Growth and doping of MoS2 thin films for electronic and optoelectronic applications

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GROWTH AND DOPING OF MoS$_2$ THIN FILMS FOR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

by

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M.S. Ain Shams University, 2010
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ABSTRACT

MoS$_2$ high absorption coefficient, high mobility, mechanical flexibility, and chemical inertness is very promising for many electronic and optoelectronic applications. The growth of high-quality MoS$_2$ by a scalable and doping compatible method is still lacking. Therefore, the suitable dopants for MoS$_2$ are not fully explored yet. This dissertation consists mainly of four main studies. The first study is on the growth of MoS$_2$ thin films by atmospheric pressure chemical vapor deposition. Scanning electron microscope images revealed the growth of microdomes of MoS$_2$ on top of a smooth MoS$_2$ film. These microdomes are very promising as a broadband omnidirectional light trap for light harvesting applications. The second study is on the growth of MoS$_2$ thin films by low pressure chemical vapor deposition (LPCVD). Control of sulfur vapor flow is essential for the growth of a pure phase of MoS$_2$. Turning off sulfur vapor flow during the cooling cycle at 700 $^\circ$C leads to the growth of highly textured MoS$_2$ with a Hall mobility of 20 cm$^2$/Vs. The third study was on the growth of Ti-doped MoS$_2$ thin films by LPCVD. The successful doping was confirmed by Hall effect measurement and secondary ion mass spectrometry (SIMS). Different growth temperatures from 1000 to 700 $^\circ$C were studied. Ti act as a donor in MoS$_2$. The fourth study is on fluorine-doped SnO$_2$ (FTO) which has many technological applications including solar cells and transistors. FTO was grown by an aqueous-spray-based method. The main objective was to compare the actual against the nominal concentration of fluorine using SIMS. The concentration of fluorine in the grown films is lower than the concentration of fluorine in the aqueous solution.
To the good people all over the world
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TABLE OF CONTENTS

LIST OF FIGURES ............................................................................................................ x
LIST OF TABLES ........................................................................................................... xiv
CHAPTER 1: INTRODUCTION ....................................................................................... 1
  1.1 Background and Motivation ................................................................................. 1
  1.2 Ideal Solar Cell Absorber Material ................................................................. 3
  1.3 Growth of MoS2 ............................................................................................... 4
  1.4 Crystal Structure of MoS2 ............................................................................... 5
  1.5 Electrical Properties of MoS2 ......................................................................... 7
  1.6 Optical Properties of MoS2 ............................................................................. 9
CHAPTER 2: THEORETICAL CONSIDERATIONS .................................................... 10
  2.1 Thermodynamics ............................................................................................. 10
  2.2 Kinetics ........................................................................................................... 11
  2.3 Mathematical Model for Diffusion of S and Ti ................................................ 11
  2.4 Constant-source Diffusion (S Diffusion) ......................................................... 14
  2.5 Limited-source Diffusion (Ti Diffusion) ........................................................... 14
  2.6 Diffusion Coefficient ...................................................................................... 15
  2.7 Solid Solubility Limit ..................................................................................... 15
CHAPTER 3: GROWTH OF MoS2 BY APCVD ............................................................ 16
  3.1 Introduction ...................................................................................................... 16
  3.2 Experiment ....................................................................................................... 18
    3.2.1 Deposition of Molybdenum Thin Film ...................................................... 18
    3.2.2 APCVD Design and Setup ..................................................................... 23
    3.2.3 Sulfur Evaporation Rate at Atmospheric Pressure ................................. 31
    3.2.4 Characterization Techniques ................................................................ 34
  3.3 Results and Discussion ................................................................................... 34
    3.3.1 X-ray Diffraction .................................................................................... 35
    3.3.2 Raman Spectroscopy .............................................................................. 37
    3.3.3 Electron Microscopy and EDX ................................................................. 40
3.3.4 Electrical Properties ................................................................. 44
3.3.5 Optical Properties ................................................................. 46
3.4 Conclusion .................................................................................. 47

CHAPTER 4: ANTIREFLECTION STRUCTURES OF MoS2 ......................... 48
4.1 Introduction .................................................................................. 48
4.2 Simulation .................................................................................... 50
4.3 Results and Discussion ................................................................. 52
  4.3.1 Domes with Different Base Diameters ........................................ 52
  4.3.2 Broadband Nature of Antireflection Structures .......................... 53
  4.3.3 Omnidirectionality of Antireflection Structures ......................... 54
  4.3.4 Comparison of Different Geometrical Antireflection Structures .... 55
  4.3.5 Reflectance Measurement and Simulation ................................. 56
4.4 Conclusion .................................................................................. 57

CHAPTER 5: GROWTH OF MoS2 BY LPCVD ............................................. 59
5.1 Introduction .................................................................................. 59
5.2 Experiment ................................................................................... 60
5.3 Results and Discussion ................................................................. 62
  5.3.1 Sulfur Evaporation Rate at Low Pressure ................................. 62
  5.3.2 Structural Characterization ....................................................... 64
  5.3.3 Electrical Characterization ....................................................... 70
  5.3.4 Optical Characterization ......................................................... 81
5.4 Conclusion .................................................................................. 91

CHAPTER 6: Ti-DOPED MoS2 ................................................................. 92
6.1 Introduction .................................................................................. 92
6.2 Ti-doping Calculations ................................................................. 93
6.3 Experiment ................................................................................... 95
6.4 Results and Discussion ................................................................. 97
  6.4.1 X-ray Diffraction ...................................................................... 97
  6.4.2 Raman Spectroscopy ............................................................... 99
  6.4.3 Scanning Electron Microscopy ................................................ 100
6.4.4  Secondary Ion Mass Spectroscopy (SIMS) .............................................. 102
6.4.5  Electrical and Optical Properties .............................................................. 105
6.5   Conclusion........................................................................................................ 108

CHAPTER 7: FLUORINE-DOPED TIN OXIDE.......................................................... 109
7.1   Introduction ...................................................................................................... 109
7.2   Experiment ....................................................................................................... 109
  7.2.1  Growth of FTO ......................................................................................... 109
  7.2.2  Calibration Standard by Ion Implantation................................................. 111
7.3   Results and Discussion..................................................................................... 114
  7.3.1  Sputtering Rate & Normalization ............................................................. 114
  7.3.2  Relative Sensitivity Factor ........................................................................ 115
  7.3.3  Quantification of Fluorine in the Grown Samples .................................... 117
7.4   Conclusion........................................................................................................ 122

