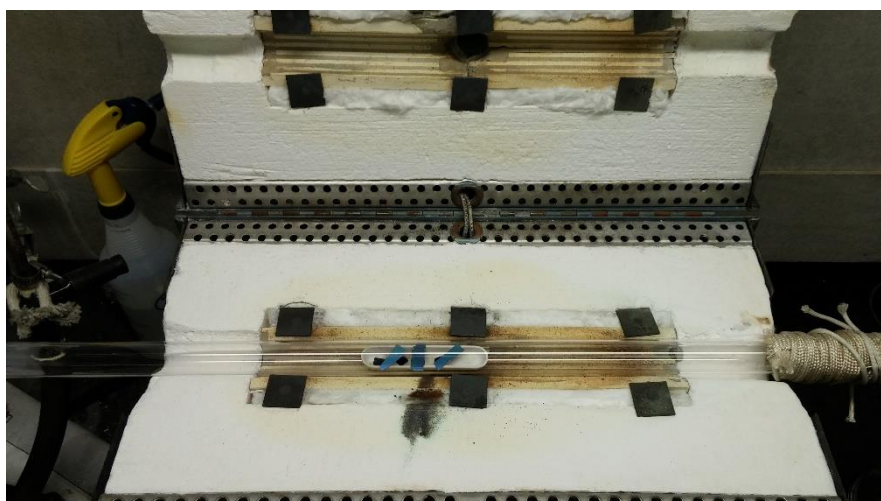
A comparison of different types of MoS<sub>2</sub> obtained by mechanical exfoliation, chemical exfoliation, and CVD are shown in Figure BB. In particular, the Raman and PL are compared.

---

<sup>1</sup> S<sub>a</sub> is the surface roughness calculated from the arithmetic mean of absolute values of deviation from the mean plane.  $S_a = \frac{1}{A} \iint_A |Z(x, y)| dx dy$

## 4.2 Chemical vapor deposition

Much of my focus was dedicated to control and optimization of experimental variables for growth of CVD MoS<sub>2</sub>. The setup I built and modified during my doctoral research is a single-zone clam-shell furnace with 1-inch quartz tube as shown photographically in Figure 25 and as a diagram in Figure 26. I developed a detailed protocol for the synthesis of MoS<sub>2</sub> by CVD. Much of the synthesis work on MoS<sub>2</sub> by CVD is empirical and the growth is dependent on empirical parameters.



*Figure 25 Photo of clamshell type furnace. In this single-zone furnace, the growth substrates are placed in the central heated zone while vapor-phase reactants are delivered via inert gas flow.*

I sought to develop methodology that could be reproduced through understanding of key variables. While this proved to be challenging, I made substantial progress towards basic understanding of the influence of key parameters on growth of MoS<sub>2</sub>. I briefly describe the protocol for CVD synthesis of MoS<sub>2</sub>. My preliminary results suggested that while single layer MoS<sub>2</sub> could be obtained, the growth was highly irreproducible for a number of reasons discussed at the end of this section.

My initial growth study started by attempting to reproduce experimental results reported in the literature. To this end, I started my depositions by utilizing the typical growth precursors used by many researchers – commercially available  $\text{MoO}_3$  and sulfur powder for Mo and S reactants respectively.  $\geq 99.5\%$  purity  $\text{MoO}_3$  powder from Sigma Aldrich and 325 mesh ( $\leq 44 \mu\text{m}$  particle size) sulfur powder was obtained from Alfa Aesar with  $\geq 99.5\%$  purity. In the initial studies, I employed several tens of milligrams of  $\text{MoO}_3$  powder, consistent with the published experiments as shown in Table 2 on page 33. The  $\text{MoO}_3$  has a much higher melting temperature of  $795^\circ\text{C}$  while sulfur melts at  $115^\circ\text{C}$ . Thus the  $\text{MoO}_3$  was placed in an alumina boat located in the center of the tube furnace (the hottest zone) and the sulfur was placed in a region upstream in the tube and out of the heated portion where the temperature was much lower. The silicon substrates on which the  $\text{MoS}_2$  was to be grown were placed face down on top of the Mo containing boat as shown in Figure 26.

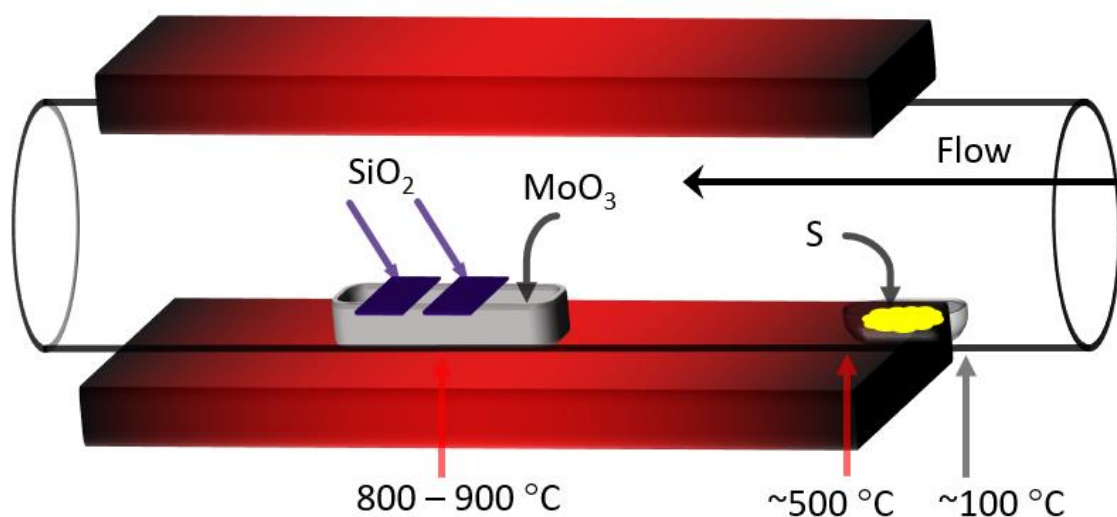
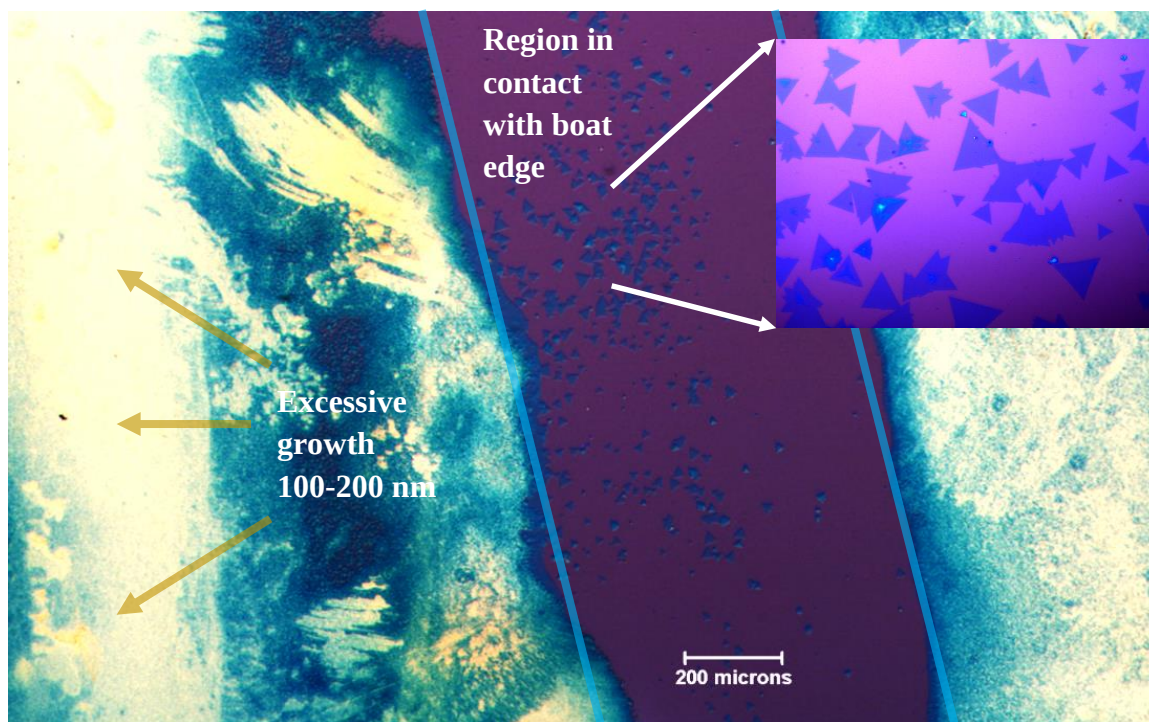


Figure 26 Diagram of early CVD  $\text{MoS}_2$  growth setup. Sulfur powder located upstream of growth zone in temperature gradient at edge of furnace.  $\text{MoO}_3$  powder placed in bottom of boat supporting substrates.

Empirical evidence suggested that the initial oxygen concentration the furnace was important in influencing the growth reactions. Thus, before beginning any deposition, the tube was purged with an inert gas to minimize unwanted oxygen from the reaction environment. The temperature of the furnace was then slowly ramped up to the growth temperature (typically 800 - 900 °C) at a rate of 20 - 25 °C/min. The temperature was then held at the growth temperature for the desired amount of time (typically 10 - 30 minutes) and finally, the tube furnace was allowed to cool to room temperature before the samples were removed. While this approach occasionally led to deposition of MoS<sub>2</sub>, inhomogeneity and variable thickness on the sample surface prompted refinement of the experimental setup. Growth on the middle of the substrate typically had bulk formations of MoS<sub>2</sub>, MoO<sub>3</sub>, and suboxides often more than 200 nm thick. See Figure 27. With this substrate-face-down approach typically single- and few-layer MoS<sub>2</sub> was only found where the SiO<sub>2</sub> surface made contact with the alumina boat.



*Figure 27 Optical image of CVD MoS<sub>2</sub> growth where SiO<sub>2</sub> contacted alumina boat. Thick growth surrounds region where tight space between boat and substrate limited diffusion of reactant vapors. Gold/yellow color indicates thickness of greater than 100 nm. Inset shows higher magnification of predominantly single-layer growth of central region.*

Many of the published CVD growth methods describe a growth time of only five minutes or less. In a single zone furnace, the heating stage will begin vaporizing MoO<sub>3</sub> long before appreciable sulfur vapor is produced. During this period, the relative partial pressures shift dramatically from sulfur deficient to sulfur rich in a short time. This and the huge variation in experimental parameters provided in the literature may indicate that single-layer growth occurs not during the dwell time, but while one of the reactant temperatures is changing, and for a brief period both partial pressures are appropriate for single-layer growth. It was thought that if the growth was occurring during temperature ramps, there must be a period during which the reactant temperatures are ideal for rapid

lateral growth. More accurately, there must be a period during which the reactant *partial pressures* are ideal for such growth.

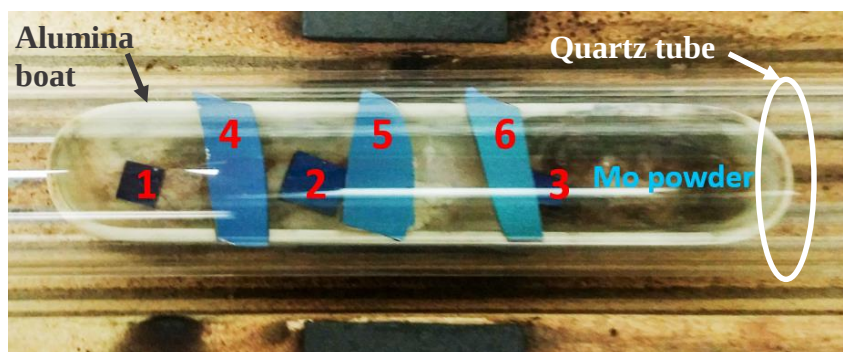
With the goal of achieving reproducible, uniform film growth, the first modification of the CVD growth setup was to move the S source outside the furnace where heating could be controlled by heating tape. Multiple heating zones (achieved in a single-zone furnace by employment of heating tape) enable more control over reactant temperature. In this way the partial pressure of one reactant relative to the other can be modified throughout the experiment. The steep temperature gradient at the sulfur source was decreased by wrapping a 10 cm section of the quartz tube just outside the furnace housing with induction heating tape controlled a proportional integral derivative (PID) device. This controller runs a continuous feedback loop that supplies power to the tape based on the difference between its set point and the thermocouple temperature (P), the integral of temperature over time (I), and the rate of change (derivative) of temperature with time (D). Instead of 100 °C/cm, the tape produced a temperature gradient at the center of less than 40 °C/cm. Following every growth experiment conducted, the furnace was set to heat to a temperature at least 100 °C above growth temperature, with air forced through the tube and all crucibles and reactant vessels inside. Adherence to this practice was intended to avoid unused reactants and deposited products from prior experiments influencing the results.

Gaining more consistent control of the sulfur temperature had no influence on the uniformity of produced films. In order to determine if the inhomogeneity in growth across substrates was due to relative precursor concentrations, an experiment was

designed to analyze multiple regions on several substrates placed in different locations both in and face-down on top of the alumina boat containing  $\text{MoO}_3$  precursor.

#### 4.2.1 Stoichiometry

Analysis of an arrangement of samples surrounding  $\text{MoO}_3$  was conducted at different sulfur temperatures to examine the influence of sample position and sulfur temperature on resulting sulfur to molybdenum ratios. At least three points per sample were averaged and compared based on each position, whether on the top (face down) or bottom (face up) in the  $\text{MoO}_3$  containing boat (see Figure 28), and by sulfur temperature.



*Figure 28  $\text{SiO}_2$  substrates positioned in alumina boat. Experimental setup to determine influence of sample height in quartz tube and distance from Mo source. Substrates 1-3 are face-up while 3-6 are face-down supported by sides of alumina boat.*

Samples were arranged as pictured in Figure 28 and experiments were carried out with sulfur temperatures of 170, 190, and 210 °C. 18 samples were then examined using XPS to correlate experimental parameters with resultant film stoichiometry. Survey spectra from XPS indicates the presence of S, Si, O, C, and Mo in all CVD experiments. (Figure 29) Survey scans only provide cursory information about material composition and cannot be relied on for quantitative values.

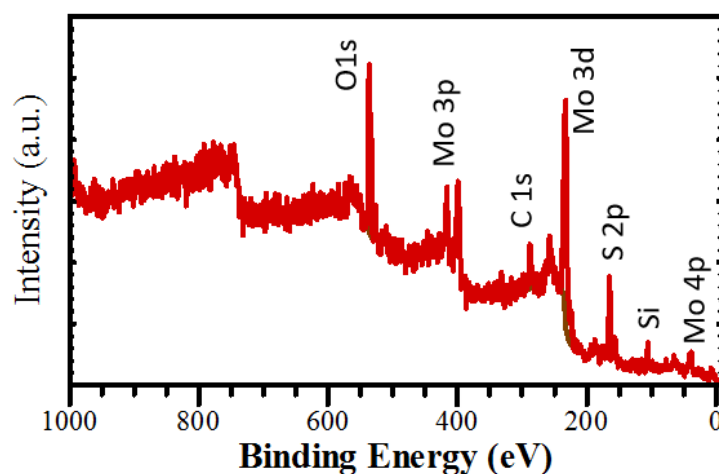


Figure 29 XPS survey spectra. Typical for CVD grown  $\text{MoS}_2$ . Four peaks are typically visible for Mo and one for sulfur. Additionally, the survey shows binding energies for silicon and oxygen from  $\text{SiO}_2$  and carbon contamination from adsorbed atmospheric  $\text{CO}_2$ .

By scanning for specified photon energies more slowly, higher resolution binding energy peaks are obtained. The Mo3d scan contains two peaks at 233.5 eV and 230.2 eV as well as a small S2s peak at 227.5 eV. The sulfur scan resolves two overlapping peaks at 163.5 eV and 162.5 eV. (see Figure 30)

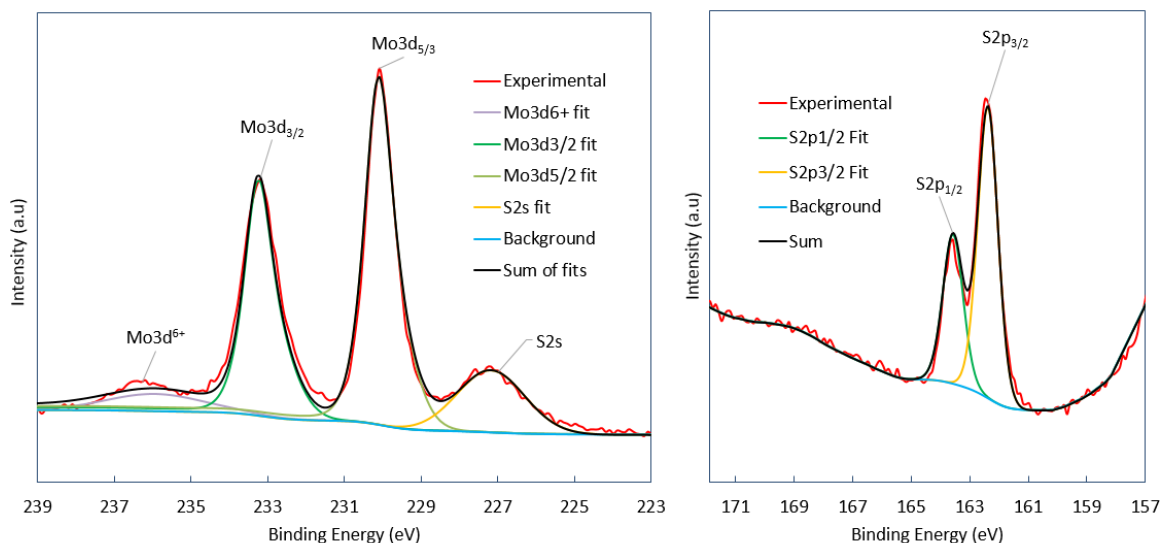


Figure 30 Mo3d and S2p XPS scans. Left: two prominent peaks from  $\text{Mo}3d_{3/2}$  and  $\text{Mo}3d_{5/2}$  electrons, small contribution from the  $\text{Mo}^{6+}$  oxidation state which indicates that some oxygen is bonded with Mo, and sulfur 2s contribution. Right: overlapping sulfur peaks from  $2p_{1/2}$  and  $2p_{3/2}$  electrons. Experimental data are in red, baseline is blue and black is the sum of fitted curves.

By fitting Gaussian curves and calculating their areas above baseline, the atomic ratios of each component can be compared directly. The relative areas of Mo and S peaks yields the ratio of the two elements which indicates the stoichiometry of MoS<sub>2</sub> films. Results indicated that there was little dependence on the distance from the Mo precursor but a significant dependence on sulfur temperature and vertical position. Position 5 (second sample on top) showed the highest average S:Mo ratio of 2.33 while position 2 (second sample on bottom) had a ratio of only 0.72. Overall the top samples had 35% greater S:Mo ratios which can be explained by the fact that unlike the Mo source, the sulfur precursor was not located inside the boat. The striking finding from the XPS analysis was that measurements made on the same exposed central region of a sample sometimes showed drastically different S:Mo ratios. Measurements separated by a few millimeters on the sample in position 2 for the 170 °C experiment showed ratios of 0.2 and 0.8 while the measured stoichiometry of a sample in position 5 of the same experiment ranged between 2.15 and 3.64.

As described in 3.5 X-ray photoelectron spectroscopy on page 50, the spot size of the x-ray beam used for this work is 400  $\mu\text{m}$  diameter. So the broad range of stoichiometries found here don't necessarily represent similar variability within individual flakes smaller than this size. Regardless, the inhomogeneity evident on millimeter scale in the same experiment is cause for concern. Published results regarding optoelectronic and catalytic properties vary substantially and stoichiometry is seldom discussed. Field effect transistors made from CVD MoS<sub>2</sub> in literature show mobilities ranging from 17 to 500  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ .<sup>181 182 183</sup> And hydrogen evolution reactions utilizing CVD MoS<sub>2</sub> are reported with Tafel slopes between 45 and 140 mV/decade.<sup>25,184,185</sup> The Tafel slope is the applied

potential necessary for a ten-fold increase in catalytic activity. The charge carrier mobility will be higher for more stoichiometric  $\text{MoS}_2$ , while lower Tafel slope is achieved as more sulfur vacancies are present. The performance of  $\text{MoS}_2$  in these applications strongly depends on stoichiometry and thus significantly improved means of controlling and characterizing it on the nanoscale must be developed.

Provided that the stoichiometric trends observed here are real and not statistical deviations, some mechanism must be responsible for inhomogeneous distribution of gaseous precursors. The density or molecular weight of each gaseous species should not produce gravimetric separation of the components, but isolated crevices smaller than the mean free path of the molecules will encourage separation because smaller molecules effuse more readily as stated in Graham's law:

$$\frac{R_1}{R_2} = \sqrt{\frac{M_2}{M_1}} \quad (4.1)$$

Where  $R_1$  and  $R_2$  are the rates of effusion through a hole smaller than the mean free path for two gasses and  $M_1$  and  $M_2$  are the molar masses of the two gasses. The experiments in this work were mostly carried out in atmospheric pressures, so the mean free paths of  $\text{MoO}_3$  and S gasses are both greater than the carrier gas, Ar, with mean free path of  $\sim 1.7 \mu\text{m}$  at 850 C. While it is generally agreed upon that all liquid and gaseous sulfur consists of rings with between 2 and 12 members, at a temperature of 850 C, the most abundant form of elemental sulfur is  $\text{S}_2$ .<sup>186</sup> Thus the molecular weight of sulfur gas is about 32 g/mol while  $\text{MoO}_3$  is 144 g/mol resulting in sulfur to  $\text{MoO}_3$  effusion ratio of

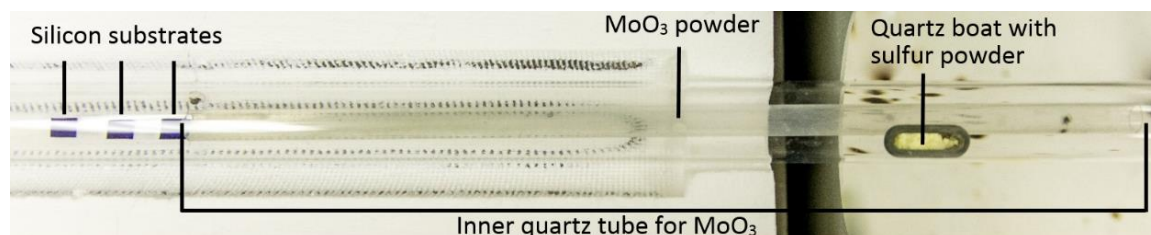
$$\sqrt{\frac{M_{MoO_3}}{M_{S_2}}} = \sqrt{\frac{144}{32}} \approx 2 \quad (4.2)$$

Adiabatic expansion of argon gas flowing at 100 SCCM and entrained vapor-phase precursors produce a drift velocity of approx. 0.8 cm/s. Though on a molecular level the RMS velocities are much higher at 440 m/s and 660 m/s for MoO<sub>3</sub> and S<sub>2</sub> respectively. Thus we can understand how the areas on growth substrates near contact with the boat or other material result in not only limited diffusion but also preferential effusion of the smaller gas species.

Considering that exposed regions near the Mo source grew bulk films and that the melting point of MoS<sub>2</sub> is significantly higher than the melting temperature of MoO<sub>3</sub> (1185 and 795 °C respectively), the second significant modification of the CVD experimental setup was to move MoO<sub>3</sub> source to a colder region of the furnace. While the large majority of published work on CVD MoS<sub>2</sub> describes experiments with Mo source in the boat at the hot reaction area, with growth substrates suspended directly above, a few recent publications have also utilized a cooler region for vaporization of the molybdenum source.<sup>32,50,149</sup>

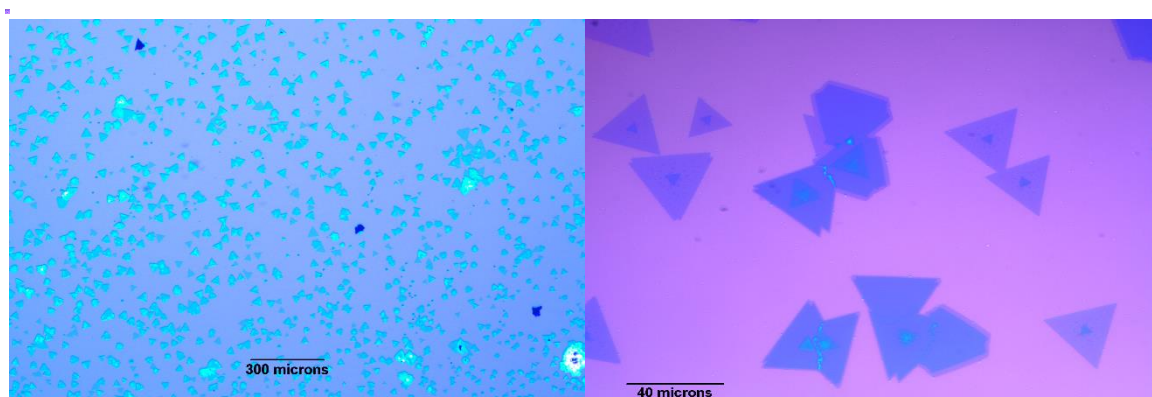
The results from this setup showed increased homogeneity across substrate surfaces, but no improvement in film quality or repeatability and there was evidence of sulfur reacting directly with Mo source by change of color as and often explosion of the MoO<sub>3</sub> pile with black bits of powder dispersed several centimeters from original location. Perhaps this resulted from vapor pressure from within the pile building up against a hardened outer layer of reacted MoO<sub>3</sub> + S. To ensure that the precursors were isolated until reaching the

substrate, I developed a design to deliver the Mo and S reactants to the substrate surface that kept both powders and vapors separated until they reached the growth zone. Figure 31 shows a photograph of the quartz tube with  $\text{MoO}_3$  powder placed inside a secondary 10 mm quartz tube and sulfur powder upstream and outside the furnace housing where a heating tape was wrapped for independent temperature control.



*Figure 31 Photograph of CVD experiment with isolated Mo source. Quartz tube in clamshell furnace with silicon substrates (left) at downstream end of 10 mm tube with  $\text{MoO}_3$  powder isolated from sulfur powder just outside furnace housing.*

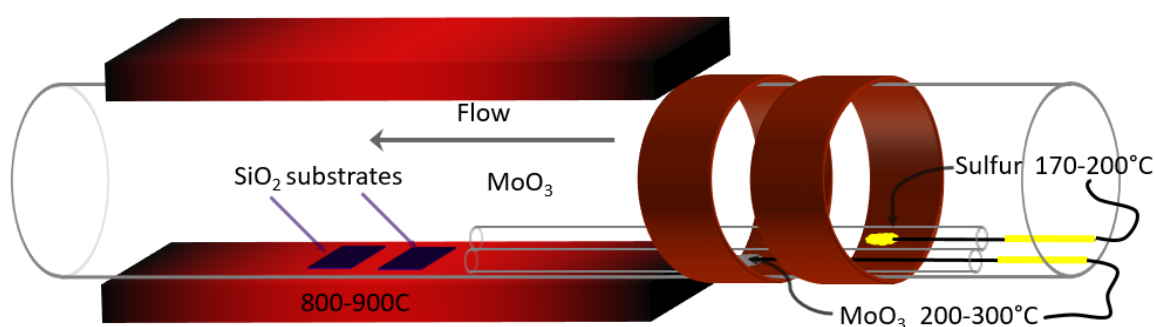
Uniformity in deposition thickness improved using this setup, but inconsistency from one experiment to the next persisted. Figure 32 (left) shows a low magnification optical image of  $\text{MoS}_2$  grown with this CVD setup with homogeneous seeding and single- to few-layer flakes that cover the entire substrate.



*Figure 32 Optical images of growth using 3 temperature zones and isolated reactants. Left: low-magnification 50x showing uniform nucleation of single and few-layer flakes over 6 mm<sup>2</sup> area. Right: 500x magnification detail.*

Compare the results here to those from earlier experimental setups where the Mo source was located directly below growth substrates in Figure 27. At this point the mass of reactants were controlled with milligram precision and vaporization temperatures were controlled using heating tape and PID controller with feedback from thermocouple wrapped between heating tape and quartz tube. Mass control using powdered precursors and a benchtop analytical balance achieved precision for measurements of several milligrams or more, but placement of powders into boats or tubes resulted in high variability in powder surface area. As optimization necessitated usage of smaller quantities of reactants, it became apparent that weighing and placing of powders with repeatable surface areas was unfeasible. Rather than further decrease  $\text{MoO}_3$  mass, it was instead kept constant at 10 mg and sublimation temperature was modified while ensuring that surface area was also consistent. This was achieved depositing packing the  $\text{MoO}_3$  powder into a small spoon, inserting it into the 10mm tube, and carefully inverting. Thus  $10.5 \pm 0.5$  mg  $\text{MoO}_3$  powder was consistently placed in a  $\sim 2.5$  mm diameter mound. Concerns arose regarding the consistency of reactant temperatures using thermocouples wrapped between heating tape and quartz tube also needed to be addressed. Dependent on the weather, temperatures in the CVD room ranged between 60 and 80 F throughout the year. This large variation in ambient temperature effects how accurately the external thermocouple represents the reactant temperature inside the quartz tube. Additionally, the potential disparity could be increased depending on how tightly the heating tape was wrapped and how many layers of tape separated the thermocouple from ambient air. To eliminate discrepancy between reactant temperature and thermocouple reading as well as inconsistencies with wrapping, the thermocouples were inserted through the end of the

tube and placed in direct contact with precursor powders. The schematic of this delivery system is shown in Figure 33, which illustrates how the precursors are supplied to the reaction area via 10 mm quartz tubes that keep the reactant vapors isolated from each other.



