# MoS2/Si Photodetector

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## Master of Technology

*in*

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# Abstract

A nano-sheet Molybdenum disulfide (MoS2) is a direct band gap semiconductor, unlike its bulk counterpart. A photodetector based on the solvent-based exfoliation technique of MoS2 nanosheet is fabricated over a SiO2 substrate. This method results in a highly pristine structure as well as a high-quality yield. For which its various structural characterization and electrical characterization are discussed in detail. This chemically exfoliated MoS2 structure shows a prominent band gap for the photoluminescence devices. All the electronic and optoelectronic properties of MoS2 are accompanied by interesting mechanical properties with monolayer MoS2 being as stiff as steel and 30× stronger.

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# Chapter 1

# INTRODUCTION

The ability to obtain single-layer graphene has opened up new possibilities and research into the physics of two-dimensional materials [1]. This is possible due to the advanced equipment and tools and a growing understanding of atomically thin layered materials. Graphene has attracted a lot of attention due to its ultrahigh mobility, good thermal conductivity and excellent mechanical properties [2].In particular, great interest has been focusing on single-layer semiconducting materials, such as Molybdenum disulfide(MoS2), one of the transition-metal dichalcogenides(TMDC), which exhibits the unique physical, optical and electrical properties correlated with its 2D ultrathin atomic layer structure. Molybdenum disulfide (MoS2) is the most studied material due to its presence in nature as molybdenite. Earlier it is used as a dry lubricant in automobile industries due to its low friction properties [3]. MoS2 which is a layered transition metal dichalcogenide (TMDC) has been explored for applications in photovoltaics and photocatalysis. TMDC are MX2-type compounds where M is a transition element from groups IV, V, and VI of the periodic table and X represents the chalcogen species S, Se, and Te [1]. These types of materials can be semiconductors, conductors or even superconductors. They show different band gaps at bulk and at monolayer i.e. the band gap changes with respect to the thickness of the material. Two-dimensional TMDCs have strong molecular intralayer bonds but weak interlayer bonds, giving rise to their layered structure and consequent anisotropic properties [1]. To get the layered MoS2 from the bulk there are several processes to achieve it among them Liquid Phase exfoliation(LPE) is found to be the simplest and most cost-effective [4]. The most attractive feature of the LPE process is that it yields suspension of TMDC nanosheets which enables easy growth of nanosheets thin films [3]. The shelf life of the MOS2 nanolayer is around a week if kept in a normal environment but it can be extended by months by keeping the solution at a controlled 5 degrees C.

# Chapter 2

# LITERATURE REVIEW

For the fabrication of the layered MoS2 from bulk MoS2, Exfoliation is the most common and widely used process. Exfoliation is the technique in which the bulk is broken into nanosheets. It is further divided into mechanical exfoliation and Liquid Phase Exfoliation (LPE). As the name suggests in mechanical exfoliation we use a mechanical parameter and in LPE we use the liquid chemical form to get the nanosheets from the bulk material.

## 2.1 MECHANICAL EXFOLIATION

Novoselov et al were among the first to use mechanical exfoliation or the "Scotch tape method" to obtain few- or even single-layer graphite [1]. In the mechanical exfoliation, a high-quality bulk MoS2 and scotch tape are used. Due to the use of scotch tape, this process is also called the scotch tape method. In this process, scotch tape is used on bulk MoS2 adhere and exfoliated in a repeat process and then the obtained result is adhered to the substrate. This results in the formation of an ultrathin layer of MoS2 on the substrate. To observe the monolayer or few-layer MoS2 flakes on the substrate, a specific thick dielectric-layer-coated substrate is needed as the exfoliated monolayer or few-layer MoS2 must have an excellent optical contrast to be easily identified under an optical microscope. Silicon oxide is the most commonly used substrate [1]. The MoS2 obtained through mechanical exfoliation is mainly used for lab purposes, for research purposes as it has the perfect crystalline structure and pristine quality. However, the yield of the process is extremely low.

## 2.2 LIQUID PHASE EXFOLIATION

Another exfoliation technique used for peeling single layer MoS2 is the Liquid Phase exfoliation(LPE), sometimes known as chemical exfoliation. In this process, chemicals are used for the fabrication of single-layer MoS2. this process is further divided into ion intercalation and solvent-based exfoliation(sonication process). LPE is the simplest

and most cost-effective process of all the processes. For this article, we are using the sonication process as it requires less time in nanolayer formation and provides a high yield as compared to mechanical exfoliation.