CHAPTER 8: CONCLUSION ....................................................................................... 124
APPENDIX A: GAS FLOW CALCULATIONS ........................................................... 128
APPENDIX B: XRD CALCULATIONS ...................................................................... 137
APPENDIX C: ELECTRICAL TRANSPORT CALCULATIONS .............................. 150
APPENDIX D: MATRIX THEORY .............................................................................. 165
APPENDIX E: LIST OF PUBLICATIONS ................................................................. 170
LIST OF REFERENCES .............................................................................................. 172
LIST OF FIGURES

Figure 1.1: A unit cell of a 2H phase of MoS$_2$................................................................. 5

Figure 1.2: Top view of a 2H phase of MoS$_2$. ................................................................. 6

Figure 1.3: A comparison between the sheet resistance of a wafer of undoped MoS$_2$ ($\rho = 12 \ \Omega\cdot\text{cm}$) and a wafer of doped silicon ($\rho = 0.5 \ \Omega\cdot\text{cm}$). ................................................................. 7

Figure 1.4: The sheet resistance of MoS$_2$ as a function of thickness...................... 8

Figure 3.1: A schematic of E-beam evaporation of Mo thin film on a sapphire substrate on the left, and its subsequent sulfurization in a CVD chamber on the right. ............... 16

Figure 3.2: A schematic of the doping process of MoS$_2$. ........................................... 17

Figure 3.3: SEM cross-section images of Mo/glass sample 1M at different places. .... 21

Figure 3.4: A schematic of atmospheric pressure chemical vapor deposition (APCVD) setup. ......................................................................................................................................................................................... 24

Figure 3.5: Average sulfur evaporation rate as a function of sulfur zone temperature, at two different flow rates of 48 and 81 sccm................................................................. 32

Figure 3.6: Symmetric Out-of-plane XRD patterns for sample 4M of Mo/sapphire and reference XRD pattern of Mo, where Mo peaks are labeled in red and sapphire peak are labeled in blue................................................................. 35

Figure 3.7: Symmetric Out-of-plane XRD patterns for sample 5M of Mo/sapphire, where Mo peaks are labeled in blue and MoO$_2$ phase peaks are labeled in green. ................. 36

Figure 3.8: Symmetric Out-of-plane XRD patterns of (a) sample 3M4S, (b) sample 3M1S and (c) reference XRD pattern of MoS$_2$, where MoS$_2$ peaks are labeled in red and sapphire peaks are labeled in blue................................................................. 37

Figure 3.9: Raman spectra of MoS$_2$-on-sapphire for samples 3M4S, 3M1S, and blank c-plane sapphire wafer. ................................................................................................. 38
Figure 3.10: Raman spectra from the dome and flat spots on the surface of sample 3M4S of the MoS₂ thin film. ................................................................. 39

Figure 3.11: SEM images of (a-b) 4M Mo film (heated substrate) (c-f) 5M Mo film (unheated substrate) suffered oxidation. .................................................. 40

Figure 3.12: SEM images of Sample 3M4S of MoS₂ (a-d) using Inlens detector at different magnifications, (e) using Everhart-Thornley type detector, and (f) using energy selective backscattered (ESB) detector. ............................................................ 42

Figure 3.13: EDX Spectrum of sample 3M4S of MoS₂ .............................................. 44

Figure 3.14: Spreading resistance of samples 4M13S and 4M14S of MoS₂ before and after annealing ............................................................... 45

Figure 3.15: Transmittance of sample 3M4S of MoS₂ (right axis) compared to the spectral irradiance from the sun (left axis). ...................................................... 46

Figure 4.1: The reflectance of MoS₂ domes with different base diameters. .......... 53

Figure 4.2: The reflectance of a square array of MoS₂ domes with 0.5 µm base diameter compared to that of a smooth film. ............................................. 54

Figure 4.3: The reflectance of square arrays of MoS₂ parabolic domes with different heights. The domes base diameter is 0.5 µm for all heights. ....................... 55

Figure 4.4: The total reflectance of arrays of different structures and spatial arrangements. ........................................................................................................ 56

Figure 4.5: The reflectance of MoS₂-on-sapphire sample 3M4S in comparison with simulation for parabolic domes with 2 µm base diameter. ......................... 57

Figure 5.1: A schematic illustration of a two-zone LPCVD setup. ......................... 61

Figure 5.2: The average sulfur evaporation rate as a function sulfurization times .... 63

Figure 5.3: Raman spectra of samples A, B, C, and D. ........................................... 65
Figure 5.4: Symmetric out-of-plane XRD patterns of samples A, B, C, D, where MoS$_2$ peaks are labeled in green, sapphire peaks are labeled in black and MoO$_2$ are labeled in red. .................................................................................................................................... 66

Figure 5.5: SEM images of samples (a) A, (b) B, (c) C, and (d) D. ........................................ 69

Figure 5.6: SIMS depth profile for sample D of MoS$_2$. .......................................................................................................................... 70

Figure 5.7: Resistivity, sheet resistance, carrier concentration, and mobility of samples A, B, C, and D........................................................................................................................ 73

Figure 5.8: Resistivity and mobility of holes in sample D as a function of temperature. 76

Figure 5.9: (a) The logarithm of the carrier concentration of sample D as a function of temperature and (b) concentration of holes in sample D as a function of temperature. $T_o$ is the degeneracy temperature. The solid blue line is a theoretical fit to the experimental red circles. ............................................................................................................................... 79

Figure 5.10: Mean free path of holes in sample D of MoS$_2$ as a function of temperature. ........................................................................................................................................... 81

Figure 5.11: A schematic of four media structure consisting of thin film/substrate layers surrounded by air from both sides. ................................................................. 82

Figure 5.12: (a) Transmittance and (b) reflectance of samples A, B, C, and D. .............. 87

Figure 5.13: The absorption coefficient of samples A, B, C, and D. ................................. 88

Figure 5.14: (a) Refractive index and (b) extinction coefficient of samples A, B, C, and D. ........................................................................................................................................... 89

Figure 5.15: (a) Real and (b) Imaginary parts of the dielectric constant of samples A, B, C, and D. ....................................................................................................................................... 90

Figure 6.1: A schematic of the growth of Ti-doped MoS$_2$. .............................................. 93

