Isolation, Identification, and Characterization of Molybdenum Disulfide Atomically Thin Layers

Alex Freedman
Dravid Group
Department of Materials Science and Engineering
Northwestern University
10 June 2013
Isolation, Identification, and Characterization of Molybdenum Disulfide Atomically Thin Layers

Alex Freedman
Dravid Group
Department of Materials Science and Engineering
Northwestern University
10 June 2013

Summary

In this report, a methodology to isolate, identify, and characterize atomically thin layered materials such as MoS$_2$ is presented. MoS$_2$ exhibits drastically different properties when atomically thin as compared to bulk, so it is necessary to develop such a methodology to perform reliable and repeatable measurements exploring these properties.

Synthesis is done using micromechanical exfoliation and chemical vapor deposition growth. Though chemical vapor deposition is much more efficient for obtaining monolayer flakes, it is a much more complicated method requiring additional infrastructure and optimization. Also, the triangular shape of the flakes presents additional contacting challenges. A combination of optical microscopy, atomic force microscopy, and Raman spectroscopy are used to identify and characterize thin flakes. Thin flakes can be identified on the substrate using optical contrast. Flakes that have been identified this way can be further characterized using AFM to confirm their thickness. Raman spectroscopy can further confirm the thickness and the electronic quality of the flake. Contacts can be patterned using e-beam lithography and thermal evaporation. The EBL is used to design and pattern contacts based on the constraints of each flake. Ti/Au contacts deposited with thermal evaporation ideally give high-quality, Ohmic contacts. Experimentally, the contacts made this way proved to be Schottky type, but this may due to contamination or damage to the flake during the patterning process. The transport measurements that can be performed depend on the contact geometry. The four-point probe configuration allows for I-V characterization of FET devices and the isolation of sheet and contact resistance. The van der Pauw configuration allows for Hall effect and mobility measurements in addition to contact and sheet resistance measurements.
# Table of Contents

Summary .......................................................................................................................... i
Table of Contents ........................................................................................................... ii
Introduction ...................................................................................................................... 1
   Overview ...................................................................................................................... 1
   Background ............................................................................................................... 1
   Purpose ..................................................................................................................... 3
Methods ............................................................................................................................. 4
   MoS\textsubscript{2} Synthesis .......................................................................................... 4
      Micromechanical Exfoliation ............................................................................... 4
      Chemical Vapor Deposition ................................................................................. 5
   Characterization ......................................................................................................... 6
      Optical Microscopy ............................................................................................... 6
      Atomic Force Microscopy ................................................................................... 7
      Raman Spectroscopy ............................................................................................ 8
   Contact Fabrication ................................................................................................... 9
      Electron Beam Lithography ............................................................................... 10
      Thermal Evaporation ......................................................................................... 12
      Contact Geometry ............................................................................................... 14
Results and Discussion .................................................................................................... 16
   Exfoliated Samples .................................................................................................. 16
   CVD Grown Samples ............................................................................................. 19
Conclusion ....................................................................................................................... 23
Acknowledgements ....................................................................................................... 23
References ...................................................................................................................... 24
Introduction

Overview

Two-dimensional (2D) materials have been some of the most comprehensively studied materials in the past decade due to the abundance of unusual physical phenomena that arise when charge and heat transport are confined in a plane. This new effort into exploring 2D materials, begun by the work on graphene by Novoselov and Geim in 2004, has led to significant interest in the transition metal chalcogenides (TMCs) due to their ease of synthesis and their suitability for nanoelectronic devices\(^1\). MoS\(_2\) is a TMC of particular significance since it possesses a bandgap of around 1.8eV\(^2\), making it suitable for field effect transistor (FET) and optoelectronic applications\(^3\). MoS\(_2\)-nanoparticle composites offer a promising and as-yet unexplored avenue for understanding charge transport and surface interactions in 2D materials. This project develops a methodology for isolation, identification, and characterization of MoS\(_2\) and other 2D layered materials.

Background

Many 2D materials exist as stacks of strongly bonded layers with weak interlayer bonding in bulk form. Graphene, a conducting 2D material with a wealth of novel physics, is the most well-known of these, but others with different electronic characteristics exist in abundance. Transitional metal chalcogenides are a class of such materials that exhibit a wide range of electronic, optical, and mechanical properties\(^3\). Recent advances in sample preparation and nanofabrication have prompted renewed interest in these materials. Unlike graphene, TMCs such as MoS\(_2\) have a bandgap, making them suitable for FETs and other electronic devices.