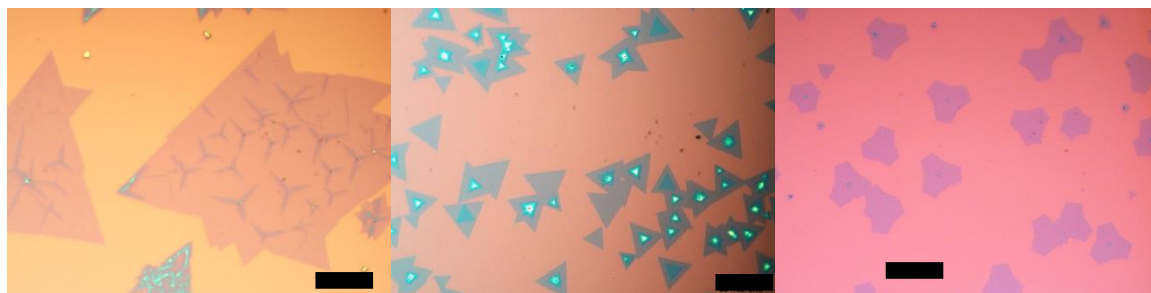
*Figure 33 Diagram of CVD setup with isolated reactants.  $\text{MoO}_3$  and S powders placed in 10mm quartz tubes with thermocouples inserted from upstream end. Red bands on right end of tube represent heating used to control temperature of reactants independently. Black rods with yellow ends represent thermocouples inserted through coupling at tube end.*

In this way, the carrier gas flows over both powders while keeping them isolated until reaching the downstream reaction zone. Many (>100) successful growths of large area (>10 micron) single- and few-layer  $\text{MoS}_2$  crystals resulted from this technique using both  $\text{MoO}_3$  and  $\text{MoO}_2$  as molybdenum sources with clean, oxidized tubes.

With these instabilities in mind, experiments were developed in such a manner as to avoid or mitigate them as much as possible. Growth (dwell) times were altered and even eliminated, but resultant crystal growth remained inconsistent. The inconsistency from cycle to cycle could not be eliminated during my tenure as a PhD student.

Despite this, I was able to get single layered  $\text{MoS}_2$  on most occasions. However, the nucleation and growth structure and size of the flakes was not consistent throughout the

successful runs. Examples of this are provided in Figure 34 which shows optical images of various growth morphologies produced by CVD. The center image in Figure 34 shows triangles with bright core centers. The bright cores or central seeds arise from nucleation sites and are well known in the literature.<sup>21,31,35,104,187,188</sup>

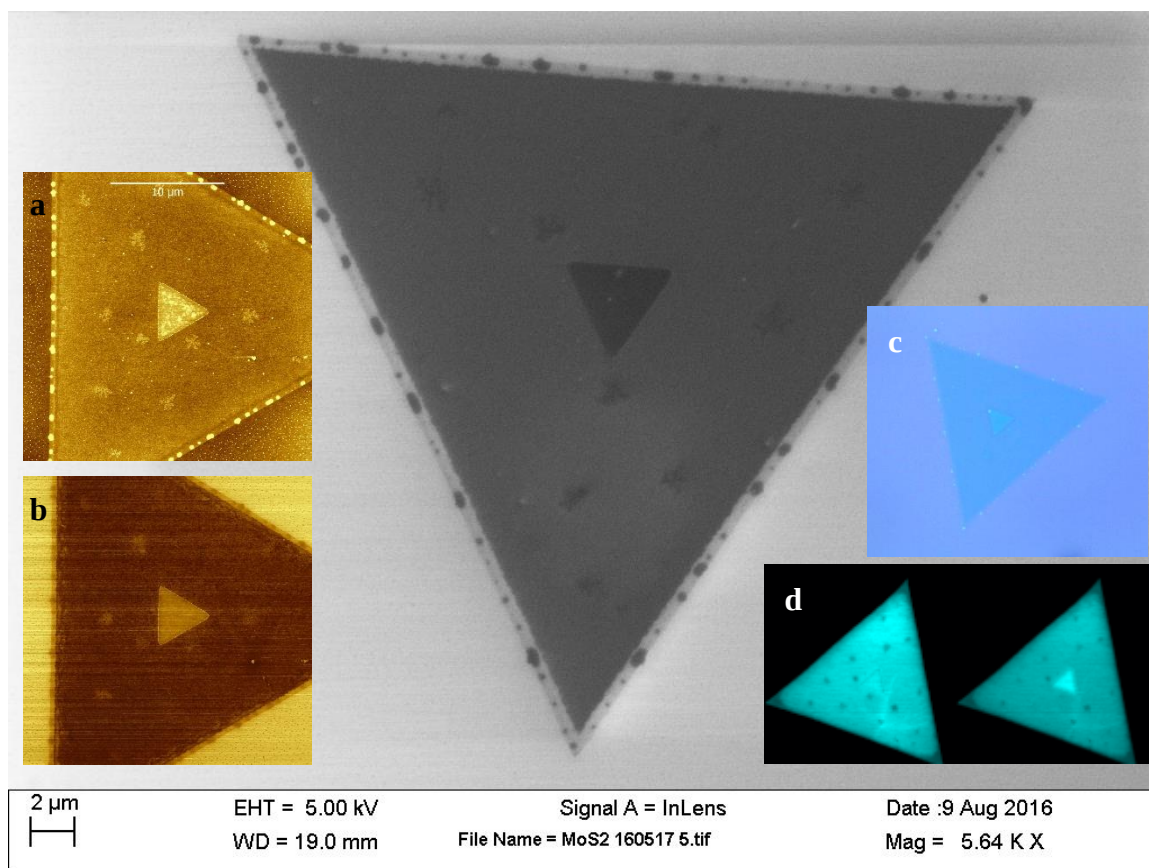


*Figure 34 Optical images of CVD MoS<sub>2</sub> captured with 50x objective lens showing several growth patterns of CVD MoS<sub>2</sub>. Dendritic formations and multilayer growth at grain boundaries (left), pyramids grown from screw dislocations seen as bright cores on triangles (center), and hexagonal single layers evolving into triangles (right). Optical interferometry allows for easy differentiation of layers despite their sub-nanometer thickness. Scale bars are 30 microns.*

Closer examination by AFM has been performed and will be presented later in the thesis in section 4.4 Atomic force microscopy. The analyses show that the seeds are Mo-rich cores. For monolayer MoS<sub>2</sub> growth to occur, the seed forms not from reactant partial pressures climbing high enough for a cluster of Mo and S atoms to reach critical radius but instead from a MoO<sub>(3-x)</sub>S<sub>y</sub> core and a MoS<sub>2</sub> fullerene shell.<sup>21</sup> For small seeds (~1 nm), mild out-of-plane distortion and local strain overcome lattice mismatch between seed and monolayer (more on this below). For intermediate seeds (~10 nm), the seed becomes a defect site allowing for bilayer, trilayer, and quadrilayer flakes to grow with 60-degree rotational symmetry. Intermediate seeds may also result in a screw dislocation and pyramid shape, which is actually a single layer of MoS<sub>2</sub> in a spiral pattern. Larger seeds cannot be accommodated by strain and line defects to form single crystals with high

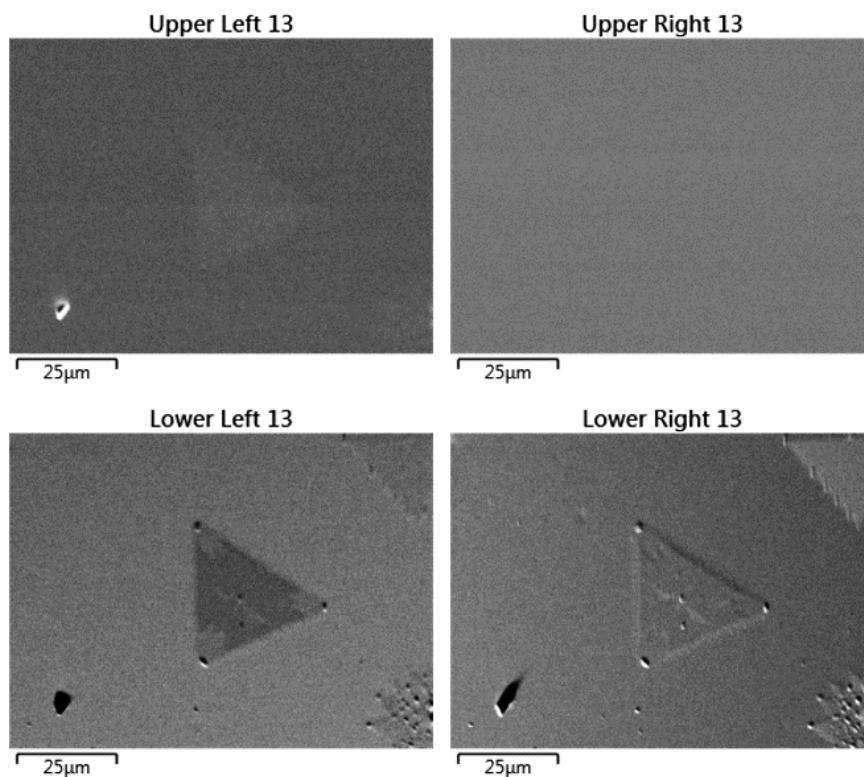
symmetry, but instead result in star shapes and dendritic formations as multiple grains compete for real estate on the  $\text{SiO}_2$  surface.

Optical microscopy alone often gives the impression that large-area uniform  $\text{MoS}_2$  flakes have been grown while further examination by SEM and other techniques can reveal a different perspective. A Zeiss Sigma Field Emission SEM was used to investigate grown films as shown in Figure 35. Optically this bilayer flake appears mostly uniform with some bright regions of excessive growth on the perimeter, but much more detail is revealed via SEM. The perimeter of this flake shows higher intensity with low intensity spots indicating an intermediate stage of growth with subnanometer thickness highlighted by tall vertical pillars surrounding the first layer of  $\text{MoS}_2$ . AFM topography confirms the thin perimeter and pillars as shown in Figure 35a. Often asperities on a material surface result in higher friction values, but interestingly these pillar structures show lower friction than both the  $\text{SiO}_2$  substrate and the sub-monolayer perimeter. (Figure 35b)



*Figure 35 SEM micrograph of 3-layer MoS<sub>2</sub>. SEM contrast from irradiation by electrons accelerated with 5 kV and detected using InLens. Insets: a), b) AFM height and friction. c) Optical image. d) Raman maps of 383 and 409 cm<sup>-1</sup> intensity.*

Attempts were made to utilize electron backscatter deflection (EBSD) as described in 3.3 Scanning Electron Microscopy on page 44 in order to determine layer stacking. The sample was mounted in a pre-tilted holder at 63.3 degrees and exposed to high current electrons accelerated with 20 kV through a 120 mm aperture. Unfortunately the ultrathin few-layer MoS<sub>2</sub> did not provide strong enough signal against the background to resolve the Kikuchi lines that indicate crystal structure. The peripheral photodiodes surrounding the EBSD phosphor screen produced some qualitative data via contrast between layers of MoS<sub>2</sub> (see Figure 36), but this sort of contrast was also obtained through Raman spectroscopy.

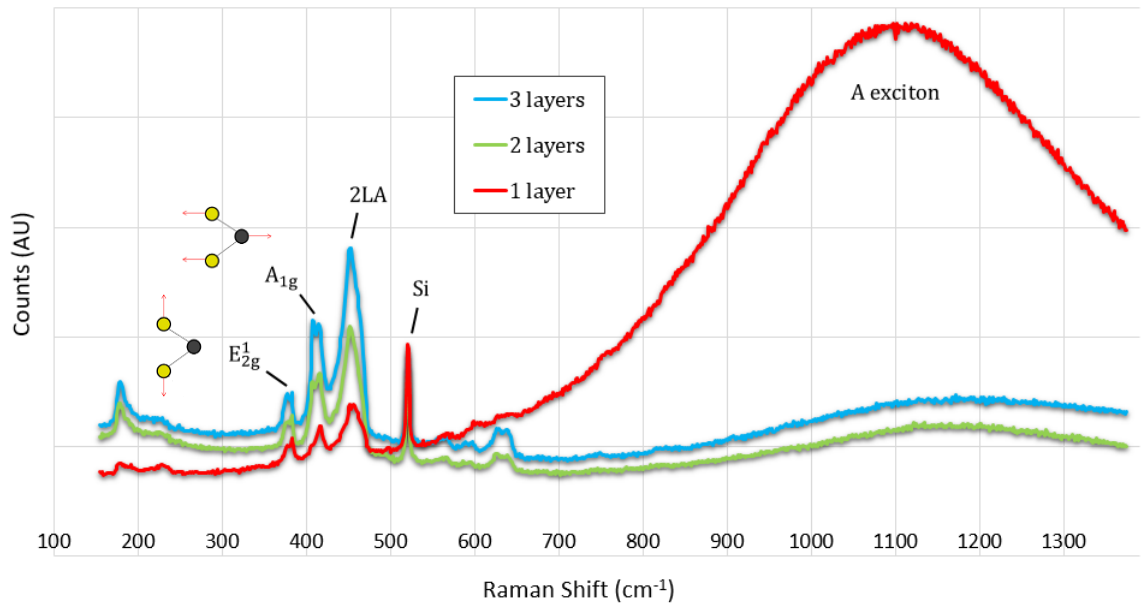


*Figure 36 Contrast images from EBSD peripheral photodetectors. Contrast between the two layers can be seen from the lower left image indicating more diffuse scattering from the second layer.*

Further efforts to conclusively determine stacking order and interlayer twist with TEM described ahead in section 4.4.4 *Tribology on a TEM* grid on page 98. While the SEM provides great insight into surface composition and morphologies for certain applications, this work did not benefit significantly from the technique but instead relied primarily on optical, Raman, and AFM.

As described in Chapter 3, Raman microscopy provides a unique means of exploring the vibrational modes and electromagnetic scattering mechanisms of 2D materials.

The quality of MoS<sub>2</sub> can be assessed comparing the relative heights of the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> and for single layers, the quality is often demonstrated by presence of strong photoluminescence (PL). The absolute intensity at a given wave number or integrated counts over a range depends not only on the sample quality but the total energy delivered through laser irradiation. Comparing the PL relative to the 520 cm<sup>-1</sup> silicon peak provides a simple means of evaluating one single layer sample to another independent of Raman exposure settings. Figure 37 shows Raman spectra for 1, 2, and 3 layer MoS<sub>2</sub> with out of



*Figure 37 Raman spectra for 1, 2, and 3 layer MoS<sub>2</sub>. Single layer MoS<sub>2</sub> in red shows photoluminescence peak at 1100 cm<sup>-1</sup>. As layers increase, the characteristic MoS<sub>2</sub> peaks for the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> modes (385 and 408 cm<sup>-1</sup> respectively) increase while photoluminescence disappears on account of the transition to indirect band gap in multilayer MoS<sub>2</sub>.*

plane E<sub>2g</sub><sup>1</sup> and in-plane A<sub>1g</sub> mode identified. Single layer spectra in red shows the broad peak from the A exciton at 1100 cm<sup>-1</sup> which corresponds to 680 nm or 1.8 eV band-gap

using a 633 nm excitation laser. The reader may notice a splitting of the  $E_{2g}^1$  and  $A_{1g}$  peaks for 2 and 3 layer spectra which indicate that stacking faults have resulted in a mix of 2H and 3R polytypes.<sup>189</sup>

On any given sample (especially those grown with Mo source in growth zone), the morphology, stoichiometry, thickness, and compounds formed were invariably heterogeneous. All varieties of structures, from triangles to hexagons, stars and dendrites can be found with thicknesses from 1 layer (<1 nm) to bulk (>100 nm) alongside  $MoO_2$  polyhedra, nanowires, and amorphous deposits.

In short, attributing a particular growth formation to an experimental parameter could not be supported by simply looking a few microns or millimeters away or attempting to recreate the growth in a subsequent identical experiment.

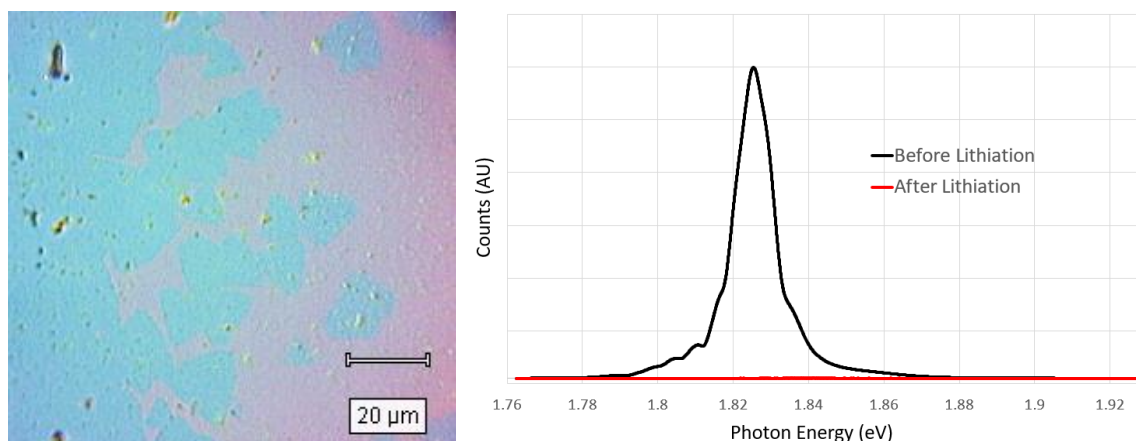
#### 4.2.2 Experimental variability

While it is possible to exercise moderate control over the highest contributing variables – temperature, mass, surface area of reactants, flow rate, sample position, and cleaning – there are many more factors that are harder to manage. The role of ambient temperature and humidity, which range from 13-27 °C and 20-100% respectively, necessarily impact CVD growth. Ambient temperature combined with uncontrolled circulation could change reactant temperatures in the steep gradient at the furnace edge, which can be as much as 200 °C/cm. Even after moving the thermocouple probes inside the individual 10mm quartz reactant tubes, the temperature read when the probe is in contact with the tube (conductive heating) is higher than when it is free-floating and thus subject to slower convection heating and constantly cooled by forced induction of inert gas.

### 4.3 Phase transformations

The ability to produce two electronically dissimilar phases of MoS<sub>2</sub> provides unique opportunities for 2D electronics as an electrode material <sup>67</sup> and relevant to this work as a means to examine electronic friction. As discussed in section 2.4 Phase transformations (page 35), n-butyl lithium (BuLi) is used not only as an exfoliating agent for bulk MoS<sub>2</sub> but also produces a phase change from 2H to 1T resulting from charge transfer from the lithium ions into MoS<sub>2</sub> sheets. CVD MoS<sub>2</sub> samples were grown and submerged in 1.6 molar n-butyl lithium in hexane solution from Sigma Aldrich. As an organometallic superbases, BuLi has a strong affinity for protons and violently reacts with water and may spontaneously ignite in air due to water vapor. Therefore, all BuLi transformation experiments were carried out in the inert atmosphere of a nitrogen filled glovebox. The MoS<sub>2</sub> on SiO<sub>2</sub> samples were typically soaked for 24 hours. This amount of time was shown to be sufficient for complete transformation to 1T as evidenced by Raman spectroscopy and XPS. For single layer samples, the phase transformation was easily confirmed via examination of photoluminescence (PL): the semiconducting 1H phase shows strong PL peak near 1.8 eV owing to its direct band gap, but the metallic 1T phase will produce no PL. Though some untransformed 1T phase may remain, defect sites in the crystal introduce additional mid-gap energy states for photoexcited electrons to occupy while relaxing non-radiatively.<sup>118,190</sup> Thus lack of PL will indicate that a single layer of MoS<sub>2</sub> has been transformed but cannot conclusively determine complete transformation. By irradiating monolayer MoS<sub>2</sub> with laser light of wavelength less than 690 nm (1.8 eV per photon), the Raman microscope can indicate that a single layer sample of MoS<sub>2</sub> has been substantially transformed to 1T phase if no peak is produced

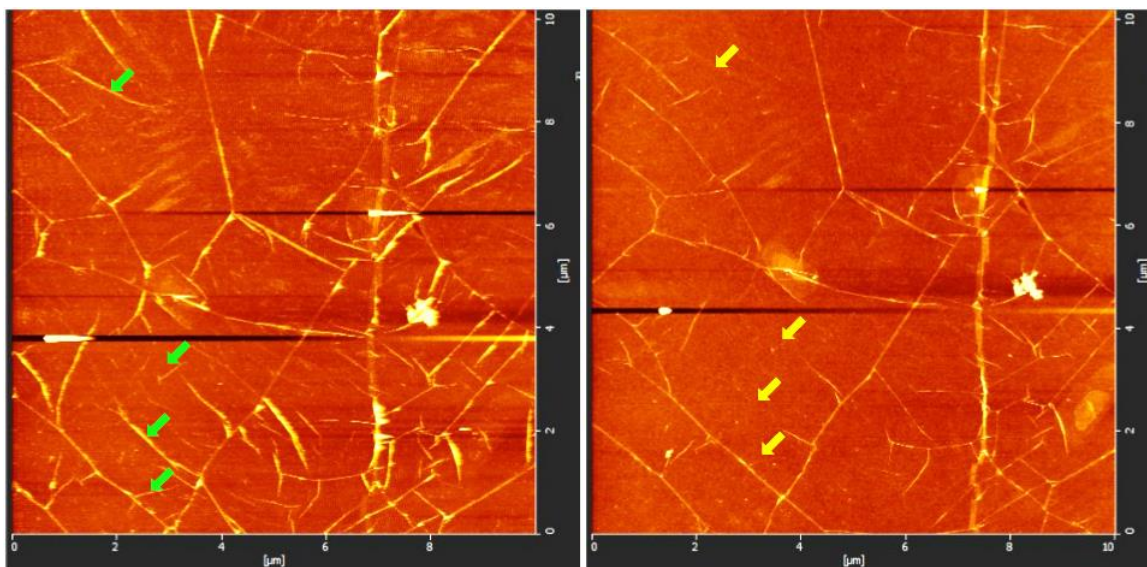
near 1.8 eV. Figure 38 Shows an AFM micrograph of a 1T flake of MoS<sub>2</sub> with height profile and the quenching of photoluminescence as a result of the phase transformation.



*Figure 38 1T MoS<sub>2</sub> from butyllithium intercalation. Left: optical micrograph showing single layer MoS<sub>2</sub> as well as debris and residue following BuLi soak and wash. Right: photoluminescence (PL) of MoS<sub>2</sub> before and after transformation. Quenched PPL indicates that the sample has been transformed.*

Through AFM analysis and particularly tribological studies, it became apparent that single-layer MoS<sub>2</sub> samples distort heavily at some point in the transformation process to the 1T phase. Typically, the thickness of a single layer of MoS<sub>2</sub> measured by AFM ranges between 0.6 and 1 nm, but after BuLi intercalation, single-layer regions often measured upwards of 1-2 nm with average roughness often exceeding five times that of as-grown 2H MoS<sub>2</sub>. In-situ experiments that monitor single-layer MoS<sub>2</sub> on SiO<sub>2</sub> during lithiation have yet to be conducted, so the precise mechanisms for planar distortions have not been elucidated, but it is clear that separation from the substrate from insinuated BuLi combined with transformation induced interlayer stresses both play primary roles in increased layer thickness and wrinkling of the nanosheets respectively. Experiments were conducted with the goal of reducing the planar distortion following lithiation, including varying concentration of BuLi, the time submerged in solution, and the washing/drying methods. BuLi concentrations were tested from 0.016 to 1.6 molar, soak times were

varied from 1 hour to 3 days, and a variety of solvents and washing procedures were tested. Because the BuLi solvent was hexane, the first rounds of washing also involved hexane, but subsequent washing steps were varied with methanol, isopropanol, acetone, and water to remove residual BuLi, lithium salts, and other organic compounds left by the BuLi. Distortions from planar could be significantly reduced through annealing at high temperature as demonstrated with graphene in Figure 39, but unfortunately annealing at temperatures of 300 °C or higher would quickly result in relaxation back to the more-stable H phase.<sup>118</sup>

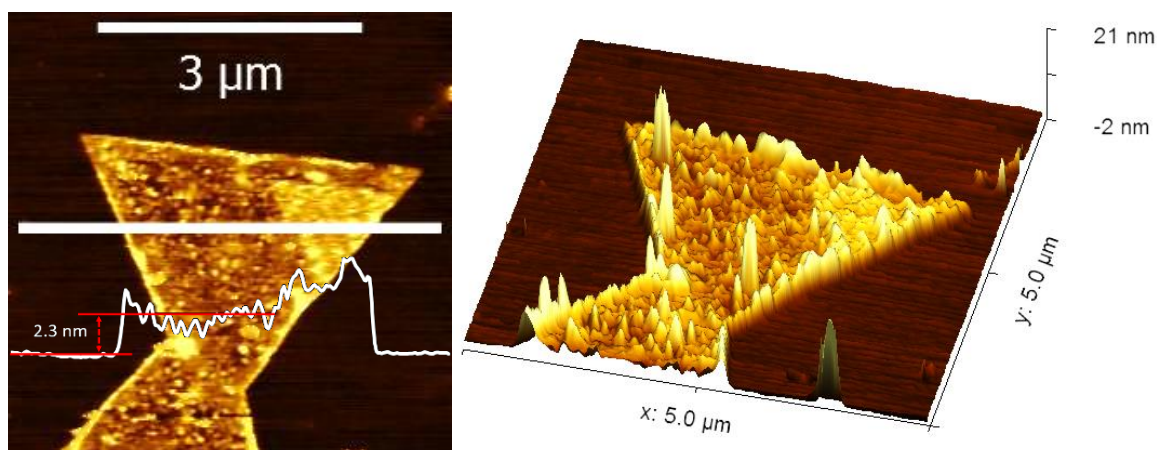


*Figure 39 AFM topography of graphene sheet after annealing. Topography after annealing in high vacuum at 300 °C for 2 hours (left) and 24 hours (right). Green and Yellow arrows highlight wrinkles that were removed after annealing.*

Regardless of the methods tested, significant morphological changes to the CVD grown monolayers were observed after the transformation process which reduced the significance of tribological findings discussed below.

#### 4.4 Atomic force microscopy

AFM was used to characterize layer thickness, roughness, surface morphology, grain size, and frictional force of both phases of MoS<sub>2</sub>. It was found that the lithium intercalation used to transform 2H into 1T phase MoS<sub>2</sub> left the nanosheets wrinkled, blistered, corrugated, or otherwise distorted from pristine, planar CVD MoS<sub>2</sub>. (See Figure 40)



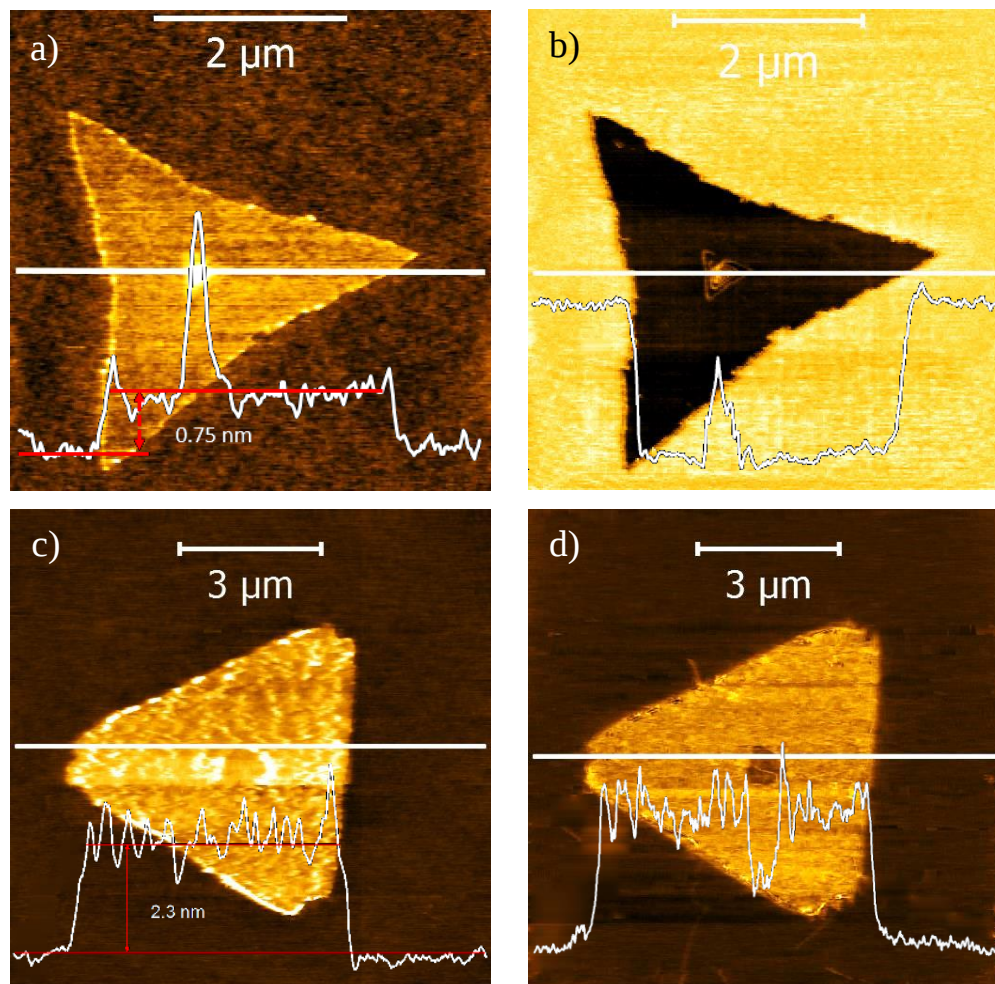
*Figure 40 1T MoS<sub>2</sub> topography. Left: AFM micrograph of 1T MoS<sub>2</sub> with height profile overlaid showing monolayer average thickness of greater than 2 nm. Right: 3d representation of 1T flake.*

Average height as measured by AFM for 1H MoS<sub>2</sub> was just under 1 nm whereas the average for the lithiated samples was over 1.8 nm. Additionally, AFM studies revealed residues from the BuLi persisting on substrate surfaces after washing that was not apparent from optical microscopy. While the AFM was useful for examining layer thickness, growth patterns, and surface morphology, its largest contribution to this research was in collection of friction data from CVD-grown MoS<sub>2</sub> for tribological study.

