CVD molybdenum disulfide: material and device engineering

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CVD Molybdenum Disulfide:
Material and Device Engineering

by

Eui Sang Song

A Dissertation
Submitted to the University at Albany, State University of New York
in Partial Fulfillment of
the Requirements for the Degree of
Doctor of Philosophy

College of Nanoscale Science and Engineering
2019
Abstract

Molybdenum disulfide (MoS$_2$) is a semiconducting 2D layered material that has attracted a lot of attention due to its material properties for electronics and optoelectronics device applications. These include a layer-dependent band gap, an indirect to direct energy transition at monolayer state, and strong light-matter interaction. A large majority of 2D materials and devices have been studied through micromechanical exfoliation for extraction and electron beam lithography for device fabrication. These methodologies while able to generate high quality materials and precisely fabricated devices, are not suitable for large scale production. Efforts have been made to make MoS$_2$ and other 2D materials commercially viable both in performance and production. This thesis explores these aspects through synthesis, fabrication, and device performance. First, a new chemical vapor deposition process for MoS$_2$ is introduced using a defect-rich MoS$_2$ bulk source through an oxidation and re-sulfurization process. Second, we investigate the effects of the photolithography process on the material properties on MoS$_2$ through Raman and photoluminescence spectroscopy. Lastly, we investigate carrier transport mechanisms of CVD MoS$_2$ and its device behavior as a phototransistor.
Acknowledgements

I would like to express my gratitude to the many people that have contributed and provided assistance towards this work. First is my advisor, Prof. Bin Yu, who introduced me to this field of research and how to approach research. He was always supportive towards my research goals and was patient when I ran into challenges. I would like to also thank my committee members: Prof. Ernie Levine, Prof. Carl Ventrice, Dr. Vadim Tokranov, Prof. Tong Zhang for taking the time out to review my dissertation and overlook my thesis defense.

No student would be able to perform any research at CNSE without the support of the faculty and staff. Natalya Tokranova, Suhasini Gattu, Steven Warfield, Stephen Stewart, Kenneth Roth, Miguel Rodriguez, and Michael Gardner have all provided technical assistance and insights for the different equipment and processes needed to obtain samples and data. I would also like to thank Prof. Harry Efstathadis for his support as my advisor the first few years in the graduate program.

I want to express my appreciation for my labmates who have worked alongside me and shared in my successes and failures. Dr. Bhaskar Nagabhirava and Dr. Tianhua Yu helped me get started when I first got to CNSE by teaching me many of the basics in synthesis and processing. Dr. Mariyappan Shanmugam and Dr. Fan Yang provided many insightful discussions on my research and its methodologies. My fellow students Nikhil Jain, Robin Jacobs-Gedrim, and Asish Parbatani worked late nights with me and held enjoyable discussions on research and life which I will always cherish.

Special thanks towards Karen Torrejon, Brendan O’Brien and baby Isabel O’Brien for welcoming me into their warm and loving home the last few years of my studies.
Lastly, I would like to thank my family for their endless support and patience with me.
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Chapter 1

Introduction

1.1 Introduction to Two Dimensional Layered Materials

The advancement of silicon-based electronics the past few decades has made it an indispensable part of modern life through computation, communications, sensors, power generation and many others. As the technology matures, improvements to better performance and cost value become more difficult and resource intensive while also nearing theoretical physical limitations. Examples of this include the performance of crystalline silicon solar cells for which devices are nearing the Shockley Queisser efficiency limit of $32\%^{1,2}$ and transistors nodes under 5 nm expecting to have problems with quantum tunneling effects. In order to overcome those limitations researchers have turned to alternative materials and sophisticated device designs using nanotechnology and low dimensional structures. Reduction in dimensionality allows for further miniaturization of devices and the emergence of new material properties that differs from the bulk state such as thermal transport, mechanical strength, electronic band structures and electrical transport. While these new properties can be used to further tailor electronic devices, reduction in size also means the loss of volume quality which in
turn affects total current flow and optical absorption as well the potential for leakage and tunneling effects. In such cases sophisticated designs are required to make up the loss, such as the FinFET structure\textsuperscript{34}, nanowire transistors, waveguides, or plasmonic nanostructures\textsuperscript{5,6}.

\textbf{Figure 1.1}: Structure of a 2D layered material. Image by Benjah-bmm27, distributed under public domain.

With the only requirement for low dimensional effects for a material system being limited in length, generally any material can be reduced to nanoscale dimensions through synthesis\textsuperscript{7} or reduction\textsuperscript{8} techniques. Layered materials are a unique class of materials due to their inherent lack of surface states and dangling bonds. Such materials are defined by strong in-plane covalent bonding weak out-of-plane van der Waal coupling (Fig. 1.1). This crystal structure allows for a high degree of flexibility\textsuperscript{9} and atomically sharp junctions\textsuperscript{10,11}, permitting precisely designed and constructed devices. Layered materials have been researched throughout the 20\textsuperscript{th} century since Bernal first discovered the structure of graphite\textsuperscript{12} in the 1920s and calculation of the band structure\textsuperscript{13} by Wallace in the 1940s. It has only been recently that the reduction of these layered materials all the way down to a single layer has been accomplished. This was a feat once thought impossible due to thermodynamic instability if not on a matching lattice, as attempts to
do so would lead to agglomeration and island formation. As such isolated monolayer states had long since been considered theoretical constructs.

The isolation of freestanding graphene\textsuperscript{14}, a single atomic layer of graphite, in 2004 by Geim and Noselov by micromechanical exfoliation broke this long-standing idea and opened an entirely new field of science generating enormous amounts of research interest and publications[]. Graphene’s structure as a single atomic layer of sp\textsuperscript{2} bonded carbon atoms in a hexagonal lattice has demonstrated many amazing physical properties as well as insight into physics that hadn’t been previously discovered including the fractional quantum hall effect\textsuperscript{15} and Berry’s phase\textsuperscript{16} of massless fermions. The charge carriers in graphene are described by the Dirac equation\textsuperscript{14,17}, mimicking relativistic particles with zero rest mass and moving with an effective speed of light. This results in carrier mobility exceeding 200,000 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}\textsuperscript{18} and ballistic transport at room temperatures in the sub-micron length scale\textsuperscript{19}. Additional properties such as high thermal conductivity of 5,000 W m\textsuperscript{-1} K\textsuperscript{-1}\textsuperscript{20}, optical absorption of 2.3\%\textsuperscript{21} and optical transmittance of 97.7\% makes graphene an attractive material for many different types of device applications. The lack of band gap due to its semi-metallic nature however limits its potential as the active material in basic electronic devices to radio frequency (RF) devices\textsuperscript{22} and interconnects\textsuperscript{23}. 
1.2 Types of Two Dimensional Layered Materials

![Image of 2D materials]

**Figure 1.2:** Different classes of 2D materials discovered\(^{24}\). Reproduced from Ref. [24] with permission from The Royal Society of Chemistry.

Since the initial discovery of graphene, numerous layered 2D materials have since been studied by numerical simulations\(^ {25}\) and direct experimentation. The array of materials discovered can be categorized by their chemical structures in which each group and subgroup have distinct traits. Elemental materials like graphene were found in groups III, IV, and V. Group IV materials such as silicene\(^ {26,27}\) and germanene\(^ {28,29}\) demonstrate a 2D layered form with a hexagonal lattice similar to graphene but with the lattice buckled due to the preference of \(sp^3\) hybrid bonds. Similar to graphene, this group has a linear electronic dispersion relation, high mobility and very
small or no band gap. Phosphorene or black phosphorus\(^\text{30}\) in Group V A drew much interest due to its intrinsic layer-dependent band gap which spans from mid-infrared to the visible spectral range. Such a property is highly valued for optoelectronic applications. A unique exception amongst single atomic layered materials is hexagonal boron nitride. Known as “white graphene”, it is an isomorph of graphene with a flat hexagonal lattice structure of alternating boron and nitride atoms\(^\text{31}\). It is an insulating material with a band gap of 5.97 eV. Boron nitrides’ insulating nature and matching lattice makes it highly complementary to graphene as demonstrated by the many studies pairing them together\(^\text{32}\).

Compounds make up the majority of layered 2D materials with varying chemical families that have unique electrical and physical properties within and in-between different groups. The most notable and studied group is the transition metal chalcogenides (TMC). One of the most studied types of TMCs is \(\text{MX}_2\) where \(\text{M}\) is a transition metal ranging from groups 4-10 and \(\text{X}\) is a chalcogenide from group 16 of the periodic table. The wide range of combinations available results in a material base that covers almost all electrical properties including insulators (\(\text{HfS}_2\)), semiconductors (\(\text{MoS}_2\), \(\text{WSe}_2\)), semimetals (\(\text{MoTe}_2\)) and metals (\(\text{NbS}_2\), \(\text{VSe}_2\))\(^\text{33}\). Beyond the typical conductive states, exotic behavior such as superconductivity, charge density wave, and Mott transition has also been observed. Another prominent class of TMC is \(\text{M}_2\text{X}_3\) including materials like \(\text{Sb}_2\text{Te}_3\) and \(\text{Bi}_2\text{Te}_3\) which have shown to behave as topological insulators which are materials insulating in the bulk phase with conductive surfaces possessing a linear dispersion relation electronic band structure. \(\text{In}_2\text{Se}_3\) is a direct band gap material through all layer thicknesses and has been of interest in optoelectronics\(^\text{34}\). Transition metal oxides have been used as both precursors to transition metal dichalcogenides\(^\text{35}\), and as hole transport layers in organic solar cells\(^\text{36}\) due to their wide band gaps and high work function\(^\text{37}\).
The number of 2D materials can further be extended by the manipulation of the pristine materials. This includes creating alloys\textsuperscript{38,39}, surface functionalization\textsuperscript{40} and formation of derivatives\textsuperscript{41}, in-plane superlattice formations\textsuperscript{42}, and Janus monolayer compounds\textsuperscript{43}. In addition to standalone monolayers, coupling between different layers have been demonstrated to form their own unique material systems due to interlayer interactions\textsuperscript{44}. These interactions also inhibit transport properties between 2D materials and traditional 3D materials when compared to all-2D material systems\textsuperscript{45,46}. So not only are individual materials themselves numerous in number but the formation of heterostructures produce material structures with varying properties. All these possibilities exist and can be utilized for device and material studies.