MoS\(_2\) is a typical member of the TMC family. Crystals of MoS\(_2\) are comprised of vertically stacked, weakly interacting layers held together by van der Waals forces, just as graphene is. The atoms within each layer are covalently bonded in hexagonally packed MoS\(_6\) trigonal prisms, essentially resulting in an S-Mo-S “sandwich” (Fig. 1). The weak van der Waals interlayer bonding, the energy of which is on the order of 50meV, allows for easy micromechanical exfoliation (“scotch-tape method”) of large area, high-quality, atomically thin crystals. The structure of MoS\(_2\) gives rise to its notable mechanical and electronic properties.

![Figure 1. MoS2 Structure\(^4\)](image)
MoS$_2$ has exceptional mechanical strength, making it attractive for use in flexible electronics and optoelectronic devices. The Young’s modulus of MoS$_2$ nanosheets was found to be $0.33\pm0.07$ TPa. The nanosheets were also found to have low pre-strain and high strength and were able to undergo elastic deformations of tens of nanometers without breaking (Fig. 2)$^5$. These mechanical properties mean that it is possible to make flexible, high-mobility FETs. Potential applications include flexible screens and digital “paper”$^6$.

Bulk MoS$_2$ is an indirect bandgap semiconductor with bandgap energy of 1.2eV$^7$. With decreasing thickness, the indirect gap, which is lower in energy than the direct gap in bulk MoS$_2$, shifts upwards in energy by more than 0.6eV due to dimensional confinement effects as the material becomes 2D. This change in energy causes a crossover to a direct gap material in monolayers of MoS$_2$, since the electronic states near the K-point in the Brillouin zone are more localized within the layer and only slightly shift up in energy with decreasing layer thickness (Fig. 2)$^8$. As a result of this crossover, the monolayer material exhibits bright photoluminescence$^9$.

![Figure 2. Band structure of MoS2 in a) bulk, b) 4 layer, c) 2 layer, and d) monolayer forms$^9$](image)

One of the most important applications for semiconductor materials is in transistors for digital electronics. MoS$_2$ shows great promise for use in transistors. Non-equilibrium Green’s function transport calculations show an extremely large maximum on/off ratio of $10^{10}$ and a near-immunity to short channel effects due to the atomic layer thickness$^{10}$. The first implementation of a top-gated MoS$_2$ FET (Fig. 3) showed excellent on/off ratio of $10^8$, a mobility of 200 cm$^2$V$^{-1}$s$^{-1}$, and n-type conduction. This study used HfO$_2$, a high-$\kappa$ dielectric, as a top-gate to improve mobility and to reduce the voltage needed to switch the device$^4$. The same researchers also demonstrated that they could build basic integrated circuits capable of performing digital logical operations using MoS$_2$$^{11}$. MoS$_2$ transistors show hysteretic effects under ambient environment. It has been shown that these effects are due to absorption of water on the surface. Passivation with Si$_3$N$_4$ was shown to eliminate these effects$^{12}$. Due to its photosensitivity, there has been an
interest in MoS$_2$ based optoelectronics. Monolayer MoS$_2$ has been used to fabricate a phototransistor with fast photoswitching and good photoresponsivity$^{13}$.

![Top-gated MoS$_2$ FET with HfO$_2$ top gate dielectric](image)

Figure 3. Top-gated MoS$_2$ FET with HfO$_2$ top gate dielectric$^4$

The high surface-to-volume ratio of MoS$_2$ and other TMCs make them especially sensitive to changes in their surroundings. Exposure to various gases can lead to changes in charge transfer, doping, permittivity, and lattice vibrations. Changes to the electronic properties can be detected electrically by measuring changes in the I-V characteristics of TMC-based transistor devices or optically by measuring changes in Raman spectra, photoluminescence, or absorbance$^3$. Transistors made from MoS$_2$ have been shown to be sensitive detectors for NO and NO$_2$ gases$^{14}$. The humidity dependent hysteresis in MoS$_2$ transistors can also be used to measure humidity$^{12}$.

