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SynThesis, Device Fabrication, and Characterization of Two-Dimensional Molybdenum Disulfide

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SYNTHESIS, DEVICE FABRICATION AND CHARACTERIZATION OF TWO-DIMENSIONAL MOLYBDENUM DISULFIDE

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DEDICATION

This thesis is dedicated to my family, especially to my mother Etelvina Saenz, my role model. Thanks to her I have been able to reach my goals, and I am the person who I am because of her inspiration. In addition, this thesis is dedicated to all the academic mentors in my life who have guided my way up to this point, principally Dr. Jose Mireles from the Universidad Autonoma de Ciudad Juarez and my research advisor at UTEP, Dr. Anupama B. Kaul.
SYNTHESIS, DEVICE FABRICATION AND CHARACTERIZATION OF TWO-DIMENSIONAL MOLYBDENUM DISULFIDE

by

GUSTAVO ALBERTO LARA SAENZ
BS in Mechatronics Engineering

THESIS

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The work described in this thesis was made possible through the support and advice of my research mentor Dr. Anupama B. Kaul. Several research grants have enabled us to set up the Nanomaterials and Devices Laboratory which has allowed me to have access to research facilities and equipment in the Kaul Research Group at UTEP. We specifically acknowledge financial support from the University of Texas STARS program (EC284802), U.S. Air Force Office of Scientific Research (grant number FA9550-15-1-0200). The other agencies that provided support to me personally for my education include: CONACYT (National Council of Science and Technology of Mexico), Chihuahua’s government, and the SEP (Secretary of Public Education in Mexico). The collaboration with Dr. Aditya Mohite’s group at Los Alamos National Laboratory for Raman spectroscopy measurements was very valuable. In addition, I wish to acknowledge Dr. Deidra Hodges at UTEP who provided assistance in the deposition of molybdenum metal using sputtering. I also would like to thank my colleague, PhD candidate Eva Deemer, for measurements using the Atomic Force Microscope.
ABSTRACT

The miniaturization of electronic devices according to Moore’s Law has been propelled by the continuous demand for faster and smaller devices which continue to advance technology. One recent contribution to this trend was the isolation and characterization of one atom thick of graphite, known as graphene, which led to the Nobel Prize in physics in 2010 being awarded to Andre Geim and Konstantin Novoselov. Graphene and its related nanocarbon derivatives have exceptional mechanical, thermal, optical and electronic properties, making them a potential candidate for electronics and optoelectronics applications. However, this material has no intrinsic bandgap and complicated processes are required to open up a bandgap in graphene to make it attractive for semiconductor device applications. Nevertheless, the body of work on graphene has enabled researchers to investigate a new family of non-carbon based layered materials with a wide variety of compositions. Given that these 2D layered materials include, semiconductors, insulators, and semimetals, their potential applications include devices such as transistors, integrated circuits, sensors, solar cells, flexible electronics, and optical devices. Therefore, 2D materials is a multidisciplinary research area for their synthesis, characterization, simulation, and implementation. Moreover, a subcategory of 2D materials that have attracted significant attention are the TMDCs (Transition Metal Di-Chalcogenides). In addition, among this subcategory, the 2D semiconductor that has involved special interest since the demonstration of high performance for electronic and optoelectronic applications is molybdenum disulfide (MoS$_2$), the focus of this research. In this work, we have developed a process for the vapor phase synthesis of single-layer MoS$_2$. These process parameters have been analyzed in detail and the samples obtained have been characterized using Raman spectroscopy and Atomic Force Microscope. Following on from this synthesis work, we have developed a fabrication process to integrate few-layered MoS$_2$ for electronic and opto-electronic device applications.
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CHAPTER 1. INTRODUCTION

The synthesis, fabrication, and characterization of devices based on two-dimensional (2D) materials is a research area of interest in electrical engineering since these novel materials have the potential for many novel nano-electronic and optoelectronic devices, as is demonstrated by the exponential growth in publications emerging from these materials. In this work, in Chapter 1 a brief description, background, review, and applications of these materials is provided, that exhibit outstanding optical, mechanical, and electrical properties. Often times, these properties change immensely from the bulk to monolayers, reaching the ultimate miniaturization limit. From this broad family of materials, a subcategory has drawn special attention of researchers in multidisciplinary areas, the Transition Metal Di-Chalcogenides (TMDCs), emphasizing in monolayer molybdenum disulfide (MoS$_2$), material in which this work is focused. In chapter 2, the basics of a selection of characterization techniques, including electron microscopy and spectroscopy, applied in this novel family of materials is explained. As in the previous chapter, it is focused on their application in 2D MoS$_2$ by highlighting some interesting properties of the material to analyze the information provided by these characterization tools. Next, the synthesis approach for 2D MoS$_2$ (some of them applied for layered materials in general) is discussed in Chapter 3. Here, the specifics are explained for the synthesis in vapor phase. Then, the experiments developed and results obtained using this approach are described in detail, including the material characterization techniques utilized, such as Raman spectroscopy and Atomic Force Microscopy. Chapter 4 provides details of the process for device fabrication based on MoS$_2$. In addition, electrical characterization of MoS$_2$ devices as a function of temperature and optical response is shown, including the data analysis and extraction of key parameters of the device, such as contact resistance, Schottky barrier, and photoresponsivity. Finally, the conclusions from the research developed are discussed in Chapter 5, including some comments on future directions for this work.
1.1 Two-Dimensional Layered Materials

The advance in science and technology thanks to research have allowed a tendency in the miniaturization of electronic devices following Moore’s Law, at the same time, the cost of semiconductor technology is decreasing among with the power consumption. A significant contribution for the development of a new generation of devices was the isolation of graphene, a monolayer of sp2-bonded carbon atoms arranged in a hexagonal lattice. The finding and characterization of this allotropy of carbon have demonstrated its exceptional mechanical, optical, thermal, and electrical properties. This study lead to a Nobel Prize in physics in 2010 [1], [2]. The investment and intensified research in graphene led to the exploration of other two-dimensional materials, introducing to the discovering of a complete family of materials with outstanding properties, including semiconductors, insulators, and semimetals [3], [4]. The application of these materials have demonstrated their applications in novel electronic devices such as transistors [5]–[7], integrated circuits [8], [9], sensors [10], [11], optical devices [12]–[14], solar cells [15], [16], flexible electronics [17]–[19] and spintronic devices [20], [21]. The research areas of interest for these new materials encompass: exploring their novel properties, developing scalable approaches to synthesize these materials, the creation of new compounds, study their properties, attributes and characteristics by simulation and characterization, and integrating them into a new generation of nanodevices. The crystallographic structure of the layered material is composed by weak van der Waals out-of-plane bonding and ionic or covalent bonding in-plane [22], property used in mechanical and liquid exfoliation for the top-down synthesis approaches for these new generation of materials. All in all, 2D materials are anticipated to have a significant impact in a vast diversity of applications continuing with the exponential development of science and technology.

1.2 Transition Metal Di-Chalcogenides (TMDCs)

The family of two-dimensional materials that have attracted considerable attention are the TMDCs (transition metal dichalcogenides). These materials, relatively abundant in earth, consist
of hexagonal structure of metal M atoms (from group 4B and group 5B or group 6B, typically molybdenum, niobium, tungsten, and nickel) which are sandwiched between two layers of chalcogen X atoms (usually, sulfur, selenium or tellurium) with stoichiometry MX$_2$ [23], [24] (see Figure 1.1). MX$_2$ can form two crystal structures: a trigonal prismatic (polytype 2H or 3R) and octahedral (phase 1T), depending on the atomic stacking configurations [25]. Currently, there are 40 different combinations of TMDCs with an extensive diversity of properties. Depending on the compound, TMDCs can be insulators (HfS$_2$), semiconductors (WS$_2$, MoS$_2$), semimetals (WT$_2$, TiSe$_2$), true metals (TaSe$_2$) or exhibit superconductivity at low temperatures such as NbSe$_2$ [26], [27].

Figure 1.1. Transition Metal Di-Chalcogenides, elements located in the periodic table and the resulting combination.

Mono- and few-layers TMDCs exhibit a wide range of properties that in their bulk counterparts is not seen due to quantum confinement and surface effects. Materials, such as MoS$_2$, WS$_2$, WSe$_2$, MoSe$_2$ and MoTe$_2$, switch from indirect band gap semiconductors to direct band gap semiconductors in going from the bulk to monolayer, a characteristic that leads to enhanced photoluminescence [28]. Additionally, the band gap is tuned by the number of layers [29]. Some bilayer TMDCs band gaps can be tuned through the application of an external electrical field [30].
Moreover, research in monolayer TMDCs have demonstrated the great potential they have for the next generation of ultrathin and flexible optoelectronic devices [15], for instance, it has been proven that they are prospects for multi-junction solar cells since they capture photons from a broad band spectra from visible to near infrared [31]. The crystalline structure control, morphology, controlled synthesis still require further research for future implementation in chemical, catalytic, electronic, optical, and biological applications.