#### 4.4.1 Friction and Phase

Initial experiments to explore the tribological properties of MoS<sub>2</sub> were designed to compare the relative nanoscale friction characteristics between the semiconducting 2H phase and metallic 1T phase. These experiments were chosen as a means of exploring the influence of electronic properties on friction. Lateral force measurements were collected at Argonne national laboratory using a Bruker/Nanoscope Multimode 8 AFM and Nanosensors PPP-CONT-SPL n-doped Si (0.01-0.02 Ωcm) 0.02-0.77 N/m cantilevers. The friction of both phases of MoS<sub>2</sub> were measured and qualitatively compared. The

semiconducting phase of MoS<sub>2</sub> produced much lower friction relative to the surrounding SiO<sub>2</sub> substrate as shown by dark triangle surrounded by bright substrate in Figure 41b. Whereas compared to the friction between AFM tip and bare SiO<sub>2</sub> substrate, it was found that the friction of 1T MoS<sub>2</sub> was substantially greater as shown by bright triangle surrounded by dark substrate in Figure 41d.



*Figure 41 Friction of 1T and 1H MoS<sub>2</sub>. a) 1H MoS<sub>2</sub> height with overlaid line profile. b) Corresponding friction micrograph showing lower friction than surrounding SiO<sub>2</sub>. c) 1T MoS<sub>2</sub> with overlaid line profile showing increased thickness resulting from BuLi transformation. d) 1T friction map showing high friction relative to SiO<sub>2</sub>.*

In every flake examined by lateral force microscopy (LFM), the 1T phase exhibited higher friction and the 1H phase exhibited lower friction relative to the substrate. Thus

the transformed 1T metallic phase exhibits higher friction (dissipates kinetic energy more quickly) than the 1H phase. This finding corroborates previous hypotheses that electronic friction plays a major role in nanoscale friction.<sup>49,50</sup> As they are composed of the same elements in similar ratios, the only significant difference between these two phases of MoS<sub>2</sub> is their electronic behavior.

In addition to identifying the large disparity in nanoscale friction between 1H and 1T phases of MoS<sub>2</sub>, friction AFM experiments conducted here displayed no frictional force dependence on the number of layers of MoS<sub>2</sub> and interesting multilayer growth mechanisms. Figure 42 shows a ten-layer thick MoS<sub>2</sub> pyramid via AFM topography and corresponding LFM map.

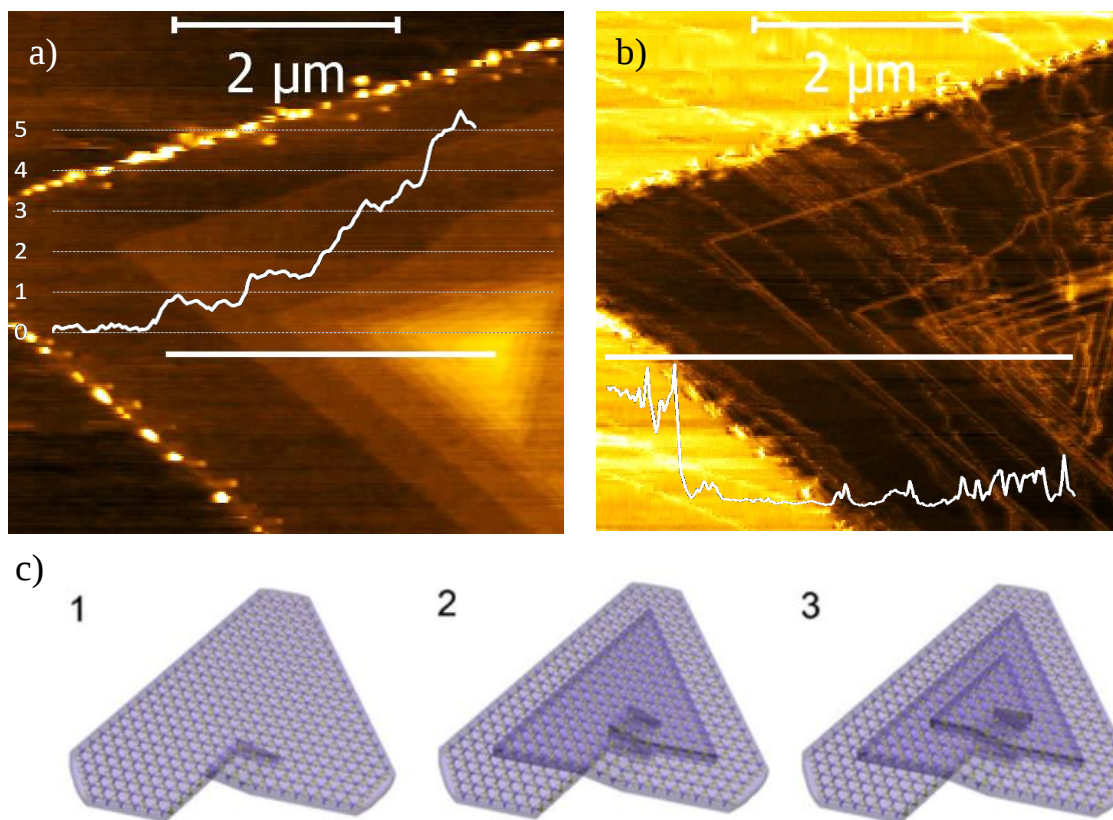


Figure 42 Friction of a multilayered MoS<sub>2</sub> pyramid. a) Height micrograph of pyramid-shaped MoS<sub>2</sub> crystal with overlaid height profile and nm gridlines; nine layers at 5.4 nm yielding average thickness of 0.6 nm per layer. b) Corresponding friction micrograph showing spiral layer boundaries with overlaid friction profile showing approximately equivalent friction force at all layers. c) Model of pyramid formation due to screw dislocation.<sup>12</sup>

Two things are evidenced here: The MoS<sub>2</sub> has grown in a spiral pyramid pattern indicating a screw dislocation which results in one continuous 2D sheet of MoS<sub>2</sub> growing into a 3D pyramid.<sup>191</sup> (see Figure 42c); CVD MoS<sub>2</sub> friction behavior shows no appreciable dependence on number of layers. Frictional force rises abruptly and briefly when the tip traverses from one layer to another, but friction did not appear to vary from one layer plateau to the next. (Figure 42b)

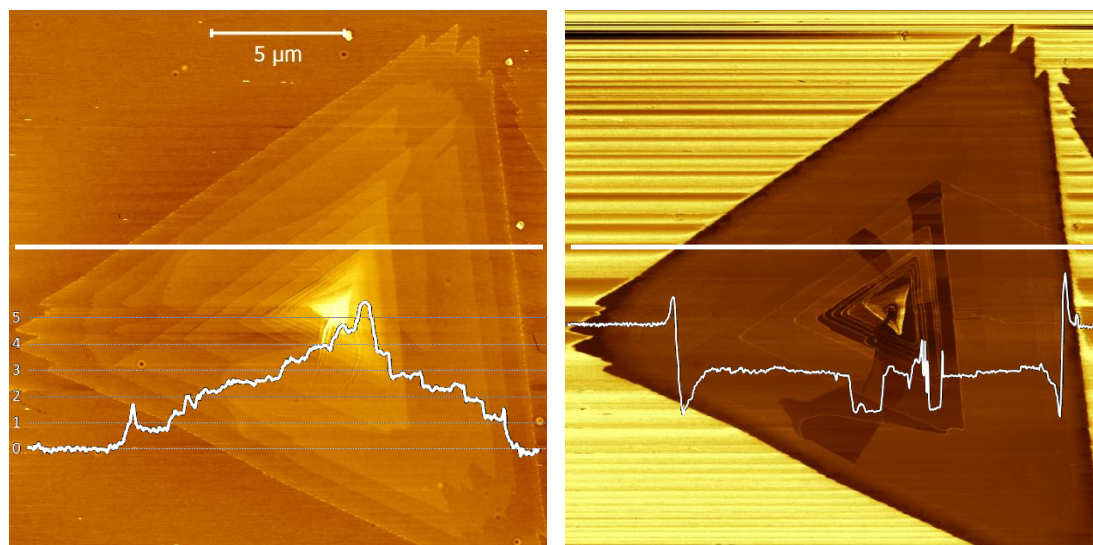
This finding is in contrast to work by Carpick et al., who found that frictional force decreased monotonically as the number of layers of atomically thin sheets increases.<sup>10</sup>

Samples analyzed in this work were prepared by CVD, whereas those in the Carpick study were mechanically exfoliated. Both should be almost if not entirely composed of the 2H polymorph, but the layer stacking and possibly substrate adhesion were likely different. Carpick et al.'s observation of a greater than 50% reduction in friction from one-layer to five-layer MoS<sub>2</sub> prompted further exploration to discover why no frictional dependence on layer number was seen here.<sup>10</sup> Unfortunately for the experiments comparing friction behavior between the two phases of MoS<sub>2</sub>, morphology and roughness should be controlled and not be variable if the correlation is to be attributed to crystal structure alone. Further friction experiments and testing of hypotheses for the disparity in measurements between phases required morphologically equivalent samples of both phases.

#### 4.4.2 Friction and polytype

Beginning in 2016, a Park Systems NX-10 AFM became available in the Chemistry and Chemical Biology Department at Rutgers. This machine was utilized to explore the dependence of friction on number of layers and resolve the discrepancy between the findings from Argonne lab and those in published literature.<sup>10</sup> CVD MoS<sub>2</sub> samples were grown with a variety of experimental parameters until single-layer, few-layer, and pyramid-shape MoS<sub>2</sub> flakes were identified. Using a “soft”, 0.2 N/m, antimony n-doped Si (0.01 – 0.025  $\Omega$ cm) CONTV-A cantilever manufactured by Bruker with the NX-10 in friction force microscopy (FFM) mode, data were collected to reveal relative differences in friction between layers of MoS<sub>2</sub> flakes. With these spiral shapes, the finding was the same as from the Argonne data: friction does not follow a monotonic trend from one layer plateau to the next. More interestingly from this data, it was found in one particular

pyramid that there were two discrete values of friction apparent across many layers. This seemed to be less a result of layer dependence but rather two possible characteristic values of friction transmitted from one layer through the next. The line profile in Figure 43 (right) shows high friction on both ends from the SiO<sub>2</sub> substrate and lower on the MoS<sub>2</sub> flake, but near the middle of the profile there is a second lower friction value.

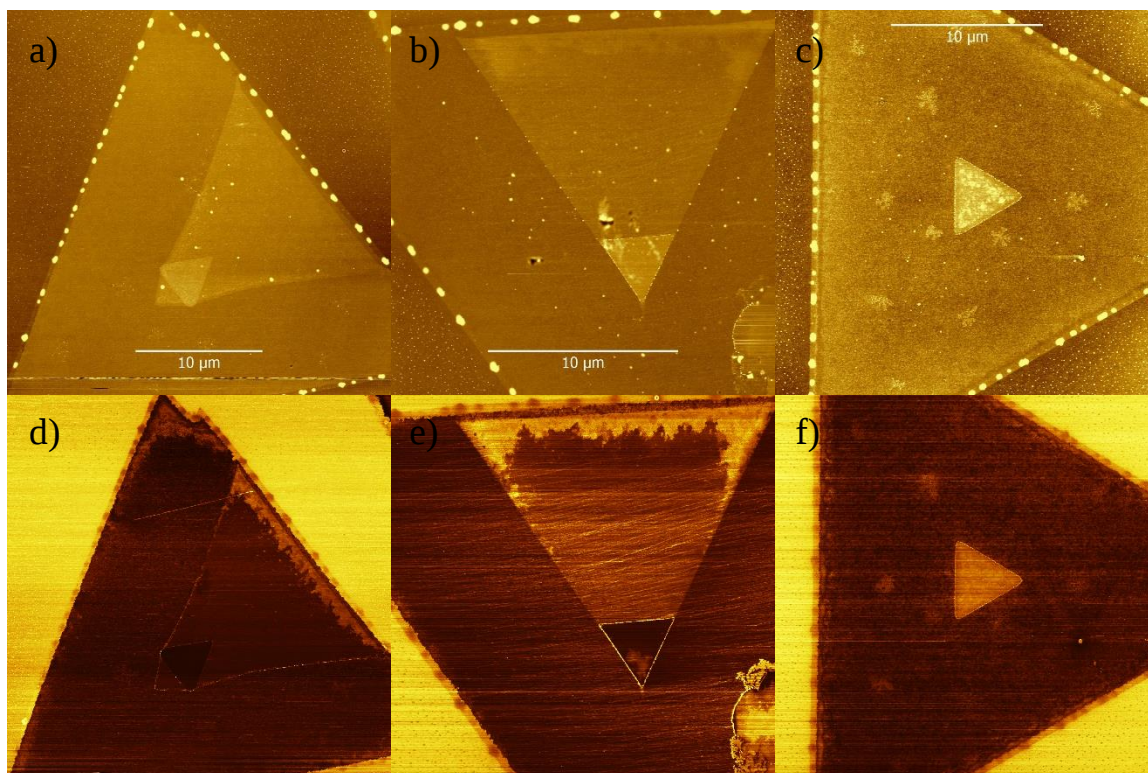


*Figure 43 AFM data from Park NX-10 of a MoS<sub>2</sub> pyramid. Height with line profile overlaid (left, gridlines are in nm) and friction with line profile (right) micrographs showing two discrete values for friction on the MoS<sub>2</sub> flake. Gridlines in height profile are nanometers.*

The low friction values appear to originate on the second layer (middle of friction map just below line profile) where the screw dislocation resulted in the overlap of layer one onto layer two. This finding further fueled the curiosity to explore the possibility that the stacking arrangement as well as coupling between the layers could account for a frictional dependence on the number of layers as discussed above when comparing the nanoscale friction of CVD-grown MoS<sub>2</sub> pyramids to mechanically exfoliated sheets from naturally occurring bulk material. More experiments were needed to explain these strange and incompatible results.

In order to explore the effect of stacking arrangement, or polytype, of MoS<sub>2</sub> on friction, samples were selected with multilayer MoS<sub>2</sub> flakes, particularly those with 0-degree relative rotation between layers and 60 degrees between layers. It was thought that a layer at 60 degrees relative to its supporting layer should have a different stacking than one with a 0-degree twist. The rotational symmetry will be broken for all rotations other than multiples of 120 degrees. Figure 44 shows topography and friction for two CVD grown trilayer flakes and one bilayer flake all with a second layer of 0-degree twist relative to the bottom single layer. These were grown on SiO<sub>2</sub> substrates face-up in an empty alumina boat with the setup shown in Figure 31 on page 75 using 20 mg MoO<sub>3</sub> in quartz boat placed outside the furnace insulation, 80mg S in 10 mm quartz isolation tube, S thermocouple wrapped under heating tape. High purity argon was injected into the right side of the tube at >300 SCCM while the center of the furnace was ramped from room temperature to 870 °C in 30 minutes. While the center cooled to 850 °C in 5 minutes, the heating tape was turned on to heat the sulfur from 50 °C to 200 °C. Over the next 30 minutes, the center of the furnace was slowly heated from 850 °C to 860 °C at a reduced argon flow of 100 SCCM while sulfur temperature was held constant. At 65 minutes total time the furnace was turned off, but sulfur temperature was maintained for another 5 minutes. Finally at 70 minutes, the flow was increased to >300 SCCM, heating tape was

turned off, and furnace lid was propped open 3 cm for rapid cooling from 720 °C.



*Figure 44 Friction of MoS<sub>2</sub> with 0-degree twist between 1st and 2nd layer. Top row shows topography of 3-, 3-, and 2-layer MoS<sub>2</sub> with tall pillar structures and sub-nanometer perimeters on all. Friction maps on bottom row show predominantly low friction first layer but high and/or low friction on second layer.*

In Figure 44, friction on the second layer is low in *d* and *e* except near the edge coinciding with the edge of the first layer but high on the second layer in *f*. What is interesting about *d* and *e* is that the second layer showed preferential growth to only one of three sides of the triangle assuming that growth originated from a seed at the center of the first layer triangle. From the time of these analyses until shortly before the present, no explanation was made that fit the growing volume of data and no trends were identified in friction behavior. Aside from the finding of two discrete values of friction in multilayer MoS<sub>2</sub>, the friction behavior seemed to be as unpredictable as seen by the data points scattered in Figure 45.

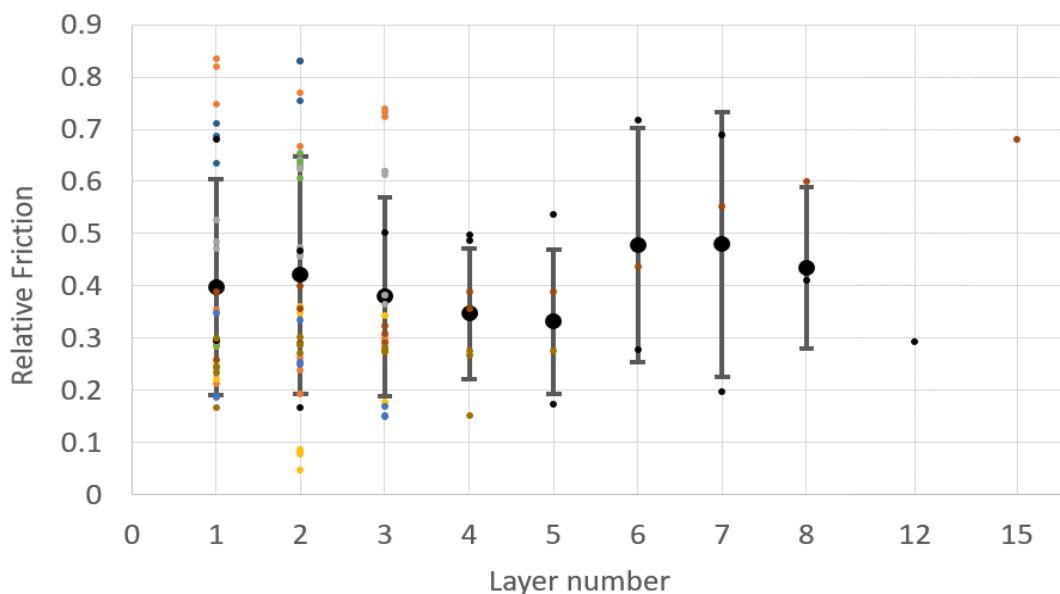


Figure 45 Scatter plot of friction vs layer number. Large black points are the average friction relative to SiO<sub>2</sub>. Error bars are 1 standard deviation from average of measurements. All measurements with more than 4 layers were from pyramid-shaped MoS<sub>2</sub> flakes resulting from screw dislocations.

Further efforts to reconcile this range of data and correlate it with other material properties prompted utilization of another tool available on the Park AFM: electrostatic force measurement.

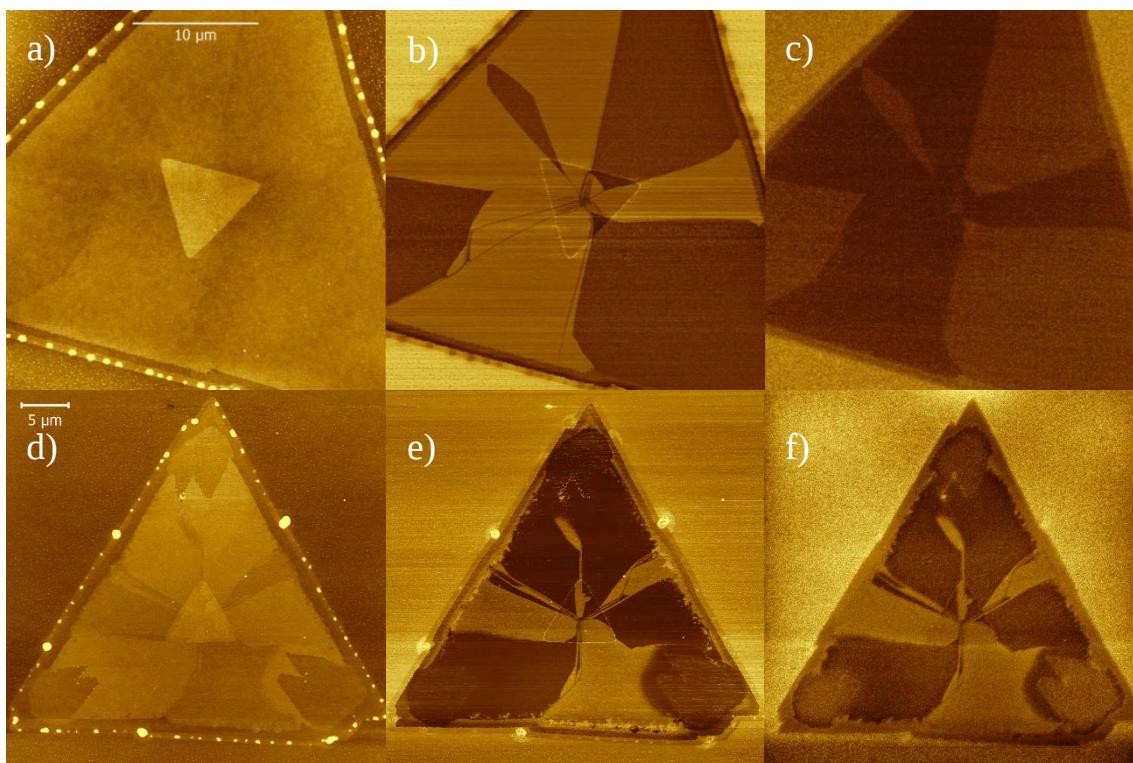
#### 4.4.3 Friction and Electrostatic Force

Refitting the NX-10 with a conductive and stiffer cantilever, the AFM can collect information about the surface charge on an MoS<sub>2</sub> flake. The Park system first scans a line to collect topographic information about the surface and then scans the same line a second time with a bias applied to the tip, while maintaining it at an increased distance above the surface to gather information about the surface charge. This is due to the different relationships of van der Waals and electrostatic forces with respect to distance. Van der Waals forces vary in proportion to  $r^{-6}$ , whereas electrostatic force is proportional

to  $r^{-2}$ . Thus, in close proximity to the surface, the dominant force is van der Waals, while further away the electrostatic force dominates.

After scanning an MoS<sub>2</sub> flake in lateral force mode using the CONTV-A to capture topography and friction (Figure 46a-b,d-e), the tip was changed to an antimony (n) doped Si 3 N/m Bruker SCM-PIT-V2 with conducting platinum-iridium coating. Then a second scan was performed at the same location to gather the electrostatic potential over the same flake. Obvious correlation was found between friction force and electrostatic potential, as seen in Figure 46b,c which shows an inverse correlation between electrostatic potential and friction on the second layer. Strangely, though, this correlation was often reversed from one sample to the next (Figure 46e, f) and occasionally surface

potential was completely uncorrelated with friction behavior.

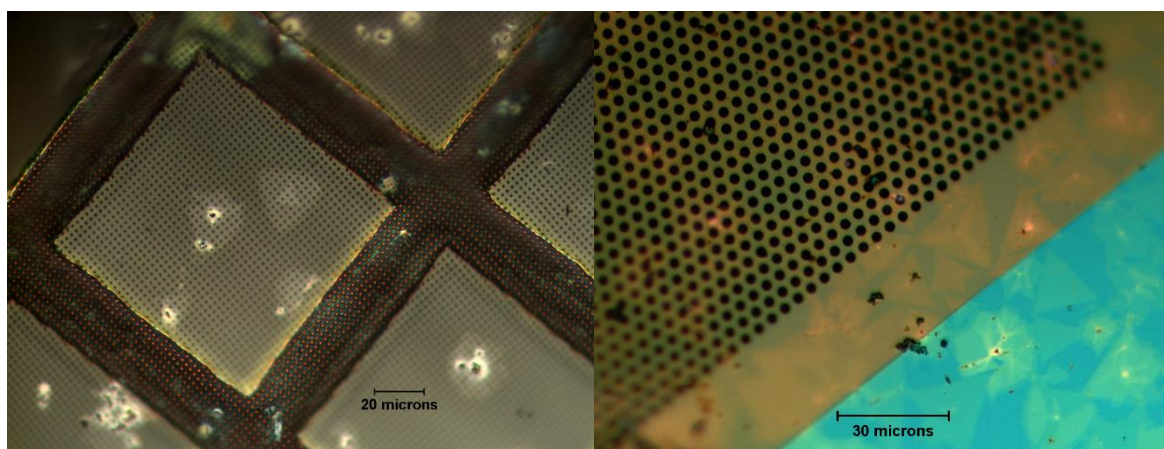


*Figure 46 Electrostatic potential of trilayer MoS<sub>2</sub> flakes. a), d) topography b), e) lateral force (friction) c), f) electrostatic potential. Note inverse correlation between friction and electrostatic potential in b) and c) vs. proportional correlation between e) and f).*

#### 4.4.4 Tribology on a TEM grid

Considering the problem of identifying the layer stacking and how to measure and correlate it with friction behavior, TEM was the obvious technique for conclusive characterization. TEM data would provide evidence as to the real stacking arrangement and help determine if it indeed affects friction behavior. CVD-grown MoS<sub>2</sub> was transferred onto a TEM grid composed of a copper grid with a carbon mesh. Several efforts resulted in some success, and few-layer MoS<sub>2</sub> flakes were identified on the mesh (Figure 47). AFM data was even more difficult to acquire and, worse still, Raman

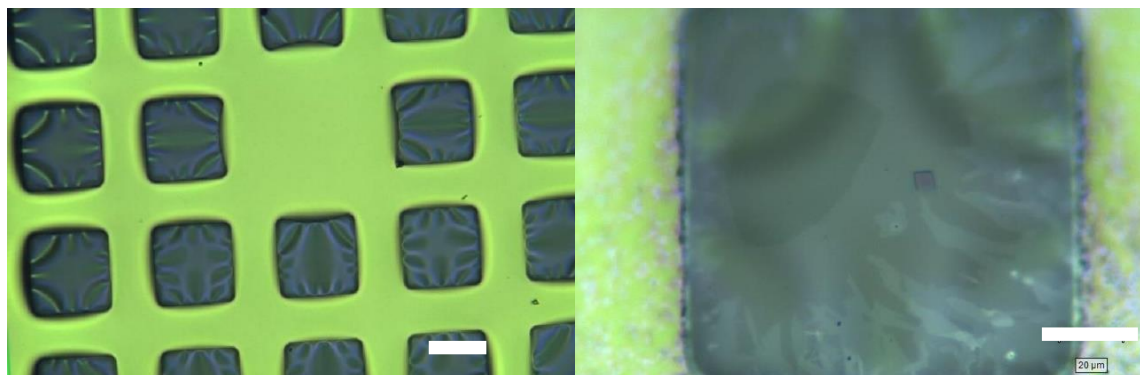
characterization proved catastrophic. Coaxing the AFM into scanning a grid with voids in it without puncturing the MoS<sub>2</sub> film resulted in relatively poor quality data in general, and additionally it seemed that the conductive nature of the mesh and grid quenched friction contrast. When Raman analysis was performed on the samples transferred to TEM grid, the carbon mesh heated to the point of burning away both mesh and sample before appreciable signal was collected using a 15 mW 633nm laser at 10% power and exposed for 1 second.



*Figure 47 MoS<sub>2</sub> flakes wet transferred onto TEM grid. Holey carbon mesh supported by copper grid left and holey silicon nitride grid, right.*

Having found that the carbon/copper TEM grids unsuitable for these experiments, TEM grids with thin SiO<sub>2</sub> membranes were procured. This provided the opportunity to grow CVD MoS<sub>2</sub> directly onto the grid for AFM, TEM, and Raman analysis without the need for transfer. The transfer process used here involved coating the MoS<sub>2</sub> on SiO<sub>2</sub> with the polymer, or acrylic glass, poly(methyl methacrylate) (PMMA), etching the SiO<sub>2</sub> with potassium hydroxide, transferring MoS<sub>2</sub> and PMMA to grid, and dissolving PMMA with acetone. For tribological analysis of 2D materials, this process is not ideal because of residues left from the acid, polymer, and solvent, and because of the morphological changes (wrinkles, strain, folds), and the non-uniform adhesion to the new substrate.

MoS<sub>2</sub> was grown on TEM grids from Ted Pella with continuous 18 nm thick windows. While single- and few-layer regions were found on these grids, the growth occurred from the edges of the windows inward, so that no clear indication of layer twists was found. (see Figure 48)



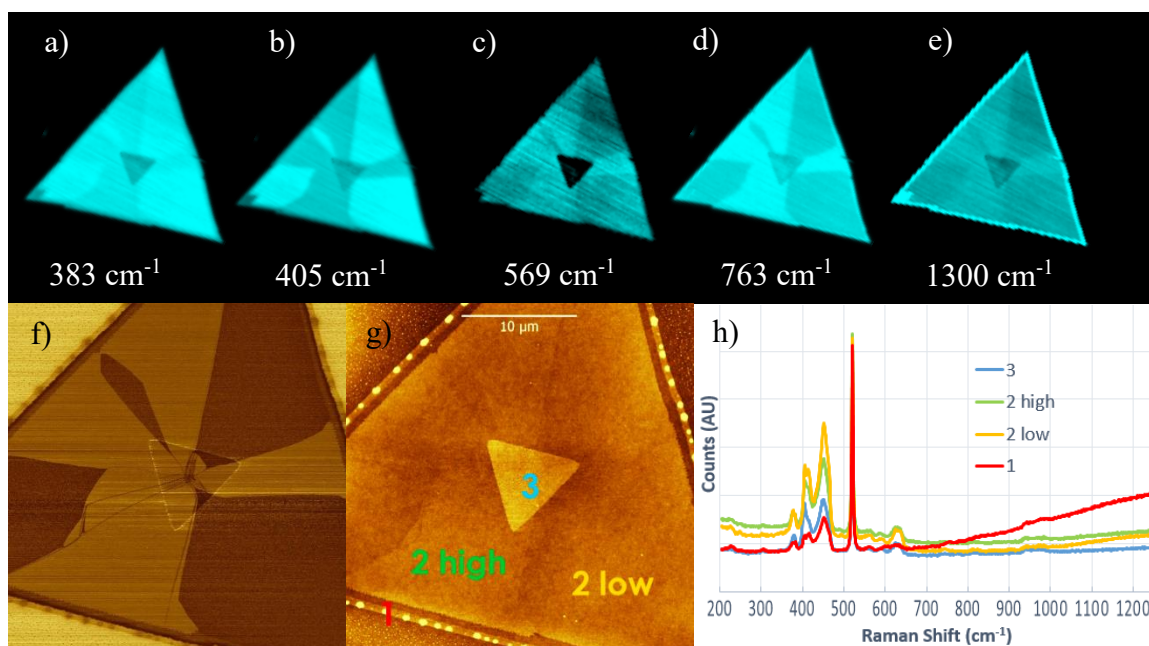
*Figure 48 MoS<sub>2</sub> on continuous SiO<sub>2</sub> window TEM grid. SiO<sub>2</sub> TEM grid prior to deposition (left) and SiO<sub>2</sub> with CVD MoS<sub>2</sub> (right). Scale bars are 50  $\mu$ m (left) and 20  $\mu$ m (right).*

Furthermore, analysis with a field emission TEM/STEM (JEOL 2010F) failed to produce image contrast to corroborate the single- and few-layer MoS<sub>2</sub> evident optically in Figure 48.

