Tunable Gas Sensor

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in

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by

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Abstract

Two dimensional(2D) materials has been extensively researched in the field of gas sensing due to their layered structure. MoS2 attracts a lot of attention due to their high surface to volume ratio with tunable band gap. The present article is aim to fabricate the MoS2 nanosheet based chemiresistive gas sensor from its bulk counterpart for the detection of various toxic gas by varying the temperature level. The article reviews the various gas sensing mechanism and synthesis techniques of single sheet MoS2.

Contents

Chapter 1

INTRODUCTION

Sensing gas molecule, especially toxic gas, is critical in environment pollution monitoring, agricultural and medical applications [1]. Due to this gas sensor with low noise and low power is high in demand in present time. In past times sensors were made from metal oxides due to the stability of the device. Schedin et al. [2] demonstrated that a micro meter-sized graphene transistor can be used to detect the ultimate concentration of molecules at room temperature, presenting a pronounced sensitivity many orders of magnitude higher than that of earlier sensors [1]. Since a lot of research is going on the field of Transition metal dichalcogenides they are now the preferred choice for the gas sensing device due to high response and recovery time. Recently two dimensional Molybdenum disulfide(MoS2) has grabbed a lot of attention due to its unique properties which can be used in design of gas sensors as resistive gas sensor, optoelectronic sensors, photodiode. 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]. Unlike graphene which lacks band gap, Pristine MoS2 has a direct band gap of 1.9eV which is totally different from its bulk counterpart which exhibits 1.2eV indirect band gap. These type of materials are called Transition Metal dichalcogenides(TMDC). 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 [4]. These types of materials can be semiconductors, conductors or even superconductors. As MoS2 also contains high surface to volume ratio comparable to graphene, expected that it will have excellent sensing performance as well. It works on the phenomenon of accepting and donating electron on coming in contact with the gas due to which there is change in the resistance(resistive gas sensor) of the device resulting in current change on exposure to gases like H2,NO2,NO,CO,NH3,O2.

Chapter 2

LITERATURE REVIEW

A gas sensor is a device that detects and estimates the presence of gas species. It transforms chemical information into useful signals for accurate monitoring. The steering committee of National Academies of Sciences, Engineering and Medicine in 1995 defined chemical sensors "as a device or instrument that determine the detectable presence, concentration, or quantity of a given analyte. The development of gas sensor technology has gained importance in last two decades for various application specific-areas. This includes environment monitoring for both outdoor and indoor air and healthcare in non-invasive diagnosis of several diseases . The quality of a gas sensor depends on several parameters which provide efficiency of the gas sensing device. All the parameters are discussed below:

2.0.1 Response:

It is the ratio of the resistance of the device when exposed to the analyte (Rgas) to the baseline resistance (Rbase) of the device (generally in presence of air or oxygen).

$$Response(intimes) = R_{gas}/R_{base}$$
$$Response(in\%) = ((R_{gas} - R_{base})/R_{base}) * 100$$

2.0.2 Sensitivity:

Senstivity is the change in the response of the sensor per unit concentration of the analyte.

$$Senstivity = Response/Concentration$$

2.0.3 Limit of Detection (LOD):

The lowest concentration of an analyte which can be detected by the sensor is known as its detection limit.

2.0.4 Selectivity:

Selectivity is the ability of the sensor to respond to a certain gas over other similar gas when in presence of mixture of gases. Apart from these, sensor performance is evaluated in terms of operation voltage, temperature, response time and recovery time.

2.1 Device classification:

Based on the sensing techniques of gas by the device the gas sensor is divided into following:

2.1.1 Electrochemical Sensors:

Electrochemical-type gas sensor consists of two electrode cells. The basic components of this type of gas sensors are (i) a working electrode (ii) a counter electrode, and (iii) an ion conductor in between them. It utilizes the humidity in atmosphere for gas sensing. When a toxic gas comes in contact with the working electrode, it gets oxidized by the water molecules in air.

$$XO + H_2O - - - -- > XO_2 + 2H^+ + 2e^-$$

The working electrode and the counter electrode are connected through a short circuit which allows protons (H+) generated on the working electrode to flow towards the counter electrode through the ion conductor and the connecting wire. On the counter electrode, the generated protons will react with oxygen from the air.

$$O_2 + 4H^+ + 4e^- - - - - - - > H_2O$$

The variation of current generated between the working and the counter electrodes would give the gas sensor response. This type of gas sensors are most abundantly fabricated in the industry. Ideally, a linear relationship exists between response and concentration of gas. o Engineering Inc., Japan). Electrochemical gas sensors can also be three electrode system.