1.3 Synthesis Methods of 2D Materials

The synthesis of ultrathin 2D materials originates with micromechanical exfoliation, a technique in which individual layers can be separated due to weak van der Waal bonds\textsuperscript{47}. This technique has been demonstrated to be robust and transferable, and has been used to study many 2D materials beyond graphene. It is however incompatible with semiconducting manufacturing processes due to the random and non-uniform deposition results. An exfoliation method with more potential for wide area deposition is liquid exfoliation, which separates 2D materials into thin layers by high frequency sonication in a solvent solution\textsuperscript{48}. This solution is then deposited onto a target substrate using a spray\textsuperscript{49}, drop cast\textsuperscript{50} or spin cast\textsuperscript{51} method. This method is a low cost method to synthesize thin wide area 2D materials at low temperatures. However, similar to micromechanical exfoliation, the resultant depositions are non-uniform with inconsistent thickness and can only be used for situations where uniformity is not essential.
The most reliable and consistent synthesis method for 2D materials has been through thin film deposition techniques. This field has been successful in the growth of monolayer and few layer single crystals to large area films\textsuperscript{35,52–54}. Large area graphene has been grown using a metal catalyst through a carbon coalescence and precipitation mechanism using a wide range of metals including copper\textsuperscript{52}, nickel\textsuperscript{55}, molybdenum\textsuperscript{56} etc. This method is performed on high purity metal foils at high temperatures of \(\sim 1000 \, ^\circ C\) to produce high quality films. The growth on a foil however requires transferring the film onto a target substrate\textsuperscript{57}, typically performed by a polymer assisted transfer method\textsuperscript{58} which can leave behind residues\textsuperscript{59} as well as create tears and wrinkles. Unlike graphene and other elemental layered materials which require a catalyst for synthesis, single crystal flakes and films of compound 2D materials have been synthesized directly on various common substrates such as silicon, silicon dioxide, quartz, and alumina\textsuperscript{60,61}. The techniques used include direct evaporation\textsuperscript{60}, chemical vapor deposition\textsuperscript{62}, and atomic layer deposition\textsuperscript{63}, all of which are processes that are compatible with IC fabrication. This growth of highly crystalline flakes without the need for lattice matching is one of the great advantages of 2D materials and their potential implementation in electronics over other novel materials.

1.4 2D Materials Based Electronics

The diversity of properties in 2D materials makes them potentially applicable in near all fields of electronics\textsuperscript{64}. A common trend in newly discovered 2D materials is the fabrication of field effect transistors due to the importance of the device as well as the ability to extract electrical properties. The first devices studied were graphene field effect transistors which demonstrated ambipolar field effect and carriers with extremely high mobility\textsuperscript{47}. Unfortunately
graphene’s inherent lack of band gap limited its on-off ratio to the $10^2$ range which is not suitable for switching applications. Its semi-metallic nature also affects its performance in other applications limiting its potential application to high speed RF devices, interconnects and as a complementary material for other active materials. The discovery of monolayer MoS$_2$\textsuperscript{65} provided a way to increase the on-off ratio for better switching with a band gap of 1.8 eV. While the on-off ratio greatly improved to $10^6$, the carrier mobilities in the 0.5–3 cm$^2$ V$^{-1}$s$^{-1}$ range were too low for practicality\textsuperscript{66}. It would be realized that the poor performance of the devices were due to external factors and many improvements were made. Metal contacts typically using titanium were replaced with noble metals such as silver for a better wetting increased the on-current by 60\textsuperscript{67,68}. Encapsulation or top gates with high-K dielectrics reduce coulomb screening effects and enhance mobilities to upwards of 1,090 cm$^2$ V$^{-1}$s$^{-1}$\textsuperscript{69}. Alternative substrates were also used to reduce interfacial traps\textsuperscript{46}. 2D materials transistors show potential to scale very well with strong resistance to drain induced barrier lowering effects because of charge carrier with high effective mass and lower dielectric constants\textsuperscript{70}.

Another highly researched area for 2D materials is in the field of optoelectronics\textsuperscript{71}. 2D layered materials have Van Hove singularities in their density of states leading to strong light-matter interaction increasing absorption\textsuperscript{72}. Photodetectors is one of the applications that can take advantage of this property and has shown promise for highly responsive sensors across a broadband spectrum. Graphene photodetectors demonstrate broadband photoresponse from 0.5 - 10 μm\textsuperscript{73}. MoS$_2$ photodetectors demonstrated high responsivity upwards of 2200 A W$^{-1}$ with CVD grown devices at room temperature\textsuperscript{74}. In$_2$Se$_3$ with its direct band gap has also demonstrated extremely high responsivities of $3.95 \times 10^2$ A·W$^{-1}$ at 300 nm along with fast response times in the range of $10^{-2}$ seconds\textsuperscript{34}. Many designs to enhance absorption previously studied for use in
thin film solar cells\textsuperscript{5} have been incorporated into 2D materials. Heterostructures\textsuperscript{75} and quantum dots\textsuperscript{76} allow for an additional material to generate photocurrent while plasmonic nanoparticles\textsuperscript{77} and light trapping designs enhance scattering at the material surface\textsuperscript{78}.

One of the main driving forces in 2D materials research is its flexible implementation. The layered structure allows for quality growth on various amorphous substrates\textsuperscript{35}, physical transfer between substrates\textsuperscript{57} and high bendability\textsuperscript{79}. This makes them an appealing material base for low cost, portable and flexible electronics\textsuperscript{80}.

1.5 Overview of Molybdenum Disulfide

![Figure 1.3: Molybdenum disulfide: (a) unit cell\textsuperscript{81} and (b) electronic band structure\textsuperscript{82}. (a) Reproduced from Ref. [81] with permission from The Royal Society of Chemistry. (b) Reprinted with permission from Ref. [82]. Copyright 2010 American Chemical Society.]

The material of focus in this work, molybdenum disulfide (MoS\textsubscript{2}), is a 2D layered semiconductor that is part of the transition metal dichalcogenide family\textsuperscript{83}. Its crystal structure is
composed of a plane of molybdenum atoms sandwiched between sulfur atoms in a prismatic trigonal crystal system (Fig 1.3a). This structure has broken inversion symmetry at odd layer numbers, leading to valley polarization\textsuperscript{84}, peizoresponse\textsuperscript{85}, and second harmonic response\textsuperscript{86} which can be used for novel device applications in valleytronics\textsuperscript{87} and piezoelectricity\textsuperscript{88}. Like many other 2D materials the electronic band structure is layer-dependent, with a band gap that ranges from 1.3 eV in the bulk state to 1.8 eV\textsuperscript{65} at monolayer thicknesses. In the electronic band structure of a monolayer (Fig. 1.3a), the minimum of the conduction band and maximum of the valence band both exist at the K point of the Brillouin zone, leading to a direct band gap (Fig. 1.3b)\textsuperscript{82}. As the layer number increases, these points shift leading to an indirect band gap. The electronic band structure also demonstrates large energy splitting in the conduction and valence bands due to strong spin-orbit coupling\textsuperscript{89}. The coupling in the valence band derived from the d-orbitals is particularly strong, resulting in an energy difference over 100 meV which can be probed by photoluminescence spectroscopy\textsuperscript{82}.

**Figure 1.4:** Raman spectroscopy of molybdenum disulfide\textsuperscript{90}. Layer-dependent (a) spectra and (b) peak frequencies. Reproduced from Ref. [90] with permission from The Royal Society of Chemistry
The physical properties of MoS\textsubscript{2} and other 2D materials can be probed by Raman spectroscopy. This nondestructive technique probes physical states by detecting in inelastic scattering of vibrational bonding modes through a laser source. In few-layer MoS\textsubscript{2}, the characteristic peaks are generated by the in-plane and out of plane vibrational modes\textsuperscript{90-92}. The number of layers can be determined by calculating the difference in those peaks, ie 17-21 cm\textsuperscript{-1} for monolayer, 22-23.5 cm\textsuperscript{-1} for bilayer, 23.5 cm\textsuperscript{-1} for trilayer, and > 25 cm\textsuperscript{-1} for bulk (Fig. 1.4). In addition this technique is able to detect lattice strain\textsuperscript{93} with the E\textsubscript{12g} peak position, carrier concentration\textsuperscript{94} with the A\textsubscript{1g} peak position, and defects\textsuperscript{95}.

1.6 Thesis Overview

The objective of this work is to study MoS\textsubscript{2} at the different stages required for implementation in device applications: synthesis, device fabrication, and device analysis.

In the second chapter, we study the synthesis process and analyze the resultant crystal flakes of MoS\textsubscript{2} grown using a defect-rich bulk MoS\textsubscript{2} precursor through an oxidation and re-sulfurization process.

In the third chapter, we study the effects of the photolithography process on the material properties of MoS\textsubscript{2}.

In the fourth chapter, we study the transport mechanism and device behavior of MoS\textsubscript{2} phototransistors.

In the final chapter, we summarize the studies that have been made as well as look at the future prospects of 2D layered semiconductors.
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Chapter 2

CVD MoS$_2$: Synthesis by Oxidation and Re-Sulfurization Method

2.1 Introduction

Scalable synthesis of high quality films is essential for the implementation of molybdenum disulfide and other 2D materials for use in commercial applications. So far several different methods have demonstrated successful synthesis of MoS$_2$ including chemical vapor deposition (CVD)$^1$, metal-organic chemical vapor deposition (MOCVD)$^2$, and physical vapor deposition (PVD)$^3$. Amongst the different techniques, the single step CVD method has stood out due to the growth of large single crystal flakes and wafer-scale films ranging from monolayer to few layers in thickness$^4$. In this method, a molybdenum-based precursor such as MoO$_3$$^1$, MoO$_2$$^{5,6}$, and MoCl$_5$$^7$ reacts with sulfur vapor to nucleate and grow MoS$_2$ crystals on targeted substrates$^8$. A less explored avenue for MoS$_2$ synthesis is through the thermal evaporation of a bulk MoS$_2$ source but studies have been limited$^{9,10}$. The major advantage of such a method would be the simplicity of utilizing a single source which would reduce the number of precursors required in doping$^{11}$ and synthesizing of alloys$^{12,13}$. An issue with MoS$_2$ flakes grown by thermal evaporation however, is the presence of anti-site defects which limits their performance in
An unexplored method that stands in-between the CVD method and the single source evaporation method could be through the oxidation of a bulk MoS$_2$ source into volatile subspecies and re-deposition through sulfurization. This method could potentially allow for depositions at lower temperatures as well as provide alternative pathways to synthesizing other 2D materials.