1.2.1 2D Molybdenum Disulfide (MoS₂)

The MoS₂ has been used as lubricant and intercalation agent in industry for many years in its bulk form. Recently, it has been converted in one of the most studied monolayer TMDCs, semiconductor analogue to graphene. It attracted scientists and researchers attention since the discovery of direct band gap in single layers [32] and the demonstration of high performance single-layer transistor in 2010 [7], this drove to an exponential increasing number of publications on this topic. The MoS₂ phase utilized as two-dimensional material is the 2H, where 2 denotes the number of layers in a unit cell and H describes the hexagonal crystallographic structure. This polytype is the most abundant in earth, it is a diamagnetic semiconductor [32], inert chemically, and reacts with oxygen at temperatures around 400 – 600°C [33]. In addition, the heavy nature of Mo atom facilitates a strong interaction with visible light and a ~10% absorption in single-layer due to van Hove singularities to its density of states [[34], [35]]. The thickness of each layer is 3.15Å, while the distance between adjacent layers is 3.49Å, suggesting the van der Waals interlayer interaction [3]. Also, it has been demonstrated the energy bandgap of MoS₂ varies in function of the number of layers from indirect bandgap of 1.2eV in bulk to direct bandgap of 1.8eV in monolayer [36], and by applying an external electrical field the bandgap can be tuned [30]. Therefore, by using different thicknesses of MoS₂, photo-detection can be tuned for different frequencies where single- and double-layer were shown to be effective for detecting green light, while triple-layer was well suited for red light [37]. Additionally, MoS₂ possess great mechanical
properties: it has an outstanding flexibility, it can sustain a large strain greater than 25%, and it has an extremely high Young’s modulus of 0.30 TPa, 50% larger than steel [38], making it suitable for flexible electronics applications. All these factors, including the appreciable carrier mobility, have been made of mono- and few-layer MoS$_2$ a promising candidate for research and its application in nano-electronics, flexible electronics, and optoelectronics, among others.

Figure 1.2. MoS$_2$ monolayer in top, side and 3D view; yellow spheres represent the Mo atoms and purple spheres represent S atoms.

The indirect to direct band gap transition is one of the key attributes of the 2D MoS$_2$. As the number of layers is reduced to one, the maximum valley in the valence band that is located in $\Gamma$ point is lowered, and the minimum energy required changes to the $K$ point, changing from indirect band gap energy of 1.2eV to direct band gap of 1.8eV [39]. This resulted because of the interlayer interactions disappearing in the monolayer state [32].

Figure 1.3. Transition from indirect to direct bandgap in the electron band structure, from bulk to monolayer. $E_g$(bulk) $\approx$ 1.2eV, $E_g$(monolayer) $\approx$ 1.8eV. Figure taken from reference [39].
CHAPTER 2. PROPERTIES AND CHARACTERIZATION TECHNIQUES OF 2D MOS₂

The investigation of the properties of these novel two-dimensional materials is a multidisciplinary research area. There exists a series of characterization techniques to describe these materials in their mono- and multilayer structure. These methods are commonly applied to analyze and study the morphology, topology, chemical structure, optical, and electrical properties of thin films. Furthermore, the examination of the vibrational and molecular structure of 2D structure is interesting due to their nano-metric scale. In this chapter, a brief description and basic principles are discussed of the selected characterization methods such as electron microscopy and spectroscopy techniques.

2.1 Optical microscope

The optical microscope is the first instrument that is non-destructive, rapid, and low cost characterization technique used when synthesizing one or few layers of 2D materials for the detection of the material [3]. Two important parameters of this instrument are the depth of focus and resolution. The resolution is the minimum distance between the object and objective at which the object is still visible, this parameter is restricted by the diffracted light. The depth of focus is the range of image plane positions at which the object can be viewed without appearing out of focus. Large depth of focus and resolution cannot be obtained at the same time. The most common substrate utilized for the detection of single-layered materials is the silicon with a thin film of silicon dioxide (SiO₂/Si). By measuring the contrast between the substrate and the monolayer, M. Benameur et al. [40] calculated the optimal thickness for the visibility of TMDCs, including MoS₂, reaching a positive maximum contrast between 25-30% with an oxide thickness of 90 and 270nm.
2.2 Atomic force Microscope (AFM)

The AFM, a member Scanning Probe Microscope (SPM), utilizes a sharp tip with a radius in the nanoscale attached to a cantilever to scan the surface and obtain a topography of the sample. The displacement of the cantilever is detected by the deflection of the laser beam [41]. The near field forces that action the tip against the surface are: the short range forces, the forces between atoms (due to the overlap of the electron clouds creating attractive or repulsive forces); electrostatic forces (interaction between the electric charges of the tip and the surface), van der Waals forces (the force between dipoles of molecules affected by the medium in which the measurement is done), and capillary forces (resultant from the water vapor condensation between the tip and the sample) [42]. AFM can be divided in two operational modes, static or dynamic. In static mode (contact type) the tip touches the surface physically while in dynamic mode (contact or non-contact type) the cantilever is excited at a certain frequency by a piezoelectric material. The most common technique is the tapping mode to reduce the damage during the measurement. The AFM is used to measure the thickness of 2D layers with a high resolution [43]. Nevertheless, the dissimilarities of interaction between the tip, the substrate, and the layered materials originate inconsistencies in the topographic measurements [44].

Figure 2.1. Mechanically exfoliated MoS$_2$ a) optical microscope image b) AFM image c) optical contrast from (a) and thickness measurement from (b). Image taken from reference [40].
2.3 Electron Microscope

Electron microscopes are capable of achieving higher spatial resolutions compared with optical microscopes, where the image is captured from the scattering of electrons instead of photons. This is based on the de Broglie relationship (Equation (1)), where $\lambda$ is the electron wavelength, $m$ is the electron mass, $q$ is the electron charge, and $V$ is the potential in which the electrons are accelerated. In addition, electron microscopes in low resolution are able to provide a three-dimensional appearance of the sample.

$$\lambda = \frac{h}{\sqrt{2mqV}}$$ (1)

Transmission Electron Microscope (TEM) has higher resolution than Scanning Electron Microscope (SEM) by using shorter wavelength. High voltage TEM instruments have point-to-point resolutions better than 0.2 nm. Additionally, contrasting to SEM, in TEM electrons are transmitted through the entire sample. The thickness of the sample has to be thinned to less than 200 nm, a disadvantage and a time-consuming sample preparation [45]. These techniques can provide information about the interlayer stacking relationships, crystalline nature, elemental configuration, and layer sizes [41]. The TEM of MoS$_2$ vapor phase grown sample, shown in Figure 2.2, along with the Selected Area Electron Diffraction (SAED) shows the hexagonal structure lattice with a spacing of 0.27 nm and for (100) plane and 0.16 nm for (110) plane.
Figure 2.2. Electron microscopy on monolayer MoS2 samples synthesized by Chemical Vapor Deposition. a) SEM image of triangular flakes. b) TEM image and SAED spectra. Figure (a) and (b) ref. [46] and [47] respectively.

2.4 Scanning Tunneling Microscopy

Scanning Tunneling Microscope (STM) is a probe based characterization technique to evaluate the electronic and topographic structure of single layered materials. Detached atoms from the substrate at exact points can be controlled using this technique in order to characterize the two-dimensional materials [48]. Epitaxial layers are the most commonly studied samples in STM due to the alignment challenge in specific parts of the substrate. This technique (imaging and spectroscopic combined) is very useful to find defects and grain boundaries in TMDC layers [49].

2.5 Raman Spectroscopy

Raman spectroscopy is a technique to analyze the molecular structure of materials by their interaction with electromagnetic radiation. It is based on the inelastic scattering of monochromatic light which is a result of the interaction of the incoming electric field with the polarizability of the medium. In other words, the Raman spectroscope irradiates the sample with a laser beam, this incident light couples with the electric field associated with periodic excitations of the sample. Most of the light is absorbed and a small proportion is scattered at an inelastic shifted wavelength
in Stokes (output energy smaller than input energy) and AntiStokes (output energy larger than input energy) scattering. The difference between the input and output light provides information of vibrational modes which is unique for each material [50].

The Raman peak frequencies are used to determine the thickness of molybdenum disulfide since the spectra is thickness dependent [51]. The MoS$_2$ Raman spectrum in bulk shows two strong vibration peaks, the in-plane $E_{12g}^1$ at 382 cm$^{-1}$ and the out-of-plane $A_{1g}$ at 407 cm$^{-1}$. The $E_{12g}^1$ shifts to 385 cm$^{-1}$ and $A_{1g}$ shifts to 403 cm$^{-1}$ in single-layer, with a frequency difference $\Delta k$ of 20 cm$^{-1}$. The shift-thickness dependency can be a result from the thermal effect of the incident laser for the measurement that softens the bond [52]. Another possible reason of this frequency shift is that the atom vibration suppressed as the thickness is increased because of the interlayer van der Waals interaction [53].

![Figure 2.3.](image.png)

Figure 2.3. (a) Thickness dependent MoS$_2$ Raman spectra, and (b) frequency difference between $E_{12g}^1$ and $A_{1g}$ mode. Image take from reference [51].

### 2.6 Photoluminescence Spectroscopy

Photoluminescence (PL) occurs in a semiconductor when a photon stimulates an electron from the valence band to the conduction band. The photon energy must be equal or higher to the
material bandgap [54]. The radiative recombination of the electron-hole pair is preceded by a non-radiative relaxation mechanism which leads to the emission of photons in direct bandgap semiconductors such as TMDCs. On the other hand, in indirect bandgap semiconductors, the emission of a particle requires additional emission of phonon to conserve momentum where a lower emission rate of photon is produced [55]. PL in single-layer MoS$_2$ is another important characteristic. In this material, two prominent absorption peaks are identified, one at 670nm (A1) and the second one at 627nm (B1) shown in Figure 2.4. The magnitude of these peaks is related to the MoS$_2$ thickness, showing the maximum values in monolayer structure [39]. These peaks are generated from the direct band gap transition due to direct gap hot luminescence [32].