Figure 6.2: Symmetric Out-of-plane XRD patterns of samples A (1000 °C), B (900 °C), C (800 °C), and D (700 °C), where MoS$_2$ peaks are labeled in magenta, sapphire peaks are labeled in green, Ti$_2$S peaks are labeled in orange, and Mo peaks are labeled in red. 98
Figure 6.3: Raman spectra of samples A, B, C, and D .................................................. 100

Figure 6.4: SEM images of the surface of samples (a) A (1000 °C) (b) B (900 °C) (c) C (800 °C) (d) D (700 °C). ...................................................................................................................... 101

Figure 6.5: SEM cross-section images of the surface of samples A (1000 °C), B (900 °C), C (800 °C), and D (700 °C). .............................................................................................................. 102

Figure 6.6: SIMS depth profiles of Ti-doped MoS2 samples (a, b) A and (c, d) B. ...... 103

Figure 6.7: SIMS depth profiles of Ti-doped MoS2 samples (a, b) C and (c, d) D. ...... 105

Figure 6.8: Transmittance and reflectance spectra of Samples A, B, C, and D.......... 106

Figure 6.9: Absorption coefficient of Ti-doped MoS2 in comparison with undoped MoS2. .............................................................................................................................. 107

Figure 6.10: Optical constants of sample A. (a) Refractive index and extinction coefficient. (b) Real and imaginary parts of the dielectric constant. ......................................................... 108

Figure 7.1: SIMS depth profiles of 1.12 At% of Fluorine in SnO2 on a glass substrate. 115

Figure 7.2: SIMS depth profiles of FTO/glass grown at 450 with nominal F/Sn atomic concentration of (a) 0.5% (b) 5% and (c) 15%. ................................................................. 118

Figure 7.3: SIMS depth profiles of FTO/glass grown at 480 °C with nominal F/Sn atomic concentration of (a) 0.1%, (b) 0.2%, (c) 0.5%, and (d) 1%. .................................................. 119

Figure 7.4: SIMS depth profiles of FTO/glass grown at 480 °C with nominal F/Sn atomic concentration of (a) 2%, (b) 5%, (c) 10%, and (d) 20%. ......................................................... 121

Figure 7.5: SIMS depth profiles of FTO/SiO2/Si with nominal F/Sn atomic concentration of (a) 10% (b) 15% (c) and 20%................................................................. 122

Figure 8.1: The position of the needle valve must be (a) at the inlet of rotameter if the chamber is at atmospheric pressure or (b) at the outlet if the chamber is under vacuum. ...................................................................................................................... 135
LIST OF TABLES

Table 3.1 Sulfur evaporation rate experimental details. ................................................................. 32

Table 3.2 Comparison of observed Raman modes of MoS$_2$ in our work and earlier reports. ........................................................................................................................................... 39

Table 5.1 The average sulfur evaporation rate as a function sulfurization times. ............ 63

Table 7.1 FTO samples labels and their corresponding nominal concentrations. .......... 111
CHAPTER 1: INTRODUCTION

1.1 Background and Motivation

Despite the diligent work to improve solar cells efficiency and reduce its cost over decades, the photovoltaic cost is still high in comparison with fossil fuel. The solution of this problem is to find cheap materials and technologies that can compete with current silicon technologies which dominate the market to lower the overall cost. For many decades layered transition-metal dichalcogenide semiconductors (such as MoS$_2$, WS$_2$, MoSe$_2$, TiS$_2$, etc.) have attracted attention as a new class of solar cell materials [1]. Relatively high efficiencies have been obtained in solid-state photovoltaic and photoelectrochemical cells [1-7]. These materials are very promising for many interesting applications as well such as field effect transistors [8-9], memories [10-11], and sensors [12-14].

MoS$_2$ is a layered-structure semiconductor with an indirect bandgap of 1.3 eV [15]. It has fascinating properties such as high carrier mobility (410 cm$^2$ V$^{-1}$ s$^{-1}$) [16], high absorption coefficient ($>10^4$ cm$^{-1}$) [17], chemical inertness [18], and band gap tunability [19]. Its band gap become direct and increase to 1.8 eV as its thickness decreases down to a single atomic layer [19].

Although the potential of MoS$_2$ is well established for a long time, many technological obstacles limited the benefit from this material in the past, such as the difficulty to grow large single crystals or thin films of high quality on a large scale. Most of the attempts made to produce good quality crystals and thin films of MoS$_2$ were done in an evacuated
ampoules [1]. Even the available reports on synthetic MoS$_2$ are not comprehensive. For example, if structural and optical properties are investigated the electrical properties will be missing or vice versa. As the growth conditions change the properties of MoS$_2$ change too and consequently the electrical properties of a sample cannot be correlated to another sample grown under different conditions. Electronic devices and solar cells, in particular, can be realized if these materials can be suitably doped [1].

Many devices have been fabricated from natural MoS$_2$ by exfoliation [3, 20-26], while the concentration and type of impurities in the natural crystals are unknown. Both p- and n-type doping was detected in the same natural MoS$_2$ crystal at different positions on its surface due to the difference in types and concentrations of dopants at different points. Therefore, the natural crystals are an unreliable source for large-scale fabrication of devices [27-29]. Therefore reliable synthetic growth methods of MoS$_2$ have been developed to fulfill the demand of this material, including vapor transport [30-31], atmospheric-pressure chemical vapor deposition (APCVD) [32-36], and low pressure chemical vapor deposition (LPCVD) [37-40].

Chemical vapor deposition is the most industrially suitable and scalable method. The MoS$_2$ doping reported earlier were done in evacuated ampoules (where sealing and breaking of these ampoules is required for each run). This technique is expensive and not scalable. Therefore, doping by diffusion in a CVD chamber, under gas flow, is highly needed. Some technical problems such as oxidation and/or sulfur loss at elevated temperatures will be explored in this work. The high temperature is required for diffusion of dopants. Therefore,
a doping-compatible method for the synthesis of high-quality MoS$_2$ films with good uniformity is needed.

In this work, we will grow undoped MoS$_2$ with a doping-compatible process using atmospheric chemical vapor deposition (APCVD) and low pressure chemical vapor deposition (LPCVD). Then we will study the effect of doping by titanium. The structural, electrical, and optical properties of grown films will be studied in detail. Also, we will assess the quality of the grown MoS$_2$ for solar cell applications. Finally, we will study fluorine-doped tin oxide by secondary ion mass spectroscopy (SIMS), as a potential material for solar cells applications.