**Purpose**

The goal of this project was to develop a methodology for isolating and identifying MoS$_2$ atomic layers and for creating devices and performing transport measurements on these layers. This method includes synthesis, characterization, and device fabrication. While this project focused on MoS$_2$, the method should be effective with only minor modification for use with other layered materials such as graphene, GaS, WS$_2$, and other similar materials. Devices made using this method can provide information about contact resistance, sheet resistance, FET performance, mobility, and Hall coefficient. The devices could also be tested under various conditions, such as illumination, nanoparticle decoration, and gas exposure, to see how electron transport is affected. These experiments would indicate how device performance and electron transport change based on these interactions and hopefully give information about the underlying mechanisms. This information could suggest avenues for future research and lead to the development of new applications for MoS$_2$ and other similar layered materials.
Methods

MoS\textsubscript{2} Synthesis

The goal of the synthesis processes was to obtain high-quality thin MoS\textsubscript{2} sheets at least 10µm by 10µm in area to facilitate patterning and to allow for accurate transport measurements. Solution-based methods produce flakes that are too small and high in defects to be used. Though solution-based methods are less complicated and more consistent, the flakes obtained through these methods are usually less than 1µm in size\textsuperscript{1}. Both micromechanical exfoliation and chemical vapor deposition (CVD) synthesis methods were used to obtain MoS\textsubscript{2} nanosheets of sufficient size for this project. The CVD samples were provided by the Ajayan Research Group at Rice University. All samples were deposited on 285nm SiO\textsubscript{2} on doped Si substrates.

Micromechanical Exfoliation

The micromechanical exfoliation method, commonly known as the scotch-tape method, was pioneering by Novoselov and Geim in their original work on graphene. Since this method requires little infrastructure and material, this is the primary synthesis method used in the Dravid Group. The substrates are prepared by dicing them into approximately 1cm by 1cm pieces and by cleaning them with ultrasonication for 15 minutes in consecutive acetone, isopropanol, and deionized water baths and then with Ar/O\textsubscript{2} plasma at 50W for 5 minutes in an SBT PC2000 plasma cleaner. This process removes any contaminants on the surface. To exfoliate the MoS\textsubscript{2}, a piece of ordinary scotch-tape is applied to the surface of a single crystal of MoS\textsubscript{2} and peeled off. The tape is then applied to the substrate and carefully peeled back by applying force as close as possible to parallel with the substrate surface to minimize adhesive residue. This method yields relatively large area and very low defect flakes (Fig. 4). However, the shapes are very irregular, and the thicknesses are non-uniform. In addition, the yield is very low, as most of the flakes are quite thick, usually tens or hundreds of layers. Exfoliating MoS\textsubscript{2} and searching for thin flakes using optical contrast is quite inefficient and time-consuming.
Figure 4. Optical micrograph of a typical micromechanically exfoliated MoS$_2$ sample on 285nm SiO$_2$ on Si. The thickness of the flake decreases as the color changes from gold (>50 layers) to metallic green (~10-50 layers) to deep green (<10 layers).

Chemical Vapor Deposition

While chemical vapor deposition synthesis requires more equipment and is a much more complicated process, the yield and consistency are greatly superior to that of the micromechanical exfoliation method. The VPD Group has not optimized the parameters for efficient CVD growth of MoS$_2$, so all CVD grown samples are provided by the Ajayan Research Group at Rice University. In this method, a ~1-5nm layer of Mo is pre-deposited on the SiO$_2$/Si substrate using an e-beam evaporator. The substrates are placed in a ceramic boat in the center of a tube furnace. Another ceramic boat containing sulfur powder is placed upwind in the low-temperature zone, the temperature of which is maintained just above the melting point of sulfur (113°C). N$_2$ flowing at 150-200 sccm is used as the carrier gas. After 15 minutes of N$_2$ purging, the furnace temperature is slowly increased to 500°C over a period of 30 minutes. The temperature is then increased to 750°C over 90 minutes and is held there for 10 minutes before being cooled back to room temperature of a period of 120 minutes. The flakes grown with this method are very uniform, usually 1-2 layers, approximately in the shape of equilateral triangles with blunted corners that can reach up to 20µm per side (Fig. 5). This shape mirrors the underlying crystal symmetry. The MoS$_2$ produced by this method is of high electronic quality with a low defect density.
Characterization

Once the MoS\(_2\) has been synthesized, it is necessary to locate thin flakes and quantitatively determine their thickness. It is especially important for mechanically exfoliated samples to have a fast, accurate method to differentiate flakes based on their thickness since the flakes vary widely in thickness and to have an accurate method to quantitatively confirm the thickness and uniformity. A combination of optical microscopy, atomic force microscopy (AFM), and Raman spectroscopy is used to accurately determine the thickness of MoS\(_2\) flakes.