#### 4.4.5 Friction: Raman correlation

Raman analysis of few-layer samples that exhibited the two discrete friction behaviors showed marked differences in vibrational behavior at the same boundaries. Mapping of nearly any Raman shift over a few-layer sample showed contrast at the same location where friction abruptly changed. This was not a surprising result in itself, because it is known that friction results from electronic and phonic contributions. What sparked curiosity, though, was that different contrast boundaries on the friction map were evidenced by some Raman shifts but not by others. For instance, the A<sub>1g</sub> peak map

(Figure 49a) shows the opposite contrast behavior on layer two relative to the friction map, but the  $763\text{ cm}^{-1}$  peak intensity map (Figure 49d) showed the same contrast behavior as friction for layer two. Each map of peak intensity shows some correlation to the friction behavior, but any one alone cannot account for the entire friction map. Several Raman shift intensity maps from a 3-layer  $\text{MoS}_2$  sample and corresponding friction map are shown in Figure 49.

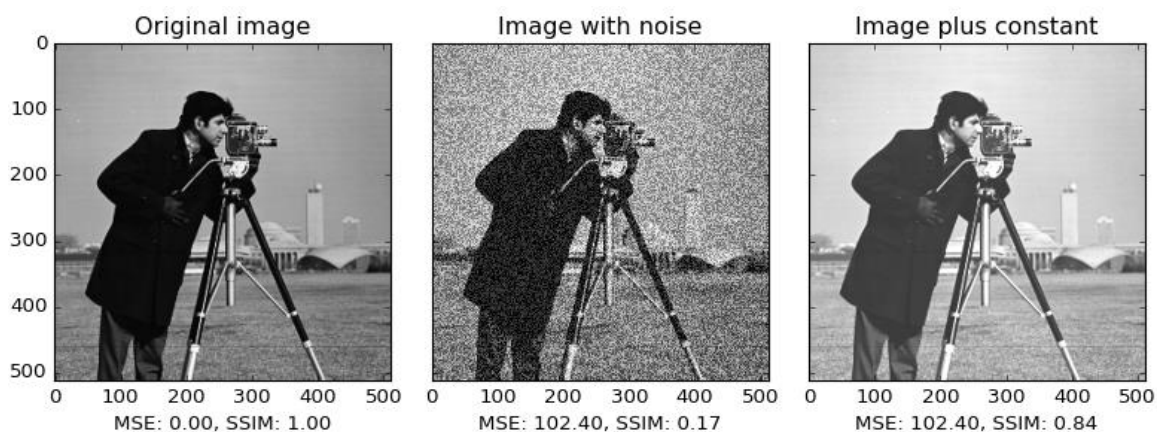


*Figure 49 Raman mapping and friction. Raman maps created from selected peak intensities (a-e), corresponding friction and topography micrographs (f, g), and Raman spectra for select points (h).*

If a major contribution of the friction behavior comes from vibrations in the lattice, probing the vibrational behavior of a crystal could be used (at least in special cases) to determine its frictional response.

A script was created in Python<sup>192</sup> version 3.5 utilizing image analysis libraries and some basic functional structures for optimizing the linear combination of maps that best recreated a friction map. Because the scan size, resolution, and scan directions were

different from the AFM and Raman mapping, affine transformations to one of the maps were necessary in order to correlate the two. Affine transformations are any transformations that can be constructed as a linear map from the original to new coordinates. In this case, translations, scaling, shear mapping, squeeze mapping, and cropping were used to reshape the Raman map to fit the friction map. Next, the Raman maps from 226, 250, 300, 376, 383, 405, 415, 462, 569, 600, 820, 1300  $\text{cm}^{-1}$  were manually selected and input to an algorithm to optimize their linear combinations. Through a series of random assignment of coefficients, each iteration additively combined the Raman maps and compared the result with the friction map. During each iteration, the composite raman map and friction map were compared to determine if the current linear combination improved their match. To make this comparison two criteria were used: structural similarity (SSIM) and mean squared error (MSE). The commonly used method of comparing images is the mean squared error (MSE), but often this does not accurately portray the true similarity between images. Figure 50 Shows the MSE and SSIM values produced when an image of a cameraman is compared to itself, a copy with added noise, and a copy with an added constant (increased exposure compensation).



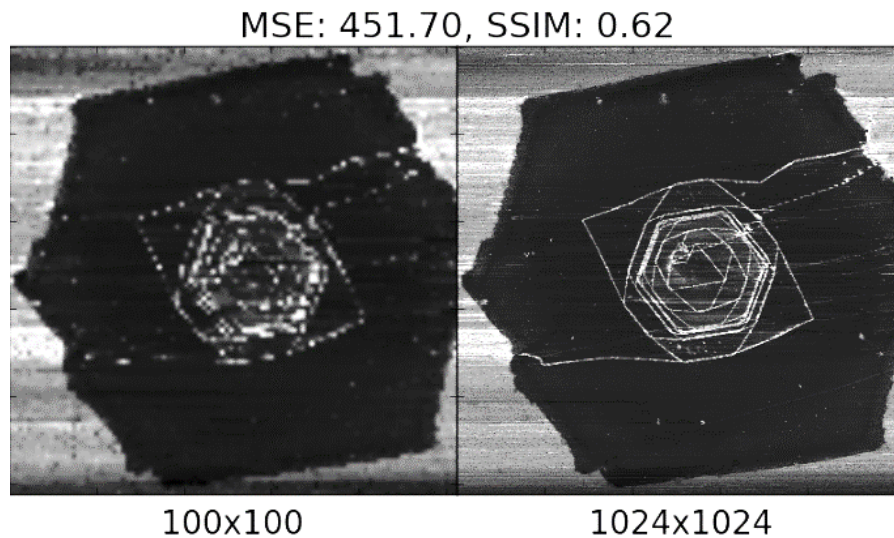
*Figure 50 Mean square error vs structural similarity. MSE and SSIM between an image of a cameraman when compared with original (left), with added noise (center), and with added constant (right). Note high MSE in middle image despite obvious similarity with original.*

It is clear that both MSE and SSIM values should be considered when quantitatively comparing one image to another.

Thus to optimize the linear combination of Raman maps to best recreate friction behavior, the coefficients of the Raman composite were iteratively modified to with the goal of reducing MSE and maximizing SSIM between Raman composite and friction map. This was accomplished by assigning a random set of coefficients to the selected maps and these were passed to a secondary loop where fine adjustments to each coefficient tuned in the linear combination to highest structural similarity and lowest mean square error relative to the friction map. As shown in Figure 50 (left), the lowest value obtainable for MSE is zero and highest SSIM is one for parity. These minimum and maximum values can only result when the compared images are of the same dimensions, with exactly the same intensity for every correlated pixel. Comparing the maps from Raman and AFM data was limited by the disparate resolving powers of each system and therefore the resolution of maps obtained. The Renishaw Invia with a 633 nm laser

produces a spot of approximately  $1\mu\text{m}$  in diameter, so reducing the step size below this length results in smoothing but negligible improvement of resulting map detail.

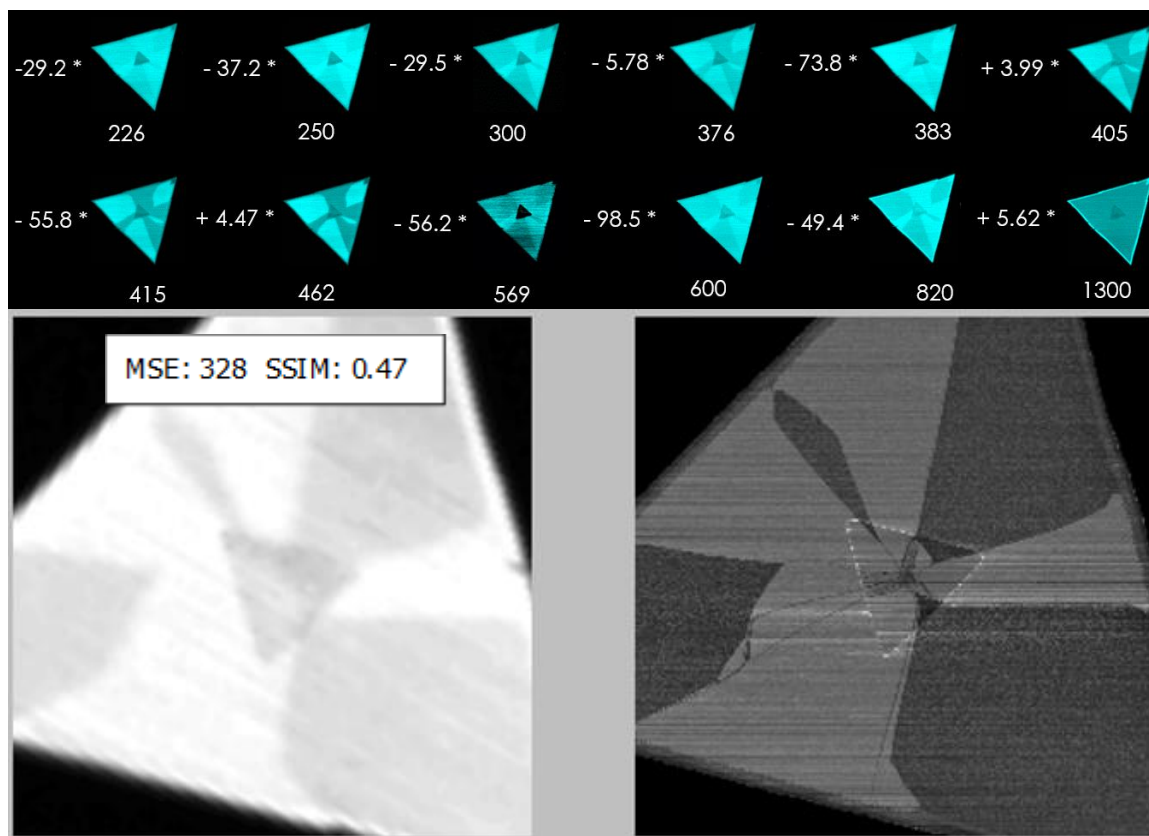
Typically, the step size for Raman measurements was  $0.5\mu\text{m}$  and  $\text{MoS}_2$  flakes were  $10 - 50\mu\text{m}$  laterally. On the other hand, AFM produces much higher resolution and maps were typically produced at  $1024 \times 1024$  pixels. Given the different resolutions between the Raman and AFM, the min MSE and max SSIM for comparison is equal to the values obtained when comparing an image with  $1024^2$  pixels to a compressed  $100^2$ -pixel version of itself. By comparing several  $1024 \times 1024$  images to their compressed  $100 \times 100$  versions, the lower limit for MSE and upper limit for SSIM were found to be around 250 and 0.7 respectively as illustrated in Figure 51.



*Figure 51 MSE and SSIM of  $1024^2$ -pixel vs  $100^2$ -pixel images. Comparison of a  $1024 \times 1024$  FFM friction micrograph to a  $100 \times 100$  compressed version of itself. Mean square error (MSE) and structural similarity (SSIM) values above.*

Through the optimization procedure described above, using a linear combination of intensity maps of 12 Raman shifts, the best coefficients found were -29.2, -37.2, -29.5, -5.78, -73.8, 3.99, -55.8, 4.47, -56.2, -98.5, -49.4, and 5.62 as illustrated in Figure 52

which shows each Raman intensity map at the specified shift with corresponding coefficient for the linear combination. Summing these maps together in this combination produces a composite image with MSE of 328 and SSIM of 0.47 when compared to the AFM generated friction map in Figure 52.

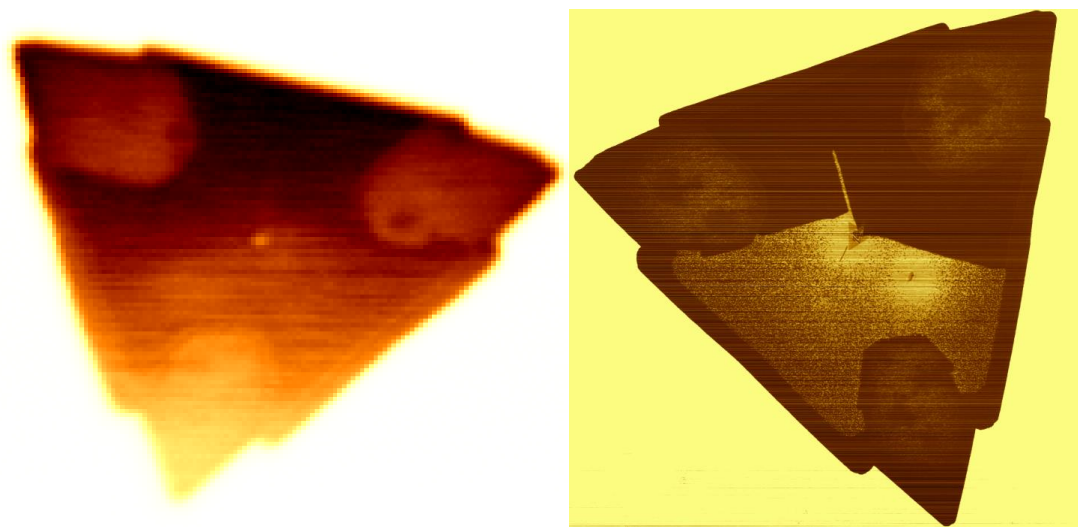


*Figure 52 Raman generated friction map. Top: intensity maps used to optimize linear combination that best recreates friction contrast. Numbers below each map are respective Raman shifts in  $\text{cm}^{-1}$ . Left: resultant map created from superposition of intensity maps. Right: Corresponding friction map acquired by AFM.*

This result demonstrates that friction response on a multilayer  $\text{MoS}_2$  sample can be modeled by analyzing the electromagnetic emission spectra from monochromatic laser irradiation. When considering the resolution-limited MSE and SSIM values generated using this procedure, this recreation of the friction map appears remarkable. What will make these findings outstanding and the procedure potentially useful is its applicability to

unbiased Raman data and predictive accuracy in creating friction behavior maps from Raman analysis.

Using the coefficients optimized for the trilayer flake in Figure 52, their applicability to several other MoS<sub>2</sub> flakes was tested. CVD grown MoS<sub>2</sub> nanosheets were mapped with LFM and Raman microscopy and a Python script was written to parse the 4 channels of the Raman file. The four channels are for lateral location (x, y), Raman shift, and intensity. The parsing script simply created one intensity map file for every Raman shift collected by the microscope. Then the maps with Raman shifts corresponding to the 12 selected waves shown in Figure 52 were weighted by their respective optimized coefficients and summed into one intensity map. Result of weighted Raman composite and corresponding friction map are shown in Figure 53.



*Figure 53 Composite Raman map for predicting friction behavior. Left: linear combination of 12 Raman shift intensities. Right: friction map produced by AFM.*

The Raman composite shows clear indication of similar contrast to the AFM friction map across the multilayer flake. This confirms that the Raman spectra and specifically the 12 wavenumbers analyzed here are indeed correlated with the friction behavior. The script was further modified to optimize the rotation and scaling of the Raman maps to make them coincide with friction data. This allowed for friction and Raman data to be more quickly analyzed. Coefficients for randomized sets of wave numbers from the full 1023-wave spectra were selected and optimized for prediction of friction behavior for seven different multilayer MoS<sub>2</sub> samples. The optimized coefficients were saved in a spreadsheet to be tested against the other six (unbiased) samples. AFM friction maps of select samples are shown in Figure 54 with predicted Raman friction and maps of the difference between the two.



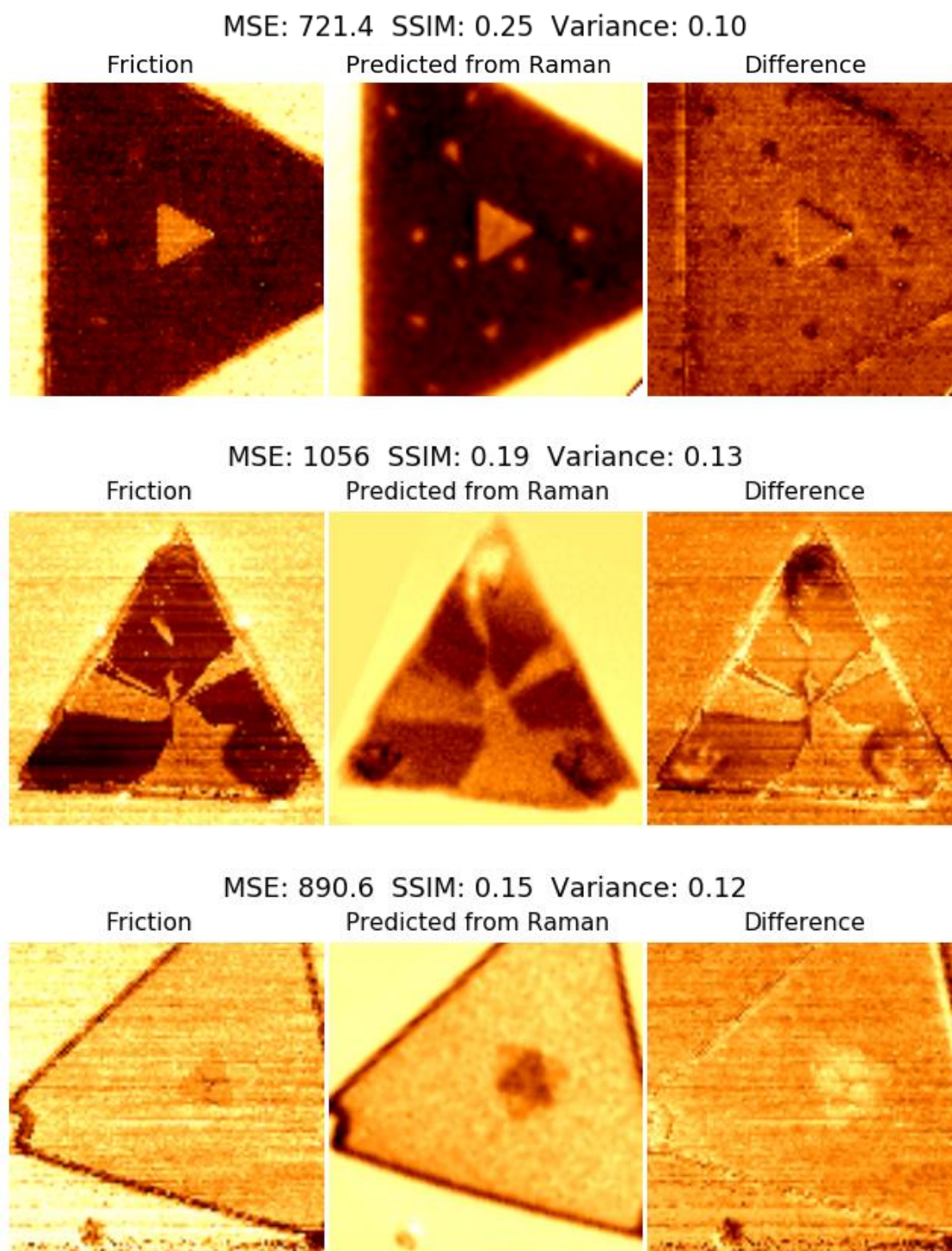


Figure 54 Friction predicted by Raman. AFM friction data (left), predicted friction via Raman (center), and the difference between AFM friction and Raman prediction (right) with calculated mean squared error (MSE), structural similarity (SSIM), and variance above each set. Top: 25x25  $\mu\text{m}$  maps of bilayer flake with no relative rotation. Middle: trilayer sample with no relative rotation between layers. Bottom: quadrilayer sample with 60 degree relative rotation of layer 3.

Many of the wave/coefficient sets show appreciable predictive value across all seven samples, but optimization of wave selection from all 1023 spectral lines rather than a smaller sample was conducted. Unfortunately, the Raman maps produced for each sample did not all possess the same set of wavenumbers because the center position for spectra acquisition was not constant. Thus, creating a set of wavenumbers applicable to all seven samples produced some gaps in the spectra. After rounding each wavenumber to the nearest integer and given that the spacing between consecutive wavenumbers for each spectrum is  $\sim 1.3 \text{ cm}^{-1}$ , the 1023 lines were pared down to a 704 integer wavenumber set between 204 and  $1374 \text{ cm}^{-1}$  present in all 7 Raman maps. Thus the coefficients plotted as black points in Figure 55 show regular gaps on the wavenumber axis. A sample spectrum from a bilayer region of CVD  $\text{MoS}_2$  is shown in the same plot to correlate statistics drawn from the coefficients and the vibrational modes of  $\text{MoS}_2$  grown on  $\text{SiO}_2$ .

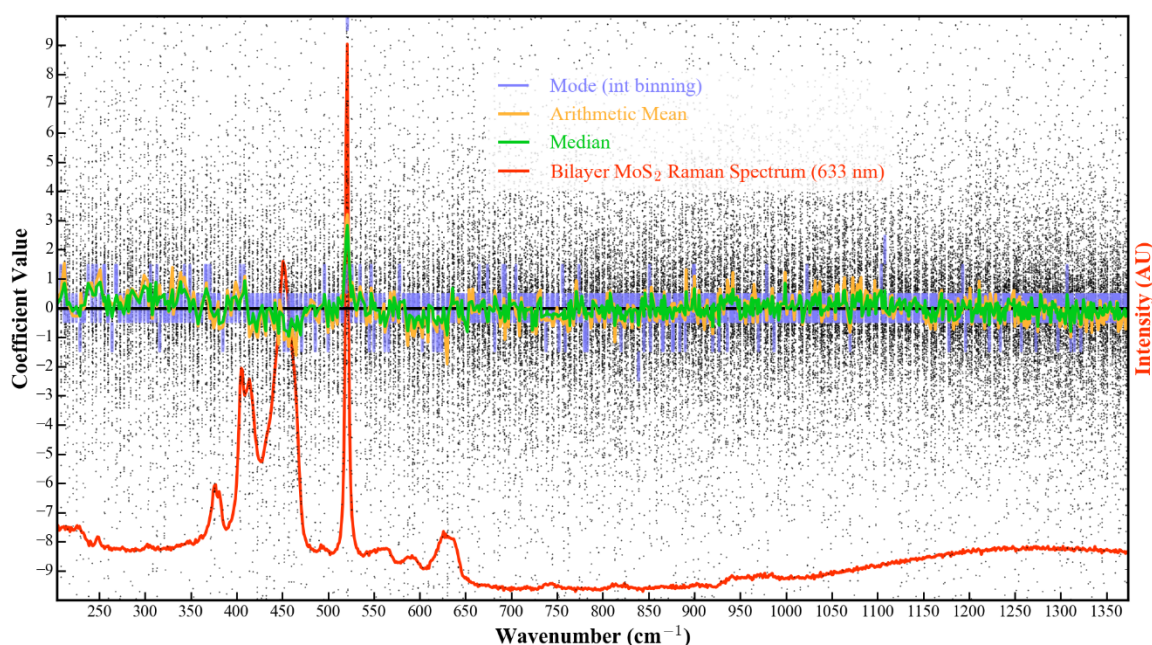


Figure 55 Coefficient values vs wavenumber. Plot of 100 best coefficient sets found for correlation of Raman spectra maps with friction behavior with coefficient mean, median, and integer mode. Clear indication of a negative friction dependence on  $\text{MoS}_2$  signature Raman peaks between  $400$  and  $470 \text{ cm}^{-1}$ .

It can be seen that the best coefficient sets give a high weight to the wavenumbers near  $520\text{ cm}^{-1}$  because this wavenumber corresponds to the silicon Raman mode. It should be noted that the absolute intensity at 520 is actually higher as measured on few-layer  $\text{MoS}_2$  than the bare substrate because the entire spectrum is increased from additional scattering sites contributed by the mostly transparent  $\text{MoS}_2$ . This plot also indicates that statistically, friction is inversely proportional to the Raman intensity between 400 and  $470\text{ cm}^{-1}$  because the large majority of coefficients in this range are negative. But the particular modes most strongly correlated with friction are not obviously apparent. By more closely at the coefficients and Raman spectrum in the range  $350\text{--}550\text{ cm}^{-1}$ , additional dependencies began to emerge. Figure 56 shows this portion of the spectrum with the Raman modes annotated.

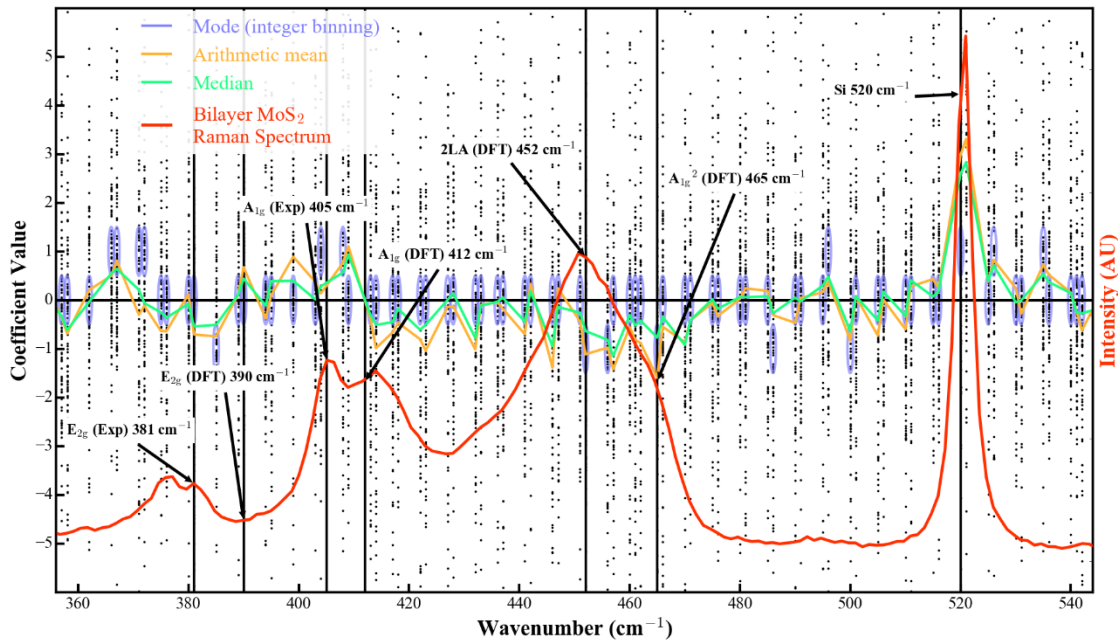


Figure 56 Coefficient values vs wavenumber detail. Black scatter points are coefficient from best performing coefficient sets. Most frequently occurring whole-number coefficients are shown in ellipses. Average and median of coefficients are in orange and green respectively. Red curve is a bilayer Raman spectrum with features annotated.

It can be seen that the peak formed by the 2LA (lateral acoustic) and  $A_{1g}^2$  modes (450-470  $\text{cm}^{-1}$ ) statistically seem to reduce friction as well as blue-shifted  $A_{1g}$  mode. The blue shift of the  $A_{1g}$  mode results from out of plane confinement as a result of substrate proximity as well as proximity to neighboring sulfur atoms from in adjacent  $\text{MoS}_2$  layers. Thus, it appears that more out-of-plane confinement of the  $\text{MoS}_2$  produces a lower friction surface. The distance between sulfur atoms from one layer to the next depends on the orientation between stacked layers. This is the reason that the  $A_{1g}$  peak show obvious splitting for multilayer  $\text{MoS}_2$  samples stacked with 0-degree relative twist (3R configuration). Looking at the red-shifted portion of the split  $A_{1g}$  peak, it is apparent that on average, the friction is enhanced with higher intensity near 405  $\text{cm}^{-1}$ .

The influence of the in-plane  $E_{2g}$  mode is less clear. Strong intensity at the experimentally observed 381  $\text{cm}^{-1}$  shift contributes to lower friction. While a blue-shifted  $E_{2g}$  peak that approaches the DFT calculated 390  $\text{cm}^{-1}$  seems to contribute to higher friction. The experimental  $E_{2g}$  peak is typically in the range of 380 to 385  $\text{cm}^{-1}$ ; lower than DFT likely because vacancies at sulfur sites allow for larger amplitude, lower frequency oscillation of neighboring sulfur atoms. Further red-shifted at 376  $\text{cm}^{-1}$  higher contribution to the Raman spectrum shows as inverse relationship with friction. This indicates that the layer stacking can also have an influence on the lateral motion of sulfur atoms between the  $\text{MoS}_2$  layers. We can expect that because the 2H stacking allows for this closest packing of two layers, the sulfur atoms should be more confined laterally because the sulfur atoms of the opposing  $\text{MoS}_2$  layer do not lie in the same z-axis. Further red-shifted, Raman intensity at 366, 367, and 371  $\text{cm}^{-1}$  strongly enhance friction.