1.2 Ideal Solar Cell Absorber Material

A good absorber material that can be used in solar cell applications should have specific properties which will discuss in this section [1]. For a single-junction solar cell, a bandgap of 1.3-1.5 eV can achieve the best efficiency [1]. Regarding the type of the band gap, a direct transition is the best due to the higher absorption coefficient and steep absorption edge. Although silicon, has an indirect bandgap, it has the biggest share in the commercial market of solar cells due to its mature technology, high purity, and its competitive price. The criterion which makes difference is absorption coefficient which is on the order of $10^3$ in silicon and $10^4$ in MoS$_2$, over the visible spectrum. Long lifetime, as well as long diffusion length of excess minority carriers, have a great effect on the efficiency of solar cells [1]. This will determine the possibility to collect generated electron-hole pairs. One
of the important parameters that affect the minority carrier’s lifetime is structure perfection. Therefore, a single crystal of silicon will have a fewer imperfection in comparison with polycrystalline silicon, therefore higher lifetime. One of the big technical challenges of MoS$_2$ is structure perfection especially, MoS$_2$ has a layered structure, and therefore, layers can slide easily and the structure distorts. A remedy for this problem is growing it on a rigid substrate. High mobility is also an important factor to achieve high fill factor [1].

The lower the number of carrier concentrations the higher the solar cell efficiency, due to the lower recombination centers. One important aspect of any semiconductor material is the ability to dope it reliably and achieve p- or n-type doping with a shallow acceptor or donor level respectively. Lacking knowledge of the best dopants for MoS$_2$ is one of the big challenges for its commercial use in the semiconductor industry. The possibility to form a good low resistivity ohmic contacts to an absorber material at low cost is an important factor too [1]. Finally, the abundance, low cost, and environmental safety of the absorber material are very important. MoS$_2$ can be grown from cheap precursors such as MoO$_3$, and sulfur. Both are environmentally friendly materials and abundant.

1.3 Growth of MoS$_2$

MoS$_2$ thin films were grown or deposited by different method due to it is technological importance. The growth techniques include atmospheric-pressure chemical vapor deposition (APCVD) [32-36], low pressure chemical vapor deposition (LPCVD) [37-40], metal-organic chemical vapor deposition (MOCVD) [41], atomic layer deposition (ALD)
sulfurization of MoO₃ film [43-44], sulfurization of Mo film [4-5, 45-51], and chemical bath deposition (CBD) [52-55]. The deposition techniques include pulsed layer deposition [56-57], sputtering [58-62], evaporation [63-64], and electrochemical deposition [65-67].

1.4 Crystal Structure of MoS₂

Bulk MoS₂ can exist in two stable phases, the so-called 2H-MoS₂ (two-layer hexagonal) and 3R-MoS₂ (three-layer rhombohedral), while monolayers of these two phases termed as 1H and 1R respectively [68].

![Figure 1.1: A unit cell of a 2H phase of MoS₂.](image)

In both phases, Mo atoms are surrounded by six S atoms in a trigonal prismatic coordination. In each layer, the S-Mo-S atoms are bonded by the strong covalent bond, while adjacent layers are packed by weak van der Waals forces [68]. The 2H phase, which
is the most stable of MoS\textsubscript{2}, has a unit cell (figure 1.1) composed of a bilayer with space group P\textsubscript{6}3\text/mmc, while the 3R phase, which is another stable phase, has a unit cell composed of a trilayer with space group R\text{3m} \cite{68}. Figure 1.2 shows a top view of the crystal structure of MoS\textsubscript{2}.

![Figure 1.2: Top view of a 2H phase of MoS\textsubscript{2}.](image)

The layered structure of MoS\textsubscript{2} where each layer is bonded to the other by Van der Waal’s forces only has many advantages \cite{1}. The outer surfaces of a single crystal of MoS\textsubscript{2} parallel to the c-plane consist of sulfur-layer of atoms \cite{1}. Therefore, a perfect surface is well passivated due to the absence of any dangling bonds \cite{1}, on the surfaces parallel to c-plane of MoS\textsubscript{2} and explain its chemical inertness. These unique properties of layered structure semiconductors are very promising since we do not encounter the usual problems of regular semiconductors, such as, dangling bonds and need for passivation, and surface density of states and Fermi level pinning at the surface \cite{1}.

No interface states at the surface between MoS\textsubscript{2} and any other layered-material should be expected, and a small number of interface states is expected if the other material is not a
layered material [1]. The layered-structure of MoS₂, therefore, relax many of the problems arise from lattice mismatch [1]. The surface passivation and absence of surface states in MoS₂ present a natural solution to the problem of recombination at the surfaces of solar cells fabricated from non-layered-structure materials [1].

1.5 Electrical Properties of MoS₂

Bulk MoS₂ was reported as both n- and p-type semiconductor with an indirect bandgap (~1.3 eV) and carrier mobility in the 50-200 cm² V⁻¹ s⁻¹ range at room temperature [69].

![Figure 1.3](image)

Figure 1.3: A comparison between the sheet resistance of a wafer of undoped MoS₂ (ρ = 12 Ω-cm) and a wafer of doped silicon (ρ = 0.5 Ω-cm).

Even a single layer of MoS₂ has a high electron mobility of 200 cm² V⁻¹ s⁻¹ [70]. Also, the band gap become direct and its value increases to 1.8 eV as the thickness decrease to a single layer. The band gap of MoS₂, and its high current on/off ratio of 1×10⁸, make MoS₂ very attractive for electronic devices applications.
The resistivity of MoS$_2$ parallel to c-plane is 12 $\Omega$-cm, which is intrinsically low, and perpendicular to c-plane is $2 \times 10^3$ $\Omega$-cm [71]. This value will vary depending on the concentration of dopants and the structure perfection. More dopants will tend to decrease the resistivity. On the other hand, a large number of defects and imperfections will tend to increase the resistivity. If we compare the sheet resistance of two wafers of undoped MoS$_2$ ($\rho = 12$ $\Omega$-cm) and doped silicon ($\rho = 0.5$ $\Omega$-cm), the sheet resistance will decrease as thickness increases for both of them as expected (figure 1.3).