**Optical Microscopy**

Optical contrast can be used to differentiate MoS\(_2\) flakes on SiO\(_2\)/Si substrates based on thickness (Fig. 6). Late et al found that the level of contrast depends on the thickness of the oxide layer and that the optimal oxide thickness for identifying MoS\(_2\) is ~250-300nm. The choice of 285nm SiO\(_2\) on Si substrates is based on this effect. On 285nm SiO\(_2\)/Si substrates, monolayer flakes appear as a nearly translucent purple. As thickness increases, the color changes from purple to green to gold as a result of optical interference effects with the oxide layer.

Figure 5. Optical micrograph of CVD-grown MoS\(_2\) flake
This technique is especially important for the mechanically exfoliated samples to locate viable flakes, namely those of sufficient thinness and area, for further investigation. Samples are manually scanned for viable flakes at 200x magnification. Images are taken at 1000x to get a detailed image of the flake of interest and at 200x and 50x to be able to locate the flake again for subsequent measurements. Promising flakes are further characterized using AFM and Raman spectroscopy. For CVD grown samples, large-area thin flakes are very common. Optical microscopy is used to locate especially large triangular flakes that are relatively isolated from other flakes to simplify device patterning.

![Figure 6. Thickness dependence of color and contrast in optical microscopy](image)

**Figure 6.** Thickness dependence of color and contrast in optical microscopy

Atomic Force Microscopy

Once a flake of interest has been located using optical microscopy, the exact thickness needs to be confirmed. Standard tapping mode atomic force microscopy (AFM) is a scanning probe microscopy technique that non-destructively provides very precise measurements in the z-
direction. AFM can quantitatively determine the thickness of MoS$_2$ down to the individual layer. It provides a 2D height map of the flake (Fig. 8). Analysis software is used to perform specific quantitative measurements on the height maps. Usually, AFM is sufficient to characterize the thickness and any irregularities such as cracks.

![AFM Height Map of MoS$_2$ Flake](image)

**Figure 8.** AFM height map of a mechanically exfoliated MoS$_2$ flake

**Raman Spectroscopy**

Raman spectroscopy is another useful technique for quantitatively determining layer thickness. It relies on inelastic scattering of monochromatic light from a laser. The laser interacts with phonons and other vibrations in the system, resulting in the energy of the photons being shifted up or down. With varying layer thickness between bulk, few, and single layer flakes, the Raman spectra differ in spectral width and intensity. There is also a Raman shift as a function of the thickness, which allows the thickness to be determined (Fig. 9). The system used for this report utilizes a 514.5nm laser. It is necessary to use a low laser power to prevent sample decomposition in monolayers.
Since the laser can potentially destroy the sample, Raman spectroscopy is not always used if the AFM results are conclusive. Once the spectrum is recorded (Fig. 10), the peak locations can be compared against known values for specific thicknesses.

Contact Fabrication

Once a flake of suitable thinness and size is found, contacts must be fabricated in order to perform transport measurements and obtain data. Contacting 2D flakes about 10µm by 10µm in size presents special challenges in terms of fabrication and processing. The flakes are
relatively fragile, and the contact geometries must be quite precise in order to obtain reliable data. Since all the flakes are different shapes and since the area of interest may not be isolated from thicker parts of the flake, any contacting technique must allow for simple and quick pattern design and implementation. The technique that best meets these constraints is electron beam lithography (EBL).