### 2.2.1 ION INTERCALATION

Ion intercalation is a process in which ions are used for the formation of single-layer MoS2. In this process, ions are introduced externally in the gaps between MoS2 which widen the gaps and finally, we get the single-layer MoS2. In this n-butyl lithium is a commonly used solution as a source of lithium due to the small size of the lithium. After the lithium-ion intercalation, water is used which reacts with the lithium and forms hydrogen. This hydrogen gas between the layers pushes the MOS2 layers apart resulting in the singelayer MoS2. Methanol, ethanol, isopropyl alcohol, or rapid heating in a vacuum at around 600℃ can also be used to release MoS2 layers instead of water [1]. This process holds several drawbacks which are-

- High-temperature requirement of around 600℃
- Longer reaction time of approx 3 days
- Little control over the intercalation process
- Causes structure conversion from hexagonal to octahedral

A low level of intercalation results in a low yield of single-layer sheets, while excess intercalation causes the decomposition of MoS2 into metal nanoparticles along with the generation of Li2S.

### 2.2.2 SOLVENT BASED EXFOLIATION(SONICATION)

Solvent-based exfoliation is relatively new which was first proposed in 2011 and is often referred to as the Coleman process. This process is also known as the sonication process as the major process is done using the sonicator. For the formation of the MoS2 single layer, we are using this process as it consumes much less time and provides better yield. In this process, the bulk MoS2 is introduced into the inorganic solvents to form a solution at a certain ratio followed by the process of sonication at a certain rpm and time. For the selection of inorganic solvents, the surface tension plays a vital role as the primary function of the solvent is to decrease the energy required for layer separation. The surface tension of the MoS2 is 46.5 mJ/m2 so we have to choose a solvent whose surface tension matches it. There are very limited no of inorganic solvents which are explored for the exfoliation process some of them are N-methyl-2- pyrrolidone (NMP), N-cyclohexyl-2-pyrrolidone (CHP), isopropanol(IPA), ethanol and even water. NMP and CHP can not be used as their boiling point is above 200C. Water can be used as a solvent but it has its limitations as long process time and most importantly the large surface tension mismatch. At room temperature surface tension of the water is 70 mJ/m2. So for the exfoliation of MoS2 aqueous ammonia(NH3)(50%v/v) solvent is

the best suited as its surface tension is approx 49 mJ/m2 which facilitates the efficient exfoliation of MoS2. In comparison with water-only exfoliation, the aqueous ammonia method offers important advantages such as shorter sonication times, higher yield, and improved suspension stability even at low temperatures [2]. This method is sometimes also preferred as the use of the organic solvents preserves the 2H-MoS2 (hexagonal) crystal structure, the semiconducting structure of MoS2, unlike ion intercalation which tends to render metallic MoS2 with 1T-MoS2 (octahedral) crystal structure [1]. Apart from several advantages sonication process also has a flip side, including the low yield of single-layer sheets and low MoS2 flake concentration in the solution (0.25 to 0.3 mg/mL) [1]. The major drawback of the sonication process is it causes the tearing of 2D material sheets reducing their dimension to a few thousand nanometers and even smaller. So the small-sized MoS2 layers can not be used for electronic devices that are directly built on them.