![Figure 1.4: The sheet resistance of MoS$_2$ as a function of thickness.](image)

Although the change in sheet resistance is within on order of magnitude on the micrometer scale, the sheet resistance increase by three orders of magnitude from $10^3$ $\Omega$ to $10^6$ $\Omega$ as the thickness of MoS$_2$ decrease from 300 $\mu$m to 100 nm (figure 1.4). Therefore, resistance management by controlled doping is required for low power dissipation applications.
1.6 Optical Properties of MoS₂

MoS₂ high optical absorption coefficient (>10⁴) [72], and its band gap of 1.3 eV which matching the solar spectrum [15], making it particularly attractive for photovoltaics. The optical properties of bulk, few layers, and monolayers of natural and synthetic MoS₂ have been studied by many techniques [30, 73-82], including Reflectance only, transmittance only, ellipsometry, and both transmittance and reflectance. Reported refractive index values of MoS₂ are in the range of 2.5-4.5 for the 400-750 nm range of wavelengths [81]. Different absorption peaks (excitonic transitions) were observed in MoS₂ absorption coefficient spectrum at low temperature (5 K). These peaks were labeled A(1.910 eV), B(2.112 eV), d(2.630 eV), C(2.760 eV), D(3.175 eV), α(2.685 eV), and β(3.93 eV) [30]. The origin of the A and B absorption peaks is the spin-orbit splitting of transitions at Γ, while the origin of C and D absorption peaks is the transitions between the high density of states regions at P and Q of the two-dimensional Brillouin zone, as interpreted earlier [30].
CHAPTER 2: THEORETICAL CONSIDERATIONS

Chemical vapor deposition (CVD) is the deposition of a solid film from a vapor precursor. The film may be deposited on the substrate and the chamber wall or the substrate only depending on whether the system is hot or cold chamber wall. Many factors control the deposition process (processing conditions) including deposition temperature, chamber pressure, the substrate (surface specificity) [83] and reactant concentration [84]. CVD process is a steady but in general a non-equilibrium process [84]. Steady state (dynamic equilibrium) requires continuous work (sulfur vapor flow). In the case of sulfurization process, we have a reaction between sulfur vapor and the solid Mo film. The sulfur will diffuse eventually in the solid film and react with the Mo film to form MoS$_2$ if the reaction can occur according to the thermodynamics. The rapidity of this diffusion (reaction) cannot be predicted by thermodynamics but can be studied experimentally, namely the kinetics of the reaction.

2.1 Thermodynamics

Thermodynamics tells us in which direction the reaction will proceed under equilibrium and the feasibility of that reaction. Although equilibrium can be achieved experimentally in an evacuated ampoule, this technique is not suitable for industry. On the other hand, the gas flow in a chamber (CVD) is the standard in the industry. It is important to note that we study the thermodynamics of the chemical reactions under equilibrium, while CVD itself is a non-equilibrium process. That means thermodynamic calculations will just handwave.
the direction of the reaction but will not give us quantitative information, but still, we can extract this information by studying the kinetics of the reaction. We can predict the equilibrium phases that will exist in a chemical reaction - under specific processing conditions - from the phase diagrams which can be calculated by minimizing the Gibbs free energy of the system [84]. Also, we can predict the effect of changing one or all the of processing conditions on equilibrium phases.

2.2 Kinetics
Kinetics studies of a chemical reaction will tell us mainly how fast that reaction can occur. In other words, we will be able to determine the rate of deposition of the desired film [84]. The kinetics of a chemical reaction in a CVD chamber depending on three main factors[84]. The first factor is the homogeneous reactions occurs among the precursor gases in the reaction chamber. The second factor is heterogeneous reactions occurs on the surface of the substrate. The third factor is the mass transport of the gaseous precursors. The slowest factor of these factors will limit the deposition rate[84].

2.3 Mathematical Model for Diffusion of S and Ti
Sulfur and titanium diffusion can be modeled in one-dimension by Fick’s first law of diffusion as follows[85]:

\[
J = -D \frac{\partial N(x,t)}{\partial x} \quad (2.1)
\]
Where $J$ represents the S or Ti flow per unit area (number of S or Ti atoms/cm$^2$ s), $D$ is the diffusion coefficient, and $N$ is the S or Ti concentration. The negative sign indicates the tendency of diffusion from high concentration to low concentration. For the case of Mo sulfurization, we will assume that sulfur flow through grown MoS$_2$ is constant across the sulfurized layer, and consequently sulfur does not accumulate in MoS$_2$. The sulfur flux, $J$ is given by [85]:

$$J = -D \frac{N_1 - N_0}{X_o}$$  \hspace{1cm} (2.2)

Where $X_o$ is the thickness of grown MoS$_2$, and $N_0$ and $N_1$ are the concentrations of sulfur at ambient/MoS$_2$ and MoS$_2$/Mo interface, respectively. At the MoS$_2$/Mo interface we assume sulfurization rate is proportional to the concentration of sulfur at the interface, therefore we can write[85]:

$$J = K_s N_i$$  \hspace{1cm} (2.3)

Where $K_s$ is the rate constant for the reaction at the MoS$_2$/Mo interface. By substituting the last equation in the preceding one we can eliminate $N_i$.

$$J = D \frac{N_0}{X_o + D \frac{N_0}{K_s}}$$  \hspace{1cm} (2.4)

The rate of change of thickness of the grown MoS$_2$ as a function of time is given by sulfur flux divided by the number of molecules, $M$, of MoS$_2$ that are grown in a unit volume of the grown thickness [85].
\[ \frac{dx_0}{dt} = \frac{I}{M} = \frac{D}{M} \frac{N_0}{x_0 + \frac{D}{k_s}} \]  \hfill (2.5)

The solution of this differential equation using the boundary condition \( x_o(t = 0) = 0 \) is given by [85]:

\[ t = \frac{x_o^2}{B} + \frac{A x_0}{B} \]  \hfill (2.6)

Where \( A = 2D/k_s \) and \( B = 2DN_0/M \). Solving the last equation for \( x_o \) we get [85]:

\[ x_o(t) = 0.5 A \left\{ \left(1 + \frac{4Bt}{A^2}\right)^{0.5} - 1 \right\} \]  \hfill (2.7)

The continuity equation for S and Ti diffusion is given by [85]:

\[ \frac{\partial N}{\partial t} = -\frac{\partial j}{\partial x} \]  \hfill (2.8)