2.7 UV-Visible-NIR Spectrophotometer

The UV-visible-NIR spectrophotometer is quantitative way to determine the materials absorption using the Beer-Lambert law $\alpha = \log_{10}(I_o/I)$, where $\alpha$ is the absorbance, $I_o$ is the incident intensity, and $I$ the transmitted intensity. The characteristic spectra observed in the absorption and emission spectra of nearly isolated atoms and ions due to transitions between quantum levels are extremely sharp. As a result, their wavelengths or photon energies can be determined with great accuracy. Excitons dynamics (the excitonic absorption) can be described applying this technique [56], which is the reverse process of the direct band gap hot luminescence. Therefore, in addition to the photoluminescence spectra, the two emissions A1 and B1 of MoS$_2$ can be determined using this tool (Figure 2.4). Hence, this characterization technique is frequently utilized for the study of 2D materials dispersed in solution to explore their quality and properties [57], [58].
Figure 2.4. Photoluminescence spectrum dependent to the number of layers in MoS$_2$ showing the A1 and B1 excitons at 670 and 627 respectively. Figure taken from reference [59].

In addition, the band gap can be extracted from optical absorption by using the Tauc plot $(a\gamma)^2$ (in eV/mm$^2$) versus energy (in eV). Where $a$ is the absorption coefficient of the material, $h$ is the Planck constant and $\gamma$ is the photon wave frequency [60]. Technique applied for the characterization of TMDCs.
CHAPTER 3. 2D MOS$_2$ SYNTHESIS

In this chapter, it is described the synthesis approaches for two-dimensional MoS$_2$: micromechanical exfoliation, liquid exfoliation, and vapor phase reaction. The last approach, emphasized in the manuscript, can be divided in two routes, the sulfurization of metal oxide and the vapor phase reaction of precursors. Next, the review and discussion of the synthesis variables involved in the growth of 2D MoS$_2$. Later in this chapter, based in that study, it is explained the design of the Chemical Vapor Deposition system. Finalizing the chapter with the explanation of the experiments and characterization techniques executed (Raman and AFM) that yielded to the vapor phase synthesis (via sulfurization of metal oxide and vapor phase reaction) of MoS$_2$.

3.1 Synthesis Approaches for 2D MoS$_2$

The synthesis of 2D materials, including the MoS$_2$, is a research of interest where the objective is to obtain high quality material to study their properties, then the large area growth for scalable manufacturing for future application in industry mass production. Three general approaches have been proposed for the investigation of these materials: mechanical exfoliation, liquid exfoliation, and vapor phase synthesis.

3.1.1 Micromechanical Cleavage

Mechanical exfoliation, also known as mechanical cleavage or scotch tape method, is a technique utilized since 2004 with the isolation of monolayer of graphite, graphene. This method to synthesize 2D layered materials is the cheapest and simplest used only in research laboratories due to the low yield in this process, allowing the application of characterization techniques for their study [64] (steps of this technique are shown in Figure 3.1). However, the 2D flakes obtained with this technique are high quality. The weak out of plane van der Waals bonding of the crystal
allow the peeling off of the few- and mono-layer flakes using blue tape to avoid residuals during the process. Then, the flakes are transferred to the desired substrate. In the case of MoS$_2$, the most common is 270nm SiO$_2$/Si where the highest contrast is obtained to facilitate the identification of flakes under the optical microscope, as explained in section 2.1.

![Mechanical exfoliation of 2D crystals](image)

Figure 3.1. Mechanical exfoliation of 2D crystals. (a) Adhesive blue tape is pressed against a 2D crystal, (b) the top few layers are attached to the tape, (c) the tape with crystals of layered material is pressed against a surface of choice, (d) upon peeling off, the bottom layer is left on the substrate. Figure taken from reference [67].

### 3.1.2 Chemical Exfoliation

A second low cost approach for the scalable manufacture of 2D materials is the chemical exfoliation. In this technique the 2D layered material powder is dispersed in a solution with solvent and surfactant to avoid agglomeration. Intercalation, a method for liquid exfoliation, is a widely used technique to obtain TMDCs monolayers [63]. During the intercalation process, ions intercalate between the layers, causing weakening of interlayer adhesion due to the increase of the interlayer spacing and energy barrier [68]. The disadvantage of this process is the contamination of the MoS$_2$ flakes with the solvents, which could affect their properties and reduce the current because after the evaporation of the solvents it is obtained a film with discrete flakes.
Figure 3.2. Liquid exfoliation, ion intercalation method for the synthesis of single-layer MoS$_2$. The ultrasonication separates the layers resulting in an exfoliated dispersion. Figure taken from reference [68].

3.1.3 VAPOR PHASE DEPOSITION

Chemical Vapor Deposition (CVD) has been introduced as the most efficient method in synthesizing two-dimensional MoS$_2$ compared with chemical and mechanical exfoliation. The vapor phase reaction is divided in three approaches: vapor phase reaction, sulfurization of metal or metal oxide, and the evaporation and recrystallization of precursor. In this section, the first two methods will be discussed.

3.1.3.1 Vapor phase reaction

In the vapor phase reaction, the precursors (usually molybdenum trioxide (MoO$_3$) and sulfur (S)) are evaporated at different temperatures in a reaction chamber. Next, the vapor of the two precursors is transported with an inert gas, argon or nitrogen, leading to the chemical reaction. This reaction consist in the reduction of the MoO$_3$ to MoO$_2$ with S. Then, the last two gases react to form MoS$_2$ and oxisulfides by-products (Equation (2)). Afterwards, the MoS$_2$ in vapor phase is condensed and growth in triangular crystal domains on the surface of the substrate such as SiO$_2$/Si, mica, sapphire or quartz (schematic shown in Figure 3.3). The last three substrates are preferred due to the lattice matching with the MoS$_2$ crystallinity, chemical inertness, high thermal stability,
and surface flatness, that assists the precursor migration to improve the thickness uniformity and nucleation sites [69].

\[ MoO_2 + 3S \rightarrow MoS_2 + SO_2 \]  

(2)

### 3.1.3.2 Sulfurization of Metal or Metal Oxide

The sulfurization of the metal or metal oxide is one of the first approaches for MoS\(_2\) CVD synthesis. The process consists on the evaporation of MoO\(_3\), then it is reduced with S vapor. Next, the MoO\(_{3-x}\) is deposited on the substrate, resulting in rhomboidal crystals. Then, the sulfur in vapor phase is flowed with an inert gas, as in the previous process, to sulfurize the surface of MoO\(_{3-x}\) crystals by the reaction shown in Equation (3) and (4) [70] (schematic shown in Figure 3.3)

\[ 2MoO_3 + xS \rightarrow 2MoO_{3-x} + xSO_2 \]  

(3)

\[ 2MoO_{3-x} + (7 - x)S \rightarrow 2MoS_2 + (3 - x)SO_2 \]  

(4)

Figure 3.3. Vapor phase reaction and sulfurization techniques for MoS\(_2\) mono-layer synthesis. Figure taken from reference [71].

### 3.1.3.3 Synthesis Parameters for MoS\(_2\) CVD Synthesis

In this section, the study and review of the synthesis process parameters and variables has been done in order to a better understanding of the mechanism of synthesis and to obtain the
requirements for the CVD system design. A summary of the synthesis parameters review is shown in Table 3.1 in which triangular single crystals domains are grown using these processes [72], [73]. CVD synthesis allows to obtain high quality MoS$_2$, however, it is still challenging to grow large-scale and continuous films [74].

Table 3.1. Review of synthesis parameters for CVD synthesis of monolayer MoS$_2$.

| MoO$_3$ (mg) | S (g) | Substrate | Gas     | Flow (sccm) | Pressure (Torr) | T rate ($^\circ$C/min) | Tmax, MoO$_3$ ($^\circ$C) | Tmax, S ($^\circ$C) | t @ Tmax (min) | Seed promoter | Heat zones | Ref |
|------------|-----|----------|---------|-------------|----------------|----------------------|------------------------|-------------------|---------------|---------------|------------|----------|-----|
| 15         | 1   | 285nm SiO$_2$ | N$_2$   | 200         | 760           | 50                  | 850                  | 150              | 5             | -            | 1         | [75]    |
| -          | 1   | Si       | N$_2$   | 200         | -             | -                   | 850                  | 600              | 10            | -            | 1         | [46]    |
| 30         | 0.01 | Si       | Ar      | 10          | 760           | 15                  | 650                  | -                | 5             | -            | 1         | [76]    |
| -          | -   | 300nm SiO$_2$ | N$_2$   | 233.33      | -             | -                   | 880                  | -                | -             | 1         | [77]    |
| 35         | 0.6  | 300nm SiO$_2$ | Ar      | 130         | 0.67          | 25                  | 450-600              | 120-130          | 20            | -            | 3         | [78]    |
| 100        | 0.4  | 300nm SiO$_2$ | Ar      | 100         | 760           | 11.3 and 3.1        | 700                  | 100              | 20            | -            | 1         | [79]    |
| -          | -   | Sapphire | Ar / H$_2$ | 700         | 600           | 15                  | 1000                 | -                | 30            | -            | 1         | [80]    |
| 400        | 0.8  | Si treated | N$_2$   | 1           | 760           | 15                  | 650                  | -                | 15            | PTAS and PTCAD | 1         | [47]    |
| -          | -   | 300nm SiO$_2$ | -       | -           | 760           | -                   | 650                  | -                | -             | PTAS         | 1 / heat belt | [81]   |
| 25         | 0.5  | 300nm SiO$_2$ | Ar      | 150         | -             | 20 and 10           | 850                  | 145              | 180           | -            | 1 / heat belt | [82]   |