Thus it appears that lowest friction should be observed when there are minimal sulfur vacancies and the stacking is 2H.

The Python scripts used to optimize and test coefficients for creation of predicted friction map from Raman map is provided in Appendix A: *Python Scripts*. Prediction results figures for the other four regions tested can be found in Appendix B.

## 5. Discussion and Conclusions

CVD-grown MoS<sub>2</sub> was characterized with all analysis methods described above: optical microscopy, XPS, SEM, Raman, and AFM. Through this in-depth analysis a better understanding of the kinetics of crystal growth mechanisms and electromechanical properties of CVD MoS<sub>2</sub> was gained. Exploration of the methods and parameters to grow CVD MoS<sub>2</sub> produced not only optimized crystal growth with reasonable control over resulting nanoscale 2D films but also a deeper understanding of how each of the parameters influence growth and its mechanisms. CVD-synthesized samples were transformed from stable 2H MoS<sub>2</sub> into the metastable 1T phase, and both phases were characterized using optical microscopy, Raman microscopy, XPS and AFM in a systematic manner with the focus on nondestructive phase transformation. Tribological study of two phases of MoS<sub>2</sub> as well as a multitude of morphologies, stacking arrangements (polytypes), and layer numbers via LFM corroborated previous literature on nanoscale friction and the present hypothesis explaining the large disparity in nanoscale friction between phases of MoS<sub>2</sub> as well as variations resulting from polytype/layer stacking.

### 5.1 Controllable CVD growth

CVD synthesis of single and multi-layer MoS<sub>2</sub> films were prepared using a wide range of experimental parameters. Repeatability was only weakly established and it was found that changing one or both of the vapor partial pressures of reactants through the duration of experiments was the best way to assure single- and few-layer growth of MoS<sub>2</sub>. In this way the optimal ratio of partial pressures would be achieved (if only briefly) at some

point in the experiment. Because attempts to reduce the range of temperatures during experiments did not uncover more specific relative vaporization temperatures, it can be assumed that even in the absence of controlled temperature ramps, the vaporization rate of reactants were not constant. Particularly for the sulfur reactant, the vaporization rate depends strongly on the exposed surface area of sulfur.

Even if we only consider the published works with silica above  $\text{MoO}_3$ , there is a vast range of parameters: growth/substrate temperatures ranging from 650-1000 °C;  $\text{MoO}_3$  temperatures ranging from 300-1000 °C; and S temperatures ranging from 100-600 °C have been published.<sup>5,29-46</sup> There are several apparent reasons for this large range of experimental parameters producing similar results. As mentioned in *Chemical vapor deposition* on page 31, single-layer growth may occur during temperature ramps rather than during dwell period. If the stoichiometric growth happens during heating or cooling ramps, then the reported growth temperature is not a meaningful parameter. Additionally, most experiments in the literature were conducted in single-zone furnaces, so the reported sulfur temperatures are unreliable on account of the steep temperature gradient at the furnace edge. Considering the temperature immediately inside the furnace edge to be approximately 500 °C and that of the tube in the ambient air only a few centimeters away as cool as 100 or 200 °C, the resulting 100°C/cm gradient produces vastly different temperatures for deviations in reactant position by only millimeters. Descriptions of prior cleaning or oxidation procedure for the CVD tube are seldom provided, so it cannot be assumed that residue from previous experiments was not involved. Surface areas of reactants were not measured/controlled. When dealing with vaporization/sublimation

rates, it is not only the temperature of the material that matters but also the vapor pressure immediately above and the exposed surface area.

In this work, the major inconsistencies mentioned above were marginalized and some control of pertinent variables was gained. It was found that more consistent and uniform growth could be achieved by controlling three different heated zones to accommodate the optimal growth temperature and vaporization temperatures of both reactants.

Additionally, the reactants were isolated in solid and vapor phase until they were transported to the growth zone. By beginning the CVD experiment with a high relative partial pressure of the Mo source (via delayed heating of S source), the Mo-rich  $\text{MoO}_{(3-x)}\text{S}_y$  cores were allowed to form from which the  $\text{MoS}_2$  flake could grow.

## 5.2 Friction vs. Phase

Synthesized of two differentiable phases of  $\text{MoS}_2$  (2H and 1T) in thin nanosheets provided a unique means of exploring nanoscale friction and its dependencies. Composed of the same elements in similar ratios, these two phases of  $\text{MoS}_2$  only differ significantly in their electronic behavior. For weak electric fields, the 2H  $\text{MoS}_2$  behaves as an insulator with localized, discrete orbitals. Under the influence of small electric fields, instantaneous dipoles are formed, but the nanosheet recovers its original, unperturbed electronic configuration once sufficiently weak electronic phenomena pass. In this way, the repulsive force of dipole moments created at the leading edge is reversed as dipoles disperse and electronic configuration returns to its unperturbed state at the trailing edge. The electric field from the local charge density of the sample opposes the incoming local charge density of the AFM tip; this results in a change of the charge density of the sample

which stores kinetic energy lost from the tip as its approach slows. If the change in charge density (dipole moment) remains localized (i.e. does not conduct or transfer to neighboring atoms), the stored energy will be returned to the tip as it passes and the induced dipole moment relaxes. In this scenario, energy is conserved by shifting kinetic energy to electrodynamic potential energy and finally back to kinetic energy. Low sliding friction between dry surfaces of electrically insulating materials is evidenced in compounds such as polytetrafluoroethylene (PTFE) and polycarbonate-polypropylene with macroscale friction coefficients as low as 0.2<sup>51</sup> and 0.08<sup>52</sup>, respectively.

The Fermi electrons of 2H phase MoS<sub>2</sub> are below the conduction band and are thus localized to their orbitals unless excited above the band-gap. This is not the case for 1T MoS<sub>2</sub> which has a Fermi level above the conduction band. Electrons in the metallic 1T phase are delocalized and thus free to move in a reactionary manner to the local electric field of the n-type silicon AFM tip scanning across the MoS<sub>2</sub> surface. The kinetic energy that would be stored as reversible dipole moment in a nonconductive material is instead transferred to local unbound charge that is free to diffuse within the 1T nanosheet.

Electric fields from instantaneous dipole moments, coulombic interactions, and/or excess charge of the scanning tip cause charge density in the 1T MoS<sub>2</sub> to redistribute in an irreversible manner. These interactions allow dissipation of the tip's kinetic energy, which equates to higher friction. Electronic contribution to macroscopic friction is evidenced by the ubiquitous and often catastrophically high friction of unlubricated steel on steel sliding contact, which can be upwards of 0.8. Silver, aluminum, and copper sliding against a counterpart of the same metal have friction coefficients of 1.4, 1.2, and 1, respectively. These values are virtually independent of surface roughness.

A larger number of layers could only decrease tip-sample adhesion and deformation if the attraction between layers is greater than that between sample and substrate. Assuming that is the case, decreasing friction with increasing layers would likely not be monotonic. That work <sup>10</sup> also ruled out substrate effects by testing suspended regions of samples as well as various substrate materials. If increased friction is indeed the result of more puckering or adhesion to the AFM tip, then one might expect the pull-off force of the tip to follow the same trend as friction, but pull-off force was shown to be layer independent in a subsequent paper by the same group on layer dependent friction of graphene.<sup>193</sup> Raman studies have demonstrated a reduced band-gap and modified resonance Raman peaks in AB-stacked (2H, mechanically exfoliated) vs AA'-stacked (3R) CVD MoS<sub>2</sub> due to variations in interlayer coupling.<sup>122</sup> If CVD-grown MoS<sub>2</sub> layers are sufficiently decoupled relative to mechanically exfoliated layers, a frictional dependence on layers could be found in the latter while not in the former.

The effect of phase change from 1H to 1T MoS<sub>2</sub> on friction was drastically evident as high friction for the metastable 1T conducting phase and low for the stable, semi-conducting 1H phase relative to the silicon dioxide substrate. This disparity in behavior between two phases of the same chemical composition emerges due to the divergent electronic properties upon transformation. With a band-gap of approximately 1.8eV, 2H MoS<sub>2</sub> acts as an insulator for sufficiently weak electromagnetic phenomena. Since the electrons participating in coulombic repulsion with the counterpart (AFM tip in this case) are bound to their valence bands, the kinetic energy they receive during approach remains localized and is returned to the counterpart during departure. Conversely, the electrons and their electric fields of the conducting 1T phase MoS<sub>2</sub> are free to capture kinetic

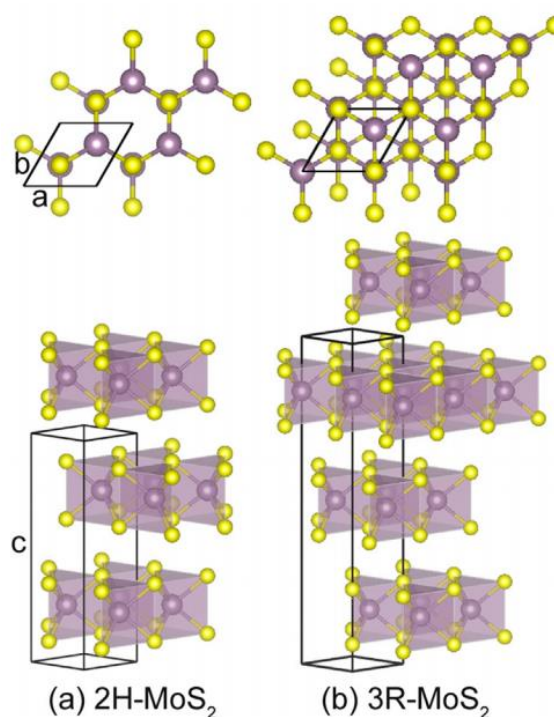
energy from the counterpart and flee like billiard balls following a break. Though the chemical composition of 1T and 2H MoS<sub>2</sub> is the same, difference in electronic structure produces vastly different tribological behavior.

### 5.3 Friction vs Polytype

Examining tribological differences between semiconducting MoS<sub>2</sub> phases shed some light on the phononic contribution to friction generation. Building multilayered MoS<sub>2</sub> from the same single-layer polymorph as 2H MoS<sub>2</sub> produces various polytypes notably 3R. These polytypes are differentiated by a shift or rotation between layers. In regard to tribological behavior, the electronic contribution is fixed with the semi-conducting polymorph, but the phononics vary with polytype. It was observed that two contrasting friction values may occur on bilayer CVD MoS<sub>2</sub>. Depending on how the second layer is translated or rotated relative to the first, the interaction between the two layers varies significantly as evidenced by the Raman spectra shown in Chapter 4.

There are two low-energy energy arrangements for multiple layers of MoS<sub>2</sub>: 2H and 3R. The 2H and 3R portions of Figure 6 are reproduced below in Figure 57 for this discussion. Projected from the z axis, the yellow points represent sulfur atoms and the purple points represent molybdenum atoms. A second layer of MoS<sub>2</sub> will either shift by 3.2Å (-3.2Å) along a direction of translational symmetry so that the sulfur (Mo) atoms of the second layer fall into the hexagons of the first layer as viewed from above or the second layer crystal will be rotated by 60 degrees so that Mo(S) atoms of the second layer

lie on the same z axis as S(Mo) from the first layer when viewed from above.



*Figure 57 Stacking of MoS<sub>2</sub> layers. Bilayer MoS<sub>2</sub> can occur with either a rotation (a) or translation (b) of the second layer.*

This is the lower energy (2H) stacking because the intralayer spacing is minimized while distance between intralayer sulfur atoms is maximized. Thus the long time-scale that produced naturally occurring MoS<sub>2</sub> (the source for mechanically exfoliated flakes) results predominantly in this more stable stacking arrangement and is referred to as AB stacking. Layer twists of 0 degrees comprises the 3R phase of MoS<sub>2</sub> which is also found naturally but less frequently owing to its decreased stability. Considering only two layers of 3R MoS<sub>2</sub> with there are two possible lateral shifts of the second layer relative to the first:  $\pm 3.2\text{\AA}$  along any of the three directions of translational symmetry. Thus the drastic contrast in friction sometimes observed on the second layer of untwisted bilayer samples could arise from strain upon merging of the two energy-equivalent stackings.

## 5.4 Predicting Friction Behavior Remotely

Friction behavior was correlated with Raman spectroscopy results, and through algorithmic optimization of Raman data, a means for predicting friction behavior via monochromatic visible excitation was found. Python scripting language was used to test randomized adjustments to an initial set of coefficients for a linear combination of Raman shift intensities. Each coefficient represents the relative Raman shift dependence of the friction force observed by a silicon tip sliding on the sample surface. Since many of the Raman intensities likewise depend on an associated vibrational mode, these coefficients indicate the relative strengths of associated modes in observed friction response.

Never before has a method been described to predict friction behavior remotely. In order to examine the friction forces encountered on a material surface, physical contact and relative motion with a counter surface were necessarily employed. With even the most sensitive equipment, some amount of chemical and/or physical changes would unavoidably result from friction testing. In addition to its potential utility in predicting dissipative surface forces in specialized systems, the coefficient optimization method used here can give useful insight into interlayer coupling of 2D materials and phonon dispersion for general materials.

## 6. Future Work

If MoS<sub>2</sub> continues forward towards replacement of silicon as the transistor material for improved performance in CMOS devices, significant advances in synthesis methods must be realized. While the mechanical exfoliation, chemical exfoliation, and CVD have been shown to produce MoS<sub>2</sub> satisfactory for research purposes, none can achieve the uniformity and scale necessary for technology applications. A similar method that allows for more precise control over the growth conditions is metal-organic chemical vapor deposition (MOCVD) which enables more precise control and in-situ monitoring of vapor phase reactant flow, pressure, and deposition thickness using gaseous precursors such as Mo(CO)<sub>6</sub>, MoCl<sub>5</sub>, H<sub>2</sub>S, and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S. But the complexity of MOCVD, its high cost, and use of toxic gases reduces its appeal. Molecular beam epitaxy (MBE) allows for finer control of deposition by utilizing solid reactant sources but necessitates ultra-high vacuum. Both MBE and MOCVD have recently been used to produce thin films of MoS<sub>2</sub>, but the issue of small grain size and performance inhibiting grain boundaries has not been addressed. Thus regardless of the methods used, means of growing large-scale, single-crystal, monolayer MoS<sub>2</sub> have yet to be developed. Approaches to this problem may include epitaxial growth on a suitable substrate, reduce nucleation to a singular site, or coherent alignment of grain growth with applied electromagnetic.

Regarding the exploration of MoS<sub>2</sub> as a media for tribological discovery, several experimental opportunities are apparent for the near term. Given the seemingly unavoidable distortions and morphological changes induced to a thin film of MoS<sub>2</sub> upon transformation to the 1T phase via butyllithium, the striking contrast between friction behaviors of the two phase were not found to be compelling enough for publication

considering the potential influence of surface roughness and topography. While distortion of MoS<sub>2</sub> nanosheets may invariably result from the transformation, it ought to be possible to instead make tribological comparisons of the 1T phase and 1H phase produced from relaxation of the already distorted 1T sample. This can simply be achieved by annealing the 1T sample in an inert gas environment at 300 °C for one hour. Perhaps even more enticing is the prospect of performing these tribological measurements while the relaxation occurs. This in-situ experiment and many others will be possible at Rutgers MSE by end of Summer 2017 upon installation of the new Park Systems NX-Hivac with environmental control and heating stage. Additionally, the recently acquired 3-zone, programmable furnace will enable finer control of future CVD experiments to explore the polytypes of MoS<sub>2</sub> which can be conclusively characterized with further efforts to grow films directly on TEM grids.

With TEM evidence used in conjunction with AFM, optical imaging, and Raman spectroscopy, the method of predicting friction behavior based on layer-stacking and resulting phonon modes can be advanced. Truly utilizing the predictive power of electromagnetic excitation to determine the close range interactions of two bodies will require modeling systems beyond the 2D regimes explored in this work. At the time of writing, there have been no published studies linking the tribological and Raman behavior of 2D materials. Raman microscopy has been used in conjunction with tribological studies only for its ability to characterize material composition. This presents a unique opportunity to advance the field of tribology by elucidating its dependencies on various phononic surface characteristics. With further insight into the mechanisms that

influence friction, intelligently designed materials will enable the next generation of miniature electronics.

## Appendix A: Python Scripts

```
# Python scripts for reading Raman map data saved as .txt document & optimizing shift  
intensity components for linear combination to predict friction behavior  
  
# Sol Torrel  
  
# 6/28/17  
  
from scipy import stats  
import matplotlib  
matplotlib.use('Agg')  
import matplotlib.pyplot as plt  
from mpl_toolkits.axes_grid1.inset_locator import inset_axes  
from mpl_toolkits.axes_grid1.inset_locator import mark_inset  
from skimage.measure import compare_ssim as ssim  
import pandas as pd  
import random  
import math  
import numpy as np  
from scipy import stats  
from statistics import stdev  
from openpyxl import load_workbook  
import winsound  
import cv2  
import csv  
import os  
import shutil
```

```

import psutil

import glob

import re

from time import sleep

from datetime import datetime

from skimage.measure import compare_ssim as ssim


def set_cpu_affinity():

    utilizations = psutil.cpu_percent(interval=1, percpu=True)

    min_utilized = min(utilizations)

    min_utilized_index=utilizations.index(min(utilizations))

    print(utilizations,min_utilized_index,min_utilized)

    psutil.Process().cpu_affinity([min_utilized_index])


def decimal(places,number):

    # return string from number with 1 decimal places

    return format(number,'.'+str(places)+'f')


def sig_figs(figs,number):

    # return string from number with 6 sig digits

    return format(number, '.'+str(figs)+'g')


def average(li): # return arithmetic mean of list

    return sum(li)/len(li)


def load_xlsx(file):

```

```

# load .xlsx spreadsheet for reading and writing

print("Loading workbook:",file)

global prev_wb,prev_ws

attempts=0

while attempts<10:

    try:

        wb=load_workbook(filename=file)

        ws=wb.active

        prev_wb,prev_ws=wb,ws

        return wb,ws

    except:

        attempts+=1

        winsound.Beep(2000,200)

        seconds=random.uniform(1,100)

        print('Error loading workbook; '

              'trying again in',decimal(2,seconds),'seconds')

        sleep(seconds)

        #print(traceback.format_exc())

def get_row(ws,col,value):

    for row in range(2,ws.max_row+1):

        if str(ws.cell(row=row,column=col).value)==str(value):

            return row

    return 0

def get_col(ws,row,value):

```

```

for col in range(1,ws.max_column):
    if str(value)==str(ws.cell(row=row,column=col).value):
        return col

return 0

def get_value(ws,row,col):
    return ws.cell(row=row,column=col).value

def mse(img_1,img_2):
    # compare two images of same dimensions and return
    # mean square error (MSE) between them
    # MSE is the average of the squared difference each pixel
    err=np.sum((img_1.astype("float")-img_2.astype("float"))**2)
    err/=float(img_1.shape[0] * img_1.shape[1])
    return err

def compare_images(img_1,img_2):
    # compute and return mean squared error
    # and structural similarity index between two images
    m=mse(img_1,img_2)
    s=ssim(img_1,img_2)
    return m,s

def scale_rotate_translate(img,scale,deg_ccw=0,dx=1.,dy=1.):
    # return scaled, rotated, and translated image
    # note: numpy uses (y,x) convention; OpenCV functions use (x,y)

```

```

(old_y,old_x)=img.shape[:2]

center=(old_x/2,old_y/2)

# rotate about center of image

M=cv2.getRotationMatrix2D(center=center,angle=deg_ccw,scale=scale)

new_x,new_y=old_x*scale,old_y*scale # new image size.

r=np.deg2rad(deg_ccw)

new_x,new_y=(abs(np.sin(r)*new_y)+abs(np.cos(r)*new_x),
             abs(np.sin(r)*new_x)+abs(np.cos(r)*new_y))

# the warpAffine function call applies the M transformation
# on each pixel of the original image and saves everything
# that falls within the upper-left "dsize" portion of the
# resulting image. So we must find the translation that moves
# the result to the center of that region.

(tx,ty)=((new_x-old_x)/2,(new_y-old_y)/2)

# third column of matrix holds translation
# which takes effect after rotation.

M[0,2]+=tx*dx

M[1,2]+=ty*dy

return cv2.warpAffine(img,M,dsize=(int(new_x),int(new_y)))

def map_per_wave(path,map_file_name):

    # write map file for each Raman shift from Wire .txt export

    start_time=datetime.now()

    print('Reading map.')

    maps=pd.read_csv(path+map_file_name, delim_whitespace=True)

    print(datetime.now()-start_time, 'to read into pandas')

```

```

maps.columns=['x','y','Wave','Intensity']

x_range=maps['x'].iloc[-1] - maps['x'].iloc[0]
y_range=maps['y'].iloc[-1] - maps['y'].iloc[0]

dimensions=decimal(1,x_range)+'x'+decimal(1,y_range)

print('Finding minimum intensity...')

min_intensity=maps['Intensity'].min()

print('Minimum intensity=',min_intensity,

      'Computing harmonic mean of max 3 values...')

hmean=stats.hmean(maps['Intensity'].nlargest(3).values)

print('Max for normalization:',hmean)

normalization=(hmean-min_intensity)/1000

print('Creating individual files for each shift. '

      'Normalization constant:',normalization)

new_path=path+'/map_per_wave '+dimensions+'/'

if not os.path.exists(new_path):os.makedirs(new_path)

waves_present=maps.Wave.unique()

print(len(waves_present),waves_present)

for wave in waves_present:

    new_map=open(new_path+decimal(2,wave)+

                  '.csv', 'a',newline=")

    writer=csv.writer(new_map)

    subset=maps.loc[maps['Wave']==wave]

    y_values=subset.y.unique()

    #print(len(y_values),y_values)

    for y in y_values:

        row=subset.loc[subset['y']==y]['Intensity'].tolist()

```

```

        #print(len(row),row)

        writer.writerow([min(999,int((float(i)-min_intensity)/
                                normalization)) for i in row])

    print('Created',len(waves_present),'maps in',datetime.now()-start_time)

def create_results_file():
    # create file for storing coefficients to be tested against unbiased data

    wb,ws=load_xlsx(file_name)

    waves=[]

    for sample in samples:

        raman_maps_path=path+sample+'/map_per_wave '+\
            raman_resolutions[samples.index(sample)]+'/'

        for map_file in os.listdir(raman_maps_path):

            wave=round(float(map_file[:-4]))

            waves.append(wave)

    waves=sorted(list(set(waves)))

    print(waves)

    header=['avg']+samples

    ws.cell(row=1,column=1).value='timestamp'

    for col in range(len(header)):

        ws.cell(row=1,column=col*2+2).value='MSE '+header[col]

        ws.cell(row=1,column=col*2+3).value='SSIM '+header[col]

    for c in range(len(waves)):

        ws.cell(row=1,column=c+4+2*col).value=waves[c]

        print(waves[c])

    wb.save(file_name)

```

```

def compare_100_1024():
    # used to estimate upper limits of MSE and SSIM
    # considering different resolution of Raman vs AFM

    large_img=cv2.imread('DSC_6028.jpg')
    large_img_bw=cv2.cvtColor(large_img, cv2.COLOR_BGR2GRAY)

    small_img=cv2.imread('DSC_6028-2.jpg')
    small_img_rotated=scale_rotate_translate(small_img,10.24,0)
    small_img_bw=cv2.cvtColor(small_img_rotated, cv2.COLOR_BGR2GRAY)

    print(compare_images(small_img_bw,large_img_bw,"100x100 vs. 1024x1024"))

def crop(img,x_size=100,y_size=100):
    # crop image after transformation to 100x100

    y,x = img.shape
    startx = x//2-(x_size//2)
    starty = y//2-(y_size//2)
    raman=img[starty:starty+y_size,startx:startx+x_size]

    y,x=raman.shape

    y-=1
    x-=1

    corner1_avg=average([raman[i][j] for i in range(3) for j in range(3)])
    corner2_avg=average([raman[x-i][j] for i in range(3) for j in range(3)])
    corner3_avg=average([raman[i][y-j] for i in range(3) for j in range(3)])
    corner4_avg=average([raman[x-i][y-j] for i in range(3) for j in range(3)])

    raman[raman==0]=max(corner1_avg,corner2_avg,corner3_avg,corner4_avg)

    return raman

```

```

def normalize(img):
    # normalize image intensities to standard 8-bit 0-255 values

    return (img-img.min())*255/(img.max()-img.min())

def three_point_level(P1,P2,P3):
    # Level the plot to a plane through the following three points

    (p1x,p1y)=P1
    (p2x,p2y)=P2
    (p3x,p3y)=P3

    print(Z[p1y][p1x],Z[p2y][p2x],Z[p3y][p3x])

    p1 = np.array([p1x,p1y,average([Z[k][i] for i in range(p1x-3,p1x+3)for k in range(p1y-
3,p1y+3)])])

    p2 = np.array([p2x,p2y,average([Z[k][i] for i in range(p2x-3,p2x+3)for k in range(p2y-
3,p2y+3)])])

    p3 = np.array([p3x,p3y,average([Z[k][i] for i in range(p3x-3,p3x+3)for k in range(p3y-
3,p3y+3)])])

    print(p1,p2,p3)

    # These two vectors are in the plane

    v1 = p3 - p1
    v2 = p2 - p1

    # the cross product is a vector normal to the plane

    cp = np.cross(v1, v2)

    a, b, c = cp

    # This evaluates a*x3 + b*y3 + c*z3 which equals d

    d = np.dot(cp, p3)

```

```

print('The equation is {0}x + {1}y + {2}z = {3}'.format(a, b, c, d))

Z2 = (d - a * X - b * Y) / c

Z-=Z2

Z-=np.amin(Z)

print(datetime.now()-start_time)

plt.scatter([p1x,p2x,p3x],[p1y,p2y,p3y],s=100,c='blue',marker=(5,0))

def load_maps(path): # loads intensity maps for waves in waves_to_use list

    global waves_to_use,coefficients

    wave_maps=[None]*len(waves_to_use)

    for map_file in os.listdir(path):

        # iterate through maps and select those closest to waves

        wave_file=round(float(map_file[:-4]))

        #print(wave_file,wave_file in waves_to_use)

        if wave_file in waves_to_use:

            wave_maps[waves_to_use.index(wave_file)]=(np.genfromtxt(path+map_file,delimiter=',')

            )

    # for s,ind in enumerate([i for i,x in enumerate(wave_maps) if x==None]):

    #     #print(waves_to_use[index-s],'not mapped')

    #     del coefficients[ind-s]

    #     del waves_to_use[ind-s]

    #     del wave_maps[ind-s]

    if not len(coefficients)==len(waves_to_use)==len(wave_maps):

        print(len(coefficients),len(waves_to_use),len(wave_maps))

    print(len(waves_to_use),waves_to_use)

```

```

# print(len(coefficients), [decimal(2,c) for c in coefficients])

return wave_maps

def save_coefficients(sample,mse,ssim,timestamp):
    # save optimized coefficients to spreadsheet
    wb,ws=load_xlsx(file_name)
    row=ws.max_row+1
    print('Writing coefficients to row',row,timestamp,sample,mse,ssim)
    for c in range(1,ws.max_column+1):
        header=ws.cell(row=1,column=c).value
        if c==1:ws.cell(row=row,column=c).value=timestamp
        elif header=='MSE '+sample:ws.cell(row=row,column=c).value=mse
        elif header=='SSIM '+sample:ws.cell(row=row,column=c).value=ssim
        elif any(header==w for w in waves_to_use):
            ws.cell(row=row,column=c).value=sig_figs(6,coefficients[waves_to_use.index(header)])
    wb.save(file_name)

def load_coefficients(sample):
    # Find starting coefficients within one standard deviation
    # of those saved in spreadsheet
    global waves_to_use,coefficients,var_devs
    # waves_to_use=[]
    # waves_to_use=[x for x in range(300,600)]+[random.randint(154,350) for _ in
    range(20)]+[random.randint(550,1400) for _ in range(50)]
    # waves_to_use=sorted(list(set(waves_to_use)))

```

```

wb,ws=load_xlsx(file_name)

num_rows=ws.max_row

num_cols=ws.max_column

waves_to_use=[get_value(ws,1,c) for c in
range(get_col(ws,1,204),ws.max_column+1)]

coefficients=[None]*len(waves_to_use)

var_devs=[None]*len(waves_to_use)

parent_rows=random.sample([r for r in range(2,102)],random.randint(2,50))

for col in range(1,num_cols+1):

    coefficient_list=[]

    if ws.cell(row=1,column=col).value in waves_to_use:

        wave_number=get_value(ws,1,col)

        for row in parent_rows:

            if ws.cell(row=row,column=col).value:

                coefficient_list.append(float(ws.cell(row=row,column=col).value))

        if len(coefficient_list)>1:

            avg=average(coefficient_list)

            dev=stdev(coefficient_list)*random.uniform(.1,2)

            var_devs[waves_to_use.index(wave_number)]=dev

            coefficients[waves_to_use.index(wave_number)]=max(-
10,min(10,random.uniform(max(-1,avg-dev),min(1,avg+dev))))

        else:coefficients[waves_to_use.index(wave_number)]=(random.uniform(-1,1))

    for s,ind in enumerate([i for i,x in enumerate(coefficients) if x==None]):

        #print(waves_to_use[index-s], 'not mapped')

        del coefficients[ind-s]

        del waves_to_use[ind-s]