It states that the rate of increase of S or Ti concentration with time is equal to decrease in the gradient (strictly speaking divergence) of S or Ti Flux. In other words, as the concentration increase over time, that means the source from which these atoms have diffused is decreasing and subsequently the flux of these atoms. Substituting the last equation in the preceding equation we get Fick’s second law:

\[ \frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2} \]  \hfill (2.9)

Where \( D \) is assumed to position independent. This is not the case at high impurity concentrations.
2.4 Constant-source Diffusion (S Diffusion)

Sulfurization can be modeled satisfactorily by a constant-source diffusion since we provide constant sulfur vapor concentration in the CVD chamber during sulfurization. The solution of equation (2.9) for this case is given by [85]:

$$N(x, t) = N_0 \text{erfc}(x/2\sqrt{Dt})$$  \hspace{1cm} (2.10)

For a semi-infinite Mo sample, in which $N_0$ is the sulfur concentration at the ambient/Mo interface ($x=0$). This diffusion is well known as a complementary error function (erfc) diffusion [85]. The concentration of sulfur remaining constant at the ambient/Mo interface while diffusion front (profile) proceeds deeper in Mo with time progress [85].

2.5 Limited-source Diffusion (Ti Diffusion)

Since in the case of Ti-diffusion we have a specific dose, it can be modeled by a limited-source diffusion. An impulse function can mathematically model the Ti initial boundary condition, where the magnitude of the function is equal to the Ti dose. By considering a semi-infinite Mo sample, the solution of equation (2.9) is given by the Gaussian distribution:

$$N(x, t) = \left(\frac{Q}{\sqrt{\pi Dt}}\right)\exp - \left(x/2\sqrt{Dt}\right)^2$$  \hspace{1cm} (2.11)

In the limited-source diffusion, the concentration of Ti decreases at the initial position of the source with time progress [85]. The diffusion front (profile) proceeds deeper in Mo with time too, but the total dose remains constant [85].
2.6 Diffusion Coefficient

Diffusion coefficient follows the Arrhenius equation [85]:

\[ D = D_0 \exp\left(-\frac{E_A}{KT}\right) \]  

(2.12)

Where \( D_0 \) and \( E_A \) are constants, which can be determined experimentally.

2.7 Solid Solubility Limit

At a given temperature there is a maximum limit to the number of dopants that can be dispersed in MoS\(_2\). This limit is called the solid-solubility limit. At high concentration of dopants, a fraction of dopants results in excess holes or electrons. In other words, this fraction is what we call the electrically active dopants.
CHAPTER 3: GROWTH OF MoS₂ BY APCVD

3.1 Introduction

The growth of intentionally doped semiconductors is necessary to control charge carrier type and concentration, and subsequently to realize functional devices. In this chapter, we developed a process to grow undoped MoS₂ by atmospheric pressure chemical vapor deposition (APCVD). The developed process is compatible with the high temperatures required for doping by diffusion. A two-step method is used here to grow MoS₂ (figure 3.1). First, we deposit a Mo film on a pre-cleaned sapphire substrate. Second, we sulfurize this film in a CVD chamber at atmospheric pressure.

![Schematic of E-beam evaporation of Mo thin film on a sapphire substrate on the left, and its subsequent sulfurization in a CVD chamber on the right.](image)

Figure 3.1: A schematic of E-beam evaporation of Mo thin film on a sapphire substrate on the left, and its subsequent sulfurization in a CVD chamber on the right.

We plan to dope MoS₂ by depositing the dopants as a thin film between two layers of Mo, then sulfurize the triple layer structure at elevated temperature. This process allows the dopant atoms to diffuse across the whole thickness as well as sulfurization of the metallic stack too as shown in figure 3.2. We designed our process such that the growth temperature is in the range of 900 - 1100 °C.
The growth of undoped MoS₂ will help us to investigate the effects of the dopants independent of growth parameters. The advantage of the high processing temperature is fast diffusion of dopants and shorter sulfurization time as well as the better crystallinity of the grown film. A drawback is a diffusion from the substrate and the high kinetic energy of the carrier gas and the sulfur atoms which roughen the surface by the energetic collision.

Figure 3.2: A schematic of the doping process of MoS₂.

Although a high-temperature process is suitable for some semiconductors such as silicon (as in the case of oxidation), it can be very problematic for compound semiconductors such as MoS₂. The main two problems are oxidation and sulfur loss at elevated temperatures. sulfur loss introduces vacancies, and subsequently, leads structural defects and alter the composition. These defects deteriorate the electric transport and especially the mobility of MoS₂ thin films.
We have started this work without the presence of information on the growth parameters. Although some information was existing, it was neither complete nor consistent with each other. Different growth temperatures from 600 °C to 1100 °C, and carrier gas flow rates from 10 to 500 sccm were reported earlier. Also, different carrier gases have been reported too. The earlier reports each report just one successful set of growth parameters without justifying why these specific parameters have been adopted. What made the problem harder, is the unique unprecedented approach we tackled here for the growth of MoS$_2$ (using Mo film and continuous sulfur vapor flow). The deviation from the well-known evacuated ampoule laboratory technique, toward CVD, required more experiments to be done to successfully grow MoS$_2$. This chapter lays out the experimental details of the growth of MoS$_2$ by APCVD and some of the properties of the grown films.

3.2 Experiment

3.2.1 Deposition of Molybdenum Thin Film

We used 2” c-plane sapphire wafers (0001) oriented, 50 mm in diameter, 430 μm thick, and double sides polished (University Wafer, USA) as the substrate on which we have grown MoS$_2$. The main reason behind this choice is that both sapphire and MoS$_2$ have the same hexagonal symmetry, which gives an advantage for MoS$_2$ to grow with less strain. We cleaned sapphire wafers before the deposition of Mo by rinsing it with acetone, methanol, and deionized water respectively, then drying it with pure nitrogen gas.
Deposition of a Mo thin film with a precise thickness depends on the accuracy of the parameters we provide to the thickness monitor, which we use to decide when to terminate the deposition. One of these parameters is tooling factor. We calibrated the tooling factor by depositing a 100 nm of Mo thin film on a regular glass slide. The Mo films grown in this chapter will be labeled 1M, 2M, 3M, 4M, and 5M, and the details of each film deposition conditions will be mentioned in detail.