From this study, it was conclude that the synthesis parameters that affect the growth during the CVD synthesis are: the substrate, the pressure, mass load of precursors, flow rate of transport gas, temperature of precursors and substrate, position of precursors, substrate, time of process, and substrate treatment. The role of these variables help us to understand the synthesis mechanism for future experiments. The most common substrate used for the CVD synthesis of MoS$_2$ is the SiO$_2$/Si with a thickness of 270nm, which is the optimal thickness for obtaining the highest optical contrast to identify MoS$_2$ monolayers under the optical microscope [40]. However, this substrate entails some disadvantages: the MoS$_2$ crystallites grow in random orientations, since the nucleation points are sparsely located over the substrate, and the area of single domains is small and the crystals overlap each other. The synthesis on SiO$_2$ can be improved with the application of aromatic molecules used as seed promoters such as perylene-3,4,9,10-tetracarboxylic acid tetrapotassium
salt (PTAS), reduced graphene oxide (r-GO), and 3,4,9,10-perylene-tetracarboxylic acid-dianhydride (PTCDA). Ling et al [83] reported the PTAS as the best seed promoter for SiO$_2$ substrates. In contrast, it has been obtained satisfactory result on SiO$_2$ substrate without the use of any seed promoter, with a triangular flake size of $\sim120\mu$m [72]. This positive result was obtained through the substrate treatment which consisted in ultrasonic bath with solvents, followed by two hours of piranha solution, and finishing the cleaning process with an O$_2$ plasma, indicating that the substrate treatment is crucial for the quality of the growth. Better growth results can be obtain in substrates such as mica, quartz, and sapphire due to the lattice matching with MoS$_2$, high thermal stability, flat surface, and chemical inertness that assists the precursor migration to improve the thickness uniformity [69].

The temperature of the precursors is one of the most important parameters for the synthesis. This can be controlled by changing the position of the precursors and the temperature profile set in the furnace. The temperatures required for sulfurization ($\sim850 – 950^\circ$C) are higher than the temperature for reduction of MoO$_3$ ($\sim650 – 850^\circ$C) [47]. Additionally, low temperatures in precursors results in a low vapor concentration in the reaction chamber. Another element that is affected by the process temperature is the substrate, which influences the adsorption and desorption of the MoO$_3$ and MoS$_2$ clusters and hence the nucleation density and domain size of the MoS$_2$ flakes. On the other hand, the pressure during the growth process alters the crystallinity, the density, and the single domain size of the MoS$_2$. This parameter is increased by evaporation of the sulfur in the reaction chamber. As the pressure increases, the vaporization of Mo is reduced and consequently the vapor concentration that leads to the change of shape of the single domain from hexagons to triangles, to three point stars [46]. Furthermore, the flow rate of the transport gas is an important parameter to control the deposition rate. A high flow rate contributes to a high deposition rate. Nevertheless, high flow rate results in unstable growth and at the same time creates defects such as dendritic morphologies due to the crystal growth driven more by reaction kinetics than equilibrium thermodynamic processes [84]. Finally, the mass load of the precursors is directly related to the their vapor concentration which at the same time is related to the morphology of the
domains with different terminations, Mo-zigzag or S-zigzag [84]. Low load reduces the deposition rate that can be compensated by increasing the flow rate of the transport gas. When the sulfur supply is insufficient, it grows rectangular oxisulfides instead of MoS$_2$ [46].

### 3.2 CVD System Design

The design and assembly of the CVD system was necessary to start the experimentation in the synthesis of 2D MoS$_2$. Also, it has been a contribution for the development of the laboratory and future research. This work consisted on the selection of the material and equipment based on the technical requirements from the literature study for two CVD systems, one for sulfurs and selenoids and the second one for graphene, the design of the layout, and the supervision of the installation.

The key parameters for the system design were defined in the section 3.1.3.3. This system consists in two furnaces, one for sulfurs and the second one for graphene. Both furnaces have a built-in single-zone temperature controller and a quartz tube capable to reach a maximum temperature of 1200ºC. A total of 5 gases (CH$_4$, C$_2$H$_2$, Ar, N$_2$, H$_2$) are connected into the system, among which the last three are shared between the two furnaces. The sequence of connection starting from the gas cylinder is: the pressure regulator with their gauges, a mass flow controller with a range of 0 – 200 sccm calibrated for each gas, a check valve to prevent flow on the opposite direction, and a plug valve to open and close the gas flow. Furthermore, in the inlet and outlet of both furnaces it is installed two solenoid electro-valves, two needle valves, and a digital pressure gauge. The pressure controller manipulates the two solenoid valves by the feedback from the digital pressure gauge where the pressure range is defined. Finally, one vacuum pump for each furnace is installed at the end which at the same time is connected to a general exhaust. The schematic is shown in Figure 3.4.
Figure 3.4. Pneumatic schematic of the two CVD systems designed for sulfurs and carbons.

The first furnace (model MTI OTF-1200X-80SL), for the MoS$_2$ synthesis, includes a rail for rapid cool down with manual positioning, a quartz tube 80cm of outside diameter, 72 mm of inside diameter, and a length of 1.4 m. It also includes, a temperature controller to set the temperature profile with feedback from one thermocouple type K (maximum temperature of 1350$^\circ$C). A second thermocouple was installed in a flange feedthrough to use the furnace as a two-zone. The precursors for the synthesis of sulfurs and selenoids are powders. Therefore, it is only necessary to install the transport gas (inert gases such as nitrogen and argon) and hydrogen, which in some cases is used as a reductor element [80]. The second furnace, the model OTF-1200X-50SL-UL, is a small version of the previous one. One difference is that includes an electronic control for the rails with a small fan to increase the cool down rate and a 50 cm outside diameter quartz tube. As stated before, this furnace is dedicated to graphene synthesis, so that argon, nitrogen, hydrogen, methane, and acetylene are installed.
In addition, a 3D model was designed to construct the system and position of the components considering the dimensions and that way prevent mistakes on the installation and assembly (Figure 3.5). Also, it was used as a reference for the technical installation from facilities and can be used as a future resource for upgrading the system.

![3D model of the prototypes of two CVD systems.](image)

### 3.3 CVD Synthesis of 2D MoS2

Two synthesis routes of MoS$_2$ were developed using the system described in the previous section: the sulfurization of molybdenum oxide and vapor phase reaction or precursor [62], [65], mechanisms explained in detail in section 3.1.3. Optical microscopy, Raman spectroscopy and AFM were used to characterize the material synthesized.

The procedure steps for the synthesis experiments are: clean the alumina (AlO$_3$) boats, clean the substrate and cut it, weight the desired mass load of precursors in boats, vent the system, place substrate and precursors in the position required, purge the system, reach and control at 760 Torrs, program the furnace, run program and control pressure during the process, slide the furnace
for fast cool down at ~500°C, remove the sample and boats from the reaction chamber at a maximum temperature of 100°C. The detailed procedure is shown in appendix A.

From our experiments, it was confirmed that the triangular crystals grow at the vicinity of the edges, on dust particles, on scratches, and random orientations (see Figure 3.6). The synthesis of MoS$_2$ was done in SiO$_2$/Si (270 nm of thickness oxide) substrates. The precursor utilized are the MoO$_3$ (sigma Aldrich 99.9995%) and S (sigma Aldrich 99.5%) with a mass of 0.4g and 0.8g deposited on alumina (AlO$_3$) boat of dimensions 100 x 40 x 18mm and 50 x 20 x 20mm respectively. After each experiment, the alumina boats were cleaned in piranha solution at 100°C for 40-60 minutes.

![Figure 3.6. MoS$_2$ triangular crystals on SiO$_2$/Si substrate grown in a) dust particles, b) scratches, and c) vicinity of edge. d) Random crystal growth orientation of domains. The bright spots corresponds to the original nucleation sites of the crystal. The scale for all images is 60μm.](image)

During the experiments, the AlO$_3$ boat with the MoO$_3$ powder was invariably placed in the middle of the quartz tube, where the highest temperature, measured with the built-in thermocouple, is obtained. The substrate in all the experiments was facing down, located at the top of the MoO$_3$ precursor. The position of boat with the S powder has been tuned during the experiments, obtaining MoS$_2$ by two different approaches (see Figure 3.7).
Figure 3.7. Position of substrate and precursors in alumina boats inside the CVD furnace. Long distance between the precursors assure homogeneous concentration of sulfur vapor. By changing this distance it is modified the route of MoS$_2$ synthesis.