2.1.2 Capacitive Sensor:

In this type of gas sensors, the change in the capacitance of a solid state capacitor (used here as gas sensor) is studied. It detects the change in the capacitance due to presence of the gas molecules. Capacitive type CO2 sensors are often fabricated by organically modified silicates as gas sensitive dielectric layers on interdigitated designs. As the gas comes in contact to the dielectric layer, CO2 being an oxidising gas reduces the dielectric thereby changing its capacitance [5].

2.1.3 Thermoelectric Sensors:

A thermoelectric sensor uses the heat of reaction on the sensor surface. It is mostly used to detect combustible gases at high operating temperatures. These sensors are easy to fabricate and highly stable and hence can be used easily. However, these sensors are generally power hungry and hence have limited use.

2.1.4 Chemiresistive Sensors:

Chemiresistive gas sensors consist of (i) a non-conducting substrate (typically ceramic or Si/SiO2), metal interdigitated electrodes (typically Au or Pt are used) and (iii) resistive gas sensing layer. There are various types of sensing materials that can be used depending on the end application of the gas sensor. These are (i) metal oxide (for high and fast response but poor selectivity) and (ii) polymers and 2D materials (for room temperature sensing but poor response). The mechanism of these gas sensors are based on the phenomenon of adsorption of oxygen species onto the sensing layer surface. Depending on the type of sensing layer (p or n type), the resistance of the layer decreases or increases.

2.2 MoS2 sythesis(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 [6]. 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 [7]. 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) [7]. 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.