In this section, we demonstrate a CVD process to synthesize monolayer MoS$_2$ flakes using defect-rich MoS$_2$ as a precursor source through an oxidation and re-sulfurization mechanism. Material characterization of the synthesized crystals is performed through different spectroscopic techniques. The growth process is run under different parameters to investigate the growth mechanism and the effects of sulfur concentration. Device transport properties is studied and compared between flakes grown under different sulfur flow conditions.

## 2.2 Experimental Methods

### 2.2.1 Chemical Vapor Deposition of Molybdenum Disulfide

![Figure 2.1: Schematic of the CVD growth setup.](image)
The setup for the growth process starts with cleaning 300 nm SiO$_2$/p++ Si substrates in piranha solution. Then 2 substrates are stacked facing each other with a piece of aged MoS$_2$ crystal (SPI Supplies) in between them. These are loaded in a 1 inch quartz tube and placed at the center of a Lindberg Blue tube furnace along with 5-15 mg of sulfur powder (Sigma Aldrich) in an alumina boat (Sigma Aldrich) placed at the edge of the furnace. Once the setup is complete the system is pumped down to base pressure under a flow of 100 sccm of ultrahigh purity argon. The growth process begins with the furnace heating up to 300 °C in 6 minutes and held for 15 minutes to help reduce moisture. While the furnace increases to the target temperature of 600 °C at 30 C/min, the pressure is increased to 20 Torr with the flow reduced to 12 sccm at 400 °C. At the target temperature of 600 °C, the sulfur is positioned to melt between 2-5 minutes for a high sulfur flow growth and 10-15 minutes for a low sulfur flow growth. Once the sulfur melts, the synthesis is allow to continue for 10-25 minutes. After which the furnace is allowed to cool down to 350 °C. The flow rate increased back to 100 sccm and the pressure is reduced back to the base pressure. A constant flow of atmospheric air is bled into the chamber as an oxygen source. The bleed-in rate is 26 mTorr/min. In comparison, the pressure build-up rate at 30 sccm argon in our setup is 10 Torr/min. Schematic of the setup is shown in Figure 2.1.

2.2.2 Material Characterization

Images were obtained using Leica DM 8000M optical microscope and Leo1550 scanning electron microscope. Chemical analysis was performed using a ThetaProbe X-ray photoelectron spectroscopy system. Raman and photoluminescence spectroscopy was performed with a Horiba Labram HR800 using a 532 nm laser source. Surface morphology scans from atomic force
microscopy were obtained using a Bruker Dimension Icon system. Electrical transport measurements were made using a probe station under vacuum (>10^-6 Torr) with Agilent B1500A analyzer.

2.2.3 Device Fabrication

Back-gated field effect transistor (FET) devices were fabricated by photolithography. A trilayer resist structure of AZ5206, PMMA A4, and Lor3A was used. The Lor3A was spun on at 3000RPM for 1 minute and baked at 170 °C for 3 minutes. PMMA A4 is spun on twice under the same conditions and then baked at 170 °C for 2 minutes. For AZ5206, the resist is spun at the same conditions and baked at 80 °C for 1 minute. Patterning of the contacts was done using an OAI 800 mask aligner. The exposed patterns on the resist were developed using base developer AZ300 MIF to open up to the PMMA layer. The PMMA layer is then etched using O2 plasma in a Trion Micro RIE system for 75 seconds. The remaining Lor3A in the patterned area is removed using Remover 1165 for 3 minutes, after which the substrate is sprayed with remover 1165, sprayed with isopropanol (IPA), immersed in IPA for 30 minutes, and finally dried with nitrogen. Metal layers of 30 nm Ag / 30 nm Au are deposited using e-beam evaporation to form the contacts. After deposition the sample is covered in Lor3A and the back oxide of the substrate is etched using droplets of hydrofluoric acid. The remaining acid is dried with a wipe, followed by a gentle cleaning with a wet wipe. Liftoff is done immersing the sample in Remover 1165 to remove the top Lor3A, acetone to remove the PMMA, and once again in Remover 1165 to remove the bottom Lor3A. Afterwards the sample is immersed in acetone, IPA and dried with nitrogen.
2.3 Results and Discussion

2.3.1 Material Characterization

Figure 2.2: SEM image of triangular flakes grown. (scale bar: 10 μm)

The synthesis process results in flakes with triangular or star-like shapes which are indicative of single crystal MoS₂ growth (Fig. 2.2). The shape originates from the trigonal crystal structure and the growing rate of different crystal faces or edge terminations.

Figure 2.3: X-ray photoelectron spectroscopy of the synthesized crystals.
Spectroscopic analysis is undertaken to analyze the resultant material. Compositional analysis of the flakes is made using x-ray photoelectron spectroscopy (XPS). The spectra for the triangular flakes exhibit molybdenum (Mo) 3d doublet peaks with binding energies positioned at 233.3 eV and 230.2 eV corresponding to Mo$^{4+}$ and sulfur (S) 2p doublet peaks positioned at 162.7 eV and 163.9 eV. The S 2s peak can also be observed at 227.4 eV. The peaks can be quantified to show an atomic concentration ratio of \(~1:1.93\) of molybdenum to sulfur, demonstrating some sulfur depletion.

![Graph of Raman spectra](image)

**Figure 2.4:** Raman spectra of a MoS$_2$ flake showing its characteristic peaks

Raman spectroscopy analysis of MoS$_2$ flakes provides information about physical and electrical properties of the materials. The characteristic peaks for monolayer MoS$_2$ are the in-plane vibrational mode E$_{2g}^1$ which is sensitive to strain$^{16}$ and the out-of-plane vibrational mode A$_{1g}$ which is affected by charge carrier concentration$^{17}$. The frequency difference $\Delta$, has been observed to range from 17 cm$^{-1}$ to 21 cm$^{-1}$ for monolayer MoS$_2$. Further increase in difference signifies an increase in the number of layers. The peak positions of the flake shown in Figure 2.4 are 384.3 cm$^{-1}$ and 405.3 cm$^{-1}$ for the E$_{2g}^1$ peak and A$_{1g}$ peak respectively.
2.3.2 Effects of Sulfur Flow Conditions

One of the most important parameters in CVD MoS$_2$ synthesis is the amount of precursors flowed down to the target substrates. For synthesis involving a MoO$_3$ source as an example, low sulfur flow induces the formation of undesired MoO$_2$ and MoOS$_2$ crystals, while too high of a sulfur flow will suppress the growth. We control the sulfur flow by adjusting the position of the sulfur precursor along the furnace which effects its melting time and temperature. For a growth with low sulfur flow, the sulfur is positioned to melt at 10-15 minutes after the furnace reaches 600 °C, while a growth with high sulfur flow the sulfur is positioned to melt at 2-5 minutes after the furnace reaches 600 °C.

Figure 2.5: (a) Overall image of growth under low/late sulfur flow. (scale bar: 200 μm) (b) Respective location of distinct growth regions under precursor.

Another factor of CVD synthesis that affects the shape, distribution, and thickness of MoS$_2$ crystals is the configuration between the Mo precursor and the substrate. Different arrangements affect the local concentrations of reagents on the substrate which in turn influences
nucleation and growth\textsuperscript{18-21}. Non-uniform growth distribution with different distinct regions due to these local concentrations can be observed in Figure 2.5a of a synthesis grown under low sulfur flow. The different regions are related to their relative positions with the MoS\textsubscript{2} precursor (Fig. 2.5b). Region A has highly dense growth of smaller flakes and is located by the edge of the precursor where the sulfur would meet with the Mo source. In the interior is region C where larger flakes are grown with low nucleation density. The flakes in this region can be discerned even under the low magnification imaging of Figure 2.5. Flakes of Region B are observed randomly at both the interior and outer edges where the flakes are smaller like region A but more spread out. We believe these flakes appear when there is a low concentration of Mo precursor source due to the inhomogeneous nature of precursor source and its distance to the substrate.

\begin{center}
\textbf{Figure 2.6:} Optical image of flakes grown under low/late sulfur flow. (Scale bars: 20 μm)
\end{center}

Optical images of individual flakes in different growth regions grown under low sulfur flow are shown in Figure 2.6a-c. The flakes grown in region A are not only highly dense but also diverse in shapes and sizes. Flakes in Region B have similar star shapes to region A but the flakes are larger with more consistent geometry. The biggest contrast is found with flakes in region C due to their larger triangular geometry with sharp edges which is normally seen in synthesis at higher pressures\textsuperscript{22}. Additionally the flakes in region C is observed to have more
particles on the surface, which will be discussed in the next section, which along with its morphology suggests higher molybdenum concentration compared to the other 2 regions\textsuperscript{20}.

**Figure 2.7:** Raman spectroscopy analysis of growth regions under low sulfur flow. (a) Raman spectra of flakes with varying peaks positions, (b) plot of the distribution of the E\textsubscript{12g} and A\textsubscript{1g} peak positions, (c) FWHM of the different E\textsubscript{12g} and A\textsubscript{1g} peaks.