In the first method, the sulfurization of MoO$_2$, the furnace was heated up to 850°C on a rate of 15°C/min, temperature in which was kept for 15 minutes. This is the temperature in which the substrate and the molybdenum trioxide were exposed. Then it was cool down naturally until ~500°C, then rapid cool down was applied. The maximum temperature of the sulfur was ~170°C, measured with the second thermocouple. This temperature was controlled by the position of the precursor inside the chamber with respect the center of the furnace, in this case was 36cm. These conditions yielded to the growth of rhomboidal MoO$_2$ crystals, in which some of them were sulfurized and obtained MoS$_2$. The previous statement was confirmed with the Raman spectrum of these samples. They show peaks that correspond to MoO$_2$ and MoS$_2$ for some rhomboidal flakes and just MoO$_2$ for others (Figure 3.10), agreeing with previous synthesis reports using this technique [80][70].
In contrast, in the second mechanism, the vapor phase reaction, the temperature ramp rate was programmed to 17.6°C/min up to 550°C, temperature in which the sulfur begins to evaporate; then the ramp was decreased to 5°C/min until a temperature of 850°C was reached; this temperature was kept for a duration of 15 minutes. In this process, the sulfur reached a temperature of 600°C by changing the position to 17cm from the center of the reaction chamber (this distance should be long enough to obtain an homogenous concentration of S vapor throughout the quartz tube). This process yielded to the synthesis of triangular crystals, corresponding to the morphology of MoS$_2$. We have confirmed that monolayer MoS$_2$ was synthesized as in this samples where the strong vibration modes $E_{12g}$ and $A_{1g}$ corresponds to the characteristic Raman peaks of 388.4 and 408.4 cm$^{-1}$ respectively (see Figure 3.10). This results in a $\Delta k = 20$ cm$^{-1}$, which agrees well with previous reports for monolayer MoS$_2$ [51].
Figure 3.9 Temperature profile of precursors and pressure inside the chamber that lead to the synthesis of 2D MoS$_2$ crystals.

The sharp edges triangular flake crystals in our samples from Figure 3.9b indicate that the orientation is molybdenum zigzag (Mo-zz), the termination can be easily identified in optical microscope image [72].

![Figure 3.9](image)

Figure 3.10 Raman spectrum of the two samples obtained by different synthesis routes. The blue spectrum corresponds to MoS$_2$, the red with section highlighted in blue to MoO$_2$/MoS$_2$, and the black on to MoO$_2$.

Additional to the Raman spectroscopy analysis, AFM topography analysis was done on the samples (Figure 3.11). Verifying a thickness of ~7 Å, corresponding to previous reports [3]. It is important to highlight that the process described in this chapter is repeatable, making it a contribution for the development of future projects.
Figure 3.11. AFM topography of MoS$_2$ synthesized by vapor phase reaction.
CHAPTER 4. MOS₂ DEVICE FABRICATION AND CHARACTERIZATION

In this chapter, it is discussed a background on the integration of 2D MoS₂ in transistors and photodetector devices and the importance in the material selection for the junction with the semiconductor. The next section consists in the description of the metal contact design for the study of the 2D layered materials obtained in the NDL. Later, the procedure to align and transfer mechanically exfoliated layered materials, final step of the device fabrication, is showed. Finally, in the last section of the chapter, the few-layered MoS₂ device characterization procedure is discussed among with the parameters obtained that describe in detail the device.

4.1 Electrical Properties for Device Application

Most of the reports in literature have described that monolayer MoS₂ has an n-type semiconductor. Yin et al [85] suggest that the n-type doping could come from impurities atoms, such as halogen (Cl or Br), which could replace S atoms in the natural MoS₂ crystals or exist as the interstitial atoms in the interlayer gap of MoS₂. However, it has been reported also p-type semiconductivity in 2D MoS₂. This phenomena is explained by the intrinsic defects in the stoichiometry of the crystal, doping from the metal contacts, or the Schottky barrier from the metal-semiconductor junction [86].

The performance of the 2D MoS₂ device is related to the properties of the materials in which it is in junction, such as the metal contacts and the dielectric materials. The fabrication and characterization of filed effect transistors (FET) is applied to demonstrate the performance and quality of single-layer MoS₂. A key parameter of FET devices is the field effect mobility, which can be extracted from the current – gate voltage curve (I_DS-V_GS) at a constant drain-source voltage V_DS using the equation
\[
\mu = \frac{1}{C_i} \frac{L}{W} \frac{dI_{DS}}{dV_{GS}} \frac{1}{V_{DS}}
\]

(5)

Where,

\[
C_i = \frac{\varepsilon_0 \varepsilon_r}{d}
\]

(6)

Where \( C_i \) is the capacitance per unit area between the conducting channel and the back gate, \( L \) is the channel length, \( W \) is the channel width, \( \varepsilon_0 \) is the permittivity in vacuum, and \( \varepsilon_r \) is the relative permittivity of the semiconductor. The FET mobilities for MoS\(_2\) reported are from a range of .1 to 10 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) and on/off ratio up to \( 10^{10} \) [3], [7], [72] for semiconductor exposed to air. However, it has been demonstrated that with the use of hafnium oxide as dielectric material, the electron mobility of MoS\(_2\) can be increased up to 168 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) due the capacitive coupling of the transistor channel of the top gate to the back gate [87]. Other materials such as Al\(_2\)O\(_3\) and h-BN have been applied as dielectric materials for FET transistors [88]. In addition, the performance can be increase by double gate fabrication, phenomena attributed to suppressed charged impurity scattering [89].

Furthermore, the selection of the best metal contact is crucial for the performance of FET devices, where minimum Schottky barrier height \( \phi_B \) is desired. This parameter is defined with the Schottky-Mott model shown in Equation (7), which is based on the difference of metal work function \( \phi_M \) and the electron affinity \( \chi \) of the MoS\(_2\) (4eV) [90], [91]. The most common metal utilized for this purposes is the Ti/Au, Ti the first one as an adhesion metal to the surface which has a lattice mismatch with MoS\(_2\) of 1\% [92]. Other material such as Pd, Mo, has been reported in MoS\(_2\) devices [93], [94].

\[
\phi_B \approx \phi_M - \chi
\]

(7)

Furthermore, the unique photo-electron interaction in mono- and few-layer MoS\(_2\) have attract special interest in optoelectronic applications. Several mechanisms contribute to the generation of photocurrent: the photovoltaic effect (attributed to the shift in transistor threshold voltage due to
charge transfer from the channel to nearby molecules), photoconductivity (attributed to the trapping of carriers in band tail states in the molybdenum disulfide itself), and photothermoelectric effect (under sub-band gap illumination, attributed to the mismatch in the Seeback coefficients between the contacts and the semiconductor) [95], [96]. From previous manuscripts, it has been reported MoS$_2$ photodetectors that under illumination energy above the bandgap the photoresponsivity varies from $7.5 \times 10^{-3}$ to 880 A/W [85].

4.2 Metal Contacts

4.2.1 Photolithographic Mask Design

The electrical measurements and characterization for the mechanically exfoliated two-dimensional materials require metal contacts to avoid the damage of the monolayer by using probe tips directly on the material [66]. There are several structures that help to the characterization these materials. A dark field 4” photolithographic for 3” wafer mask was designed for this purpose on the software L-Edit from Tanner ED with several contacts configurations fabricated in quartz by Toppan Mask. The polarization of the mask is considered for its application in lift-off process, but also it can be applicable for positive and negative photoresists, depending on the process sequence selected. Several arrays of structures were designed for the metal contacts included van der Pauw, four-point contact, contacts for anisotropic electrical transport measurements, and contacts mechanical exfoliation transfer with random distribution in form of a die. For all the cases the pads are 150µm squares for the contact with the micromanipulator probe tips and the transmission lines are 20µm thick.

The first structure is for the case where the mechanically exfoliated flakes are transferred directly from the tape to the metal contacts patterned on a substrate. It consist in a die with 28 pads to form 13 crosses for 4 point measurement (Figure 4.1). The die also includes 4 test structures, one resistance, three different van der Pauw configurations for resistivity measurement of the
metal, and crosses as alignment marks. The biggest number on the left upper corner indicates the distance in micrometers between the contacts translated in some structures as the channel length. The array designed consists in distances from 1 to 10μm with increments of 1μm, 12 to 30μm with increments of 2μm, and 35 to 50μm with increments of 5μm. The even pads are enumerated for easy read and detection under the optical microscope.

![Figure 4.1. Metal contacts layout for random distribution and size of mechanically exfoliated flakes.](image)

The second structure consist in a van der Pauw (Figure 4.2). This design is suggested for the alignment of the contacts with a single flake, regardless of the first step on the process either exfoliation or metal deposition. The four-point of this structure allows Hall Effect measurements in the samples. The number on top of each cross indicates the separation distance between the contacts, as in the previous design. A die consist in 5 crosses with different dimensions and two test structures. The small crosses are the alignment marks for each of the group of contacts and the
distance between the metal contacts in micrometers are 1 to 10μm with increments of 1μm, 12 to 30μm with increments of 2, 35 to 50 with increments of 5μm.

![Figure 4.2](image2.png)

Figure 4.2. van der Pauw configuration for Hall effect and resistivity measurements in two-dimensional flakes.

Some 2D materials exhibit an anisotropic electrical transport or optoelectrical behavior. For this scenario, eight contacts arrange in a circle was designed for measurements at different angles to allow the comparison of the carrier transport in function of the material orientation (Figure 4.3). As in the previous layouts, the number corresponds to the distance between the contacts which start from 4 to 52μm with increments of 4μm for a big range of flake dimensions.

![Figure 4.3](image3.png)

Figure 4.3. Metal contacts for anisotropic electrical transport in 2D materials.

The last design for the photolithography mask layout is for four-point measurements. This structure is commonly used to obtain the electrical resistivity of the material under test (see Figure
4.4. The label corresponds to the distance between the two vertical contacts, the distance between the horizontal contacts is 2μm for all the cases. The array designed consists in vertical distances between contacts from 8 to 32μm with increments of 4μm.