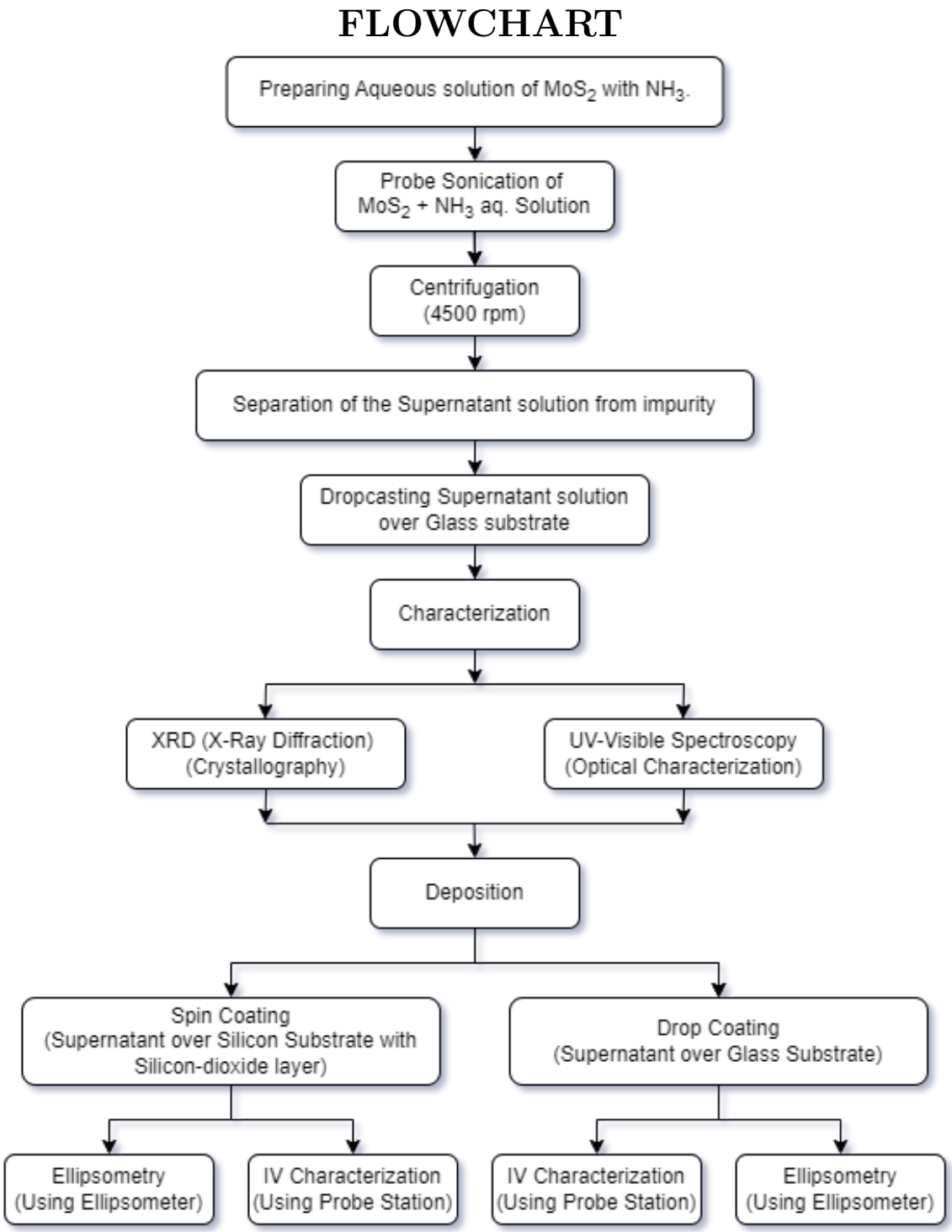


Figure 2.1: Flowchart of MoS2 Fabrication over SiO2 Substrate.

# Chapter 3

# CHARACTERIZATION

Characterization involves finding the various characteristics of the formed material via different processes. In the MoS2 solution, we are performing crystallization characterization using X-ray diffraction(XRD) techniques and optical characterization using UV-visible spectroscopy.

## 3.1 CRYSTALLIZATION CHARACTERIZATION

The crystallisation characteristics of any sample are determined with the help of the X-ray diffraction process. XRD is a technique to determine the crystallographic structure of a substance using the X-ray beam. It is a non-destructive technique. An XRD machine consists of an X-ray source that emits X-rays on the substrate and a detector that detects the scattered rays from the substrate. When the X-ray is incident on the substrate at different angles by moving in the measuring circle then every plane on the substrate reflects the light which is then analyzed by the detector. The reflected rays form constructive or destructive interference. According to Bragg's law [6] for constructive interference-

$$n\lambda = 2dsin\theta$$

The pattern of reflected rays provides the blueprint of the material's structure. Thus, we can find the lattice distance as well as the distance between the planes. To perform the XRD process, we first drop-cast supernatant over a glass substrate at a temperature of 50°C for 10 layers. This will act as a material in which we will perform XRD. On performing the XRD we get a graph between the angle and intensity in which several peaks are at different points. If these peaks are shifting then it represents the homogeneous strain and if these peaks are broadening then it represents the heterogeneous strain. We can observe in Figure 3.1 that we are getting three peaks achieved via the XRD process. The two peaks which are 38.248° and 44.487°represent the MoS2 with the glass substrate. The first peak is at 14.72° which represents the MoS2 layers. So for MoS2, we have calculated the distance using Bragg's law which is 0.607 nm.