**Electron Beam Lithography**

Electron beam lithography works by using the electron beam from a scanning electron microscope (SEM) to break crosslinks in a polymer coating on top of the sample in the desired pattern. The exposed regions of resist are then developed. Metal can then be deposited on top, and the resist can be dissolved away and the unnecessary metal lifted off leaving metal in the desired pattern. The resist used for this project is PMMA. The PMMA is dissolved in anisole and spin-coated onto the substrate. A two layer coating is used to aid in the lift-off process. The lower layer is a lower molecular weight PMMA (N = 495,000), which is more easily dissolved after exposure to the electron beam. The top layer is a higher molecular weight PMMA (N = 950,000). Once the resist is developed, this configuration gives some undercut in the low molecular weight layer (Fig. 11). This results in better metal deposition and more reliable lift-off.

![Figure 11. The two-layer resist coating results in undercut in the bottom layer.](image)

Each resist layer is pipetted onto the substrate and spin-coated at 4000rpm for 30s. The substrate is then annealed for 1 minute on a hot plate at 170°C to evaporate any remaining solvent.

The pattern is designed using DesignCAD LT software to give the optimal contacts for each flake. Once the design is complete, the electron beam from the SEM is used to write the pattern in the resist. The exposure dose must be carefully controlled to ensure that the exposed resist does not under- or overdevelop. To determine the correct dose for a given resist coating, a dose array can be constructed. A dose array contains a shape of similar dimensions to the intended pattern repeated at incrementally changing doses. Once this is performed, the developed resist can be examined to find the optimal dose. For the resist coating used in this report, the optimal dose was found to be around 450 µC/cm² (Fig. 12).
Figure 12. Dose array showing the optimal dose for EBL

The flakes are not visible under the PMMA since the PMMA is not electron-transparent. To ensure proper alignment of the pattern on the flake, it is necessary to measure distance from a visible landmark. A scratch on the substrate made using a diamond scriber can serve as a rough guide, but a more accurate landmark closer to the flake is needed to align the pattern. Measuring from the tip of the scratch, an initial set of markers is created closer to the flake but not contacting the flake (Fig. 13). Gold is used for these markers, since the difference in atomic number between gold and silicon provides enough Z contrast to be visible even under the resist.

Figure 13. Markers patterned around thin flake to provide landmarks during EBL
Once the markers are deposited, the contact pattern can be designed based on distance measurements between the flake and the markers. Once the design is done, the contact pattern can be written and developed. The development process works by submerging the substrate in a 3:1 isopropanol and methyl isobutyl ketone solution for 1 minute to dissolve away the exposed resist. Since the exposed resist has a lower degree of polymerization, it is more soluble in the developer solution. Once the pattern is developed, it can be checked for alignment and sufficient exposure using optical microscopy (Fig. 14). At this point, the sample is ready for metal deposition.

**Figure 14. Contact pattern written into resist**

*Thermal Evaporation*

Metal deposition on the EBL-patterned substrates is done using a thermal evaporation system. This system uses resistive heating to evaporate metal atoms from a solid source. The evaporated atoms travel across the vacuum chamber and hit the substrates, which are attached to a water-cooled plate (Fig. 15).
The thermal evaporation system allows multiple metals to be deposited sequentially. To contact MoS$_2$, a 5nm Ti/50nm Au is used. The Ti work function aligns well with the conduction band of MoS$_2$, which is important for forming an Ohmic contact. Ohmic contacts are necessary to get reliable results from the device. The Au layer is more conductive and acts as a capping layer to prevent oxidation of the Ti. Once the metal is deposited, the resist and the extra metal on top of it must be removed. This liftoff process is completed in two steps (Fig. 16). First, the sample is submerged in acetone in a vial for 1 hour. This dissolves the PMMA and breaks up the surface of the undesired metal. Then, the vial is agitated by manually moving it in a circular motion. This completes the process of separating the PMMA and extra metal from the surface, leaving only the patterned metal on the surface.
Figure 16. The liftoff process consists of two steps. The 1) substrate is placed in acetone for 1h to dissolve the 2) resist and separate the extra 3) metal. The agitation step ensures complete liftoff of the resist.