```

```

del var_devs[ind-s]

global avg_sample_mse,avg_sample_ssim

avg_sample_mse=average([float(x) for x in [get_value(ws,row,get_col(ws,1,'MSE
'+sample))for row in range(2,ws.max_row+1)] if x])

avg_sample_ssim=average([float(x) for x in[get_value(ws,row,get_col(ws,1,'SSIM
'+sample))for row in range(2,ws.max_row+1)] if x])

print(len(waves_to_use),waves_to_use)

print(len(coefficients),[decimal(2,c) for c in coefficients])

cmaps = [('Sequential',    ['Blues', 'BuGn', 'BuPu',
                             'GnBu', 'Greens', 'Greys', 'Oranges', 'OrRd',
                             'PuBu', 'PuBuGn', 'PuRd', 'Purples', 'RdPu',
                             'Reds', 'YlGn', 'YlGnBu', 'YlOrBr', 'YlOrRd']),
          ('Sequential (2)', ['afmhot', 'autumn', 'bone', 'cool', 'copper',
                              'gist_heat', 'gray', 'hot', 'pink',
                              'spring', 'summer', 'winter']),
          ('Diverging',    ['BrBG', 'bwr', 'coolwarm', 'PiYG', 'PRGn', 'PuOr',
                              'RdBu', 'RdGy', 'RdYlBu', 'RdYlGn', 'Spectral',
                              'seismic']),
          ('Qualitative',  ['Accent', 'Dark2', 'Paired', 'Pastel1',
                              'Pastel2', 'Set1', 'Set2', 'Set3']),
          ('Miscellaneous', ['gist_earth', 'terrain', 'ocean', 'gist_stern',
                              'brg', 'CMRmap', 'cubehelix',
                              'gnuplot', 'gnuplot2',
                              'nipy_spectral', 'jet', 'rainbow',
                              'gist_rainbow', 'hsv', 'flag', 'prism'])]

```

```

map_size=[2.3,2.3]

def plot_coefficients():

    global waves_to_use,coefficients,fig,ax,ax1

    waves_to_use,coefficients_list=[],[]

    df = pd.read_excel(file_name, encoding = 'utf8').iloc[:101,:])

    #write to excel

    #df.to_excel('MyOutputFile.xlsx')

    headers=list(df)

    waves_to_use=headers[headers.index(204):]

    print(waves_to_use)

    #df_sorted=df.assign(f =
abs(df[375])+abs(df[376])+abs(df[381])+abs(df[380])+abs(df[389])+abs(df[390])+abs(df[4
03])+abs(df[404])+abs(df[408])+abs(df[409])+abs(df[413])+abs(df[414])).sort_values('f',
ascending=False).drop('f', axis=1)

    df_sorted=df.sort_values(['MSE 3L060MD','MSE 3L00MD'],ascending=True)

    df_sorted=df.assign(f = df['MSE 3L060MD']*2+df['MSE 3L00MD']).sort_values('f',
ascending=True).drop('f', axis=1)

    print(df_sorted['MSE 3L060MD'],df_sorted['MSE 3L00MD'])

    #df.assign(f =
abs(df.iloc[:101,headers.index(352):headers.index(470)]).sort_values('f',ascending=False)
e).drop('f', axis=1)

    #df_sorted=df.assign(f = df[381] - df[390]).sort_values('f').drop('f', axis=1)

    #df_sorted=df.sort_values('MSE avg')

    df_coeffs=df.iloc[:101,headers.index(204):]

    #print(headers)

```

```

#print(df_sorted[headers.index(362):headers.index(490)].describe())

for column in df_coefs:

    coefficients_list.append(df_sorted[column][:80].tolist())

max_vals=df_sorted.iloc[:80,headers.index(204):].apply(max, axis=1).tolist()

print(len(max_vals),len(coefficients_list[0]),max_vals)

coefficients_list=[[coefficients_list[c][r]*10/max_vals[r]for r in
range(len(coefficients_list[0]))] for c in range(len(coefficients_list))]

binned_coefs=[]

binning=1

for c in coefficients_list:

    binned_coefs.append([round(s+.0) if 1>s>0 else (round(s-.0) if 0>s>-1 else
round(s)) for s in list(c)])

average_coefficients=[average(c) for c in coefficients_list]

modes=[mode(s)[0] for s in binned_coefs]

medians=[statistics.median(c) for c in coefficients_list]

fig,ax=plt.subplots(figsize=(19.2,10.8),dpi=100,facecolor='black',edgecolor='none')

for i,Y in enumerate(coefficients_list):

    ax.scatter([waves_to_use[i]*len(Y),Y,s=.4,color='white',marker='.')

ax.set_ylim(-10,10)

ax.set_axis_bgcolor('black')

plt.plot(waves_to_use,average_coefficients, color=(1,.7,.2,1),
lw=1.5,label="Arithmetic Mean")

plt.plot(waves_to_use,medians, color=(.1,1,.5,1), lw=1.5, label='Median')

plt.plot(waves_to_use,modes, color=(.5,.5,1,1), lw=1.5, label='Mode (integer
binning)')

plt.axhline(0, color='white',lw=1)

```

```

plt.yticks(np.arange(-9,10,1),fontsize=16,color='white')

plt.xticks(np.arange(250, 1400, 50),fontsize=16,color='white')

ax.tick_params(axis='x', direction='in', width=1, length=10,color='w', labels=16,
pad=5)

ax.tick_params(axis='y', direction='in', width=1, length=10,color='w', labels=16,
pad=4)

for spine in ax.spines.values():
    spine.set_edgecolor('white')
    spine.set_linewidth(2)

ax.get_xaxis().tick_bottom()
ax.get_yaxis().tick_left()

#ax.tick_params(direction='in', length=10, width=1, colors='w')

legend=plt.legend(fontsize=18,loc=(.02,.87))

frame = legend.get_frame()

frame.set_facecolor((.3,.3,.3,.4))

frame.set_linewidth(0)

for line,text in zip(legend.get_lines(), legend.get_texts()):
    text.set_color(line.get_color())

ax.set_xlabel('Wave Number (cm-1)',fontsize=22,color='white')

ax.set_ylabel('Coefficient Value',fontsize=22,color='white')

#for sample in samples:

#    coefficients=[1]*len(waves_to_use)

#    raman_maps_path=path+sample+'/map_per_wave

'+raman_resolutions[samples.index(sample)]+'

#    wave_maps=load_maps(raman_maps_path)

#    try: raman_sum=[raman_sum[i]+sum(sum(map)) for i,map in

```

```

enumerate(wave_maps)]

# except:raman_sum=[sum(sum(map)) for map in wave_maps]

# print(len(raman_sum),min(raman_sum),max(raman_sum))

#min_raman=min(raman_sum)

#max_raman=max(raman_sum)

#x=waves_to_use

#y=[i/max_raman*100000 for i in raman_sum]

with open("H:/Rutgers Research/MoS2/160517/3L060MD/L2 low Raman
Spectra.txt") as f:

    data = f.read()

    data = data.split("\n")

    x = [row.split("\t")[2] for row in data[1:-1]][::-1]

    y = [row.split("\t")[3] for row in data[1:-1]][::-1]

    ax2 = ax.twinx()

    ax2.plot(x,y,lw=1.5,color=(1,.184,0,1),label='Bilayer MoS $\mathrm{2}$  Raman
Spectrum (633 nm)')

    ax2.set_ylim(6700,80000)

    ax2.set_yticklabels([])

    ax2.set_ylabel('Intensity (AU)',fontsize=22,color=(1,.184,0,1))

    legend=plt.legend(fontsize=18,loc=(.4,.06))#

    frame = legend.get_frame()

    frame.set_facecolor((.1,.1,.1,.5))

    frame.set_linewidth(0)

    for line,text in zip(legend.get_lines(), legend.get_texts()):

        text.set_color(line.get_color())

    plt.subplots_adjust(left=0.04, right=0.97, top=0.98, bottom=0.08)

```

```

plt.xlim(waves_to_use[0],waves_to_use[-1])

axins =

inset_axes(ax,9,7,loc=3,bbox_to_anchor=(800,230))#,bbox_transform=ax.figure.transFi
gure) #,,no zoom

axins.set_ylim(-6.5,5.5)

mark_inset(ax, axins, loc1=2, loc2=3, fc=(.2,.2,.2,.4), ec=(1,1,1,.7))

axins.set_axis_bgcolor((0,0,0,1))

axins.set_xlim(356, 544)

# draw a bbox of the region of the inset axes in the parent axes and
# connecting lines between the bbox and the inset axes area

s=waves_to_use.index(352)
e=waves_to_use.index(550)

for i,Y in enumerate(coefficients_list[s:e]):

    axins.scatter([waves_to_use[s+i]]*len(Y),Y,s=.7,color='white',marker='.')

#X,Y=(list(t) for t in zip(*sorted(zip(X, Y))))

#plt.scatter(X[X.index(352):X.index(550)], Y[X.index(352):X.index(550)],s=.7,color='white'
,marker='.')

plt.plot(waves_to_use[s:e],average_coefficients[s:e], color=(1,.7,.2,1),
lw=2,label="Arithmetic mean")

plt.plot(waves_to_use[s:e],medians[s:e], color=(.1,1,.5,1), lw=2, label='Median')

plt.plot(waves_to_use[s:e],modes[s:e], color=(.5,.5,1,1), lw=2, label="Mode (int
binning)")

plt.axhline(0, color='white',lw=1.5)

colors=[wavelength_to_rgb(w) for w in [610,560,520,470,445,420,380]]

plt.axvline(381, color=colors[0],lw=1.1)

```

```

plt.text(376,6,'E2g (Exp) 381 cm$\mathrm{-1}$',rotation=90,color='white',fontsize=16,**hfont)

plt.axvline(390, color=colors[1],lw=1.1)

plt.text(385,6,'E2g (DFT) 390 cm$\mathrm{-1}$',rotation=90,color='white',fontsize=16)

plt.axvline(405, color=colors[2],lw=1.1)

plt.text(400,6,'A1g (Exp) 405 cm$\mathrm{-1}$',rotation=90,color='white',fontsize=16)

plt.axvline(412, color=colors[3],lw=1.3)

plt.text(407,6,'A1g (DFT) 412 cm$\mathrm{-1}$',rotation=90,color='white',fontsize=16)

plt.axvline(452, color=colors[4],lw=1.5)

plt.axvline(465, color=colors[5],lw=1.5)

plt.text(446,6,'2LA 443 cm$\mathrm{-1}$',rotation=90,color='white',fontsize=16)

plt.axvline(520, color=colors[6],lw=1.5)

plt.text(515.5,6,'Si 520.5 cm$\mathrm{-1}$',rotation=90,color='white',fontsize=16)

axins2 = axins.twinx()

#axins2.plot(x[36:136],y[36:136],lw=2,color=(1,.184,0,1),label='Bilayer
MoS2 Raman Spectrum')

axins2.plot(x[30:530],y[30:530],lw=2,color=(1,.184,0,1),label='Bilayer
MoS2 Raman Spectrum')

axins2.annotate('E2g (Exp) 381 cm$\mathrm{-1}$',
(381,y[finder(x,381)]), color=colors[0],fontsize=16,xytext=(0.01, 0.25), textcoords='axes
fraction',

arrowprops=dict(arrowstyle='simple',relpos=(.5, 0.),fc=colors[0].),
bbox=dict(boxstyle='square',pad=.2, fc=(.3,.3,.3,.8),

```

```

ec='none'),fontweight='bold',**tfont)

    axins2.annotate('E$_\mathrm{2g}$ (DFT) 390 cm$^\mathrm{-1}$',
(390,y[finder(x,390)]), color=colors[1],fontsize=16,xytext=(0.22, 0.03), textcoords='axes
fraction',

        arrowprops=dict(arrowstyle='simple',relpos=(0,
1),fc=colors[1]),bbox=dict(boxstyle='square',pad=.2, fc=(.3,.3,.3,.8),
ec='none'),fontweight='bold',**tfont)

    axins2.annotate('A$_\mathrm{1g}$ (Exp) 405 cm$^\mathrm{-1}$',
(405,y[finder(x,405)]), color=colors[2],fontsize=16,xytext=(0.15, 0.35), textcoords='axes
fraction',

        arrowprops=dict(arrowstyle='simple',relpos=(.3, 0),fc=colors[2],
),bbox=dict(boxstyle='square',pad=.2, fc=(.3,.3,.3,.8),
ec='none'),fontweight='bold',**tfont)

    axins2.annotate('A$_\mathrm{1g}$ (DFT) 412 cm$^\mathrm{-1}$',
(412,y[finder(x,412)]), color=colors[3],fontsize=16,xytext=(0.33, 0.11), textcoords='axes
fraction',

        arrowprops=dict(arrowstyle='simple',relpos=(0, 1),fc=colors[3],
),bbox=dict(boxstyle='square',pad=.2, fc=(.4,.4,.4,.8),
ec='none'),fontweight='bold',**tfont)

    axins2.annotate('2LA (DFT) 452 cm$^\mathrm{-1}$',
(x[finder(x,452)],y[finder(x,452)]), color=colors[4],fontsize=16,xytext=(0.55, 0.45),
textcoords='axes fraction',

        arrowprops=dict(arrowstyle='simple',relpos=(.5,
0.),fc=colors[4]),bbox=dict(boxstyle='square',pad=.2, fc=(.5,.5,.5,.8),
ec='none'),fontweight='bold',**tfont)

    axins2.annotate('A$_\mathrm{1g}$$_\mathrm{2}$ (DFT) 465 cm$^\mathrm{-1}$',

```

```

(x[finder(x,465)],y[finder(x,465)]), color=colors[5],fontsize=16,xytext=(0.6, 0.32),
textcoords='axes fraction',
    arrowprops=dict(arrowstyle='simple',relpos=(.5,
0.),fc=colors[5]),bbox=dict(boxstyle='square',pad=.2, fc=(.6,.6,.6,.8),
ec='none'),fontweight='bold',**tfont)

axins2.annotate('Si 520 cm $\mathrm{-1}$ $', (x[finder(x,520.5)],y[finder(x,520.5)]),
color=colors[6],fontsize=16,xytext=(0.75, 0.8), textcoords='axes fraction',
    arrowprops=dict(arrowstyle='simple',relpos=(.5,
0.),fc=colors[6]),bbox=dict(boxstyle='square',pad=.2, fc=(.7,.7,.7,.8),
ec='none'),fontweight='bold',**tfont)

axins2.set_ylim(6700,80000)
axins2.set_xlim(356, 544)
axins2.set_yticklabels([])
#axins2.set_ylabel('Intensity (AU)',fontsize=16,color=(0,1,1,1))

autoAxis = axins2.axis()
print(autoAxis)

#Rectangle((autoAxis[0]-0.7,autoAxis[2]-0.2),(autoAxis[1]-autoAxis[0])+1,(autoAxis[3]-
autoAxis[2])+0.4,fill=False,lw=2)

#rec1 = patches.Rectangle((autoAxis[0]-7,autoAxis[2]-0.),7,72000,color=(0,0,0,.9))
#rec2 = patches.Rectangle((autoAxis[1],autoAxis[2]-0.),8,72000,color=(0,0,0,.9))
rec1 = patches.Rectangle((autoAxis[0]-5.5,autoAxis[2]+1000),5.3,autoAxis[3]-
autoAxis[2]-2500,color=(.0,.0,.0,.9))

rec3 = patches.Rectangle((autoAxis[0]+.2,autoAxis[2]-2400),autoAxis[1]-autoAxis[0]-
.4,2350,color=(.0,.0,.0,.9))

axins2.add_patch(rec1)
axins2.add_patch(rec3)

```

```

rec3.set_clip_on(False)
rec1.set_clip_on(False)
for spine in axins.spines.values():
    spine.set_edgecolor('white')
    spine.set_linewidth(1)
plt.xticks(np.arange(360, 541, 20),fontsize=16,color='white')
plt.yticks(np.arange(-6,6,1),fontsize=16,color='white')
#axins.set_yticklabels(np.arange(-9,7,1))
axins.xaxis.set_ticks_position('bottom')
axins.yaxis.set_ticks_position('left')
axins.tick_params(axis='x', direction='in', width=1, length=10,color='w', labels=14,
pad=3)
axins.tick_params(axis='y', direction='in', width=1,
length=10,color='w',labels=14,pad=3)
axins2.tick_params(axis='y', direction='in', width=0, length=0)
plt.savefig('trends.png',dpi=fig.dpi,facecolor=(0,0,0,.5))
plt.show()

def initialize_figure(friction,raman,m,s,scale,rot,tx,ty,overlay_path,cmap,save=False):
    # initiates plotting for real-time visualization

    global fig,ax,ax2,axins1,axins2,axins3,axins4,co_scatt,fric_plot,t

    fig,ax=plt.subplots(figsize=(19.2,10.8),dpi=100,facecolor='black',edgecolor='none')

    co_scatt=ax.scatter(waves_to_use,[1]*len(waves_to_use),s=1,color='white',marker='.')

    ax.set_axis_bgcolor('black')

    plt.axhline(0, color='white',lw=1)

```

```

plt.yticks(np.arange(-9,10,1),fontsize=16,color='white')

plt.xticks(np.arange(250, 1400, 50),fontsize=16,color='white')

ax.tick_params(axis='x', direction='in', width=1.5, length=10,color='w', labels=16,
pad=5)

ax.tick_params(axis='y', direction='in', width=1.5, length=5,color='w', labels=16,
pad=4)

for spine in ax.spines.values():
    spine.set_edgecolor('white')
    spine.set_linewidth(2)

ax.get_xaxis().tick_bottom()
ax.get_yaxis().tick_left()

ax.set_xlabel('Wavenumber (cm $\mathrm{-1}$ )',fontsize=20,color='white')
ax.set_ylabel('Coefficient Value',fontsize=20,color='white')

ax.set_ylim(-10,10)

ax2 = ax.twinx()

x=waves_to_use

#print(len(wave_maps),len(coefficients),len(waves_to_use))

y=[sum(sum(wave_maps[w])) for w,c in enumerate(coefficients)]

fric_plot,=ax2.plot(x,y,lw=1.5,color=friction_color,label='Weighted Raman Intensity')

#ax2.set_ylim(6700,80000)

ax2.set_yticklabels([])

ax2.set_ylabel('Total Friction Contribution',fontsize=20,color=friction_color)

legend=plt.legend(fontsize=20,loc=(.4,.1))#

frame = legend.get_frame()

frame.set_facecolor((.1,.1,.1,.5))

frame.set_linewidth(0)

```

```

for line,text in zip(legend.get_lines(), legend.get_texts()):
    text.set_color(line.get_color())

plt.subplots_adjust(left=0.05, right=0.97, top=0.98, bottom=0.08)

plt.xlim(waves_to_use[0],waves_to_use[-1])

axins1 = inset_axes(ax,map_size[0],map_size[1],loc=3,bbox_to_anchor=(550,750))
axins1.imshow(friction,cmap=cmap)
axins1.yaxis.set_ticks_position('left')
axins1.xaxis.set_ticks_position('bottom')
axins1.tick_params(axis='x', direction='in', width=2, length=6,color=(.5,.5,.5))
axins1.tick_params(axis='y', direction='in', width=2, length=6,color=(.5,.5,.5),pad=1)
tick_labels=[round(y*friction_y_size/100) for y in range(90,0,-25)]
tick_locs=[y for y in range(10,100,25)]
axins1.set_xticks(tick_locs)
axins1.set_yticks(tick_locs)
axins1.set_yticklabels(tick_labels,fontsize=16,color='w')
axins1.set_xticklabels([])
axins1.set_ylabel('$\mu$M',fontsize=20,color='white')

for spine in axins1.spines.values():
    spine.set_linewidth(0)

axins1.text(20,-3, "AFM Friction",fontsize=16,color='white',ha='left')

axins2 =
inset_axes(ax,map_size[0],map_size[1],loc=3,bbox_to_anchor=(550+100*map_size[0],7
50))

axins2.axis("off")

axins2.imshow(raman,cmap=cmap)

```

```

axins2.text(5,-3, "Predicted from Raman",fontsize=16,color='white',ha='left')

axins3 =
inset_axes(ax,map_size[0],map_size[1],loc=3,bbox_to_anchor=(550+200*map_size[0],7
50))

axins3.axis("off")

axins3.imshow(friction+raman,cmap=cmap)

axins3.text(40,-3, "Sum",fontsize=16,color='white',ha='left')

axins4 =
inset_axes(ax,map_size[0],map_size[1],loc=3,bbox_to_anchor=(550+300*map_size[0],7
50))

axins4.axis("off")

axins4.imshow(friction-raman,cmap=cmap)

axins4.text(30,-3, "Difference",fontsize=16,color='white',ha='left')

t = axins1.text(0, 107, "Scale: %.3g Rotation: %.3g T$\mathrm{x}$: %.3g
T$\mathrm{y}$: %.3g MSE: %.0f SSIM: %.2f Variance: %.2f"
%(scale,rot,tx,ty,m,s,m**.5/256),color='w',fontsize=18,ha='left', va='center')

t.set_bbox(dict(facecolor='black', alpha=.8,edgecolor='none',pad=3))

fig.set_size_inches(19.2, 10.8)

#plt.draw()

plt.pause(.000001)

#plt.show(block=True)

if save:

    timestamp=datetime.now().strftime('%y%m%d%H%M%S%f')[:-3]

    plt.savefig(overlay_path+str(timestamp)+' '+str(int(m))+
'+decimal(2,s)+'+'.png',dpi=fig.dpi,facecolor=(0,0,0,.5))

plt.pause(.000001)

```

```

friction_color=(random.uniform(0,1),random.uniform(0,1),random.uniform(0,1))

def
update_figure(friction,raman,m,s,scale,rot,tx,ty,overlay_path,cmap,end=False,save=False):

    # updates figures with new maps when called

    global fig,ax,ax2,axins1,axins2,axins3,axins4,co_scatt,fric_plot,t

    co_scatt.remove()

    co_scatt=ax.scatter(waves_to_use,coefficients,s=2,color='white')

    fig.set_size_inches(19.2, 10.8)

    #print(len(wave_maps),len(coefficients),len(waves_to_use))

    y=[sum(sum(wave_maps[w]))*c for w,c in enumerate(coefficients)]

    fric_plot.remove()

    fric_plot,=ax2.plot(waves_to_use,y,lw=1.5,color=friction_color,label='Friction vs
wavenumber')

    ax2.set_ylim(average(y)-(max(y)-min(y))/2,average(y)+(max(y)-min(y))/2)

    axins2.imshow(raman,cmap=cmap)

    axins3.imshow(friction+raman,cmap=cmap)

    axins4.imshow(friction-raman,cmap=cmap)

    t.remove()

    t = axins1.text(0, 107, "Scale: %.3g Rotation: %.3g T $\mathrm{x}$ : %.3g
T $\mathrm{y}$ : %.3g MSE: %.0f SSIM: %.2f Variance: %.2f"
%(scale,rot,tx,ty,m,s,m**.5/256),color='w',fontsize=18,ha='left', va='center')

    t.set_bbox(dict(facecolor='black', alpha=.8,edgecolor='none',pad=3))

    #plt.draw()

```

```

plt.pause(.000001)

#if end:

if save:

    plt.savefig(overlay_path+str(timestamp)+' '+str(int(m))+
'+decimal(2,s)+'+'.png',dpi=fig.dpi,facecolor=(0,0,0,.5))

    plt.pause(.000001)

def optimize_translation(sample,iterations,start_sigma):

    raman_maps_path=path+sample+'/map_per_wave
'+raman_resolutions[samples.index(sample)]+'/'

    friction_fname=path+sample+'/' +sample+' LFM.txt'

    #print(raman_maps_path,friction_fname)

friction=pd.read_csv(friction_fname,delimiter='\t',skiprows=4,header=None).as_matrix()

friction=normalize(scale_rotate_translate(friction,100/friction.shape[0]))

start_scale=scales[samples.index(sample)]

start_rot=rotations[samples.index(sample)]

[start_x,start_y]=shifts[samples.index(sample)]

print(start_scale,start_rot,start_x,start_y)

wave_maps=load_maps(raman_maps_path)

orig_raman=sum(coefficients[i]*map for i,map in enumerate(wave_maps))

raman=normalize(crop(scale_rotate_translate(orig_raman,start_scale,start_rot)))

best_mse,best_ssim=compare_images(raman,friction)

best_fom=best_ssim/best_mse

#initialize_figure(sample,friction,raman,best_mse,best_ssim,predict=True,save=False)

best_transform=[start_scale,start_rot,start_x,start_y]

```

```

best_const=0

for iter in range(1,iterations):

    sigma=start_sigma*(1-iter/iterations)**1.1

    [scale,rotation,tx,ty]=best_transform

    const=random.normalvariate(best_const,2*sigma)

    kappa=10000*iter/iterations+1000

scale_adj=max(.95*start_scale,min(1.05*start_scale,(scale*random.normalvariate(1,sig
ma))))

tx_adj=max(.95*start_x,min(1.05*start_x,tx*random.normalvariate(1,sigma)))

ty_adj=max(.95*start_y,min(1.055*start_y,ty*random.normalvariate(1,sigma)))

rot_adj=max(start_rot*.95,min(start_rot*1.05,(random.vonmisesvariate(rotation*math.pi/1
80,kappa)*180/math.pi)))

raman=normalize(crop(scale_rotate_translate(orig_raman,scale_adj,rot_adj,tx_adj,ty_ad
j)))

raman+=const

try:m,s=compare_images(raman,friction)

except:

    winsound.Beep(2000,80)

    print(iter,scale_adj,rot_adj,tx_adj,ty_adj,raman.shape,raman_x,raman_y)

    continue

fom=s/m

if fom>best_fom:

    best_mse=m

```

```

    best_ssim=s

    best_fom=fom

    best_const=const

    best_transform=[scale_adj,rot_adj,tx_adj,ty_adj]

    print(iter,' '.join(sig_figs(4,f)for f in
[best_mse,best_ssim,best_mse/best_ssim,const,scale_adj,rot_adj,tx_adj,ty_adj]))

    #update_figure(friction,raman,m,s)

    [scale,rot,tx,ty]=best_transform

    composite=normalize(crop(scale_rotate_translate(orig_raman,scale,rot,tx,ty)))

    composite+=best_const

    return friction,composite,best_mse,best_ssim

def predict_friction(iterations,start_sigma):

    # loads coefficients from spreadsheet and determines

    # predictive value for unbiased samples

    print(datetime.now(),'Predicting friction behavior')

    set_cpu_affinity()

    global coefficients,waves_to_use,raman_maps_path,timestamp

    wb,ws=load_xlsx(file_name)

    first_wave=get_col(ws,1,204)

    num_rows=ws.max_row

    num_cols=ws.max_column

    row=2#num_rows

    increment=1

    while row<num_rows+1:

        if get_value(ws,row,get_col(ws,1,'MSE avg')) or not get_value(ws,row,1):

```

```

    row+=increment

    continue

start_time=datetime.now()

set_cpu_affinity()

timestamp=get_value(ws,row,1)

for s,sample in enumerate(samples):

    if get_value(ws,row,get_col(ws,1,'MSE '+sample)):

        continue

    waves_to_use,coefficients=[],[]

    print(datetime.now(),'Row:',row,'Sample:',s,timestamp,sample)

    for col in range(first_wave,num_cols+1):

        if get_value(ws,row,col):

            waves_to_use.append(int(get_value(ws,1,col)))

            coefficients.append(float(get_value(ws,row,col)))

    coefficients=[x for x in coefficients]

    print(len(waves_to_use),min(waves_to_use),max(waves_to_use),waves_to_use)

    print(len(coefficients),min(coefficients),max(coefficients),coefficients)

friction,raman,best_mse,best_ssim=optimize_translation(sample,iterations,start_sigma)

    #if best_ssim<0:

    # ws.cell(row=row,column=get_col(ws,1,'MSE
'+sample')).value=sig_figs(4,best_mse)

    # ws.cell(row=row,column=get_col(ws,1,'SSIM
'+sample')).value=sig_figs(4,best_ssim)

    # break

    avg_sample_mse=average([float(x) for x in
```

```

[get_value(ws,row,get_col(ws,1,'MSE '+sample))for row in range(2,ws.max_row+1)] if
x])

    avg_sample_ssim=average([float(x) for x
in[get_value(ws,row,get_col(ws,1,'SSIM '+sample))for row in range(2,ws.max_row+1)]
if x])

    if best_ssim/best_mse>1.5*avg_sample_ssim/avg_sample_mse:

        print('Saving figure',sample,timestamp,'MSE: {0:.4g} SSIM: {1:.4g}
avg_MSE: {2:.4g} avg_SSIM:
{3:.4g}'.format(best_mse,best_ssim,avg_sample_mse,avg_sample_ssim))

initialize_figure(sample,friction,raman,best_mse,best_ssim,predict=True,save=True)

    else:

        print(sample,timestamp,'MSE: {0:.4g} SSIM: {1:.4g} avg_MSE: {2:.4g}
avg_SSIM: {3:.4g}'.format(best_mse,best_ssim,avg_sample_mse,avg_sample_ssim))

        ws.cell(row=row,column=get_col(ws,1,'MSE
'+sample)).value=sig_figs(4,best_mse)

        ws.cell(row=row,column=get_col(ws,1,'SSIM
'+sample)).value=sig_figs(4,best_ssim)

        #update_figure(friction,raman,m,s,end=True,save=save)

        mses=[float(ws.cell(row=row,column=col).value)for col in range(4,18,2)if
ws.cell(row=row,column=col).value]

        ssims=[float(ws.cell(row=row,column=col).value)for col in range(5,19,2)if
ws.cell(row=row,column=col).value]

        avg_mse=average(mses)

        avg_ssim=average(ssims)

        wb,ws=load_xlsx(file_name)

```

```

r=get_row(ws,1,timestamp)

if not r:

    row+=increment

    continue

print('Saving row',r)

print('Average set MSE:',sig_figs(4,avg_mse),[sig_figs(4,m) for m in mses])

print('Average set SSIM:',sig_figs(4,avg_ssim),[sig_figs(4,s) for s in ssims])

ws.cell(row=r,column=2).value=sig_figs(4,avg_mse)

ws.cell(row=r,column=3).value=sig_figs(4,avg_ssim)

for c,col in

enumerate(range(4,18,2)):ws.cell(row=r,column=col).value=sig_figs(4,mses[c])

for c,col in

enumerate(range(5,19,2)):ws.cell(row=r,column=col).value=sig_figs(4,ssims[c])

ssim_avgs=[float(x) for x in[get_value(ws,r,get_col(ws,1,'SSIM avg'))for r in
range(2,ws.max_row+1)] if x]

mse_avgs=[float(x) for x in[get_value(ws,r,get_col(ws,1,'MSE avg'))for r in
range(2,ws.max_row+1)] if x]

timestamps=[x for x in[get_value(ws,r,1) for r in range(2,ws.max_row+1)]if
get_value(ws,r,2)]

if len(mse_avgs)>100:

print(decimal(4,average(ssim_avgs[:100])),int(average(mse_avgs[:100])),sorted(range(le
n(mse_avgs)), key=lambda x: ssim_avgs[x]/mse_avgs[x]):len(mse_avgs)-100])

for i in sorted(range(len(mse_avgs)), key=lambda x:
ssim_avgs[x]/mse_avgs[x]):len(mse_avgs)-100]:

    r=get_row(ws,1,timestamps[i])