Raman spectra measured of various flakes in different growth regions show a wide range of differing characteristic peak positions (Fig. 2.7a). The difference between the two peak positions Δ, ranges from 17 cm\textsuperscript{-1} to 21 cm\textsuperscript{-1} which is indicative of monolayer thickness\textsuperscript{23}. A distribution of the Raman peak positions of flakes in each region is shown in Figure 2.7b. Flakes in region B have the highest A\textsubscript{1g} peak positions (> 405 cm\textsuperscript{-1}) while the flakes in region C have the lowest (< 404 cm\textsuperscript{-1}). The A\textsubscript{1g} peak positions of the flakes in region A lie in-between, ranging from 404.1 cm\textsuperscript{-1} to 405.2 cm\textsuperscript{-1}. The relationship between the E\textsubscript{12g} peak and A\textsubscript{1g} peak shows a small trend where the smaller A\textsubscript{1g} peak positions tend to have the larger E\textsubscript{12g} peak positions, but most of the flakes are in the range of 384.4 cm\textsuperscript{-1} to 384.7 cm\textsuperscript{-1}. The full width at half maximum (FWHM) of the E\textsubscript{12g} peaks are all within ~2 cm\textsuperscript{-1} which suggests very good crystalline quality, even better than those grown at high temperature, atmospheric pressure\textsuperscript{7,24} (Fig. 2.7c). A linear
broadening effect is observed for the FWHM of the A$_{1g}$ peak, consistent with reports where charge carrier density is modulated through electrostatic gating$^{17}$.

![Figure 2.8: Overview image of a high/early sulfur flow growth. (Scale bar: 100 μm)](image)

Synthesis under increased sulfur flow is observed to change the dynamics of the growth process. The overall synthesis of MoS$_2$ flakes within the different regions is shown in Figure 2.8. In comparison to low sulfur flow growth, high sulfur flow growth appears to push in the Mo source, leading to smaller overall growth region and individual crystal sizes. The distinct regions for this growth is the center region with lobe-like shapes at low nucleation, the main central growth ring with normal triangular, star-like shapes, and the outer rim where smaller triangular flakes are observed.
Figure 2.9: Optical image of flakes grown under high/early sulfur flow. (Scale bars: 20 μm)

Optical images of the flakes under this growth condition show similar shapes to the low sulfur flow growth in regions A and B (Fig. 2.9a-b). The only difference is the triangular flakes in outer region A have corners that are rounded. The flakes in the central region C undergo dramatic changes in morphology. Instead of triangular crystals with sharp edges, we observe flakes with 3-fold symmetric lobes and multiple lobes initiated from defects\(^{25}\) (Fig. 2.9c). The formation of lobe flakes has been observed previously by Ling et al., in their synthesis using perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt as a growth promoter\(^{26}\). The results are not dissimilar to what we present; the lobe growth occurs closest to the sulfur source while triangular flakes are grown further away where the sulfur concentration would be reduced. This shape has also been observed in the synthesis of 4 and 6-lobe “flower” growths of CVD graphene caused by surface limited diffusion\(^{27-29}\). This limitation in diffusion results in each lobe and triangular or hexagonal-shaped center keeping a distinct shape rather than growing uniformly together.
Figure 2.10: Raman spectroscopy analysis of high sulfur flow growth. (a) Raman spectra of flakes with varying peaks positions, (b) plot of the distribution of the \( E_{2g}^1 \) and \( A_{1g} \) peak positions, (c) FWHM of the different \( E_{2g}^1 \) and \( A_{1g} \) peaks.

Analysis by Raman spectroscopy is repeated on these flakes as those grown under increased sulfur flow (Fig. 2.10a-c). The range of the characteristic peak positions show many similarities, with the \( A_{1g} \) peaks of Region A and B ranging from 404 – 405.2 cm\(^{-1}\) and Region C ranging from 403 - 404 cm\(^{-1}\). The divergence comes from the \( E_{2g}^1 \) peaks, where the flakes in both regions A and C have an increase in FWHM upwards of 3.0 cm\(^{-1}\). Region B remains the same as during the low sulfur flow with a FWHM at a maximum of 2.3 cm\(^{-1}\) with an occasional exception. The \( E_{2g}^1 \) peak positions for regions A and C tended to be higher 384 – 358 cm\(^{-1}\) compared to region B where it was 383.8 – 384.8 cm\(^{-1}\).
Figure 2.11: Atomic force microscopy of flakes grown by the 2 different growth conditions: (a) low sulfur flow and (b) high sulfur flow

Atomic force microscopy (AFM) is used to scan the flakes grown under low and high sulfur flow (Fig. 2.11). We observe that the flakes grown under low sulfur flow conditions are measured to have thickness of ~1.4 nm which would be near a bilayer thickness. However the characteristic Raman peaks suggests that the MoS$_2$ is a monolayer. A possible solution that would allow both conclusions to be true would be the formation of an interfacial contamination layer between the MoS$_2$ and substrate during the growth process. In comparison the flakes grown by high sulfur flow have heights of ~0.7 nm which is the expected thickness of monolayer MoS$_2$. 
The origin of the variations in the $A_{1g}$ peak frequency is from oxygen absorption on the surface of the MoS$_2$ flakes. Oxygen atoms which accept electrons from MoS$_2$ are either physisorbed onto the surface or chemisorbed onto a sulfur vacancy site$^{30}$. During synthesis those in region C are generally exposed to less oxygen due to the protection provided by the precursor flake. Additionally surface particles which are more prevalent in region C can also prevent oxygen atoms from interacting with the flakes. We observe a general trend in which over time the characteristic peak difference will eventually get to a value of 20.8 - 21 cm$^{-1}$. In Figure 2.12 we plot the Raman spectra of a flake 14 hours after growth, with approximately 12 hours in a nitrogen box. Within those 14 hours the $A_{1g}$ peak frequency shifted from 404.9 cm$^{-1}$ to 405.2 cm$^{-1}$ and the difference between the characteristic peaks increasing from 20.3 cm$^{-1}$ to 20.7 cm$^{-1}$. 

**Figure 2.12:** Raman spectra shift in MoS$_2$ flakes over time
2.3.3 Photoluminescence Spectroscopy Analysis

![Graph](image)

**Figure 2.13:** Comparison of the photoluminescence spectra of flakes grown under the 2 different sulfur flow conditions.

Photoluminescence (PL) of monolayer MoS$_2$ emerges from the radiative recombination of photoexcited carriers due to the direct band gap at the K point of the Brillouin zone$^{31,32}$. This direct band gap facilitates the 3 transitions that make up the spectrum: the A exciton, B exciton and the A$^-$ trion$^{33}$. The PL spectra of MoS$_2$ grown under the 2 different growth conditions are shown in Figure 2.13. The selected flakes had near matching Raman spectra to keep the physical properties similar for better comparison. The PL spectra measured appear to have near identical peaks and intensities, with large peaks centered by 1.84 eV which is the expected energy of the A exciton transition.
Figure 2.14: (a) Photoluminescence of monolayer MoS$_2$ at varying A$_{1g}$ peak positions. (b) Magnified view of the spectra of lower intensities

The PL spectra of flakes with varying A$_{1g}$ peak positions are shown in Figure 2.14. The reduction in intensity with decreasing A$_{1g}$ peak position is in agreement with studies where the peak position or charge carrier concentration was modulated through plasma treatment$^{34}$, chemical treatment$^{35}$, thermal annealing$^{36}$, and electrostatic gating$^{17}$. The difference in the maximum peak intensity between the 405.5 cm$^{-1}$ and 402.9 cm$^{-1}$ spectra is near a factor of 40. Additionally the maximum intensity peak positions can be observed to shift in energy from 1.84 eV to 1.78 eV. The emission intensity of these transitions is important to potential optoelectronic devices and these properties would need to be considered$^{37}$. Additionally it also appears that physical properties of each flake measured by the Raman spectroscopy are more critical to the PL spectra than the growth method itself.
Figure 2.15: Deconvolution of photoluminescence spectra. Fitted peaks of flakes with (a) $A_{1g}$ of 405.4 cm$^{-1}$ and (b) $A_{1g}$ of 403.7 cm$^{-1}$.

The PL spectra is analyzed using a Lorentzian fit to the 3 transitions$^{38}$. The PL spectrum of the flake with an $A_{1g}$ peak position of 405.4 cm$^{-1}$ (Fig. 2.15a) has a dominant A exciton peak at 1.85 eV and lower intensity transitions of the $A^-$ trion at 1.81 eV and B exciton at 2.03 eV. The difference of the 2 exciton peaks of 180 meV results from the energy difference of the split valence band due to spin orbit coupling$^{32}$. In contrast, the PL spectra of the flakes with $A_{1g}$ peak positions of 403.7 cm$^{-1}$ and below not only have dramatically reduced intensities due to Pauli blocking$^{39,40}$, but also a red-shifted $A^-$ trion transition (Fig. 2.15b). This red-shifting is from the emergence of a “free” trion transition, where the recoil electron of the three particle system goes to the Fermi level in the conduction band$^{41}$. In the other “bound” trion transition, which is also observed at higher $A_{1g}$ peak positions, the recoil electron goes to a fixed shallow trap site$^{42}$. The “bound” trion transition has a peak position remaining at 1.81 eV, while the peak position of the “free” trion transition here is observed to be 1.77 eV but ultimately dependent on the Fermi level. The B exciton transition at 1.96 eV is also observed to red-shift but has not been previously reported. Further investigation is necessary to elucidate the origin of this higher energy transition.
2.3.4 Growth Mechanism

\[ \text{(a)} \]

Figure 2.16: Synthesis with no sulfur flow. (a) SEM image of a synthesis without sulfur (scale bar 10 μm), inlet: magnified image of a single particle (scale bar: 400 nm). (b) XPS analysis of the particles.

The growth mechanism is deduced by experimental trials. By using a bulk MoS\(_2\) source, an evaporation and re-deposition mechanism would be expected to grow MoS\(_2\) flakes. However, when the synthesis was attempted without sulfur, there were no triangular flakes observed. What was observed in its place was the formation of spherical nanoparticles (Fig. 2.16a). The nanoparticles analyzed by XPS showed no sulfur peaks while Mo 3d doublet peaks were positioned at 232.9 eV and 236 eV which is associated with Mo\(^{6+}\) of MoO\(_3\)\(^{43}\) (Fig. 2.16b). This would signify that it is not direct evaporation but rather a reaction process that was synthesizing the monolayer flakes.
Table 2.1: List of conditions tested during the growth process and the resulting observations.