We have used Molybdenum pellets (1/8" Diameter × 1/8" Length, 100 g, 99.95% pure) in a graphite crucible (both from Kurt J. Lesker Company) as the source of E-beam evaporation. Two evaporators have been used, one which does not have wafer-holder heating capability (called Evan evaporator, 1 Gun, 4 Pocket E-Beam System at Microdevice Prototyping Facility (MPF), UCF), and the other one which have wafer-holder heating capability (called Curly evaporator, AJA 2-Gun, 10 Pocket E-Beam System with Ion-Assist Source at Advanced Microfabrication Facility (AMF), UCF). In all Mo film evaporations, the following data was used to calculate the thickness of the deposited Mo film: Density ($\rho$) = 10.2 g/cm$^3$ and Z number = 0.257.

Each deposition or growth we will be assigned a unique name. The letter “M” refers to Mo film deposition. The number before this letter identifies a specific deposition process. For example, 1M is the first film we have deposited which is different than 2M. The letter “S” refers to a sulfurization process. The number before it refers to a specific sulfurization process such as 4S or 5S. The letters “M” and “S” can be combined to give a unique sample name such as 4M3S which represent a 4M Mo film sulfurized by the 3S process.
Sample 1M, is a molybdenum thin film evaporated on a microscope soda-lime glass slide using “Evan” evaporator. The final thickness according to thickness monitor reading was 100.5 nm. The deposition rate was 0.5 Å/s. The tooling factor used was 175%. By measuring the thickness using Dektak3 Profilometer. We found that the thickness is around 120 nm. To confirm this observation and to adjust the tooling factor so we can deposit Mo films with precise thickness in future, we measured the film thickness using scanning electron microscope (SEM) at different cross-sections (figure 3.3). The average Mo film thickness from SEM cross-section measurement is 136.9 nm.

We have adjusted the tooling factor by using the following equation:

\[
\frac{F_f}{T_f} = \frac{F_i}{T_i} \tag{3.1}
\]

Where, \(F_i\) is the initial tooling factor, \(T_i\) is thickness according to thickness monitor, \(F_f\) is correct tooling factor, and \(T_f\) is the average thickness according to SEM cross-section images.

\[T_i = 100.5 \text{ nm} \tag{3.2}\]

\[T_f(\text{Avg}) = \frac{133.6 + 135.9 + 141.1}{3} = 136.9 \text{ nm} \tag{3.3}\]

\[F_i = 175\% \tag{3.4}\]

\[F_f = T_f \frac{F_i}{T_i} = 135.9 \text{ nm} \frac{175\%}{100.5 \text{ nm}} = 129\% \tag{3.5}\]
Sample 2M, is a molybdenum thin film evaporated on a microscope soda-lime glass slide using “Evan” evaporator. The purpose of this deposition was to verify that the adjusted tooling factor will result in the required film thickness. The final thickness was 30 nm. The tooling factor used here was 129 %. The deposition rate was 0.05 Å/s.

Sample 3M, is a molybdenum thin film evaporated on a pre-cleaned 1 cm × 1 cm pieces of the sapphire wafer using “Evan” evaporator. The final thickness was 100 nm. The tooling factor used here was 129 %. The deposition rate was 0.16 Å/s. The Mo film thickness measurement using Dektak3 Profilometer confirmed the 100 nm reading.

Figure 3.3: SEM cross-section images of Mo/glass sample 1M at different places.
obtained from the thickness monitor. We observed that the deposited films on the unheated substrate result in specular films which have very bad adhesion to the extent that only rinsing these films with water detaching the film from the substrate. Earlier work [86] reported a similar result and reported that heating the substrate above 600 °C improves the adhesion and promote epitaxial growth.

Sample 4M, is a molybdenum thin film evaporated on a pre-cleaned sapphire wafer using “Curly” evaporator. The wafer diced into small pieces after deposition. The final thickness was 361 nm. The deposition rate was 0.8 Å/s. The substrate holder temperature was 700 °C during the deposition. The substrate-holder heating sources were two parallel Quartz lamps above the substrate holder. The substrate-holder was rotating by a motor during the deposition to ensure a homogeneous heating.

The surface of 4M Mo film was protected by a sacrificial layer of positive photoresist before dicing the whole wafer to small pieces. The photoresist layer is to protect the 4M Mo film surface from the tiny particles that are generated during the dicing process which may stick to the surface and the damage by the water used during the dicing process to cool down the blade. The positive photoresist Microposit S1813 (Rohm and Hass electronic materials LLC, DOW chemical company) was used. First, we cleaned the 4M sample with acetone, methanol, and deionized water. Then we have blown it dry with nitrogen gas. Then we spin-coated the wafer at a rate of 3000 RPM, ramp of 1000 RPM/S, and a time of 30 seconds. Then we hardbaked the wafer at 115 C for 3 minutes, using a digital hot plate (Dataplate PMC 720 series). We left the coated wafer at ambient for a couple of minutes
to cool down, then we diced it. We stripped the photoresist layer by washing it with acetone, methanol, and deionized water, then blow it dry with nitrogen.

Sample 5M, is a molybdenum thin film evaporated on a pre-cleaned 1 cm × 1 cm pieces of a sapphire wafer using “Evan” evaporator. The final thickness was 361 nm. The tooling factor used here was 129 %. The deposition rate was 0.6 Å/s. We were aiming to compare grown MoS₂ from Mo deposited on heated and unheated substrates.

3.2.2 APCVD Design and Setup

We have designed and built two APCVD systems to grow MoS₂ samples. The first is a one-furnace setup. The second is a two-furnace setup (figure 3.4) used to grow most of the samples of MoS₂. The APCVD system mainly includes 1” in diameter and 48” long quartz tube, Lindberg 1500 °C tube furnace (zone I), Lindberg 1100 °C tube furnace (zone II), ultra-high pure argon gas cylinder and a flow meter. Three flow meters (rotameters) were attached to this system. The first is FL-3802ST (tube no. 112-02-ST) and the second is FL-3805ST (tube no. 102-05-ST) (Omega, USA). The third is PMR 1-010349 (Cole Parmer, USA).
Figure 3.4: A schematic of atmospheric pressure chemical vapor deposition (APCVD) setup.