![Figure 4.4. Four-point measurement structure for resistivity measurements of 2D materials.](image)

### 4.2.2 PATTERNING AND DEPOSITION OF METAL CONTACTS

The pattering consists in a photolithography, process applied in the fabrications of chip technology using the mask described in the previous section. The photolithography process was defined for the use of AZ-5214E image reversible photoresist (PR) using lift-off process. This procedure consist in the spin coating, exposure, and development of the PR. Then the metal is deposited via Physical Vapor Deposition (PVD). Finalizing with the lift-off of the PR/metal, leaving the pattern designed for the metal contacts. The process schematic is shown in Figure 4.5.
Even though the vendor suggest one procedure for the specific PR, a recipe had to be defined. The spin coater utilized was the G3P-8 from Specialty Coating Systems and the mask aligner used for the process is the Karl Suss MJB3. The UV light energy distribution (Figure 4.6) was measured using an OAI 308 UV Intensity Meter to assure the exposure dose for the PR. From the relation: Uniformity = \([\frac{H - L}{H + L}] \times 100\%\), where H is the highest intensity and L is the lowest intensity measured in the substrate chuck, it was calculated an uniformity of 1.98\%, which is less than the tolerance suggested in the manual of 5\%.

After several tests, the best parameters where found to be an exposure of 2 mW/cm\(^2\) for 35 seconds, giving a dose of 70 mJ/cm\(^2\), for a photoresists AZ5214E-IR thickness of ~1.4 \(\mu\)m, and a developing
time of 30 seconds using AZ 300 MIF developer. This process is explanted with more detail in Appendix B.

The substrate used for the fabrication of the device is a wet oxidized p-type Si substrate with 270nm of SiO$_2$. It was cleaned with ultrasonic bath in acetone, methanol and deionized water for 5 minutes each, and piranha solution for 15 minutes at 100°C, followed by dehydration for 5 minutes at 120°C. Once the PR is patterned on the 270nm SiO$_2$/Si substrate, the fabrication process is continued with the molybdenum deposition, metal chosen due to it has been reported as a potential metal contact for its lattice matching and low Schottky barrier with MoS$_2$ [94]. The deposition of the metal contacts was done via sputtering, a category of PVD, process commonly used for metal deposition where no chemical reaction is involve. In this process, on a vacuum environment, high energized argon ions bombard the target that releases material that afterward is deposited on the substrate [97]. The deposition parameters were 3mTorr of pressure and 200W of DC power for 20 minutes for the deposition of 100nm of Mo thickness.

![Figure 4.7 Molybdenum metal pattern deposited by DC sputtering compared with the mask design (black lines) after lift-off process.](image)

### 4.2.3 Resistivity Measurement of Mo Contacts

The resistivity of the metal contacts, intrinsic property of a material, was measured as an indication of its quality. For this measurement, the square van der Pauw structure was used. The
probe station Micromanipulator 450PM-B was utilized as the interface between the Semiconductor Parameter Analyzer HP 4156A and the sample for the electrical measurement. A graphic user interface (GUI) was programmed in Labview (Figure 4.8) for the data acquisition, another contribution to the NDL, by saving the data in a text file, and to control and settings of the Source Measurement Unit (SMU) such as variable definitions, channel and sweep parameters via GPIB protocol.

![Figure 4.8. Graphic user interface programmed in Labview for control and data acquisition of Semiconductor Parameter Analyzer HP 4156A.](image)

The pads were contacted with tungsten probe tips for the measurements. Although the structure is a symmetric shape, the resistivity calculations were done using arbitrary shape equations [98] to obtain a more precise estimation since it is hard to position the probe tips at equal distances. The resistance is calculated by ohms law, where the labels corresponds to the probe position in the surface,

$$R_{12,34} = \frac{V_{34}}{I_{12}}$$  \hspace{1cm} (8)
Then, the resistivity is given by

$$\rho = \frac{\pi t}{\ln(2)} \cdot \frac{(R_{12,34} + R_{23,41})}{2} F$$  \hspace{1cm} (9)

Where $t$ is the metal thickness and $F$ is the correction factor which is in function of $R_r = \frac{R_{12,34}}{R_{23,41}}$,

$$\frac{R_r - 1}{R_r + 1} = \frac{F}{\ln(2)} \cdot \text{arccosh} \left( \frac{\exp[\ln(2)/F]}{2} \right)$$  \hspace{1cm} (10)

The IV curves obtained from the structure is shown in Figure 4.9, in the van der Pauw square of 300$\mu$m$^2$.

![IV curves](image)

**Figure 4.9.** IV curves of $R_{12,34}$ and $R_{23,41}$ for the resistivity calculation in Mo using van der Paw. The inset shows the contact configuration.

The correction factor curve was programmed in Matlab (program shown in Appendix C) using Equation (10) to obtain the value for the corresponding to $R_r$ of 1.19. A correction factor of 1.1247 was obtained. Finally, with all the variables for the calculation, it was obtained a resistivity of $\rho = 24.35 \Omega \cdot \mu m$. 

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4.3 Micromechanical Cleavage and Transfer of Few Layered MoS$_2$

The last step for the device fabrication is the mechanical exfoliation and transfer of the flake MoS$_2$. It has been explain in a previous section that the micromechanical cleavage is a low yield process (Figure 4.11). In addition, the alignment process with the metal contacts usually consist in first the transference of the flake on the substrate, then the deposition of the metal contacts by e-beam evaporation. For the device fabrication, it was necessary to adapt to the laboratory restrictions.

![Optical microscope image of mechanically exfoliated MoS$_2$ flakes on SiO$_2$/Si substrate.](image)

Figure 4.11 Optical microscope image of mechanically exfoliated MoS$_2$ flakes on SiO$_2$/Si substrate.
After literature research it was found that a high yield and low time consuming procedure to transfer mono or few-layered materials exfoliated mechanically has been reported using viscoelastic material (Gel-Film x4 6.0mil) to stamp the flakes onto the substrate [99]. Our setup consist on the mask aligner Karl Suss MJB3 for the alignment and flake transference showed in Figure 4.12.

![Viscoelastic stamping setup for MoS\textsubscript{2} transfer to Mo contacts on SiO\textsubscript{2}/Si substrate using a mask aligner Karl Suss MJB3.](image)

The viscoelastic stamping consists first in mechanical exfoliation of MoS\textsubscript{2} crystal. Next, the flake thickness is reduced and transferred to the transparent gel-film that is adhered in a 4’ x 4’ glass, dimension for mask holder in mask aligner. Then, the substrate with the Mo contacts is held by double coated carbon tab on the substrate chuck and the glass positioned in the mask aligner. Finally, the alignment and the transfer of the flake is done using the micromanipulators of the system. The transfer process is constantly monitored in the optical microscope (process demonstrated in Figure 4.13).
Figure 4.13. Optical images of the viscoelastic stamping process. (a) Alignment of flake with Mo contact pattern, (b) deformation of gelfil due to pressure between the substrate and the glass, (c) flake completely in contact with substrate, (d) removal of gel film, (e) and (f) the flake transferred onto the substrate with Mo contacts. The scale bar for (a)-(e) is 200μm.

4.4 Characterization of Few Layered MoS$_2$ Photodetector

In this section, the characterization development of the devices is explained, the measurements include the electrical transport with two-terminal measurements, the optical response with a broadband light source, and the optical response at 300K under vacuum [61]. The schematic of the device and thickness specifications is shown in Figure 4.14. The MoS$_2$ flake is suspended between the contacts since it was stamped on top of Mo metal and the thickness proportion is ~100 times high.
The sample was analyzed under the optical microscope (Figure 4.15) and the software ImageJ to estimate the flake area, the channel length, and the channel width, obtaining thus magnitudes of 1,237.48 μm², 12μm, and ~17μm respectively. Back gate contact was not possible due to in this device the flake is suspended between the contacts.

Figure 4.15. Optical microscope image of the device, few layered MoS₂ flake on Mo contacts over SiO₂/Si substrate. The two terminal measurements were done using the contacts labeled as drain and source.
4.4.1 Electrical Transport

The two-terminal electrical transport measurements were done in function in temperature under vacuum conditions. The equipment and instrument utilized for this purpose are: the state of the art probe station Lakeshore CRX-4K (Figure 4.16) and the low noise Semiconductor Parameter Analyzer Keysight B1500A. Before starting the measurements, the sample was prepared. It consisted in the reduction of the contact resistance by electrical annealing and left the sample under vacuum (~10^{-6} Torrs) for two weeks to remove absorbed gases and moisture, and thus decrease the hysteresis [100]. Despite the employment of these two techniques, the device still demonstrates a small hysteresis that is reduced at higher temperatures, possibly due to the thermal annealing which leads to the reduction of impurities present during the exfoliation process.

![Cryogenic probe station system CRX-4K](image)

Figure 4.16. Cryogenic probe station system CRX-4K utilized for the device characterization.

The IV curves were acquired every 34K starting at 6K, the base temperature of the system using liquid helium, up to 346 K (see Figure 4.17) to study the electrical transport in function of temperature. As the temperature was increased the tendency approximates to ohmic contact behavior. This results show and asymmetric semi-log IV curve (Figure 4.17a), where the electrical transport has a higher magnitude in reverse bias. Consequently, it can be inferred that the device shows a p-type behavior, even though most of the previous reports in literature demonstrate a n-type semiconductivity [7]. However, it needs to be confirmed with another characterization system such as Hall Effect measurement.
Figure 4.17. Two-terminal IV characteristic curves of device in function of temperature. a. Semi-log plot of the IV measurement in which device exhibits p-type behavior, b. IV curves with VDS from -1 to 1 V, as the temperature is increased, the curve approximates to ohmic contact. The inset shows the plot with VDS from -20 to 20 V.