<table>
<thead>
<tr>
<th>Growth Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>No sulfur flow</td>
<td>MoO$_x$ particles</td>
</tr>
<tr>
<td>Freshly cleaved flakes or powder</td>
<td>No Growth</td>
</tr>
<tr>
<td>No air bled in</td>
<td>No Growth</td>
</tr>
<tr>
<td>Repeated precursor</td>
<td>Evidence not MoO$_3$</td>
</tr>
</tbody>
</table>

Several more clues to the mechanism were obtained by changing growth parameters as shown in Table 2.1. First, when the process was run without any air bled into the system, there was no growth observed, which suggests oxidation is an integral part to the synthesis process. Second, when the process was run using a freshly cleaved MoS$_2$ flake or powder, there was no growth observed once again. This eliminates pure MoS$_2$ as the molybdenum source. The original source that was used had been sitting in ambient conditions for years suggesting that the aging process of MoS$_2$ is a primary factor to this growth process. The aging process leads to defects, primarily sulfur vacancies and the formation of molybdenum oxide hydrate$^{44}$. While the molybdenum oxide could be the initial molybdenum source, it would be subsequently sulfurized and depleted. In our process we are able to use a source multiple times (~8-10 runs) before the source no longer produces flakes.
Figure 2.17: (a) Defect-rich MoS$_2$ synthesized by sulfurizing precipitated molybdenum oxide hydrate. (Scale bar: 20 μm) (b) Raman spectra of defect-rich MoS$_2$ and pristine MoS$_2$.

We were able to confirm the mechanism by synthesizing defect-rich MoS$_2$ film on a silicon substrate (Fig. 2.17a) and reproducing the synthesis. Molybdenum trioxide was dissolved in warm deionized water and droplets of the solution were evaporated on a substrate to precipitate molybdenum oxide hydrate, MoO$_2$(H$_2$O), which incidentally is a byproduct of aged MoS$_2$. E-beam evaporation of MoO$_3$ also yielded similar results. The substrate was then loaded into the CVD system and run through a typical growth synthesis used for monolayer MoS$_2$ growth under high sulfur flow. The Raman spectrum of the defect-rich MoS$_2$ film is compared to the spectra of a pristine bulk sample in Figure 2.17b. Both materials have the frequency difference of ~25 cm$^{-1}$ for their characteristic peaks which matches established literature values. The obvious difference between the two spectra is the peak intensity of the E$_{2g}^1$ peak, which is limited in the defect-rich sample because of its large FWHM of 3.7 cm$^{-1}$ compared to 1.4 cm$^{-1}$ for the pristine bulk. The FWHM of the A$_{1g}$ follows a similar pattern but the difference is not as big with 1.9 cm$^{-1}$ FWHM for the pristine sample and 2.8 cm$^{-1}$ FWHM for the defect-rich sample.
Figure 2.18: Illustration of the growth mechanism

An illustration of the overall growth mechanism and chemical pathway is shown in Figure 2.18. The synthesis of MoS$_2$ in this process is expected to following reaction steps:

\[ 2\text{MoS}_{2-x} + \text{O}_2 \rightarrow 2\text{MoOS}_2(\text{g}) \]
\[ 2\text{MoOS}_2(\text{g}) + \text{S}(\text{g}) \rightarrow 2\text{MoS}_2(\text{s}) + \text{SO}_2(\text{g}) \]

MoOS$_2$ has been demonstrated to be an intermediary species of MoO$_3$ growth\textsuperscript{45} and is likely to also be an intermediary species in our growth method. The defects in MoS$_2$ allows for oxidation of MoS$_{2-x}$ into a volatile intermediary species rather than a stable molybdenum oxide that would remain on the precursor. Further oxidation of this intermediary species leads to MoO$_3$ particles as previously discussed.
2.3.5 Device Analysis

**Figure 2.19:** Gate voltage-dependent I-V measurement at 20 V intervals (inlet: image of a device (scale bar: 10 μm)).

Transport properties are essential for potential applications of MoS$_2$ in electronics and optoelectronics. Device performance of the CVD synthesized flakes is investigated by fabricating back-gated FET devices through photolithography and making electrical measurements under high vacuum (Fig. 2.19 inlet). I-V measurements over a wide range of gate voltages show ohmic behavior between the MoS$_2$ flakes and the Ag/Au contacts (Fig. 2.19).
Figure 2.20: Electrical measurements of devices of flakes with varying Raman spectra $A_{1g}$ peak positions grown by low sulfur flow. (a) I-V sweeps and back-gate voltage sweeps in (b) linear and (c) log scales.

Electrical measurements are made on devices of flakes synthesized under the 2 different growth conditions. Prior to measurements, the Raman spectra of device channel regions were obtained to reaffirm the relationship between carrier concentration and $A_{1g}$ peak position$^{17}$ by device analysis. I-V sweeps of devices with varying $A_{1g}$ peaks are shown in Figure 2.20a. The current densities of the devices at lower $A_{1g}$ peak positions are greater than those with higher $A_{1g}$ peak positions. Back-gate sweeps of these devices (Fig. 2.20b-c) demonstrate n-type behavior and an on-off ratio of over $10^6$ for devices with off-currents within the measurement range$^{46,47}$. In
the linear scale plot, the relationship of lower $A_{1g}$ peak position devices having higher current densities remain consistent. However in the logarithmic scale plot we observe a deviation when the currents of the devices with an $A_{1g}$ position of 404.9 cm$^{-1}$ and 405.2 cm$^{-1}$ cross over at negative gate voltages. This crossover occurs within the subthreshold region and may be caused by defects or damage from the fabrication process. Additionally since the Raman spectra measurements are taken in atmosphere without any gate voltage, the relationship may only strictly hold under those conditions.

Figure 2.21: Electrical measurements of devices of flakes with varying Raman spectra $A_{1g}$ peak positions grown by high sulfur flow. (a) I-V sweeps and back-gate voltage sweeps in (b) linear and (c) log scales.
Electrical measurements of devices of flakes fabricated from high sulfur flow are shown in Figure 2.21. Typically flakes from high sulfur flow growth tended to demonstrate lower $A_{1g}$ peak positions. The devices analyzed here measured a range of 403.9 cm$^{-1}$ to 405.0 cm$^{-1}$. Attempts to fabricate devices with lower peak frequencies were met with difficulty due to environmental effects inducing a blue-shift as previously observed in Figure 2.12. The electrical measurements made for these devices were similar to the devices of low sulfur flow grown flakes. Lower $A_{1g}$ peak position devices had higher currents for both the I-V measurement and the positive gate voltage region from the voltage sweep measurement. In the negative gate voltage regime as observed by the log scale plot (Fig. 2.21c) we observe that other than the 403.9 cm$^{-1}$ device, the other 3 devices appear to converge as the currents go down to $10^{-12}$ A/μm$^2$. The subthreshold slope region is much more sensitive to trap sites induced by defects and residues. We believe this to be the cause for the inconsistency between the devices in this region.

Figure 2.22: Plots of measured (a) mobility and (b) threshold voltage vs $A_{1g}$ peak position.

Mobility and threshold voltage are key metrics that effect transistors performance such as speed and power efficiency. The mobility is calculated using the field effect equation:
where \( \frac{dI_{ds}}{dV_g} \) is obtained from the slopes of the linear regime of the transfer curves, \( C_{ox} \) value of 11.5 nF/cm\(^2\) for 300 nm SiO\(_2\), and \( V_{ds} \) of 0.5 V. Since the channel was not etched into rectangular strips, the average lengths of the widths at the contacts were used. As shown in Figure 2.22a, field effect mobility of our devices have a wide range of 5.8 – 25.3 cm\(^2\) V\(^{-1}\)·s\(^{-1}\) which is comparable to previously reported devices of back-gated exfoliated and CVD monolayer MoS\(_2\)\(^{48–50}\). We observe a linear relationship between mobility and \( A_{1g} \) peak positions in which devices with lower \( A_{1g} \) peak positions have higher mobilities compared to those with higher peak positions. This relationship appears to be applicable even when including devices of both types of growth conditions. The threshold voltages were obtained from the x-intercept of the linear extrapolation in the linear region of gate voltage sweeps (Fig. 2.22b). We observe a range of ~-8.8 V - +20.2 V and a linear relationship with \( A_{1g} \) peak positions. For the threshold voltage the lower \( A_{1g} \) peak position devices have lower threshold voltages, inverse of the trend observed in mobility. These trends confirm that the relationship between carrier concentration and the \( A_{1g} \) peak position can be observed from electrical devices and their performance metrics. We believe that deviations from the trends in mobility and threshold voltage would be due to defects or residues in the channel or contact region of the device. The performance metrics of the devices measured were comparable to previously reported devices of back-gated exfoliated and CVD monolayer MoS\(_2\)\(^{48–50}\).
2.4 Conclusion

An alternative method for CVD synthesis of monolayer MoS\(_2\) using a defect-rich bulk MoS\(_2\) precursor source is demonstrated. Unlike a direct evaporation and re-deposition mechanism that would be expected, we observe an oxidation and re-sulfurization process. The synthesis produces monolayer flakes of varying sizes, shapes, and electrical properties depending on the growth parameters and relative location to the source. Under low sulfur flow, we observe larger triangular flakes but with interfacial contamination between the flakes and the substrate. This contamination layer does not appear in flakes grown under higher sulfur flow. The MoS\(_2\) flakes probed by Raman and photoluminescence spectroscopy exhibit the characteristics of monolayer thickness and good crystalline quality. Electrical measurements of devices show n-type semiconductor field-effect transistor switching properties. The Raman A\(_{1g}\) peak position of the device channels is observed to be related to the current density, mobility and threshold voltages of the devices, with the latter 2 properties showing a linear relationship with the peak positions.

2.5 References


continuous films of monolayer MoS$_2$ by atmospheric pressure chemical vapor deposition. 