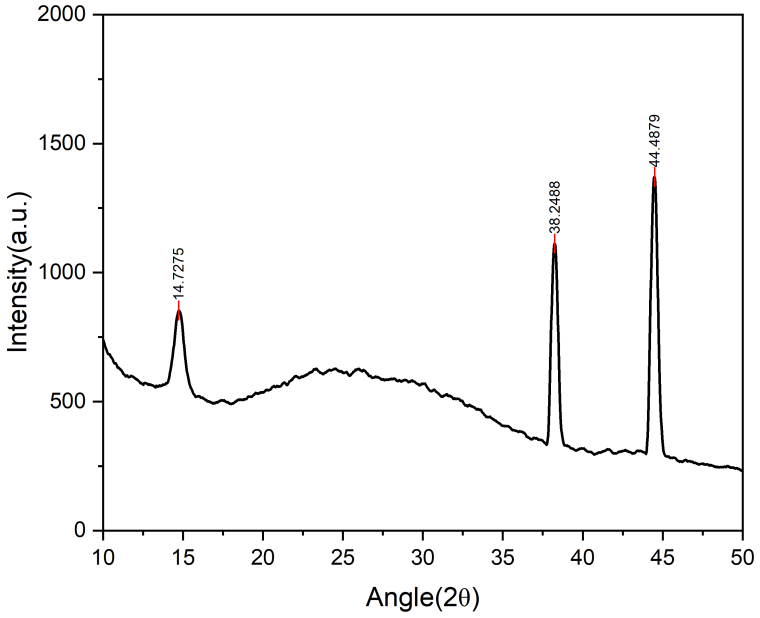


Figure 3.1: Intensity vs Angle plot obtained from XRD Technique.

## 3.2 OPTICAL CHARACTERIZATION

Optical characterization is performed on a material to get its optical characteristics like the band gap of the material and concentration of the material. In this light is transmitted from the material to determine the properties of the material by analyzing how the light interacts with the material. It is often a non-destructive process and requires a very small quantity of sample material. It can be used to probe the physical and chemical properties of the material. For our sample characteristics, we are performing UV-visible spectroscopy which ranges from 200nm to 800nm. In this, we are using a small quantity of MoS2 solution to perform the characteristics. We first set the complete system, and place the MoS2 solution in the cuvette made up of quartz or plastic. We pass the light range from 200nm to 800nm. At a particular range, the material will observe the light where we will achieve a peak. For MoS2 there peaks occur at 606nm and 667nm observable in Figure 3.2. With the help of the graph received of absorbance of light vs wavelength we can draw the Tauc plot which will help to understand the energy band. From Figure 3.3, we find out the bandgap of the material is 1.93eV which is approximately equal to the bandgap energy of single layer MoS2.

## 3.3 STRUCTURAL CHARACTERIZATION

To measure the thickness of layers that are formed over the substrate we perform the ellipsometry process. For this process, we use the ellipsometer from J.A. Woolan. It is an instrument which is used to measure the thickness of the material over the substrate with the help of a light source. This works on the phenomenon of light reflection. In