4.4.2 Calculation of Contact Resistance

The high contact resistance in 2D materials represents a problem that reduces the performance of the device. For that reason, several metal contacts have been studied, which have yield to the proposing of Mo contacts for devices based on two-dimensional MoS$_2$ [94]. In this section, the contact resistance is estimated from the IV curve at 300K under vacuum conditions. The total resistance (Equation (11)) $R_T$, is the sum of the contact resistance between Mo/MoS$_2$ interface (directly proportional to the Schottky barrier height $R_{contact} \propto \frac{1}{n} e^{\phi_B/kT}$) and the channel resistance from the MoS$_2$ flake (inversely proportional to the carrier concentration, $R_{channel} \propto \frac{1}{n}$) [101]. Where $n$ is the ideality factor and $k$ is the Boltzmann constant.

$$R_T = 2R_{contact} + R_{channel}$$ (11)

The estimation of the series resistance $R_s$, presuming that this parameter is equivalent the series resistance, $R_s \approx 2R_{contact}$, can be estimated from the two-terminal IV measurement using the Werner method [102], where from the thermionic emission model under forward bias [103] (Equation (12)) a small signal conductance $G = \frac{dI_{DS}}{dV_{DS}}$ is yielded.
\[ I_{DS} = I_s \exp \left( \frac{q}{nkT}(V_{DS} - IR_S) \right) \] (12)

Where,

\[ I_s = A^*T^2 \exp \left( -\frac{q\varphi_B}{kT} \right) \] (13)

Where \( I_s \) is the saturation current, \( A^* \) is the Richardson constant, \( A \) is the area of the junction, \( q \) is the electron charge, \( k \) is the Boltzmann constant, \( T \) is the temperature, and \( \varphi_B \) is the Schottky barrier. The series resistance and ideality factor \( n \) can be estimated with the \( x_{\text{intercept}} = 1/R_s \) and \( y_{\text{intercept}} = q/kT/n \) respectively from the fit of \( G/I_{DS} \) against \( G \) plot deducted from Equation (14) [102] where \( G \) is conductance, \( I_{DS} \) is the drain-source current, \( q \) is the electron charge, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( n \) the ideality factor, and \( R_S \) the series resistance.

\[ \frac{G}{I_{DS}} = \frac{q/kT}{n}(1 - GR_s) \] (14)

The implementation of Werner’s method (Figure 4.18a) consists in the derivative of conductance against voltage to obtain the range of voltage for the next plot. Next, \( G/I_{DS} \) against \( G \) is plotted and obtained a linear fit to acquire the intercept in \( x \) and \( y \) axis. From the IV curve at room temperature it was obtained an ideality factor of 1.36 and a series resistance of \( R_S = 0.1296 \text{ M}\Omega \), calculating a contact resistance of \( R_C = 0.0648 \text{ M}\Omega \). Next, the calculation of the contact resistivity \( \rho_C \), based on the device dimensions for 2D materials (\( \rho_C = R_C \cdot W \), where \( W \) is the channel width of 17\( \mu \)m) it is obtained a magnitude of 1.1M\( \Omega \cdot \mu \)m (see Figure 4.18). The contact resistance obtained is a value higher than in previous reports [88], [94], [104] possibly due to bottom contact configuration.

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Figure 4.18. Contact resistance estimation from the two-terminal IV curve at room temperature under vacuum conditions using Werner's method, a) IV curve under forward bias, b) conductance against forward bias, c) derivative of conductance against forward bias, d) conductance divided by drain-source current vs conductance under forward bias.

### 4.4.3 ESTIMATION OF SCHOTTKY BARRIER

To a better understanding of the device, the Schottky barrier can be estimated from the IV curves in function of temperature. The forward IV of a Schottky diode can be described with Equation (12), as the device is thin enough to be described as two-dimensional material, the drain-source current can be defined by the 2D thermionic emission model (Equation (14)) [105].

\[
I_{DS} = A A'_{2D} T^{3/2} \exp \left[ \frac{q}{kT} \left( \varphi_B - \frac{V_{DS}}{n} \right) \right]
\]  

(15)
where \( A \) is contact area of junction, \( A_{2D}^* \) is the two-dimensional Richardson constant, \( T^{3/2} \) is the reduced power law for 2D transport channel, \( q \) is the electron charge, \( \Phi_B \) is the Schottky barrier height, \( k \) is the Boltzmann constant, \( n \) is the ideality factor, and \( V_{DS} \) is the drain-source bias. As the temperature increases, so does the \( I_{DS} \), and the Schottky barrier height is reduced. Thus, this parameter of the device can be extracted by: applying Arrenius plot \( \ln(I_{DS}/T^{3/2}) vs 1000/T \), \([10][106]\) from the 2D thermionic emission model (Equation (15)); subsequently, the slopes \( S \) (Equation (16)) of the Arrenius graph are plot against the different \( V_{DS} \) magnitudes; finally, from the \( y \) intercept of \( S \) vs \( V_{DS} \) plot (Equation (17)), the Schottky barrier height can be extracted.

\[
S = -\frac{q}{1000k} \left( \Phi_B - \frac{V_{DS}}{n} \right) 
\]

(16)

\[
\text{y intercept} = -\frac{q}{1000k} \Phi_B 
\]

(17)

The implementation of the Arrenius plot requires further analysis of the device behavior. At low temperatures, the resistivity of MoS\(_2\) increases and the current does not change with temperature, reaching an off state represented in the turning point in the Arrenius plot, which can be modified by applying gate voltage \([107]\). In this case shown in Figure 4.19, the device is presenting a turning point at \( \sim 210K \). Consequently, the thermionic emission model is not suitable at this conditions. Therefore, the calculation of the Schottky barrier using this method is done above this temperature at forward voltages from 0.1 to 0.6 V.
Figure 4.19. Large range temperature in Arrhenius plot. The turning point is at ~244 K, range used for the calculation of the device Schottky barrier.

The range reduction of the previous plot was done for the Arrhenius plot and the calculation of the slopes (Figure 4.20a). Afterwards, the Schottky barrier height in the junction Mo-MoS\(_2\) with bottom contacts was obtained from the slope vs voltage (Figure 4.20b), presenting a low Schottky barrier \(\Phi_B\) of 26.78 meV.

![Diagram](image.png)

Figure 4.20. Estimation of Schottky barrier height a) Arrhenius plot \(\ln(I_{DS}/T^{3/2}) vs 1000/T\) at different drain-source voltages b) slopes from Arrhenius plot vs drain-source voltage for the calculation of the Schottky barrier.
4.4.4 Optical Response

The device under test was exposed under different white light intensities under vacuum conditions to measure the photocurrent and photoresponsivity at 300K, key parameters for photodetectors. The photocurrent $I_{ph}$ is defined as the difference between the current under exposure of light $I_{light}$ and the dark current $I_{dark}$ ($I_{ph} = I_{light} - I_{dark}$).

![Graph showing photocurrent generated at different white light intensities.](image)

Figure 4.21. Photocurrent generated at different white light intensities.

Moreover, the photoresponsivity is defined as $R = I_{ph}/P_{light}$, while the light power is the irradiance times area of the flake.

![Graph showing optical response of photodetector at 1V.](image)

Figure 4.22. Optical response of photodetector at 1V a) Photocurrent of device at different irradiance levels. b) Photoresponsivity at 0.77 nW.
The variation of $R$ as a function of applied across the device was measure. It was observed that $R \sim 60 \text{ A/W}$ can be obtained at an applied bias of 20V.

![Graph showing variation of photoresponsivity in function of applied drain-source voltage at 0.77 nW.](image)

Figure 4.23. Variation of photoresponsivity in function of applied drain-source voltage at 0.77 nW.
CHAPTER 5. CONCLUSIONS