Contact Geometry

The geometry of the contacts determines which transport measurements can be performed. Contacts must be carefully designed to give the most reliable results. The shape and accessibility of the MoS$_2$ flake determines which contact geometry is used. Two main geometries are used to contact MoS$_2$. The first of these is four-point probe, which consists of four equally spaced terminals spanning the width of the flake (Fig. 17). Current is run through the outside terminals, and the inner two terminals act as a voltmeter. The four-point probe configuration allows for separate measurement of contact and sheet resistivity. The contacts can also be used as terminals of an FET, allowing for I-V measurements and device studies. Even if one of the contacts breaks, useful data can still be obtained. Due to the shape of the flakes, most exfoliated flakes must be patterned using this geometry since often only one or two sides are available for contacting without short-circuiting the contacts on a thicker MoS$_2$ layer.
The second contact geometry that is used is the van der Pauw configuration. In this configuration, contacts are placed around the edges of the sample, overlapping the sample as little as possible. Van der Pauw requires that samples are uniform thickness, approximately two-dimensional, homogeneous, and isotropic. Two terminals serve as current source and drain, and two more serve as voltmeter leads. Van der Pauw cannot be used to perform FET measurements, but it does allow for the measurement of resistivity, doping type, sheet carrier density, mobility, and Hall coefficient. The triangular shape of the CVD grown MoS$_2$ is not optimal for four-point probe geometry since a complex geometric correction factor would have to be introduced. Since the CVD flakes are uniformly single layer and isolated from each other, van der Pauw is the preferred method.

Figure 18. Van der Pauw contact geometry

A conductive path must be completed between the contacts and the measurement device, a Keithley 4200 Semiconductor Characterization System. The contacts themselves are much too
small to be connected to the circuit. Larger contact pads (150µm by 150µm) are connected to
the contacts as part of the EBL pattern (Fig. 19). These pads can be connected to the
measurement device using either micromanipulators with conductive probes or gold wires
bonded to the pads.

![Figure 19](image)

**Figure 19.** Optical micrograph of a completed four-point probe device on exfoliated MoS₂

**Results and Discussion**

Over the course of this project, several devices were completed. Numerous samples were
exfoliated on substrates and examined using optical microscopy. Several promising sheets were
further characterized using AFM and Raman spectroscopy. Devices were fabricated, but
measurements were performed with limited success due to unreliable contacts. The CVD grown
samples were received quite late in the course of the project, but characterization was completed.

**Exfoliated Samples**

Approximately 20 substrates of exfoliated MoS₂ were made. Each substrate was
searched for large area thin sheets using optical microscopy. Factors such as the amount of
pressure applied during exfoliation, brand of scotch tape, and the number of peelings to reduce
thickness performed did not seem to have any effect on the likelihood of a large area thin sheet
being found, though this was not examined quantitatively. Promising sheets were identified for
further characterization. Fig. 20 shows several such flakes.
AFM was done on all selected flakes to confirm thickness and obtain a detailed height profile. Standard tapping mode was used. Each MoS$_2$ layer is approximately 0.68nm in thickness, so the number of atomic layers can be determined from the height. Fig. 21 shows the height profiles of several MoS$_2$ sheets. The analysis software on the AFM system allows for the quantitative examination of the height profiles.

For the exfoliated samples, Raman spectroscopy was generally not performed since it can be destructive or degrade the sample quality. Some smaller flakes were completely destroyed, while larger ones had holes and other damage. Fig. 22 shows the Raman spectrum taken from a
thin exfoliated MoS$_2$ flake and the spectrum of a thicker bulk flake, indicating the Raman shift and peak broadening.

![Figure 22. Raman spectra of a 3 layer flake and a bulk flake indicating the Raman shift and peak broadening as a function of thickness](image)

A 3 layer flake was located, and a 5-terminal device was patterned on top of it. The goal of this configuration was to allow for four-point probe measurements even if one of the contacts broke. The patterned device was completed successfully with proper alignment and no broken contacts (Fig. 23).

![Figure 23. Optical images of a completed MoS$_2$ 5-terminal device](image)

However, when initial IV characterization was performed, it became apparent that the contacts were not functioning properly. The data points were erratic and the current through the
device was three orders of magnitude lower than expected from literature and previous experiments. The device also exhibited rectifying behavior, indicating that the contacts were in fact Schottky, not Ohmic (Fig. 24). According to literature and previous experiments, Ti/Au contacts should be Ohmic. Further examination under SEM did not reveal any broken contacts or damage to the MoS₂ caused by thermal heating in the contacts. It is hypothesized that there may have been some resist or acetone residue on the surface of the flake when the contacts were deposited, resulting in the poor device performance. Subsequent samples were plasma cleaned after each EBL step to help reduce this potential source of contamination. Another possible solution is to increase the thickness of the Ti layer since the Ti is work function matched to the MoS₂ whereas the Au is not. Finally, annealing the sample in an Ar/H₂ atmosphere may increase contact performance.