40. Zhang, C., Wang, H., Chan, W., Manolatou, C. & Rana, F. Light Absorption by Excitons


Chapter 3

CVD MoS$_2$: Device Fabrication by Photolithography Process

3.1 Introduction

A noticeable trend in electronic devices based on MoS$_2$ and other 2D materials is the large range in performance metrics demonstrated, even when similar material synthesis and fabrication methods are used. Field effect mobilities have been found to range from 0.5 - 300 cm$^2$ V$^{-1}$ s$^{-1}$ just from exfoliated devices alone, without considering in the factors of material quality of thin film synthesis$^{1,2}$. Factors in these discrepancies involve intrinsic material properties$^{3-6}$, environment$^7$, metal contact material$^8,9$, and surface residues$^{10}$. One of the factors expected to be critical to the device performance is the fabrication process due to the chemicals that come into contact with the material. In this section, we investigate the effects of photolithography process on the material properties of CVD grown MoS$_2$. In particular, the application of the lift-off layer/photoresist layer and the exposure to a base developer is of interest. An alternative process where MoS$_2$ is only in contact with solvents is then demonstrated and devices fabricated by the two methods are analyzed.
3.2 Experimental Methods

3.2.1 Material Synthesis, Device Fabrication, and Characterization

Experimental methods and procedures involving material synthesis, device fabrication and characterization demonstrated here are previously referred to back in section 2.2.

3.3 Results and Discussion

3.3.1 Development with Base Solution

Figure 3.1: Intrinsic material properties of MoS$_2$ before processing: (a) Raman spectroscopy and (b) photoluminescence spectra.

The material properties of selected MoS$_2$ flakes are measured by Raman spectroscopy and photoluminescence spectroscopy as shown in Figure 3.1 prior to any processing steps. The selected flakes have characteristic Raman peaks at $\sim$384.5 cm$^{-1}$ for the E$^{1}_{2g}$ peak position and
~405.4 cm\(^{-1}\) for the A\(_{1g}\) peak position. The photoluminescence is sharp at 1.84 eV and dominated by the A exciton transition.

**Figure 3.2:** Photolithography process using a lift-off layer/photoresist bilayer and base developer.

A lift-off layer is a layer deposited underneath a photosensitive resist to provide easier removal of excess metal after deposition\(^{11}\). This is accomplished through the formation of an undercut which enables a break to occur in the metal deposition. It also has better thermal stability than photoresists to withstand the hardening effects of high temperatures during metal deposition. The photolithography process we used for MoS\(_2\) devices as shown in Figure 3.2, in which a bilayer resist structure of AZ5206E photoresist and Lor3A lift-off layer is applied onto a MoS\(_2\) flake. Following exposure to the UV light source in a contact aligner, the sample is
developed with AZ300 MIF, which is a 2.38% tetramethylammonium hydroxide (TMAH) solution.

**Figure 3.3:** (a) Optical image (Scale bar: 20 μm), (b) Raman spectra and (c) PL spectra of a flake after development in AZ300MIF.

A successful patterning process should show sharp edges of the pattern and a surface area clear of any residue as shown in Figure 3.3a. Following development, the flake in the exposed region is once again analyzed under Raman and photoluminescence spectroscopy. Significant changes are observed by both techniques. In the Raman spectra (Fig. 3.3b), the $E_{2g}^{1}$ peak is observed to blueshift 2.1 cm$^{-1}$ and the $A_{1g}$ peak is observed to redshift 0.8 cm$^{-1}$. A redshift of 0.8 cm$^{-1}$ signifies a change in carrier concentration of nearly $\sim3.6x10^{12}$ cm$^{-2}$. This charge transfer of electrons being donated to the MoS$_2$ is most likely from residual N(CH$_3$)$_4^+$ ions on the flake surface left over from the base solution. Superacids have been previously been used to enhance photoluminescence intensity by accepting electrons from MoS$_2$ in a similar manner$^{13}$. The $A_{1g}$ exciton peak from the photoluminescence spectra (Fig. 3.3c) undergoes a large intensity reduction of nearly 98% which is expected in the case of a large increase in charge carrier concentration intimated by the red-shifting of the $A_{1g}$ peak positions$^{14}$. 
The effects of the interaction with water and TMAH solution are of interest. During development, we kept the water rinse relatively short as there is a danger of the material being damaged. To study the effects of water and TMAH directly, we mix in isopropanol alcohol (IPA) to reduce the contact angle and lower chances of peeling. The effect of immersion in water/IPA is shown in Figure 3.4a. We observe that even without the base, the water/IPA solution affects the flake by slightly blue-shifting both $E_{2g}^{1}$ peak and $A_{1g}$ peak positions. It has been known that water vapor induces a charge transfer effect upon MoS$_2$ by accepting electrons$^{15}$. A fresh MoS$_2$ flake is then dipped in AZ300MIF/IPA solution for 10 seconds and then dried. The results in Figure 3.4b show the large shifts in the Raman spectra peaks that were observed during the development process. The sample is then placed in the water/IPA bath for 5 minutes in an attempt to restore the properties. Similarly to the purely water/IPA bath the final Raman peaks are slightly shifted and does not return back to its original state.
Figure 3.5: (a) Optical image (Scale bar: 20 μm), (b) Raman spectra and (c) PL spectra of device channel region.

After metal deposition and lift-off process using Remover 1165 or n-methyl-2-pyrrolidone (NMP) and acetone, flakes that were connected to the exposed region, such as the device channel region (Fig. 3.5a) are inspected. Surprisingly as shown in Figure 3.5b-c the Raman spectra peaks and PL spectra were similar to flakes that were completely exposed to the lithography processes. This would suggest that the developer solution is making contact with the flakes underneath through the interface of the flake and lift-off layer.

Figure 3.6: (a) Optical image (Scale bar: 20 μm), (b) Raman spectra and (c) photoluminescence spectra of an unexposed flake.
At the conclusion of the photolithography process, a flake in an unexposed region is analyzed as shown in Figure 3.6. The Raman spectra measured doesn’t signal any large shift and seems relatively identical from start to finish. The A exciton peak in the PL spectra did suffer a 21% loss in intensity but it is not completely quenched like those exposed to the base solution. The near unchanged Raman spectra suggests this intensity reduction is due to an increase in non-radiative recombination from either damage to the flake or surface residues acting as recombination centers.

From this information we can conclude that the positive ions from the base solution are lightly attached to the surface until it is rinsed off. This can potentially be utilized to control the doping of the channel region for modulating carrier concentration and at the contact edges for band alignment with metal contacts.
### 3.3.2 Solvent-Based Photolithography Process

![Photolithography Process Diagram](image)

**Figure 3.7**: Photolithography process using a lift-off layer/PMMA barrier layer/photoresist trilayer and solvent as patterning solution.

While the changes observed may or may not be beneficial to device behavior, a process that maintains the original state of the material could be useful. We modify the current process as shown in Figure 3.7 by adding a PMMA barrier layer between the lift-off layer and photoresist. The barrier layer has 2 functions: first is to prevent the dissolution of the lift-off layer when the photoresist is being developed, and second is to act as a patterning layer so that an undercut remains when the original lift-off layer is being dissolved in NMP. After following the original patterning step using a base developer, the PMMA layer and parts of the lift-off layer is etched away with oxygen plasma. The photoresist is more resistant to the plasma and remains through...
the etch step. Afterwards the sample is immersed in NMP to dissolve the lift-off layer in the exposed regions. To avoid potential residue from PMMA, the sample is sprayed with NMP after the immersion, sprayed with IPA, and then finally immersed in IPA solution. Afterwards the sample is dried with nitrogen air.

**Figure 3.8:** (a) Optical image (Scale bar: 20μm), (b) Raman spectra and (c) photoluminescence spectra of an exposed region under the solvent-based process.

From the results of the unexposed region in the base solution process, no shift is expected in the Raman spectra for the solvent based process. The results in Figure 3.8b support this assumption. A small loss of intensity in the photoluminescence peak (Fig. 3.8c) is also observed but remains at a higher intensity than that of Figure 3.6c. The difference could be due to the thermal effects from the metal deposition step. Further studies are required to analyze the effects of inadvertent thermal effects which include the optical camera in the contact aligner for alignment and the illumination from the plasma during the PMMA etch step. The high absorption and thermal isolation of MoS₂ flakes can rapidly heat up the material causing undesired interaction with the polymer layer.
3.3.3 Device Analysis

Figure 3.9: Electrical measurements from devices fabricated by different processes: (a) I-V sweep and (b,c) back-gated voltage sweeps. The inlet of (a) shows a magnified view of the I-V measurement of the solvent processed device.

The electrical device behavior is compared between devices fabricated by the two methods. Both devices show linear I-V behavior demonstrating ohmic contacts (Fig. 3.9a) with the base solution device having higher conductance. Back-gated sweeps from -60 V to 60 V at a $V_{ds}$ of 0.5 V are measured in Figure 3.9b-c. Both devices show n-type MOSFET behavior with on-off ratios of $\sim 10^6$. The base solution device again shows its higher conductance and
negatively shifted threshold voltage which would be in agreement with the effects of a higher carrier concentration or red-shifted Raman A_{1g} peak position.

![Graph showing mobility and threshold voltage comparison between base and solvent processes](image)

**Figure 3.10:** Comparison of the (a) mobility and (b) threshold voltage between devices fabricated by the two different processes.