In this work, the background and literature has been studied and reviewed to understand, describe, and learn about the properties, attributes, synthesis, and characterization techniques for 2D MoS2 in order to apply this knowledge for the development of the research project which consisted in the synthesis of monolayer MoS2, confirmed by characterization methods such as Raman spectroscopy and AFM, and the fabrication and opto-electro characterization of a photodetector based on micromechanically exfoliated few-layered MoS2. Two-dimensional MoS2 has been synthesized using MoO3 and S powders as precursors in a system designed in-house by two vapor phase mechanisms: vapor phase reaction (process that leads to triangular crystal domains) and sulfurization of molybdenum oxide (process that lead to rhomboidal flakes with MoS2 film on top). The synthesis of 2D MoS2 was confirmed by the characterization with Raman spectroscopy and AFM topography, where the frequency difference between the two strong vibration modes $E_{2g}^{1}$ and $A_{1g}$ was 20cm$^{-1}$ and the scanning with AFM showed a thickness of ~7Å, corresponding to previous reports in the literature. In addition, a few-layered MoS$_2$ device obtained with micromechanical cleavage was designed, fabricated, and characterized. Mo metal contacts were chosen and patterned with standard lift-off process. The MoS2 flake was transferred and aligned to finalize the photodetector fabrication process with a high yield and low time consuming viscoelastic stamping procedure, using as a set-up the mask aligner Karl Suss MJB3. Next, the electrical transport of the device was measured in function of temperature under vacuum conditions. The IV curves obtained allowed the calculations of several parameters of the MoS2 device. The Schottky barrier was estimated from the 2D thermionic emission model, exhibiting a low height. Next, the contact resistance between the Mo-MoS$_2$ was extracted utilizing Werner’s method. Finally, the optical response was obtained from the measurements at different broadband light intensities by calculating the photocurrent and the photoresponsivity at 300 K under vacuum conditions. This work has also impact on the development of the Nanomaterials and Devices Laboratory, allowing the increase of production in research.
Further experiments and analysis are proposed here for future work. Regarding the CVD synthesis of MoS$_2$, systematic studies can be done to analyze and compare how the parameters, such as transport gas and flow rate affect the growth. A comparison between the use of seed promoter such as PTAS, more compatible substrates such as sapphire can provide new dimensions to this work to allow a fuller understanding of the mechanisms that govern the CVD growth of 2D MoS$_2$. Regarding device research on MoS$_2$, set-up for Hall Effect measurements is deemed to be important to gather mobility data and carrier type. The performance of the devices can be done comparing with several metal contacts. In addition, dielectric materials can added to the fabrication process and studied to improve the device performance. Finally, an analysis of the device performance can be done, as a function of the number of MoS$_2$ layers.
REFERENCES


[13] F. H. L. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, and M. Polini,


APPENDIX A. MOS2 CVD SYNTHESIS PROCEDURE

1. Clean substrate
   1.1. Ultrasonic bath
       1.1.1. 5 min in Acetone
       1.1.2. 5 min in methanol
       1.1.3. 5 min in DI
       1.1.4. Dehydrate for 5 min @ 150 °C
   1.2. Piranha solution
       1.2.1. Pour 1 part of H$_2$O$_2$ in 3 parts of H$_2$SO$_4$
       1.2.2. Heat solution at 100 °C for 10 min
       1.2.3. Immerse substrate for 10 to 20 min
       1.2.4. Rinse in three steps of 5 min each with DI
       1.2.5. Dehydrate for 5 min @ 150 °C

2. Clean boat
   2.1. Remove residuals after process with scoop
   2.2. Piranha solution for ~45 min

3. Weight precursors in analytical balance in AlO$_3$ boats

4. Vent
   4.1. Open gas cylinder and knob
   4.2. Turn on Mass Flow Controller (MFC)
   4.3. Open the respective plug valve
   4.4. Open inlet needle valve slowly
4.5. Verify the flow rate 200 sccm and the pressure for the MFC in the cylinder (20 psi is the optimum)

4.6. Once it reaches 760 Torrs close the needle valve and close MFC

4.7. Remove flange

5. Place sample and precursors
   5.1. Locate the furnace in the desire position
   5.2. Place MoO3 boat in the middle of the furnace using a hook
   5.3. Place the S boat in the desired position
   5.4. Close the reaction chamber
   5.5. Purge system

6. Purge
   6.1. Turn on vacuum pump
   6.2. Open outlet needle valve completely
   6.3. Open right angle valve slowly
   6.4. Close inlet needle valve
   6.5. Wait until it reaches ~80 mTorr
   6.6. Open inlet valve slowly (MFC on at max flow rate)
   6.7. Leave purge system for 15 min
   6.8. Repeat two times steps 5.4 to 5.7
   6.9. Regulate inlet valves and control the pressure

7. Regulate to atmospheric pressure
   7.1. Close both outlet valves and wait until reach ~760 Torrs
   7.2. Set the MFC at the desire flow rate
   7.3. Regulate outlet valve to reach same as inlet flow rate at atmospheric pressure
8. Run process
   8.1. Program the furnace controller
   8.2. Run the program
   8.3. Control the pressure by modifying the position of the outlet needle valve during the process
   8.4. When the program fishes proceed with fast cool down

9. Fast cool down
   9.1. Wait until temperature reaches ~500 ºC
   9.2. Increase the flow rate to the maximum in the MFC
   9.3. Slide the furnace to very slowly
   9.4. Open the furnace to increase the cooling rate
   9.5. At ~100 ºC close the valves and disassembly the flange
   9.6. Remove the boats and sample
APPENDIX B. PHOTOLITHOGRAPHY PROCESS

1. Substrate cleaning
   1.1. Sonicate in Acetone for 10 min
   1.2. Sonicate in IPA for 5 min
   1.3. Sonicate in Ethanol/Methanol for 5 min
   1.4. Dry with N₂/Ar gas blow gun

2. HMDS pre-layer deposition
   1.1. Dehydration bake: Wafer on Hot Plate @ 150 °C for 4 minutes.
   1.2. Wafer Cool down: Wafer on aluminum foil covered metal work bench for 5 min
   1.3. Spin coat HMDS: a) 700 rpm for 15 sec
       1.3.1. 4000 rpm for 40 sec
       1.3.2. 500 rpm for 10 sec
   For the spin coater G3P-8 from Specialty Coating Systems the program is shown in
   Table B.1. Spin coater program for HMDS and photoresists deposition AZ5214E-IR.

<table>
<thead>
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<th>1</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<td>4000</td>
<td>4000</td>
<td>500</td>
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<td>0</td>
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<tr>
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<td>0</td>
<td>4</td>
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<td>15</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure B.1. Graphical representation of spin coater recipe for HMDS and photoresists AZ5214E-IR deposition

1.4. Hot plate bake @ 110 °C for 2 min

2. Photoresist coating
   2.1. Spin coat **AZ5214E-IR** (IR for image reversal) (Thickness = 1.4 μm)
       2.1.1. 700 rpm for 15 sec
       2.1.2. 4000 rpm for 40 sec
       2.1.3. 500 rpm for 10 sec
   2.2. **Soft Bake:** Hot plate bake @ 100 °C for 60 sec.

3. UV exposure (Karl Suss MJB 3)
   3.1. Set the exposure time to 35 sec. Since the light intensity is ~2 mW/cm², the dose will be 70mJ/cm².
   3.2. Set the exposure type to soft contact
   3.3. Contact the wafer against mask by adjusting the knob
   3.4. Exposure

4. Developing
   4.1. Development **must be completed ASAP** after exposure (no more than 5-10 min)
   4.2. Scratch outside of your pattern area to see substrate color
4.3. Completely immerse sample in “AZ 300 MIF Developer” in developing tray

4.4. Continuously shake solution until pattern color matches with scratched substrate (30 sec)

4.5. Wash sample with DI water (twice) and blow dry with N₂
APPENDIX C. LABVIEW PROGRAM FOR SEMICONDUCTOR PARAMETER ANALYZER HP 4156A

Figure C.2. Labview program, initialization and configuration of SMU channels.

Figure C.3. Acquisition, plotting and saving data in text file via GPIB communication.
APPENDIX D. MATLAB PROGRAM FOR VAN DER PAUW CORRECTION FACTOR CURVE

clear all
x = logspace(0,3,1000);
for i=1:length(x)
    Lp=@(f)cosh((x(i)-1.)/(x(i)+1))*(log(2)/f))-0.5*exp((log(2)/f));
    F(i) = fsolve(Lp,0.5);
end
semilogx(x,F,'-o')
xlabel('R_{12,34}/R_{23,41}')
ylabel('Correction Factor (f)')
grid('minor');
title('van der Pauw Correction Factor');
Gustavo Alberto Lara Saenz was born in Cd. Juarez, Chihuahua, Mexico in 1987. In 2005 he started his BS in Mechatronics Engineering at the Universidad Autonoma de Ciudad Juarez, where he had the opportunity to work in campus for 3 years and at the end of his career work as a research assistant with Dr. Jose Mireles in the Centro de Investigacion en Ciencia y Tecnologia Aplicada (CICTA) from the UACJ. In addition, he participated in academic exchange program at the Universidad Autonoma de Nuevo Leon in 2009 and in a research program at the University of Texas at El Paso working with Dr. David Zubia in 2011. At the end of his career, he won the Business Award from the Confederacion Patronal de la Republica Mexicana (COPARMEX) and the Academic Excellence Award from the Asociacion Nacional de Facultades y Escuelas de Ingenieria (ANFEI). After obtaining his BS, he worked at CICTA for three years as a MEMS Laboratory Research Technician. His activities included the design, simulation, fabrication processes, packaging, design of experiments, and electrical testing of Micro-Electro-Mechanical Systems. In addition, he worked collaborated with important institutions and universities in Mexico, such as Centro de Investigacion de Materiales Avanzados, Universidad Nacional Autonoma de Mexico (UNAM), and Instituto Mexicano del Petroleo, projects funded by the Concejo Nacional de Ciencia y Tecnologia; gain experience in staff management, training, and supervision; and participated in international conferences and journal publications. Afterwards, he decided to continue with his academic development by studying a MS in Electrical Engineering at UTEP. Since the beginning of his master’s studies, he had the fortune to work with Dr. Anupama Kaul and support her in the development of the Nanomaterials and Devices Laboratory (NDL). In April of 2015, he had the outstanding opportunity to participate as student organizer in the “NSF US-EU Workshop on 2D Layered Materials and Devices” thanks to his mentor, the US chair of this excellent event. His work during his master studies lead to the publication of 5 conference proceedings and 3 journal papers (1 in submission and 2 in process).

This thesis was typed by Gustavo Alberto Lara Saenz.