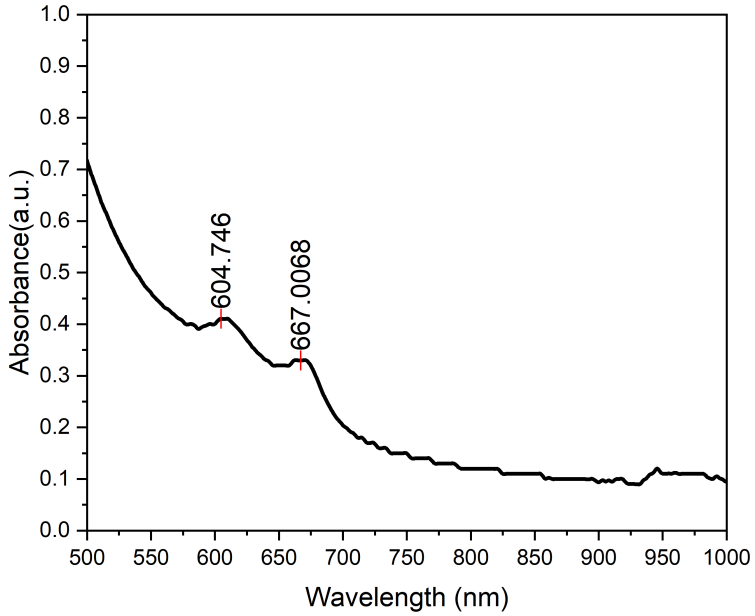


Figure 3.2: Absorbance vs Wavelength for UV Visible range.

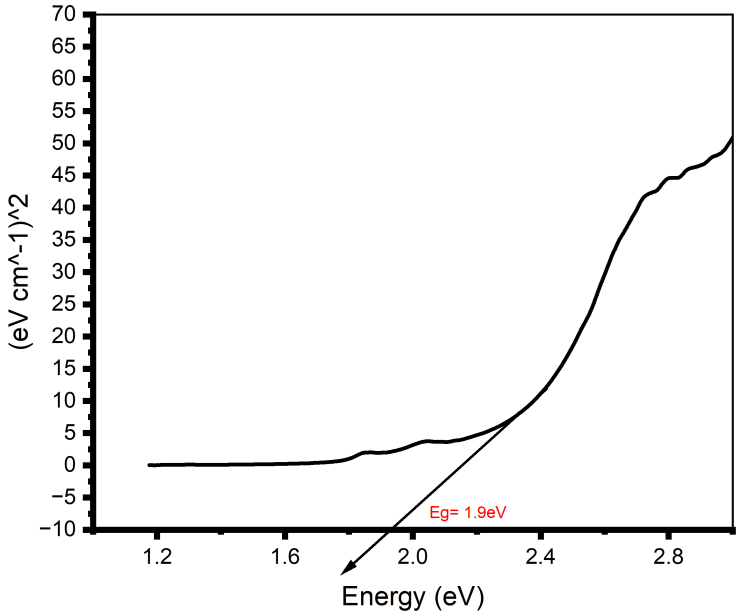


Figure 3.3: Tauc Plot for Energy Bandgap Calculation.

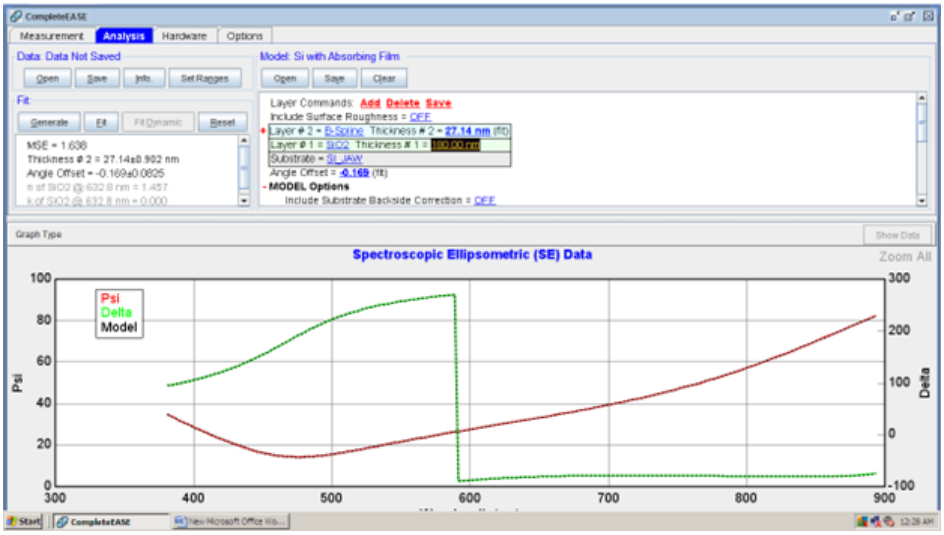


Figure 3.4: Ellipsometer thickness reading for MoS2 Layers.

this, a light source is incident onto the substrate and there is a detector on the other side which detects the diffracted light from the source. Based on diffracted light, it provides the thickness of the material formed. We first place our design over the ellipsometer and to keep it stable we use the vacuum pump followed by calibration of the transmitter and light detector. On executing the software onto the system we can easily get the thickness we have achieved after the drop-casting which can be easily seen from the Figure 3.4. The formed layer is 27.14nm thick.