The field effect mobility and threshold voltages of several devices are compiled in Figure 3.10. The calculation of the field effect mobility and measurement of threshold voltage has been discussed in section 2.3.5. The mobilities of devices fabricated by the two methods are similar, with the solvent method showing a slightly better result. The bigger difference is observed from the threshold voltage in which the solvent solution samples are very close together near ~22 V while the base solution samples are much more shifted ranging from ~-6 V to ~15 V. Considering the same material being used, we conclude that variation between the two sets originates from the fabrication process, particularly the residual ions from the base solution.
3.4 Conclusion

The effects of the base solution and water on MoS$_2$ properties is clearly observed through Raman spectroscopy, photoluminescence spectroscopy and device performance. The causes for the changes are due to charge transfer effects by residues from the base solution and damage from the photolithography process itself. While excess rinsing helps return the flake back to its original state, there will still be residual effects from adsorbed water itself. The base developer is also observed to penetrate the interface between the lift-off layer and the MoS$_2$ flake to leave residue on the surface of regions not exposed. The effects may however be beneficial as it provides an increase in charge concentration for lower threshold voltages. A solvent-based process presented allows the Raman spectra remains stable throughout the process, with the photoluminescence intensity undergoing a slight reduction. With the Raman A$_{1g}$ peak and associatively the charge carrier concentration remaining the same, the only explanation for this is non-radiative recombination centers from the residue of the lift-off layer. To reduce this effect, better cleaning processes are needed. Electrical devices from the two techniques reveal similar mobility values but the devices fabricated by the base developer demonstrate higher conduction and shifted threshold voltage most likely due to the effects of charge transfer from residue ions. Improvements to the solvent method can be possibly made by having a longer time to remove residue from the lift-off layer to make a cleaner interface with the metal contacts.
3.5 References


10. Shao, P. Z. et al. Enhancement of carrier mobility in MoS2 field effect transistors by a


CVD MoS$_2$: Phototransistor Device Analysis

4.1 Introduction

The band gap of MoS$_2$ between 1.29 – 1.9 eV makes it a suitable active material for electronic devices such as transistors and photodetectors$^1$. MoS$_2$ based photodetectors have demonstrated high responsivities upwards of 5,000 AW$^{-1}$ $^2$ however there have been difficulties in obtaining devices with fast response times. This is in large part due to interfacial charge trap sites that cause persistent photoconductivity (PPC) which can extend the response times to upwards of $10^5$ seconds$^3$.

In this chapter we investigate device behavior of CVD MoS$_2$ as a transistor and phototransistor. Low temperature electrical measurements are made to understand the carrier transport mechanisms and laser illumination is used to analyze devices as photodetectors. We confirm the persistent photoconductivity effect that is typical of MoS$_2$ photodetectors and investigate the effects of applied drain and back-gate voltages. We analyze the results and consider the potential application as an optical memory device.
4.2 Experimental Methods

4.2.1 Synthesis of CVD MoS$_2$

MoS$_2$ flakes in this chapter were grown using a conventional CVD synthesis using a MoO$_3$ precursor. The process parameters are similar to the growth process in Chapter 2, but the setup utilizes small amounts of MoO$_3$ (1 mg) loaded in a small 5 mL quartz boat which is then loaded into a larger 10 mL alumina boat. A piranha cleaned substrate is placed face down above the precursor supported by the larger alumina boat. A sulfur source of 3-4 mg is placed upstream in another alumina boat. The rest of the process recipe is identical for the growth at 600 °C and early sulfur melting time of 5 minutes except the pressure used here is 10 Torr.

Figure 4.1: Schematic of the CVD growth setup using MoO$_3$ precursor.
4.2.2 Device Fabrication

Two terminal field effect transistors (FET) structures have been fabricated as demonstrated in section 3.3.1 using the base solution based method. The devices in this chapter have been annealed in low vacuum at 0.5 Torr under 100 sccm Ar flow at 200 °C. The work in this chapter will mainly focus on 2 sets of devices, one made on 100 nm thick SiO₂ which was used for low temperature measurements and the other on 300 nm thick SiO₂ for phototransistor measurements.

4.2.3 Electrical and Optical Device Measurement

Electrical transport measurements were made using a probe station under vacuum with Agilent B1500A analyzer. Low temperature measurements are made through cryogenic cooling with liquid nitrogen. Optical sensor measurements were made using a Thorlabs 4 channel LED laser source with a 532 nm light source at a base power of 10 μW/mm² focused directly into the probe station.
4.3 Results and Discussion

4.3.1 Material Characterization

Figure 4.2: Analysis of a monolayer MoS$_2$ flake grown by MoO$_3$ precursor: (a) AFM image, (b) AFM line scan, (c) Raman spectra, (d) and photoluminescence spectra of monolayer MoS$_2$ flakes grown by MoO$_3$ precursor.

The synthesis using MoO$_3$ precursor yields monolayer flakes with similar characteristics (Fig. 4.2) to the monolayer flakes grown in Chapter 2. The general shapes are triangular/star-like and AFM analysis measures a height of ~0.7 nm which is consistent of a monolayer. Raman spectroscopy analysis demonstrates characteristic peaks positions of E$_{2g}^1$ at 384.3 cm$^{-1}$ and A$_{1g}$ at
405.0 cm\(^{-1}\) resulting in a characteristic difference of 20.7 cm\(^{-1}\). The photoluminescence spectra is dominated by the A exciton transition at \(~1.84\) eV.

4.3.2 Electrical Device Analysis

![I-V Sweep Graph]

**Figure 4.3:** Gate voltage-dependent I-V sweeps. (100 nm oxide)

Basic electrical measurements on three terminal transistor devices can elucidate a material’s electrical characteristics as well as the structural properties of an electronic device. I-V sweeps over varying gate voltages (Fig. 4.3b) show our device to have ohmic behavior across the contacts as in section 2.3.5. This is due to the use of silver as the contact material, which has a low work function and is a noble metal which has shown to wet the surface of 2D materials for better physical contact than non-noble metals such as titanium\(^4\).
Back-gated voltage sweeps of the devices between ±40 V at a $V_{ds}$ of 0.5 V is observed to have n-type behavior that is typical for MoS$_2$ FET devices (Fig. 4.4). We observe a high on-off ratio of $10^6$ and a negatively shifted threshold voltage with the minimum off-current being beyond the measurement window. This shift are due to the effects of annealing and long pump down in ultrahigh vacuum$^5$.

**Figure 4.4:** Back-gate voltage sweep measurement.

**Figure 4.5:** Temperature-dependent back-gate voltage sweeps in (a) linear and (b) logarithmic scale.
The charge transport mechanisms of materials can be extracted from temperature-dependent conduction measurements. Back-gated voltage sweeps were measured from room temperature of 296 K to the temperature of liquid nitrogen of 77.5 K. From Figure 4.5 we observe 2 trends: at higher gate voltages, conduction increases with decreasing temperatures and at lower gate voltages, conduction increases with increasing temperatures. These trends occur gradually across the gate voltages with a cross-over point at ~10 V. An increase in conduction with decreasing temperatures is typical behavior of a metal, while a decrease in conduction with decreasing temperatures is a behavior of an insulator. This phenomenon observed is called a metal-insulator transition (MIT) and is found in disordered systems where the increase in the Fermi level to the mobility edge results in non-localized conduction resulting in a band transport, while under the mobility edge the charge carriers are localized\textsuperscript{6–8}. 
Figure 4.6: (a) Conductance at different voltages at varying temperatures.
(b) Activation energy required to overcome potential barriers.

Transport mechanisms in disordered systems\textsuperscript{9} below the mobility edge can be generalized as thermally activated at higher temperatures and variable range hopping at lower temperatures. In thermally activated transport, carriers have enough energy overcome localized potentials barriers. As temperatures are lowered the carriers no longer have the energy to overcome these
potentials and hopping between local potentials becomes the dominant transport mechanism. Reports of MoS$_2$ transistors having both thermally activated and hopping transport$^6$ and only hopping transport$^7,10,11$ have been reported. Conductance at varying back-gate voltages are plotted against temperature in Figure 4.6a. It is observed that the thermally activated transport model fits conditionally at different gate voltages. From -20 V to -30 V the model fits until 220 °C before the conduction deviates. For -10 V to -15 V, the model fits until 140 °C and from -5 V to 10 V it remained within the thermally activated transport model to our measurement limit of -77.5 °C. The activation energy plotted in Figure 4.6b is calculated by Arrhenius relationship of:

$$G = G_0(T)e^{-\frac{E_A}{k_B T}}$$

where $G$ is the conductance, $k_B$ is the Boltzmann constant, $T$ is the temperature and $E_A$ is the activation energy. With the increasing energy required, it is logical that at lower voltages the carriers have insufficient energy at lower temperatures to overcome local potentials.
Figure 4.7: Conductance at different voltages at varying temperatures under $T^{-1/3}$.

The conductance measurements which do not fit with the thermally activated model are observed to fit well with 2D Mott’s variable range hopping model (Fig. 4.7). In this model the conductance follows dependence with temperature of $T^{-1/3}$. The reduction in temperature prevents carriers from overcoming potential barriers and allows them to only conduct by tunneling between localized states$^{12}$. 
Lastly the mobility at varying applied gate voltages are calculated at the different temperatures using the field effect mobility equation as previously used in section 2.3.5. This equation is normally applied in the linear regime but it is applied here at each point to observe the evolution of the mobility as we sweep the back-gate voltage. The instantaneous slope was used for each point as a substitute for the slope of the linear regime. The results shown in Figure 4.8 demonstrate that at low temperatures the mobility is continuously increasing and the device still has not reached the linear region at the gate voltages measured here. As the temperature increases the mobility is observed to level out, particularly between 20–40V from the measurements made at 260K and 295K.

### 4.3.3 Phototransistor Device Analysis

Phototransistors are photoconductors with the ability to control its charge carrier concentration to modulate the net photocurrent and response time. Several different mechanisms
for photoconduction exist for 2D materials devices. The main mechanisms for MoS$_2$ detectors are the photoconductive effect where photo-excited carriers increase the carrier concentration and conductance and the photo-gating effect where carriers from localized trap states escape create localized floating gating effects\textsuperscript{13}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_9.png}
\caption{(a) Back gate sweep under dark and illuminated conditions. (b) Calculated net photocurrent and gain. (300 nm oxide)}
\end{figure}

Transistor devices are measured under illumination by a 532 nm light source at a base power of 10 $\mu$W/mm$^2$. The dependence of the photocurrent on back-gate voltage is shown in Figure 4.9a. An illuminated photocurrent is observed throughout the gate voltage sweep. The net photocurrent shown in Figure 4.9b is calculated from a simple equation:

$$ I_{ph} = I_{illum} - I_{dark} $$

The net photocurrent is observed to saturate and even decrease at high voltages. This implies that at high gate voltages a dynamic effect is occurring and needs to be examined.
4.3.4 Time-Resolved Photoresponse and Persistent Photoconductivity

Time resolved measurements are made to study the dynamics of the photoresponse and its mechanisms. For this measurement the device is exposed to the light source for a short amount of time from 5-30 seconds. The measurement continues after the light source is turned off.