![2-Terminal Voltage Sweep Measurement](image)

**Figure 24.** IV characteristics of the exfoliated MoS₂ device

### CVD Grown Samples

Several substrates with CVD grown MoS₂ were received from the Ajayan Research Group at Rice University. Optical microscopy, AFM, and Raman spectroscopy were used to characterize these samples. Initial observations under optical microscopy (Fig. 25) found that 1-3 layer flakes up to 20μm per side in size were very common. The thinnest looking flakes were always in the shape of an equilateral triangle. Much thicker areas were also observed that appeared to be nucleation sites for further layer growth.
In order to confirm the thickness and uniformity of the flakes, AFM was also performed (Fig. 26). The flakes were either one or two layers and were very uniform. The CVD samples appear to be a good solution for efficiently obtaining monolayer samples. The triangular geometry does present additional challenges for contacting and device fabrication however. It is necessary to introduce a complex geometry factor when using a four-point probe configuration. The van der Pauw method can be used by placing a contact on each corner and each edge midpoint. The van der Pauw configuration does not allow for FET measurements, but it does enable Hall effect and mobility measurements.
Finally, Raman spectroscopy was performed on the samples to ensure that the sample was in fact MoS$_2$, as opposed to MoO$_3$ or other potential CVD products, and that the sample was sufficiently high quality. Low quality samples exhibit poor Raman signal. As can be seen in Fig. 27, the MoS$_2$ signal is quite strong and shows peaks at the proper locations. Since the flake is monolayer, the layer can penetrate it and interact with the substrate underneath, hence the SiO$_2$ peak.
The Raman peaks for the single layer flake exhibit the expected shift and signal enhancement as compared to the bulk sample. This shift indicates a high quality monolayer MoS$_2$ sample.

**Figure 27.** Raman spectrum of monolayer CVD MoS$_2$

**Figure 28.** Peak shift of monolayer MoS$_2$ as compared to bulk
Conclusion

This project sought to develop a methodology for creating devices and performing transport measurements on atomically thin layered materials. MoS$_2$ synthesis was done using micromechanical exfoliation and chemical vapor deposition. Chemical vapor deposition is a much more efficient method for obtaining single-layer flakes. However, it requires more infrastructure and optimization, and the triangular shape of flakes grown with this method presents additional contacting challenges. A combination of optical microscopy, AFM, and Raman spectroscopy were used to locate thin sheets and quantitatively determine their thickness. Optical contrast can be used to identify thin flakes on the substrate. Flakes that have been identified can be profiled using AFM to confirm their thickness. Raman spectroscopy can be used to provide an additional level of confidence in the thickness measurement and can give some indication as to the quality of the flake. Contacts can be patterned using e-beam lithography and thermal evaporation. The e-beam lithography allows for the contacts to be designed based on the constraints of each individual flake. Thermal evaporation of Ti/Au contacts gives high quality, ideally Ohmic contacts. In practice, these contacts were found to be Schottky type, but this may be due to contamination or too thin of a Ti layer. The contact geometry determines which transport measurements can be performed. The four-point probe configuration allows for the isolation of contact and sheet resistance and allows for FET performance measurements. The van der Pauw configuration allows for contact and sheet resistance measurements, as well as Hall effect and mobility measurements.

Using these techniques, it should be possible to contact and perform transport measurements on any atomically thin layered material. MoS$_2$ is quickly becoming a crowded topic of research, so this ability to contact and measure other layered materials is of great benefit for exploring novel materials. These layered materials hold great potential for the discovery of new physics and may represent the future of electronics. The ability to explore different layered materials quickly and accurately is a great opportunity for the further exploration of these promising materials.

Acknowledgements

I would like to thank Professor Vinayak P. Dravid, Dr. Kathleen Stair, Jeff Cain, Yi-Kai Huang, Dr. Bin Liu, Professor Matthew Grayson, Ben Myers, Stan Chou, Professor P.M. Ajayan (Rice University), Wang Zhou, Lintao Peng, and Jiajun Luo for all their support and assistance with my senior project.
References