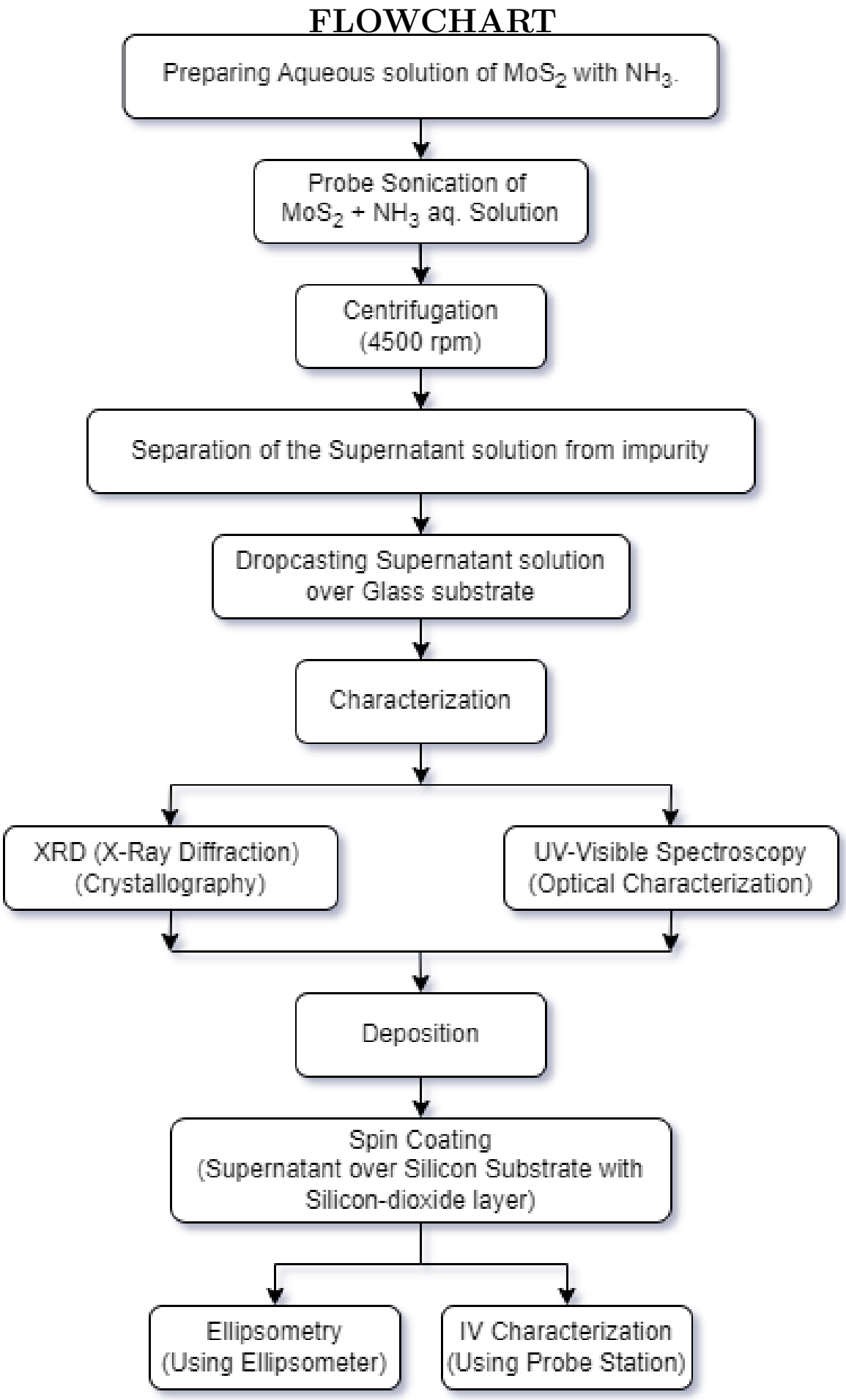

Figure 2.1: Flowchart of MoS2 Fabrication over SiO2 Substrate.

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 [8] 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.

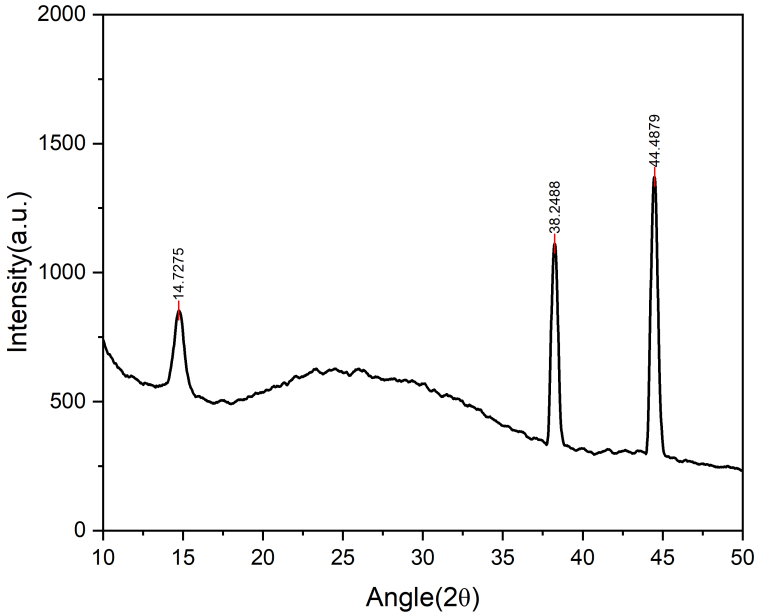

Figure 3.1: Intensity vs Angle plot obtained from XRD Technique.

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 SURFACE CHARACTERIZATION

In our mini project, we utilised a ZEISS scanning electron microscope (SEM) to analyze MoS_2 nanosheets and MoS_2 with sulfur defects. The SEM process involved preparing the samples and then imaging them at various magnifications to observe their morphology. For MoS_2 nanosheets, we expected to see layered structures with sharp edges,

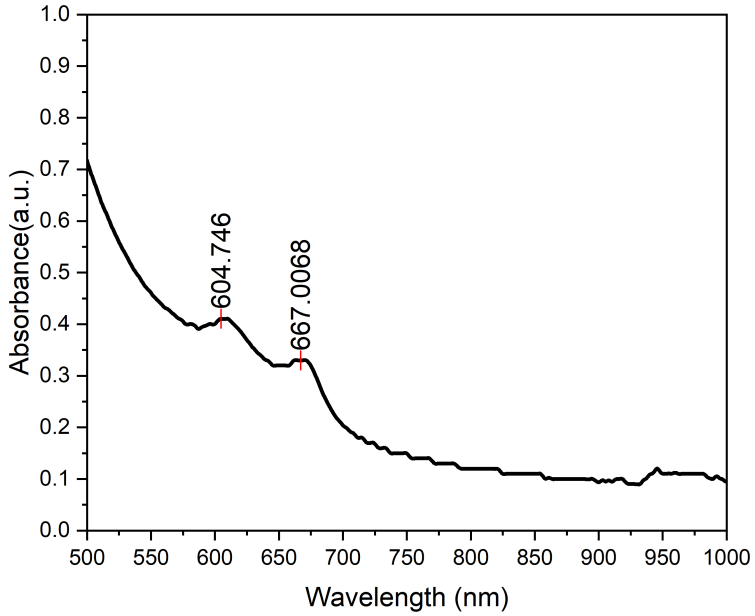

Figure 3.2: Absorbance vs Wavelength for UV Visible range.