**Figure 4.10:** (a) Analysis of the time-resolved photoexcitation behavior. (b) Band diagram illustrating the photoexcitation and relaxation process.
From Figure 4.10a, the illumination of the MoS$_2$ phototransistor induces a large photocurrent but with a slow response time while both under illumination and in darkness which is typical of the persistent photoconductivity effect$^{2,3,14}$. This behavior can be isolated into several distinct mechanisms. Initially there is a stable dark current where upon illumination the current rapidly rises within a few milliseconds. This can be interpreted as standard photoconductivity, with band to band excitation of valence electrons to the conduction band resulting in the increase in current$^{13}$. Afterwards we see a slow gain that follows a logarithmic time dependence of:

$$I = I_0 \log(t + \tau)$$

This behavior is rooted in the transfer of electrons from interfacial trap to the material channel, leaving behind net positive charges$^{15}$. When the light source is removed, the current sharply decreases due to band to band recombination but is much smaller than the initial band to band excitation. This is followed up with a very slow decay which follows an exponential time dependence of:

$$I = I_0 + A_1 e^{-t/\tau_1}$$

This slow decay is the process of negative charge carriers slowly being recaptured back into the interfacial trap sites. An illustration of the process is shown in Figure 4.10b.

**Figure 4.11:** Time-dependent photoresponse at different temperatures.
The PPC effect is further investigated through measurements at varying temperatures in Figure 4.11. As previously discussed in 4.3.2, at lower temperatures the conduction decreases as the transport mechanism switches to Mott variable range hopping. This prevents the charge carriers in trap sites from escaping, reducing the overall PPC effect both in under illumination and in darkness. At 100 K, we observe that the PPC effect is nearly gone.

4.3.5 Voltage Control of Photocurrent and PPC Effect

Persistent photoconductivity and slow response speed is an undesired trait for photodetectors. However recently it has been proposed this effect can potentially be utilized in an optical memory application\textsuperscript{16,17} particularly when the current change remains for a long time or even permanently. The persistent photoconductivity effect originates from the carriers in the interfacial traps on the SiO\textsubscript{2} surface, however the characteristic properties such as the net photocurrent and decay rate is dependent on the properties of the MoS\textsubscript{2} channel and device. This allows some form of control over the effect by applying an electrical bias.
Figure 4.12: Time-dependent photoresponse at varying gate voltages of (a) 0 V, (b) +60 V, and (c) -60 V.

The time-resolved photoresponse at varying gate voltages is plotted in Figure 4.12. Prior to any illumination there is already transient behavior observed which is induced by the gate voltages on trap sites at the interface. An applied negative gate voltage increases the total current by repulsing electrons away and creating hole trap sites while an applied positive voltage decreases the total current by attracting electrons to fill in hole trap sites. Upon illumination, we observe the transient behavior to be enhanced, where negative gate voltages continue to increase the net current and prevent recombination upon darkness while positive gate voltages reduces the net current and promotes recombination.
Figure 4.13: Time-dependent photoresponse at varying applied drain voltages of

(a) 0.25 V, (b) 0.5 V, (c) 1 V, (d) 1.5 V, (e) 2 V, and (f) 5 V.

The study is continued under different applied drain voltages which are also observed to change the behavior of the temporal response of the phototransistors. In Figure 4.13a-d, after the illumination is turned off the decay of the photocurrent appears to be steady after 20 - 25 seconds and does not fall any further. The current fluctuates and in some cases even appears to increase at times. When the applied drain voltage is increased to 2V and 5V as shown in Figure 4.13e-f, a reducing effect is observed constantly in the background. This effect appears to be similar to when a positive gate voltage was applied in Figure 4.12b. It may be possible that at these higher drain voltages the back-gate is being biased enough to affect the channel. This background current reducing affect eliminates any net photocurrent generated unlike the lower applied drain voltages.
Like for standard memory devices, key metrics for an optoelectronic memory device would be the net photocurrent and gain. These metrics are extracted from the measurements in Figure 4.13 and plotted in Figure 4.14. It is observed from Figure 4.14a that the maximum net photocurrent occurs near $V_{ds}$ of 1.0 V. At lower voltages less net photocurrent is generated while at higher voltages the amount of current that recombines increases. The gain shown in Figure 4.14b is maximized near a $V_{ds}$ of 0.5 V with a value of ~1.036. While these values are not extraordinary, modifications can potentially be made to improve the performance such as applying a negative gate voltage, increasing the power of the light source and extended exposure time.

### 4.4 Conclusion

The charge transport mechanism of CVD grown MoS$_2$ transistors are analyzed through low temperature measurements. We observed that at higher temperatures, thermally activated transport was the dominant transport mechanism while at lower temperatures the transport
mechanism switches to Mott variable range hopping. The transition temperature between the transport mechanisms also dependent on the gate voltage due to the activation energy required.

Analysis of MoS$_2$ as a phototransistor resulted in the observation of the persistent photoconductivity effect which greatly extends the response time in MoS$_2$ and other 2D material photodetector devices. The device behavior of this effect is studied at different applied gate and drain voltages. For the applied gate voltages, at -60 V the dark current is observed to increase prior to any exposure to light. After light source is turned on and off it is observed to reduce recombination effects. In contrast, at +60 V gate voltage, the dark current is observed to decrease prior to and after illumination. At measurements with varying drain voltages under 2 V we observe an eventual steady state current where the recombination ceases. When drain voltages 2 V and above were applied, we observed a constant decrease in dark current similar to the application of 60 V back-gate voltage. Calculating the net photocurrent and gain at varying drain voltages, the optimal performance as a memory device lies between 0.5 - 1.0 V. The overall performance however was limited but we believe that improvements can be made to this device by increasing the light intensity and applied a negative gate voltage where many devices have shown increase in gain$^{1,21}$.

4.5 References


5.1 Summary

In this work we have developed and analyzed new processes for 2D layered semiconductor molybdenum disulfide. Each step studied from synthesis, device fabrication, to device analysis is important towards the potential implementation of the material in commercial applications. Chemical vapor deposition of MoS$_2$ through oxidation-sulfurization process using a defect-rich bulk MoS$_2$ source provides an alternative pathway towards deposition of monolayer MoS$_2$ flakes from the current methods of using a molybdenum oxide precursor$^1$ or the direct evaporation$^2$ of MoS$_2$. The resultant flakes formed different shapes and sizes depending on the relative location of the substrate with the precursor source as well as the growth conditions controlling the sulfur flow. Varying properties from the flakes were also observed by analysis through Raman spectroscopy, AFM and photoluminescence spectroscopy. The electrical device measurements were consistent with previously observed of monolayer MoS$_2$ FET devices with n-type behavior and on-off ratios greater than $10^5$. 
An alternative photolithography process was demonstrated using a trilayer of photoresist/PMMA/lift-off layer. This method prevents contact with base solution which is used as a developer in standard photolithography processes. The base solution has been observed to change the properties of the MoS$_2$ flakes through charge transfer effects. The device performance between the devices fabricated through the two different methods was similar in terms of mobility but the base solution developed devices had higher conductance and negatively shifted threshold voltage. The solvent solution device demonstrated to be much more consistent with devices having a much narrower range of threshold voltages. In terms of yield, the solvent solution method demonstrated near 100% successful devices while many devices were damaged or broken with the base solution process due to the inconsistencies of the water rinse step.

The carrier transport mechanism and photodetector performance was investigated for MoS$_2$ devices. Analysis of low temperature electrical measurements indicated that the conduction mechanism for the MoS$_2$ devices is thermally activated at higher temperatures and variable range hopping at lower temperatures. These conduction mechanisms were observed to be connected to the photoresponse of the MoS$_2$, which upon illumination demonstrated photoconductivity but also a persistent photoconductivity effect which dramatically reduced the response time. Temperature varied time-dependent photoresponse measurements showed that the PPC effect increases when the temperature is higher due to the thermally activated transport mechanism allowing carriers to escape trap sites while at lower temperatures the dominant hopping mechanism prevents the carriers from escaping, greatly reducing the PPC effect. The behavior of the PPC effect was further investigated by applying gate and drain voltages. It was observed that the application of high positive voltages induced recombination or reduction of the dark current, while negative or low voltages prevented recombination and resulted in a net
current that reaches a steady state which could be used as an optimal memory effect. The performance metrics as an optical memory device however demonstrated a need for improvements in future works.

5.2 Future Directions

Further improvements can be made on the studies completed in this thesis. The CVD synthesis using the oxidation and re-sulfurization growth method has been shown to be limited in uniformity. We observed from continuing work that using a MoS$_2$ source grown on a substrate by the sulfurization of e-beam evaporated MoO$_3$ results in a large area, relatively uniform deposition of star-shaped flakes. Additional adjustments can also be made by changing the process conditions for the growth of the low quality MoS$_2$ film source material as well as the high quality monolayer MoS$_2$ flakes. New materials and alloys can potentially be synthesized by changing the pre-deposited metal oxide film and subsequent sulfurization or selenization. This method in particular could be useful for transition metal dichalcogenides with associated metal oxides that have high evaporation temperatures.

From our studies and literature, device fabrication processes with clean surfaces or without contact to carbon-based polymers and solvents, produce devices with better performance. In the method we demonstrated, improvements could be made by substituting the PMMA layer for a layer that is insoluble to NMP to allow for longer a clean time on the contacts. Alternatively an initial deposition of a top dielectric prior to fabrication would prevent any contact with carbon-based polymers or other chemicals with the channel region.
Improvements to phototransistors of MoS$_2$ can be split into different areas of focus. For applications as a photodetector, increase in responsivity can be assisted by light management structures such as plasmonics$^7$ and antireflective layers. The use of alternative substrates which reduces interfacial trap sites and encapsulating top dielectric layers$^8$ have been demonstrated to greatly improve response time. For optical memory devices the modification of the device structure can be tricky as while photocurrent and gain would greatly increase, it has been observed that metal nanoparticles and particularly top dielectrics not only induce charge transfer, it also increases speeds up response times. A device structure that can enhance absorption without any structures making physical contact with the material may be optimal for this type of device.

5.3 References


List of Publications


**Manuscripts in Progress**