```

```

print('Deleting row',r,i,'MSE: {} SSIM: {}'.format(mse_avgs[i],ssim_avgs[i]))

for r in range(r,ws.max_row+1):

    for c in range(1,ws.max_column+1):

        ws.cell(row=r,column=c).value=ws.cell(row=r+1,column=c).value

    num_rows-=1

    row+=increment

wb.save(file_name)

row+=increment

num_rows=ws.max_row

print('Time used:',datetime.now()-start_time,'\n')

def optimize_components(sample,iterations,start_sigma):

    # randomly adjusts transformation variables and map coefficients

    # to find best recreation of friction map

    print(datetime.now(),'Optimizing Raman coefficients for friction prediction')

    set_cpu_affinity()

    global coefficients,waves_to_use,raman_maps_path,timestamp,wave_maps

    start_time=datetime.now()

    raman_maps_path=path+sample+'/map_per_wave

'+raman_resolutions[samples.index(sample)]+'/'

    friction_fname=path+sample+'/'+sample+' LFM.txt'

    with open(friction_fname,'r')as header:

        header=header.readlines()[:4]

        global friction_y_size

        friction_x_size=float(re.findall("\d+\.\d+",header[1])[0])

        friction_y_size=float(re.findall("\d+\.\d+",header[2])[0])

```

```

print(raman_maps_path,friction_fname)

friction=pd.read_csv(friction_fname,delimiter='\t',skiprows=4,header=None).as_matrix()

friction=normalize(scale_rotate_translate(friction,100/friction.shape[0]))

load_coefficients(sample)

wave_maps=load_maps(raman_maps_path)

orig_raman=sum(map for i,map in enumerate(wave_maps))

start_rot=rotations[samples.index(sample)]

[start_x,start_y]=shifts[samples.index(sample)]

start_scale=scales[samples.index(sample)]

raman=normalize(crop(scale_rotate_translate(orig_raman,start_scale,start_rot,start_x,start_y)))

best_mse,best_ssim=compare_images(raman,friction)

colormaps=[]

for cmap_category, cm in cmaps:

    colormaps.extend(cm)

appropriate_cmaps=['Blues', 'BuGn', 'BuPu', 'GnBu', 'Greens', 'Greys', 'Oranges',
'OrRd','PuBu', 'PuBuGn', 'PuRd',
                    'Purples', 'RdPu', 'Reds', 'YlGn', 'YlGnBu', 'YlOrBr', 'YlOrRd', 'afmhot',
'autumn', 'bone',
                    'cool', 'copper', 'gist_heat', 'gray', 'hot', 'pink', 'spring', 'summer',
'winter', 'gist_earth',
                    'terrain', 'ocean', 'gist_stern', 'brg', 'CMRmap', 'cubehelix', 'gnuplot',
'gnuplot2',
                    'gist_ncar', 'nipy_spectral', 'jet', 'rainbow', 'gist_rainbow', 'hsv']

```

```

cmap=random.choice(appropriate_cmaps)

timestamp=datetime.now().strftime('%y%m%d%H%M%S%f')[:-3]

overlay_path='Raman Optimization/'+sample+' '+cmap+' '+timestamp+'/'

if not os.path.exists(overlay_path):
    os.makedirs(overlay_path)

#initialize_figure(friction,raman,best_mse,best_ssim,start_scale,start_rot,start_x,start_y,
overlay_path,cmap,save=True)

best_transform=[start_scale,start_rot,start_x,start_y]

#load_coefficients(sample)

for iter in range(1,iterations):
    [scale,rotation,tx,ty]=best_transform

    sigma=start_sigma*(1-iter/iterations)

    adjustments=np.array([random.normalvariate(1,sigma) for _ in coefficients])

    new_coefficients=[min(10,max(-
10,((coef+random.normalvariate(0,sigma)*var_devs[i]))) for i,coef in
enumerate(coefficients))]

scale_adj=max(start_scale*.95,min(start_scale*1.05,(scale*random.normalvariate(1,sig
ma/2))))

kappa=100000*iter/iterations+1000

tx_adj=max(.97*start_x,min(1.03*start_x,tx*random.normalvariate(1,sigma/2)))

ty_adj=max(.97*start_y,min(1.03*start_y,ty*random.normalvariate(1,sigma/2)))

rot_adj=max(start_rot*.97,min(start_rot*1.03,(random.vonmisesvariate(rotation*math.pi/1
80,kappa)*180/math.pi)))

```

```

    raman=sum(new_coefficients[i]*map for i,map in enumerate(wave_maps))

raman=normalize(crop(scale_rotate_translate(raman,scale_adj,rot_adj,tx_adj,ty_adj)))

#print(iter,scale_adj,rot_adj,tx_adj,ty_adj,raman.shape,raman_x,raman_y,raman.min(),ra
man.max())

    try:m,s=compare_images(raman,friction)

    except:

        print(iter,scale_adj,rot_adj,tx_adj,ty_adj,raman.shape,orig_raman.shape,
            scale_rotate_translate(orig_raman,scale_adj,rot_adj,tx_adj,ty_adj).shape,
            crop(scale_rotate_translate(orig_raman,scale_adj,rot_adj,tx_adj,ty_adj)).shape)

        #print(iter,m,s)

        if s/m>best_ssim/best_mse:

            best_mse=m

            best_ssim=s

            best_transform=[scale_adj,rot_adj,tx_adj,ty_adj]

            coefficients=new_coefficients

            print(iter,decimal(2,sigma),' '.join(sig_figs(4,f)for f in
[best_mse,best_ssim,best_mse/best_ssim,scale_adj,rot_adj,tx_adj,ty_adj]),'+'.join('{:.2f}
({:.0f})'.format(b,w)for w,b in zip(waves_to_use, coefficients)))

#update_figure(friction,raman,m,s,scale_adj,rot_adj,tx_adj,ty_adj,overlay_path,cmap,sav
e=True)

    if best_ssim/best_mse<1.2*avg_sample_ssim/avg_sample_mse and
os.path.exists(overlay_path):shutil.rmtree(overlay_path)

```

```

#update_figure(friction,raman,best_mse,best_ssim,end=True,save=True)

print('Best:',best_ssim,best_mse,best_mse/best_ssim,avg_sample_ssim,avg_sample_
mse)

print(len(waves_to_use),waves_to_use)

print(len(coefficients),[sig_figs(4,c) for c in coefficients])

if best_ssim/best_mse>avg_sample_ssim/avg_sample_mse:
    print('Saving coefficients')

    timestamp=datetime.now().strftime('%y%m%d%H%M%S%f')[:-3]

    save_coefficients(sample,best_mse,best_ssim,timestamp)

plt.close()

print(sample,'optimized. Time used:',datetime.now()-start_time,'\n')

path='H:/Rutgers Research/MoS2/160517/'

#file_name='Correlation Results.xlsx'

file_name='Correlation Results Pared.xlsx'

samples=['2L0','2L60','3L00','3L00MD','3L060','3L060MD','4L0600']

raman_resolutions=['38.0x39.2','34.2x35.8','32.5x32.5','39.0x42.6','48.8x48.8','49.5x49.
5','40.8x42.6']

scales=[1.7,1.01,2.4,.52,2.6,1.7,1.8]

rotations=[49,48.5,155,155,155,150,124]

shifts=[[.8,.9],[1.24,0.52],[.82,1.0],[.65,.65],[1.2,1.6],[1.2,.89],[1.3,1.0]]

'''

waves_to_use=[]

for sample in samples:

```

```

waves_present=[]

raman_maps_path=path+sample+'/map_per_wave

'+raman_resolutions[samples.index(sample)]+'/'

for map_file in os.listdir(raman_maps_path):

    # iterate through maps and select those closest to waves

    waves_present.append(round(float(map_file[:-4])))

    #print(samples.index(sample),wave_file,wave_file in

waves_to_use,waves_to_use)

if not waves_to_use:

    waves_to_use=waves_present

else:

    waves_to_use=list(set(waves_to_use)&set(waves_present))

print(len(waves_to_use),waves_to_use)


wb,ws=load_xlsx(file_name)

write_col=get_col(ws,1,154)

for wave in waves_to_use:

    wave_col=get_col(ws,1,wave)

    for row in range(1,ws.max_row+1):

        ws.cell(row=row, column=write_col).value = ws.cell(row=row,

column=wave_col).value

        write_col+=1

for col in range(write_col,ws.max_column+1):

    for row in range(1,ws.max_row+1):

        ws.cell(row=row, column=col).value = None

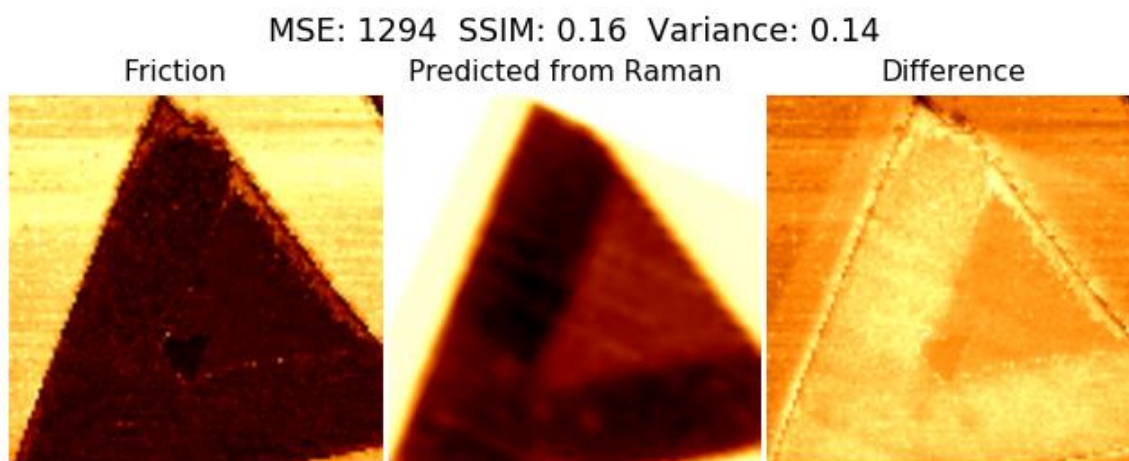
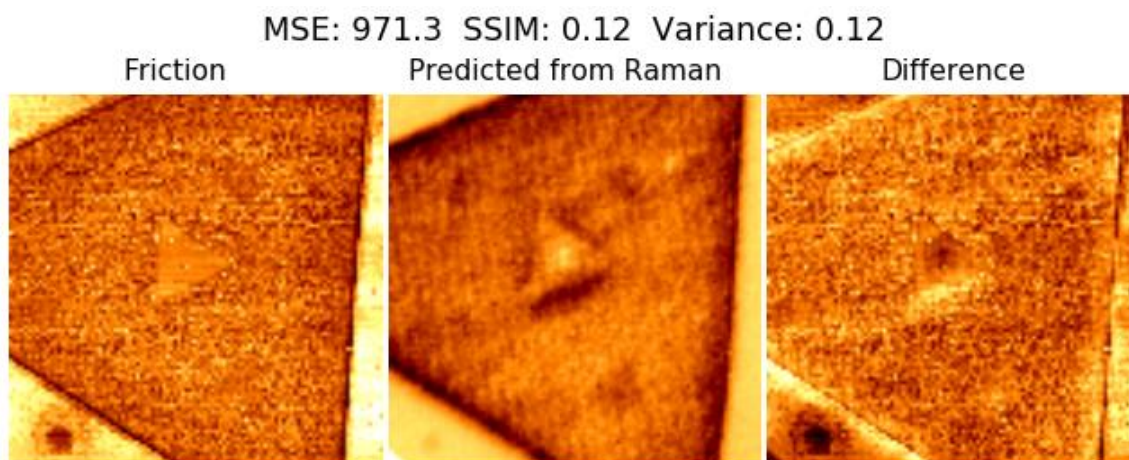
wb.save(file_name)

```

```
"""  
  
#compare_100_1024()  
  
start_time=datetime.now()  
  
while 1:  
  
    optimize_components(random.choice(samples),random.randint(5000,30000),start_sig  
    a=max(.05,random.normalvariate(.3,.1)))
```

## Appendix B: Raman generated prediction of friction

These figures show three maps: friction force obtained via Park AFM, predicted friction from linear combination of emission wavenumber intensities (Raman), and the difference between actual and predicted maps.

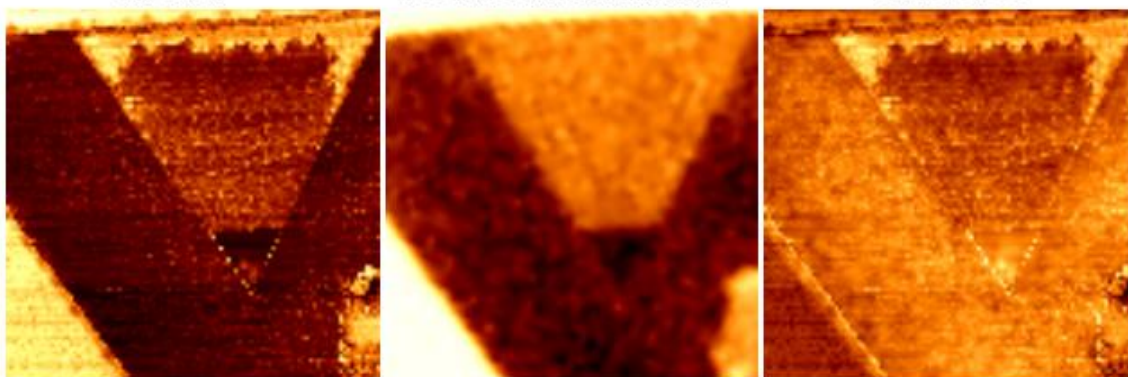


MSE: 1342 SSIM: 0.13 Variance: 0.14

Friction

Predicted from Raman

Difference

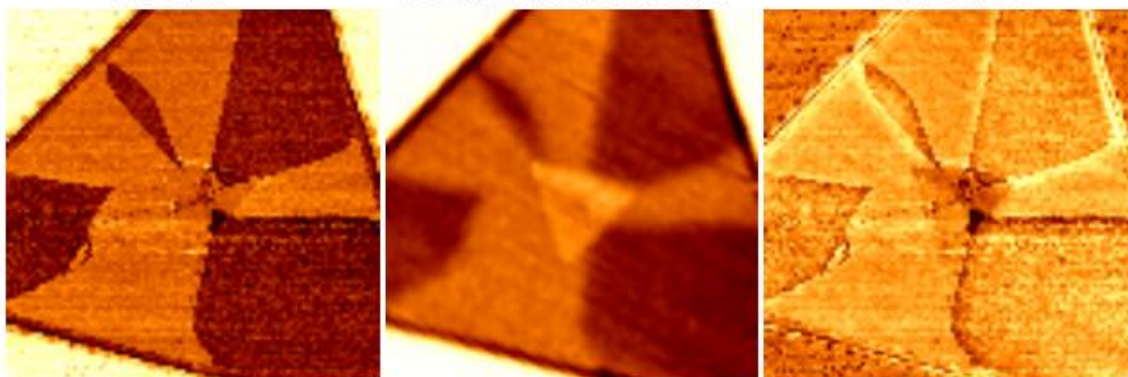


MSE: 470.7 SSIM: 0.20 Variance: 0.08

Friction

Predicted from Raman

Difference



## References

1. Wilson, L. (2013). International technology roadmap for semiconductors (ITRS). *Semiconductor Industry Association*.
2. Pendry, J. (2010). Quantum friction—fact or fiction? *New Journal of Physics*, 12(3), 033028.
3. Vašková, H. (2011). A powerful tool for material identification: Raman spectroscopy. *Int. J. Math. Appl. Math. Modell*, 5(7), 1205-1212.
4. Eda, G., Fujita, T., Yamaguchi, H., Voiry, D., Chen, M., & Chhowalla, M. (2012). Coherent atomic and electronic heterostructures of single-layer MoS<sub>2</sub>. *ACS nano*, 6(8), 7311-7317.
5. Acerce, M., Voiry, D., & Chhowalla, M. (2015). Metallic 1T phase MoS<sub>2</sub> nanosheets as supercapacitor electrode materials. *Nature nanotechnology*, 10(4), 313-318.
6. Novoselov, K., & Neto, A. C. (2012). Two-dimensional crystals-based heterostructures: materials with tailored properties. *Physica Scripta*, 2012(T146), 014006.
7. Grierson, D., Flater, E., & Carpick, R. (2005). Accounting for the JKR–DMT transition in adhesion and friction measurements with atomic force microscopy. *Journal of adhesion science and technology*, 19(3-5), 291-311.
8. Duan, X., Wang, C., Pan, A., Yu, R., & Duan, X. (2015). Two-dimensional transition metal dichalcogenides as atomically thin semiconductors: opportunities and challenges. *Chemical Society Reviews*, 44(24), 8859-8876.
9. Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, i. V., & Kis, A. (2011). Single-layer MoS<sub>2</sub> transistors. *Nature nanotechnology*, 6(3), 147-150.
10. Lee, C., Li, Q., Kalb, W., Liu, X.-Z., Berger, H., Carpick, R. W., & Hone, J. (2010). Frictional characteristics of atomically thin sheets. *Science*, 328(5974), 76-80.
11. Deng, Y., Luo, Z., Conrad, N. J., Liu, H., Gong, Y., Najmaei, S., . . . Ye, P. D. (2014). Black phosphorus–monolayer MoS<sub>2</sub> van der Waals heterojunction p–n diode. *ACS nano*, 8(8), 8292-8299.
12. Zhu, Y., Yang, J., Zhang, S., Mokhtar, S., Pei, J., Wang, X., & Lu, Y. (2016). Strongly enhanced photoluminescence in nanostructured monolayer MoS<sub>2</sub> by chemical vapor deposition. *Nanotechnology*, 27(13), 135706.
13. Philbin, T. G., & Leonhardt, U. (2009). No quantum friction between uniformly moving plates. *New Journal of Physics*, 11(3), 033035.
14. Mortazavi, M., Wang, C., Deng, J., Shenoy, V. B., & Medhekar, N. V. (2014). Ab initio characterization of layered MoS<sub>2</sub> as anode for sodium-ion batteries. *Journal of Power Sources*, 268, 279-286.
15. Katzke, H., Tolédano, P., & Depmeier, W. (2004). Phase transitions between polytypes and intralayer superstructures in transition metal dichalcogenides. *Physical Review B*, 69(13), 134111.
16. . (!!! INVALID CITATION !!! 16-18).
17. Novoselov, K. S., Fal, V., Colombo, L., Gellert, P., Schwab, M., & Kim, K. (2012). A roadmap for graphene. *Nature*, 490(7419), 192-200.
18. Chhowalla, M., Shin, H. S., Eda, G., Li, L.-J., Loh, K. P., & Zhang, H. (2013). The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature chemistry*, 5(4), 263-275.
19. Johari, P., & Shenoy, V. B. (2012). Tuning the electronic properties of semiconducting transition metal dichalcogenides by applying mechanical strains. *ACS nano*, 6(6), 5449-5456.

20. Voiry, D., Goswami, A., Kappera, R., e Silva, C. d. C. C., Kaplan, D., Fujita, T., . . . Chhowalla, M. (2015). Covalent functionalization of monolayered transition metal dichalcogenides by phase engineering. *Nature chemistry*, 7(1), 45-49.
21. Cain, J. D., Shi, F., Wu, J., & Dravid, V. P. (2016). Growth mechanism of transition metal dichalcogenide monolayers: The role of self-seeding fullerene nuclei. *ACS nano*, 10(5), 5440-5445.
22. Pumera, M., Sofer, Z., & Ambrosi, A. (2014). Layered transition metal dichalcogenides for electrochemical energy generation and storage. *Journal of Materials Chemistry A*, 2(24), 8981-8987.
23. Wang, H., Feng, H., & Li, J. (2014). Graphene and Graphene-like Layered Transition Metal Dichalcogenides in Energy Conversion and Storage. *Small*, 10(11), 2165-2181.
24. Kong, D., Cha, J. J., Wang, H., Lee, H. R., & Cui, Y. (2013). First-row transition metal dichalcogenide catalysts for hydrogen evolution reaction. *Energy & Environmental Science*, 6(12), 3553-3558.
25. Voiry, D., Fullon, R., Yang, J., e Silva, C. d. C. C., Kappera, R., Bozkurt, I., . . . Gupta, G. (2016). The role of electronic coupling between substrate and 2D MoS<sub>2</sub> nanosheets in electrocatalytic production of hydrogen. *Nature materials*.
26. Lee, K., Gatensby, R., McEvoy, N., Hallam, T., & Duesberg, G. S. (2013). High-performance sensors based on molybdenum disulfide thin films. *Advanced materials*, 25(46), 6699-6702.
27. Chhowalla, M., Liu, Z., & Zhang, H. (2015). Two-dimensional transition metal dichalcogenide (TMD) nanosheets. *Chemical Society Reviews*, 44(9), 2584-2586.
28. O'Brien, M., Lee, K., Morrish, R., Berner, N. C., McEvoy, N., Wolden, C. A., & Duesberg, G. S. (2014). Plasma assisted synthesis of WS<sub>2</sub> for gas sensing applications. *Chemical Physics Letters*, 615, 6-10.
29. Pumera, M., & Loo, A. H. (2014). Layered transition-metal dichalcogenides (MoS<sub>2</sub> and WS<sub>2</sub>) for sensing and biosensing. *TrAC Trends in Analytical Chemistry*, 61, 49-53.
30. Schaibley, J. R., Yu, H., Clark, G., Rivera, P., Ross, J. S., Seyler, K. L., . . . Xu, X. (2016). Valleytronics in 2D materials. *Nature Reviews Materials*, 1, 16055.
31. Lee, Y. H., Zhang, X. Q., Zhang, W., Chang, M. T., Lin, C. T., Chang, K. D., . . . Li, L. J. (2012). Synthesis of Large-Area MoS<sub>2</sub> Atomic Layers with Chemical Vapor Deposition. *Advanced materials*, 24(17), 2320-2325.
32. Wang, S., Wang, X., & Warner, J. H. (2015). All chemical vapor deposition growth of MoS<sub>2</sub>: h-BN vertical van der Waals heterostructures. *ACS nano*, 9(5), 5246-5254.
33. Qiu, D., Lee, D. U., Pak, S. W., & Kim, E. K. (2015). Structural and optical properties of MoS<sub>2</sub> layers grown by successive two-step chemical vapor deposition method. *Thin Solid Films*, 587, 47-51.
34. Wang, S., Rong, Y., Fan, Y., Pacios, M., Bhaskaran, H., He, K., & Warner, J. H. (2014). Shape evolution of monolayer MoS<sub>2</sub> crystals grown by chemical vapor deposition. *Chemistry of Materials*, 26(22), 6371-6379.
35. Ling, X., Lee, Y.-H., Lin, Y., Fang, W., Yu, L., Dresselhaus, M. S., & Kong, J. (2014). Role of the seeding promoter in MoS<sub>2</sub> growth by chemical vapor deposition. *Nano letters*, 14(2), 464-472.
36. Kim, I. S., Sangwan, V. K., Jariwala, D., Wood, J. D., Park, S., Chen, K.-S., . . . Jose-Yacamán, M. (2014). Influence of stoichiometry on the optical and electrical properties of chemical vapor deposition derived MoS<sub>2</sub>. *ACS nano*, 8(10), 10551-10558.
37. Kaplan, D., Mills, K., & Swaminathan, V. (2015). *Chemical Vapor Deposition of Atomically-Thin Molybdenum Disulfide (MoS<sub>2</sub>)*. Retrieved from

38. Bilgin, I., Liu, F., Vargas, A., Winchester, A., Man, M. K., Upmanyu, M., . . . Mohite, A. D. (2015). Chemical vapor deposition synthesized atomically thin molybdenum disulfide with optoelectronic-grade crystalline quality. *ACS nano*, 9(9), 8822-8832.
39. Schulz, M. (1999). The end of the road for silicon? *Nature*, 399(6738), 729-730.
40. Keyes, R. W. (2005). Physical limits of silicon transistors and circuits. *Reports on Progress in Physics*, 68(12), 2701.
41. Chen, Z., Johnson, M., Wei, L., & Roy, K. (1998). *Estimation of standby leakage power in CMOS circuits considering accurate modeling of transistor stacks*. Paper presented at the Proceedings of the 1998 international symposium on Low power electronics and design.
42. Chan, T., Chen, J., Ko, P., & Hu, C. (1987). *The impact of gate-induced drain leakage current on MOSFET scaling*. Paper presented at the Electron Devices Meeting, 1987 International.
43. Datta, S., Assad, F., & Lundstrom, M. S. (1998). The silicon MOSFET from a transmission viewpoint. *Superlattices and Microstructures*, 23(3), 771-780.
44. Wang, L. (2006). *Quantum Mechanical Effects on MOSFET Scaling*. Georgia Institute of Technology.
45. Larsen, P. M. (1980). Industrial applications of fuzzy logic control. *International Journal of Man-Machine Studies*, 12(1), 3-10.
46. Lipp, M., Gruss, D., Spreitzer, R., Maurice, C., & Mangard, S. (2016). *ARMageddon: Cache attacks on mobile devices*. Paper presented at the Proceedings of the 25th USENIX Security Symposium.
47. Holmberg, K., Andersson, P., Nylund, N.-O., Mäkelä, K., & Erdemir, A. (2014). Global energy consumption due to friction in trucks and buses. *Tribology International*, 78, 94-114.
48. Kovach, J., Tsakiris, E., & Wong, L. (1982). *Engine friction reduction for improved fuel economy* (0148-7191). Retrieved from
49. Zhan, Y., Liu, Z., Najmaei, S., Ajayan, P. M., & Lou, J. (2012). Large-area vapor-phase growth and characterization of MoS<sub>2</sub> atomic layers on a SiO<sub>2</sub> substrate. *Small*, 8(7), 966-971.
50. Zhang, J., Yu, H., Chen, W., Tian, X., Liu, D., Cheng, M., . . . Bai, X. (2014). Scalable growth of high-quality polycrystalline MoS<sub>2</sub> monolayers on SiO<sub>2</sub> with tunable grain sizes. *ACS nano*, 8(6), 6024-6030.
51. Dumcenco, D., Ovchinnikov, D., Marinov, K., Lazic, P., Gibertini, M., Marzari, N., . . . Chen, M.-W. (2015). Large-area epitaxial monolayer MoS<sub>2</sub>. *ACS nano*, 9(4), 4611-4620.
52. Koepke, J. C., Wood, J. D., Estrada, D., Ong, Z.-Y., He, K. T., Pop, E., & Lyding, J. W. (2013). Atomic-scale evidence for potential barriers and strong carrier scattering at graphene grain boundaries: a scanning tunneling microscopy study. *ACS nano*, 7(1), 75-86.
53. Snyder, G. J., & Toberer, E. S. (2008). Complex thermoelectric materials. *Nature materials*, 7(2), 105-114.
54. Wang, L., Meric, I., Huang, P., Gao, Q., Gao, Y., Tran, H., . . . Muller, D. (2013). One-dimensional electrical contact to a two-dimensional material. *Science*, 342(6158), 614-617.
55. Liu, Y., Ghosh, R., Wu, D., Ismach, A., Ruoff, R., & Lai, K. (2014). Mesoscale imperfections in MoS<sub>2</sub> atomic layers grown by a vapor transport technique. *Nano letters*, 14(8), 4682-4686.