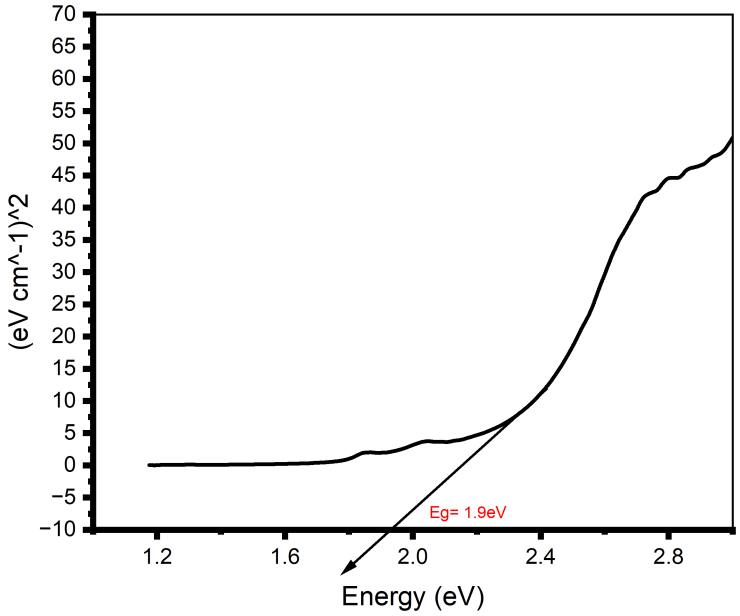

Figure 3.3: Tauc Plot for Energy Bandgap Calculation.

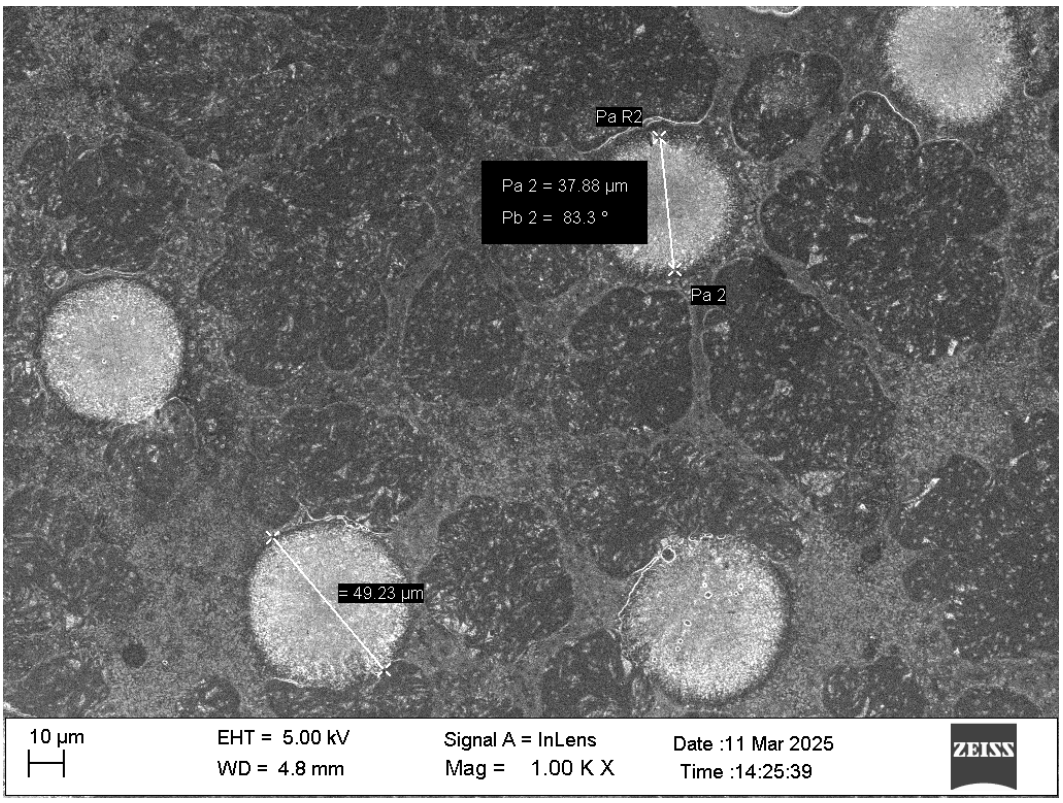

Figure 3.4: FESEM image of MoS2 (1).

potentially indicating catalytically active sites. For MoS_2 with sulfur defects, the SEM images might reveal structural irregularities or vacancies, which could enhance sensing capabilities. Observations from the SEM images can provide insights into the surface features and defects that influence the gas-sensing properties of these materials. The high-resolution images from the ZEISS SEM allowed us to assess the structural integrity and potential defects in both samples.