# Chapter 4

# ELECTRICAL CHARACTERIZATION

The electrical characterization was done using Probe Station (JANIS RESEARCH) combined with Source Measure Unit (SMU) (B2910BN). The Device under test (DUT) was put inside the source probe station and the probes were placed on the device to obtain the electrical characterization. There were two types of current calculated for the DUT:

- Dark Current.
- Current in presence of light.

The Dark current is the current obtained in a dark environment, which was found out to be nearly 1.05 nA. The dark current was taken as the baseline for the measurement of on current to off current ratio of DUT. The on current was found to be 1.9 nA. Which is calculated as:

$$A = I_{on}/I_{off} = (1.9 \times 10^{-9})/(1.05 \times 10^{-9})$$

So, the $I_{on}$ was found out to be 1.8 times $I_{off}$ (81.5%). Which is shown in the Figure 4.1. The rise time of current for the DUT was found to be $t_{rise} = 30$ sec, and the fall time of current for the DUT was found to be $t_{fall} = 120$ sec.

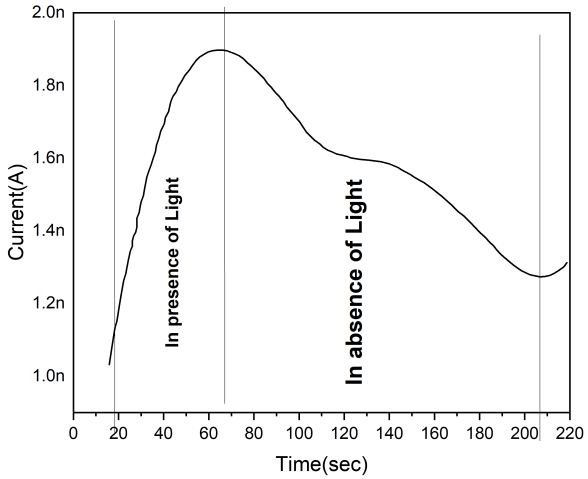

Figure 4.1: Current Versus Time.

# CONCLUSION

In this project, we have formed a Single layer MoS2 from its bulk. Followed by Crystallization and Optical characterization with the help of XRD and UV-Visible Spectroscopy. The supernatant solution was deposited over the SiO2 substrate of thickness 180 nm. Followed by ellipsometry, we found the thickness of MoS2 to be 27.14 nm. This concluded the making of our photodetector, which was followed by IV characterization. In which we observed that the photodetector showed a variation of current under the presence of light.

# References


[1] R. Ganatra and Q. Zhang, "Few-layer mos2: A promising layered semiconductor," *ACS Nano*, vol. 8, no. 5, pp. 4074–4099, 2014, pMID: 24660756. [Online]. Available: https://doi.org/10.1021/nn405938z

[2] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, and H. Zhang, "Single-layer mos2 phototransistors," *ACS Nano*, vol. 6, no. 1, pp. 74–80, 2012, pMID: 22165908. [Online]. Available: https://doi.org/10.1021/nn2024557

[3] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, and M. Chhowalla, "Photoluminescence from chemically exfoliated mos2," *Nano Letters*, vol. 11, no. 12, pp. 5111–5116, 2011, pMID: 22035145. [Online]. Available: https://doi.org/10.1021/nl201874w

[4] H. Li, J. Wu, Z. Yin, and H. Zhang, "Preparation and applications of mechanically exfoliated single-layer and multilayer mos2 and wse2 nanosheets," *Accounts of Chemical Research*, vol. 47, no. 4, pp. 1067–1075, 2014, pMID: 24697842. [Online]. Available: https://doi.org/10.1021/ar4002312

[5] Y. Yoon, K. Ganapathi, and S. Salahuddin, "How good can monolayer mos2 transistors be?" *Nano Letters*, vol. 11, no. 9, pp. 3768–3773, 2011, pMID: 21790188. [Online]. Available: https://doi.org/10.1021/nl2018178

[6] C. G. Pope, "X-ray diffraction and the bragg equation," *Journal of Chemical Education*, vol. 74, no. 1, p. 129, 1997. [Online]. Available: https://doi.org/10.1021/ed074p129