56. Ji, Q., Kan, M., Zhang, Y., Guo, Y., Ma, D., Shi, J., . . . Liu, Z. (2014). Unravelling orientation distribution and merging behavior of monolayer MoS<sub>2</sub> domains on sapphire. *Nano letters*, 15(1), 198-205.
57. Zhang, Y., Chang, A., Cao, J., Wang, Q., Kim, W., Li, Y., . . . Dai, H. (2001). Electric-field-directed growth of aligned single-walled carbon nanotubes. *Applied physics letters*, 79(19), 3155-3157.
58. Romero, L., & Binions, R. (2013). On the influence of DC electric fields on the aerosol assisted chemical vapor deposition growth of photoactive titanium dioxide thin films. *Langmuir*, 29(44), 13542-13550.
59. Wang, X., & Xia, F. (2015). Van der Waals heterostructures: stacked 2D materials shed light. *Nature materials*, 14(3), 264-265.
60. Novoselov, K., Jiang, D., Schedin, F., Booth, T., Khotkevich, V., Morozov, S., & Geim, A. (2005). Two-dimensional atomic crystals. *Proceedings of the National Academy of Sciences of the United States of America*, 102(30), 10451-10453.
61. Buscema, M., Barkelid, M., Zwiller, V., van der Zant, H. S., Steele, G. A., & Castellanos-Gomez, A. (2013). Large and tunable photothermoelectric effect in single-layer MoS<sub>2</sub>. *Nano letters*, 13(2), 358-363.
62. Mouri, S., Miyauchi, Y., & Matsuda, K. (2013). Tunable photoluminescence of monolayer MoS<sub>2</sub> via chemical doping. *Nano letters*, 13(12), 5944-5948.
63. Tran, V., Soklaski, R., Liang, Y., & Yang, L. (2014). Layer-controlled band gap and anisotropic excitons in few-layer black phosphorus. *Physical Review B*, 89(23), 235319.
64. Mas-Balleste, R., Gomez-Navarro, C., Gomez-Herrero, J., & Zamora, F. (2011). 2D materials: to graphene and beyond. *Nanoscale*, 3(1), 20-30.
65. Fei, R., & Yang, L. (2014). Strain-engineering the anisotropic electrical conductance of few-layer black phosphorus. *Nano letters*, 14(5), 2884-2889.
66. Petrone, N., Chari, T., Meric, I., Wang, L., Shepard, K. L., & Hone, J. (2015). Flexible graphene field-effect transistors encapsulated in hexagonal boron nitride. *ACS nano*, 9(9), 8953-8959.
67. Kappera, R., Voiry, D., Yalcin, S. E., Jen, W., Acerce, M., Torrel, S., . . . Najmaei, S. (2014). Metallic 1T phase source/drain electrodes for field effect transistors from chemical vapor deposited MoS<sub>2</sub>. *Apl Materials*, 2(9), 092516.
68. Sik Hwang, W., Remskar, M., Yan, R., Protasenko, V., Tahy, K., Doo Chae, S., . . . Seabaugh, A. (2012). Transistors with chemically synthesized layered semiconductor WS<sub>2</sub> exhibiting 105 room temperature modulation and ambipolar behavior. *Applied physics letters*, 101(1), 013107.
69. Tao, L., Cinquanta, E., Chiappe, D., Grazianetti, C., Fanciulli, M., Dubey, M., . . . Akinwande, D. (2015). Silicene field-effect transistors operating at room temperature. *Nature nanotechnology*, 10(3), 227-231.
70. Roy, T., Tosun, M., Kang, J. S., Sachid, A. B., Desai, S. B., Hettick, M., . . . Javey, A. (2014). Field-effect transistors built from all two-dimensional material components. *ACS nano*, 8(6), 6259-6264.
71. Kappera, R., Voiry, D., Yalcin, S. E., Branch, B., Gupta, G., Mohite, A. D., & Chhowalla, M. (2014). Phase-engineered low-resistance contacts for ultrathin MoS<sub>2</sub> transistors. *Nature materials*, 13(12), 1128-1134.
72. Krasnozhon, D., Lembke, D., Nyffeler, C., Leblebici, Y., & Kis, A. (2014). MoS<sub>2</sub> transistors operating at gigahertz frequencies. *Nano letters*, 14(10), 5905-5911.
73. Ghatak, S., Pal, A. N., & Ghosh, A. (2011). Nature of electronic states in atomically thin MoS<sub>2</sub> field-effect transistors. *ACS nano*, 5(10), 7707-7712.

74. Mak, K. F., & Shan, J. (2016). Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides. *Nature Photonics*, 10(4), 216-226.
75. Yuan, L., & Huang, L. (2015). Exciton dynamics and annihilation in WS<sub>2</sub> 2D semiconductors. *Nanoscale*, 7(16), 7402-7408.
76. Komsa, H.-P., & Krashenninnikov, A. V. (2012). Effects of confinement and environment on the electronic structure and exciton binding energy of MoS<sub>2</sub> from first principles. *Physical Review B*, 86(24), 241201.
77. Lodahl, P., Van Driel, A. F., Nikolaev, I. S., Irman, A., Overgaag, K., Vanmaekelbergh, D., & Vos, W. L. (2004). Controlling the dynamics of spontaneous emission from quantum dots by photonic crystals. *Nature*, 430(7000), 654-657.
78. Neogi, A., Lee, C.-W., Everitt, H. O., Kuroda, T., Tackeuchi, A., & Yablonovitch, E. (2002). Enhancement of spontaneous recombination rate in a quantum well by resonant surface plasmon coupling. *Physical Review B*, 66(15), 153305.
79. Ma, Y., Dai, Y., Guo, M., Niu, C., Lu, J., & Huang, B. (2011). Electronic and magnetic properties of perfect, vacancy-doped, and nonmetal adsorbed MoSe<sub>2</sub>, MoTe<sub>2</sub> and WS<sub>2</sub> monolayers. *Physical Chemistry Chemical Physics*, 13(34), 15546-15553.
80. Wachter, S., Polyushkin, D. K., Bethge, O., & Mueller, T. (2016). A microprocessor based on a two-dimensional semiconductor. *arXiv preprint arXiv:1612.00965*.
81. Narendra, S. G., & Chandrakasan, A. P. (2006). *Leakage in nanometer CMOS technologies*: Springer Science & Business Media.
82. Thompson, S. (1998). *MOS scaling: Transistor challenges for the 21st century*. Paper presented at the Intel Technology Journal.
83. Kim, N. S., Austin, T., Baauw, D., Mudge, T., Flautner, K., Hu, J. S., . . . Narayanan, V. (2003). Leakage current: Moore's law meets static power. *computer*, 36(12), 68-75.
84. Yazakis, M., Takenaka, S., & Ohshima, H. (1992). Conduction mechanism of leakage current observed in metal-oxide-semiconductor transistors and poly-Si thin-film transistors. *Japanese journal of applied physics*, 31(2R), 206.
85. Olasupo, K., & Hatalis, M. (1996). Leakage current mechanism in sub-micron polysilicon thin-film transistors. *IEEE Transactions on Electron Devices*, 43(8), 1218-1223.
86. Roy, K., Mukhopadhyay, S., & Mahmoodi-Meimand, H. (2003). Leakage current mechanisms and leakage reduction techniques in deep-submicrometer CMOS circuits. *Proceedings of the IEEE*, 91(2), 305-327.
87. Trivedi, K., Yuk, H., Floresca, H. C., Kim, M. J., & Hu, W. (2011). Quantum confinement induced performance enhancement in sub-5-nm lithographic Si nanowire transistors. *Nano letters*, 11(4), 1412-1417.
88. Hu, W., Chen, X., Zhou, X., Quan, Z., & Wei, L. (2006). Quantum-mechanical effects and gate leakage current of nanoscale n-type FinFETs: A 2d simulation study. *Microelectronics journal*, 37(7), 613-619.
89. Cassan, E. (2000). On the reduction of direct tunneling leakage through ultrathin gate oxides by a one-dimensional Schrödinger–Poisson solver. *Journal of applied physics*, 87(11), 7931-7939.
90. Ho, W., Yu, J. C., Lin, J., Yu, J., & Li, P. (2004). Preparation and photocatalytic behavior of MoS<sub>2</sub> and WS<sub>2</sub> nanocluster sensitized TiO<sub>2</sub>. *Langmuir*, 20(14), 5865-5869.
91. Zhou, W., Yin, Z., Du, Y., Huang, X., Zeng, Z., Fan, Z., . . . Zhang, H. (2013). Synthesis of few-layer MoS<sub>2</sub> nanosheet-coated TiO<sub>2</sub> nanobelt heterostructures for enhanced photocatalytic activities. *Small*, 9(1), 140-147.

92. Xiang, Q., Yu, J., & Jaroniec, M. (2012). Synergetic effect of MoS<sub>2</sub> and graphene as cocatalysts for enhanced photocatalytic H<sub>2</sub> production activity of TiO<sub>2</sub> nanoparticles. *Journal of the American Chemical Society*, 134(15), 6575-6578.
93. Zong, X., Yan, H., Wu, G., Ma, G., Wen, F., Wang, L., & Li, C. (2008). Enhancement of photocatalytic H<sub>2</sub> evolution on CdS by loading MoS<sub>2</sub> as cocatalyst under visible light irradiation. *Journal of the American Chemical Society*, 130(23), 7176-7177.
94. Badwal, S. P., Giddey, S., & Munnings, C. (2013). Hydrogen production via solid electrolytic routes. *Wiley Interdisciplinary Reviews: Energy and Environment*, 2(5), 473-487.
95. Trasatti, S. (1972). Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 39(1), 163-184.
96. Voiry, D., Salehi, M., Silva, R., Fujita, T., Chen, M., Asefa, T., . . . Chhowalla, M. (2013). Conducting MoS<sub>2</sub> nanosheets as catalysts for hydrogen evolution reaction. *Nano letters*, 13(12), 6222-6227.
97. Lukowski, M. A., Daniel, A. S., Meng, F., Forticaux, A., Li, L., & Jin, S. (2013). Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS<sub>2</sub> nanosheets. *Journal of the American Chemical Society*, 135(28), 10274-10277.
98. Kibsgaard, J., Chen, Z., Reinecke, B. N., & Jaramillo, T. F. (2012). Engineering the surface structure of MoS<sub>2</sub> to preferentially expose active edge sites for electrocatalysis. *Nature materials*, 11(11), 963-969.
99. Press, R. J., Santhanam, K., Miri, M. J., Bailey, A. V., & Takacs, G. A. (2009). Introduction to hydrogen technology. *Chromatographia*, 69(9), 1145-1145.
100. Ratha, S., & Rout, C. S. (2013). Supercapacitor electrodes based on layered tungsten disulfide-reduced graphene oxide hybrids synthesized by a facile hydrothermal method. *ACS applied materials & interfaces*, 5(21), 11427-11433.
101. Yang, Y., Fei, H., Ruan, G., Xiang, C., & Tour, J. M. (2014). Edge-Oriented MoS<sub>2</sub> Nanoporous Films as Flexible Electrodes for Hydrogen Evolution Reactions and Supercapacitor Devices. *Advanced materials*, 26(48), 8163-8168.
102. Conway, B. E. (1991). Transition from “supercapacitor” to “battery” behavior in electrochemical energy storage. *Journal of the Electrochemical Society*, 138(6), 1539-1548.
103. Kim, S., Konar, A., Hwang, W.-S., Lee, J. H., Lee, J., Yang, J., . . . Choi, J.-Y. (2012). High-mobility and low-power thin-film transistors based on multilayer MoS<sub>2</sub> crystals. *Nature communications*, 3, 1011.
104. Wang, H., Yu, L., Lee, Y.-H., Fang, W., Hsu, A., Herring, P., . . . Kong, J. (2012). *Large-scale 2D electronics based on single-layer MoS<sub>2</sub> grown by chemical vapor deposition*. Paper presented at the Electron Devices Meeting (IEDM), 2012 IEEE International.
105. Casalino, M., Coppola, G., Iodice, M., Rendina, I., & Sirleto, L. (2010). Near-infrared sub-bandgap all-silicon photodetectors: state of the art and perspectives. *Sensors*, 10(12), 10571-10600.
106. Bec, S., Tonck, A., Georges, J.-M., & Roper, G. W. (2004). Synergistic effects of MoDTC and ZDTP on frictional behaviour of tribofilms at the nanometer scale. *Tribology Letters*, 17(4), 797-809.
107. Fleischauer, P. D., & Bauer, R. (1988). Chemical and structural effects on the lubrication properties of sputtered MoS<sub>2</sub> films. *Tribology Transactions*, 31(2), 239-250.
108. Teer, D., Hampshire, J., Fox, V., & Bellido-Gonzalez, V. (1997). The tribological properties of MoS<sub>2</sub>/metal composite coatings deposited by closed field magnetron sputtering. *Surface and Coatings Technology*, 94, 572-577.

109. Spalvins, T. (1982). Morphological and frictional behavior of sputtered MoS<sub>2</sub> films. *Thin Solid Films*, 96(1), 17-24.
110. Wu, W., Wang, L., Li, Y., Zhang, F., Lin, L., Niu, S., . . . Heinz, T. F. (2014). Piezoelectricity of single-atomic-layer MoS<sub>2</sub> for energy conversion and piezotronics. *Nature*, 514(7523), 470-474.
111. Zhu, H., Wang, Y., Xiao, J., Liu, M., Xiong, S., Wong, Z. J., . . . Zhang, X. (2015). Observation of piezoelectricity in free-standing monolayer MoS<sub>2</sub>. *Nature nanotechnology*, 10(2), 151-155.
112. Gao, G., Jiao, Y., Ma, F., Jiao, Y., Waclawik, E., & Du, A. (2015). Charge mediated semiconducting-to-metallic phase transition in molybdenum disulfide monolayer and hydrogen evolution reaction in new 1T' phase. *The Journal of Physical Chemistry C*, 119(23), 13124-13128.
113. Xiao, D., Liu, G.-B., Feng, W., Xu, X., & Yao, W. (2012). Coupled spin and valley physics in monolayers of MoS<sub>2</sub> and other group-VI dichalcogenides. *Physical review letters*, 108(19), 196802.
114. Zhu, Z., Cheng, Y., & Schwingenschlögl, U. (2011). Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors. *Physical Review B*, 84(15), 153402.
115. Splendiani, A., Sun, L., Zhang, Y., Li, T., Kim, J., Chim, C.-Y., . . . Wang, F. (2010). Emerging photoluminescence in monolayer MoS<sub>2</sub>. *Nano letters*, 10(4), 1271-1275.
116. Cheiwchanchamnangij, T., & Lambrecht, W. R. (2012). Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS<sub>2</sub>. *Physical Review B*, 85(20), 205302.
117. Li, H., Yin, Z., He, Q., Li, H., Huang, X., Lu, G., . . . Zhang, H. (2012). Fabrication of single-and multilayer MoS<sub>2</sub> film-based field-effect transistors for sensing NO at room temperature. *Small*, 8(1), 63-67.
118. Eda, G., Yamaguchi, H., Voiry, D., Fujita, T., Chen, M., & Chhowalla, M. (2011). Photoluminescence from chemically exfoliated MoS<sub>2</sub>. *Nano letters*, 11(12), 5111-5116.
119. Li, H., Wu, J., Yin, Z., & Zhang, H. (2014). Preparation and applications of mechanically exfoliated single-layer and multilayer MoS<sub>2</sub> and WSe<sub>2</sub> nanosheets. *Accounts of chemical research*, 47(4), 1067-1075.
120. Joensen, P., Frindt, R., & Morrison, S. R. (1986). Single-layer MoS<sub>2</sub>. *Materials Research Bulletin*, 21(4), 457-461.
121. Plechinger, G., Mann, J., Preciado, E., Barroso, D., Nguyen, A., Eroms, J., . . . Korn, T. (2014). A direct comparison of CVD-grown and exfoliated MoS<sub>2</sub> using optical spectroscopy. *Semiconductor Science and Technology*, 29(6), 064008.
122. Xia, M., Li, B., Yin, K., Capellini, G., Niu, G., Gong, Y., . . . Xie, Y.-H. (2015). Spectroscopic Signatures of AA' and AB Stacking of Chemical Vapor Deposited Bilayer MoS<sub>2</sub>. *ACS nano*, 9(12), 12246-12254.
123. Dungey, K. E., Curtis, M. D., & Penner-Hahn, J. E. (1998). Structural characterization and thermal stability of MoS<sub>2</sub> intercalation compounds. *Chemistry of Materials*, 10(8), 2152-2161.
124. O'Neill, A., Khan, U., & Coleman, J. N. (2012). Preparation of high concentration dispersions of exfoliated MoS<sub>2</sub> with increased flake size. *Chemistry of Materials*, 24(12), 2414-2421.
125. Py, M., & Haering, R. (1983). Structural destabilization induced by lithium intercalation in MoS<sub>2</sub> and related compounds. *Canadian Journal of Physics*, 61(1), 76-84.

126. Schöllhorn, R., & Zagefka, H. D. (1977). Demonstration of the Ionic Structure of the Intercalation Compound  $\text{TaS}_2 \cdot \text{NH}_3$ . *Angewandte Chemie International Edition in English*, 16(3), 199-200.
127. Inoshita, T., Nakao, K., & Kamimura, H. (1977). Electronic structure of potassium-graphite intercalation compound:  $\text{C}_8\text{K}$ . *Journal of the Physical Society of Japan*, 43(4), 1237-1243.
128. Whittingham, M. S. (1976). Electrical energy storage and intercalation chemistry. *Science*, 192(4244), 1126-1127.
129. Silbernagel, B. (1975). Lithium intercalation complexes of layered transition metal dichalcogenides: An NMR survey of physical properties. *Solid state communications*, 17(3), 361-365.
130. Whittingham, M. S., & Gamble, F. R. (1975). The lithium intercalates of the transition metal dichalcogenides. *Materials Research Bulletin*, 10(5), 363-371.
131. Dines, M. B. (1975). Lithium intercalation via n-butyllithium of the layered transition metal dichalcogenides. *Materials Research Bulletin*, 10(4), 287-291.
132. Heising, J., & Kanatzidis, M. G. (1999). Structure of restacked  $\text{MoS}_2$  and  $\text{WS}_2$  elucidated by electron crystallography. *Journal of the American Chemical Society*, 121(4), 638-643.
133. Fan, X., Xu, P., Zhou, D., Sun, Y., Li, Y. C., Nguyen, M. A. T., . . . Mallouk, T. E. (2015). Fast and efficient preparation of exfoliated 2H  $\text{MoS}_2$  nanosheets by sonication-assisted lithium intercalation and infrared laser-induced 1T to 2H phase reversion. *Nano letters*, 15(9), 5956-5960.
134. Coleman, J. N., Lotya, M., O'Neill, A., Bergin, S. D., King, P. J., Khan, U., . . . Smith, R. J. (2011). Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science*, 331(6017), 568-571.
135. Finn, D. J., Lotya, M., Cunningham, G., Smith, R. J., McCloskey, D., Donegan, J. F., & Coleman, J. N. (2014). Inkjet deposition of liquid-exfoliated graphene and  $\text{MoS}_2$  nanosheets for printed device applications. *Journal of Materials Chemistry C*, 2(5), 925-932.
136. Zeng, Z., Yin, Z., Huang, X., Li, H., He, Q., Lu, G., . . . Zhang, H. (2011). Single-layer semiconducting nanosheets: high-yield preparation and device fabrication. *Angewandte Chemie International Edition*, 50(47), 11093-11097.
137. Bang, G. S., Nam, K. W., Kim, J. Y., Shin, J., Choi, J. W., & Choi, S.-Y. (2014). Effective liquid-phase exfoliation and sodium ion battery application of  $\text{MoS}_2$  nanosheets. *ACS applied materials & interfaces*, 6(10), 7084-7089.
138. Smith, R. J., King, P. J., Lotya, M., Wirtz, C., Khan, U., De, S., . . . Moriarty, G. (2011). Large-scale exfoliation of inorganic layered compounds in aqueous surfactant solutions. *Advanced materials*, 23(34), 3944-3948.
139. Lopez-Sanchez, O., Lembke, D., Kayci, M., Radenovic, A., & Kis, A. (2013). Ultrasensitive photodetectors based on monolayer  $\text{MoS}_2$ . *Nature nanotechnology*, 8(7), 497-501.
140. Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N., & Strano, M. S. (2012). Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature nanotechnology*, 7(11), 699-712.
141. Shi, Y., Zhou, W., Lu, A.-Y., Fang, W., Lee, Y.-H., Hsu, A. L., . . . Li, L.-J. (2012). van der Waals epitaxy of  $\text{MoS}_2$  layers using graphene as growth templates. *Nano letters*, 12(6), 2784-2791.
142. Song, J.-G., Park, J., Lee, W., Choi, T., Jung, H., Lee, C. W., . . . Kim, S.-H. (2013). Layer-controlled, wafer-scale, and conformal synthesis of tungsten disulfide nanosheets using atomic layer deposition. *ACS nano*, 7(12), 11333-11340.

143. Muratore, C., Hu, J., Wang, B., Haque, M. A., Bultman, J. E., Jespersen, M. L., . . . Voevodin, A. (2014). Continuous ultra-thin MoS<sub>2</sub> films grown by low-temperature physical vapor deposition. *Applied physics letters*, 104(26), 261604.
144. Late, D. J., Shaikh, P. A., Khare, R., Kashid, R. V., Chaudhary, M., More, M. A., & Ogale, S. B. (2014). Pulsed laser-deposited MoS<sub>2</sub> thin films on W and Si: field emission and photoresponse studies. *ACS applied materials & interfaces*, 6(18), 15881-15888.
145. Siegel, G., Venkata Subbaiah, Y., Prestgard, M. C., & Tiwari, A. (2015). Growth of centimeter-scale atomically thin MoS<sub>2</sub> films by pulsed laser deposition. *Apl Materials*, 3(5), 056103.
146. Peng, Y., Meng, Z., Zhong, C., Lu, J., Yu, W., Jia, Y., & Qian, Y. (2001). Hydrothermal synthesis and characterization of single-molecular-layer MoS<sub>2</sub> and MoSe<sub>2</sub>. *Chemistry Letters*, 30(8), 772-773.
147. Tsai, M.-L., Su, S.-H., Chang, J.-K., Tsai, D.-S., Chen, C.-H., Wu, C.-I., . . . He, J.-H. (2014). Monolayer MoS<sub>2</sub> heterojunction solar cells. *ACS nano*, 8(8), 8317-8322.
148. Van Der Zande, A. M., Huang, P. Y., Chenet, D. A., Berkelbach, T. C., You, Y., Lee, G.-H., . . . Hone, J. C. (2013). Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide. *Nature materials*, 12(6), 554-561.
149. Cheng, J., Jiang, T., Ji, Q., Zhang, Y., Li, Z., Shan, Y., . . . Wu, S. (2015). Kinetic Nature of Grain Boundary Formation in As-Grown MoS<sub>2</sub> Monolayers. *Advanced materials*, 27(27), 4069-4074.
150. Senthilkumar, V., Tam, L. C., Kim, Y. S., Sim, Y., Seong, M.-J., & Jang, J. I. (2014). Direct vapor phase growth process and robust photoluminescence properties of large area MoS<sub>2</sub> layers. *Nano research*, 7(12), 1759-1768.
151. Hell, S. W. (2007). Far-field optical nanoscopy. *Science*, 316(5828), 1153-1158.
152. Gustafsson, M. G. (2000). Surpassing the lateral resolution limit by a factor of two using structured illumination microscopy. *Journal of microscopy*, 198(2), 82-87.
153. Klar, T. A., Engel, E., & Hell, S. W. (2001). Breaking Abbe's diffraction resolution limit in fluorescence microscopy with stimulated emission depletion beams of various shapes. *Physical Review E*, 64(6), 066613.
154. Zhang, X., & Liu, Z. (2008). Superlenses to overcome the diffraction limit. *Nature materials*, 7(6), 435-441.
155. Betzig, E., & Trautman, J. K. (1992). Near-field optics: microscopy, spectroscopy, and surface modification beyond the diffraction limit. *Science*, 257(5067), 189-196.
156. Zhang, H., Ma, Y., Wan, Y., Rong, X., Xie, Z., Wang, W., & Dai, L. (2015). Measuring the refractive index of highly crystalline monolayer MoS<sub>2</sub> with high confidence. *Scientific reports*, 5.
157. Mak, K. F., Lee, C., Hone, J., Shan, J., & Heinz, T. F. (2010). Atomically thin MoS<sub>2</sub>: a new direct-gap semiconductor. *Physical review letters*, 105(13), 136805.
158. Colthup, N. (2012). *Introduction to infrared and Raman spectroscopy*: Elsevier.
159. Lee, C., Yan, H., Brus, L. E., Heinz, T. F., Hone, J., & Ryu, S. (2010). Anomalous lattice vibrations of single-and few-layer MoS<sub>2</sub>. *ACS nano*, 4(5), 2695-2700.
160. Liu, K., Zhang, L., Cao, T., Jin, C., Qiu, D., Zhou, Q., . . . Wang, F. (2014). Evolution of Interlayer Coupling in Twisted MoS<sub>2</sub> Bilayers. *arXiv preprint arXiv:1406.6487*.
161. Amani, M., Lien, D.-H., Kiriya, D., Xiao, J., Azcatl, A., Noh, J., . . . Dubey, M. (2015). Near-unity photoluminescence quantum yield in MoS<sub>2</sub>. *Science*, 350(6264), 1065-1068.
162. Bera, A., & Sood, A. (2014). Insights into Vibrational and Electronic Properties of MoS<sub>2</sub> Using Raman, Photoluminescence, and Transport Studies *MoS<sub>2</sub>* (pp. 155-215): Springer.

163. Ellis, J. K., Lucero, M. J., & Scuseria, G. E. (2011). The indirect to direct band gap transition in multilayered MoS<sub>2</sub> as predicted by screened hybrid density functional theory. *Applied physics letters*, 99(26), 261908.
164. Williams, D. B., & Carter, C. B. (1996). The transmission electron microscope *Transmission electron microscopy* (pp. 3-17): Springer.
165. Watts, J. F. (1994). X-ray photoelectron spectroscopy. *Vacuum*, 45(6-7), 653-671.
166. Binnig, G., Quate, C. F., & Gerber, C. (1986). Atomic force microscope. *Physical review letters*, 56(9), 930.
167. Freund, J., Halbritter, J., & Hörber, J. (1999). How dry are dried samples? Water adsorption measured by STM. *Microscopy research and technique*, 44(5), 327-338.
168. Asay, D. B., & Kim, S. H. (2006). Effects of adsorbed water layer structure on adhesion force of silicon oxide nanoasperity contact in humid ambient. *The Journal of chemical physics*, 124(17), 174712.
169. Zitzler, L., Herminghaus, S., & Mugele, F. (2002). Capillary forces in tapping mode atomic force microscopy. *Physical Review B*, 66(15), 155436.
170. Castellanos-Gomez, A., Cappelluti, E., Roldán, R., Agraït, N., Guinea, F., & Rubio-Bollinger, G. (2013). Electric-Field Screening in Atomically Thin Layers of MoS<sub>2</sub>: the Role of Interlayer Coupling. *Advanced materials*, 25(6), 899-903.
171. Maboudian, R., Ashurst, W. R., & Carraro, C. (2002). Tribological challenges in micromechanical systems. *Tribology Letters*, 12(2), 95-100.
172. Carpick, R., Agraït, N., Ogletree, D., & Salmeron, M. (1996). Variation of the interfacial shear strength and adhesion of a nanometer-sized contact. *Langmuir*, 12(13), 3334-3340.
173. Carpick, R. W., Agraït, N., Ogletree, D., & Salmeron, M. (1996). Measurement of interfacial shear (friction) with an ultrahigh vacuum atomic force microscope. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, 14(2), 1289-1295.
174. Carpick, R. W., & Salmeron, M. (1997). Scratching the surface: fundamental investigations of tribology with atomic force microscopy. *Chemical Reviews*, 97(4), 1163-1194.
175. Leonhardt, U. (2010). Comment on ‘Quantum Friction—Fact or Fiction?’. *New Journal of Physics*, 12(6), 068001.
176. Intravaia, F., Behunin, R., & Dalvit, D. (2014). Quantum friction and fluctuation theorems. *Physical Review A*, 89(5), 050101.
177. Intravaia, F., Behunin, R., Henkel, C., Busch, K., & Dalvit, D. (2016). Failure of local thermal equilibrium in quantum friction. *Physical review letters*, 117(10), 100402.
178. Silveirinha, M. G. (2014). Theory of quantum friction. *New Journal of Physics*, 16(6), 063011.
179. Farias, M. B., Fosco, C. D., Lombardo, F. C., & Mazzitelli, F. D. (2017). Quantum friction between graphene sheets. *Physical Review D*, 95(6), 065012.
180. Wang, T.-B., Liu, N.-H., Liu, J.-T., & Yu, T.-B. (2014). Quantum friction controlled by plasmons between graphene sheets. *The European Physical Journal B*, 87(8), 1-5.
181. Wu, W., De, D., Chang, S.-C., Wang, Y., Peng, H., Bao, J., & Pei, S.-S. (2013). High mobility and high on/off ratio field-effect transistors based on chemical vapor deposited single-crystal MoS<sub>2</sub> grains. *Applied physics letters*, 102(14), 142106.
182. Li, H., Zhang, Q., Yap, C. C. R., Tay, B. K., Edwin, T. H. T., Olivier, A., & Baillargeat, D. (2012). From bulk to monolayer MoS<sub>2</sub>: evolution of Raman scattering. *Advanced Functional Materials*, 22(7), 1385-1390.

183. Schmidt, H., Wang, S., Chu, L., Toh, M., Kumar, R., Zhao, W., . . . Özyilmaz, B. (2014). Transport properties of monolayer MoS<sub>2</sub> grown by chemical vapor deposition. *Nano letters*, 14(4), 1909-1913.
184. Li, H., Tsai, C., Koh, A. L., Cai, L., Contryman, A. W., Fragapane, A. H., . . . Abild-Pedersen, F. (2016). Activating and optimizing MoS<sub>2</sub> basal planes for hydrogen evolution through the formation of strained sulphur vacancies. *Nature materials*, 15(1), 48-53.
185. Yu, Y., Huang, S.-Y., Li, Y., Steinmann, S. N., Yang, W., & Cao, L. (2014). Layer-dependent electrocatalysis of MoS<sub>2</sub> for hydrogen evolution. *Nano letters*, 14(2), 553-558.
186. Meyer, B. (1976). Elemental sulfur. *Chemical Reviews*, 76(3), 367-388.
187. Yoo, Y., Degregorio, Z. P., & Johns, J. E. (2015). Seed crystal homogeneity controls lateral and vertical heteroepitaxy of monolayer MoS<sub>2</sub> and WS<sub>2</sub>. *Journal of the American Chemical Society*, 137(45), 14281-14287.
188. Tongay, S., Fan, W., Kang, J., Park, J., Koldemir, U., Suh, J., . . . Li, J. (2014). Tuning interlayer coupling in large-area heterostructures with CVD-grown MoS<sub>2</sub> and WS<sub>2</sub> monolayers. *Nano letters*, 14(6), 3185-3190.
189. Lee, J.-U., Kim, K., Han, S., Ryu, G. H., Lee, Z., & Cheong, H. (2016). Raman signatures of polytypism in molybdenum disulfide. *ACS nano*, 10(2), 1948-1953.
190. Kam, K., & Parkinson, B. (1982). Detailed photocurrent spectroscopy of the semiconducting group VIB transition metal dichalcogenides. *The Journal of Physical Chemistry*, 86(4), 463-467.
191. Forticaux, A., Dang, L., Liang, H., & Jin, S. (2015). Controlled synthesis of layered double hydroxide nanoplates driven by screw dislocations. *Nano letters*, 15(5), 3403-3409.
192. Van Rossum, G., & Drake, F. L. (2003). *Python language reference manual: Network Theory*.
193. Li, Q., Lee, C., Carpick, R. W., & Hone, J. (2010). Substrate effect on thickness-dependent friction on graphene. *physica status solidi (b)*, 247(11-12), 2909-2914.