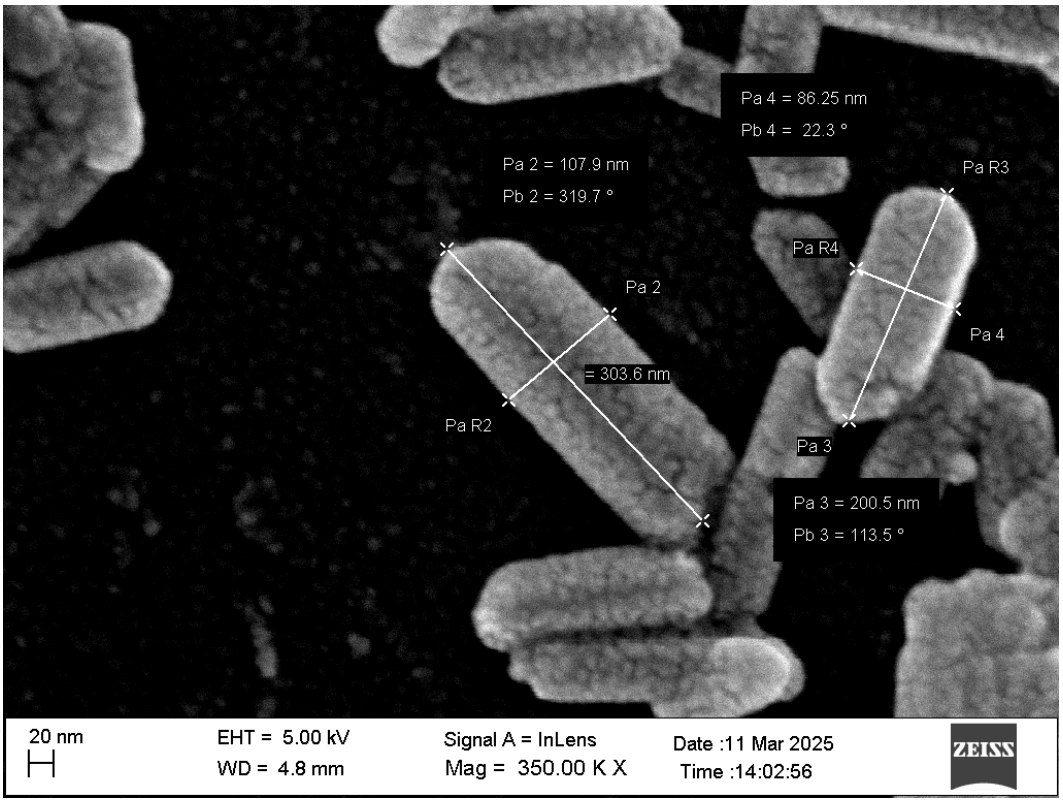

Figure 3.5: FESEM image of MoS2 (2).

Chapter 4

ELECTRICAL CHARACTERIZATION

The electrical characterization was performed using a Gas sensing system (Scientific and Analytical Instruments) combined with a Source Measure Unit (SMU) (B2910BL). The device under test was kept inside the gas sensing setup where two of the electrodes were attached, followed by sealing the sensing chamber. Then the Current vs time plot was plotted under NTP, vacuum and in the presence of NO_2 gas.

For which the obtained plots are shown in fig 4.1, 4.2.

$$test(SCCM) \; = \; required\, concentration(ppm) \times \frac{total \; flow \; rate(SCCM)}{cylinder \; conc.(ppm)}$$

but MFC can't flow above 10 SCCM. So, to get the concentration above 10 ppm, we have to use an alternate way by changing the flow rate of inert gas.

$$total \; flow \; rate(SCCM) \; = \; SCCM \; of \; NO_2(10SCCM) \times \frac{concentration \; of \; cylinder(ppm)}{desired \; ppm}$$

Response percentage of NO_2 gas:

$$Response(in\%) = ((R_{gas} - R_{base})/R_{base}) * 100$$

$$Response(in\%) = 60\%$$

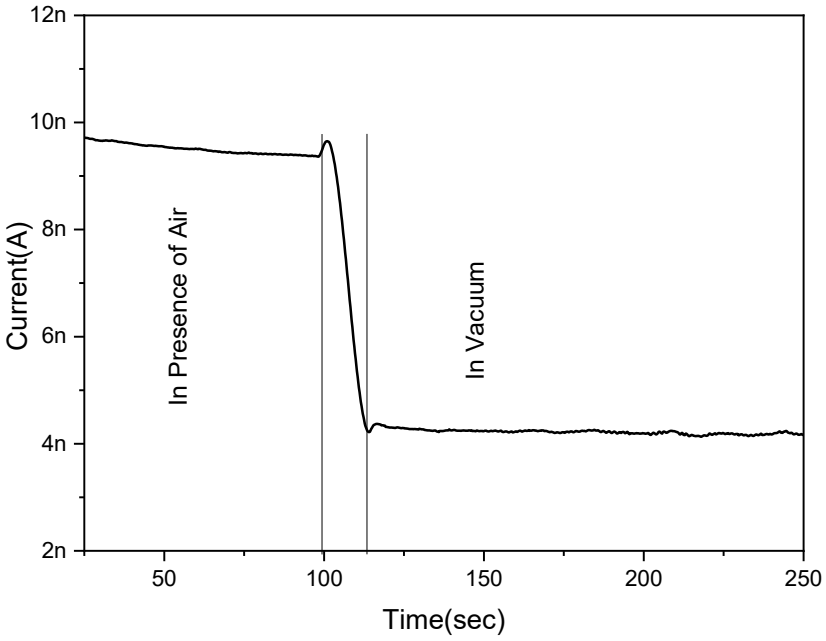

Figure 4.1: Current Versus Time in air and vacuum.

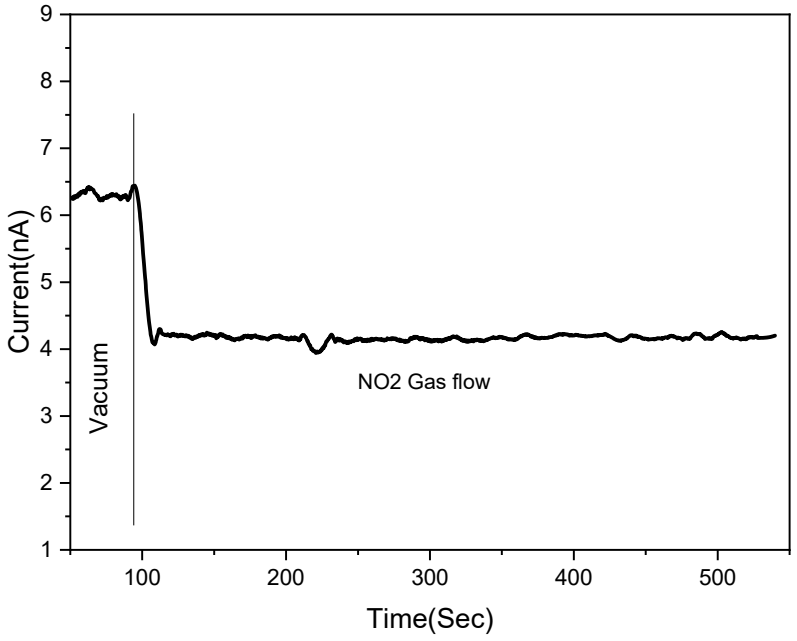

Figure 4.2: Current Versus Time in presence of NO_2 gas.

CONCLUSION

This project successfully synthesized and characterized few-layer MoS nanosheets via mechanical exfoliation, as confirmed by XRD (sharp (002) peak at 14.4°) and UV-Vis spectroscopy (A and B excitonic peaks at 670 nm and 610 nm, respectively). The transition from bulk (indirect bandgap 1.2 eV) to exfoliated MoS (direct bandgap 1.9 eV) was optically verified, aligning with its potential for gas sensing applications.

While the chemiresistive sensor demonstrated measurable responses to toxic gases (e.g., NO_2), incomplete recovery to baseline resistance was observed across tested temperature ranges. This limitation likely stems from: (1) Strong chemisorption, Gas molecules forming stable bonds with sulfur vacancies or edge sites in MoS. (2) Insufficient thermal energy, Operating temperatures may not provide adequate activation energy for desorption. (3) Structural defects, Exfoliation-induced defects could trap charges or gas molecules irreversibly.

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