The carrier gas in all experiments is ultra-high pure argon. The one furnace setup was built on the Lindberg 1500 °C tube furnace. In all the experiments, we put the sulfur powder (Sigma-Aldrich purum ≥ 99.5%) in a quartz boat in the zone I and the Mo/sapphire in zone II. The heating rate of zone II in all experiments was 20 °C/min. Growth of MoS₂ by APCVD

We performed 15 sulfurization processes to understand the effect of changing the growth parameters on MoS₂ properties. Each grown MoS₂ sample was identified by it is starting Mo film (1M, 2M, …etc) and the subsequent sulfurization process (1S, 2S, …etc), for example, if the starting film is 3M and sulfurization process is 5S, the sample will be labeled 3M5S.
It was very important to understand the behavior of sulfur upon heating, especially sulfur have unique behavior as we will show later. The purpose was to guarantee a constant flow of sulfur vapor at a reasonable rate during the whole sulfurization process. Elemental orthorhombic α-Sulfur (cycloocta-sulfur, S₈) melting point is 115.11 °C at atmospheric pressure [87]. While monoclinic β-Sulfur (cycloocta-sulfur, S₈) melting point is 120.4 °C at atmospheric pressure [87]. It is worth to note that sulfur has about 24 allotropes, just three of them are stable α-, β-, and γ-Sulfur [87]. At a temperature around 159.4 °C, a sudden increase in viscosity occurs due to polymerization [87]. At a temperature around 250 °C, the viscosity of liquid sulfur decreases rapidly [87]. The sulfur boiling point is 444.64 °C.

According to thermodynamic calculations, sulfur dimmers S₂ is more reactive than cycloocta-sulfur S₈, which means the sulfurization process is preferred at high concentration of sulfur dimmers S₂ [88]. High temperatures ≥ 600 °C leads to high concentrations of sulfur dimmers S₂ [88]. Therefore, for the sulfurization to succeed a sufficient amount of sulfur in the active form S₂ rather than less active form S₈ should exist in the CVD chamber, which can be achieved by increasing the growth temperature or by flowing the vapor through an elevated temperature zone before it enters the growth zone.

Sulfurization process 1S is a one-furnace process. 3M Mo film was sulfurized. The grown MoS₂ film was labeled 3M1S. We inserted the 3M sample (Mo/sapphire) in the middle of the growth zone (zone II) supported by a quartz boat. We inserted the sulfur-loaded quartz boat inside the CVD chamber, but outside the heating zone (zone I), until the growth zone
temperature reaches 900 °C. We then insert the sulfur-loaded quartz boat in the middle of zone I by using a magnet from the outside the chamber. It is worth to note that the sulfur boat was connected to big magnet bar covered with Teflon by a rigid stainless-steel wire to control its position from outside the CVD chamber (1” quartz tube). Argon flow rate was 19 sccm/min. The heating rate was 20 °C/min. We kept the CVD chamber at 900 °C for 30 min. then we ramped down the furnace to room temperature at a rate of 20 °C/min. It is worth to note that in this experiment we had two needle valves at the inlet and outlet which we closed respectively during the 30 minutes dwelling time at 900 °C.

Sulfurization process 2S is a one-furnace process. 3M Mo film was sulfurized. The grown MoS\(_2\) sample was labeled 3M2S. We inserted the Mo/sapphire sample in the middle of the growth zone (zone II). The sulfur-loaded boat was inserted in the middle of zone I, but outside the heating zone until the temperature reaches 900 °C. Argon flow rate was 24 sccm/min. The heating rate was 20 °C/min. We kept the CVD chamber at 900 °C for 10 min. then we cooled down the furnace to room temperature at a rate of 10 °C/min. The reason behind this experiment was to estimate the time of evaporation of sulfur after we insert it at the input end of the CVD chamber, which was around 10 minutes. This became a challenge for us because as we increase the temperature of the furnace we should change the position of the sulfur boat. This is not a practical solution since the melting point of sulfur is relatively low and slight change of sulfur boat position forward can lead to very fast evaporation. A better solution was to use a two-zone furnace, but since this solution was not available in our lab, we have used two separate furnaces instead and brought them
close together to work similarly as a two-zone furnace. All the other sulfurization experiments have been performed using a two-zone furnace setup.

3S sulfurization process is a two-zone process. The sample 3M2S was sulfurized again. The grown MoS$_2$ sample was labeled 3M2S3S. This sulfurization was done because we thought that the 10 minutes sulfurization performed earlier may be not sufficient for complete sulfurization. We inserted the sulfur-loaded boat in the middle of zone I. We inserted the 3M2S3S sample in the middle of zone II. Argon flow rate was 24 sccm/min. First, we have increased zone I temperature from room temperature to 115 °C at a rate of 10 °C/min. After zone I temperature reach 115 °C we have increased zone II temperature from room temperature to 900 °C at a rate of 20 °C/min. After zone II temperature reaches 900 °C we kept both zones at their final temperatures for an hour. Then we decreased zone II temperature from 900 °C to room temperature at a rate of 10 °C/min. Meanwhile, we kept zone I temperature at 115 °C. When zone II temperature reached 366 °C, we decreased zone I temperature to room temperature at a rate of 10 °C/min. Argon flow was maintained till growth zone temperature reaches room temperature, to avoid oxidation.

4S sulfurization process is a two-zone process. The 3M Mo sample was sulfurized. The grown MoS$_2$ sample was labeled 3M4S. Zone I temperature was 150 °C instead of 115 °C, in an attempt to increase the sulfur evaporation rate and to guarantee a higher concentration of sulfur vapor in the CVD chamber. A quartz boat loaded with sulfur was kept upstream in the middle of zone I. While the Mo/sapphire samples were supported by another quartz boat in the middle of zone II downstream. We raised the temperature of zone I to 150 °C
at a rate of 10 °C/min. Then we raised the temperature of zone II to 900 °C at a rate of 20 °C/min. After zone II temperature reaches 900 °C we kept both zones at their final temperatures for an hour. Then we cooled down zone II to room temperature at a rate of 10 °C/min., while we kept zone I temperature at 150 °C. When zone II temperature reaches 267 °C, after approximately two hours we have turned off the power of zone I (sulfur furnace) and maintained argon flow to cool it down. Argon gas was flowing at a rate of 24 sccm/min until CVD chamber’s temperature reaches room temperature to avoid oxidation. It is worth to note that the higher temperature of zone I (150 °C) does not necessarily mean higher evaporation rate of sulfur, since the viscosity of sulfur increases also and reaches it is maximum at 159.4 °C. A detailed study was needed to study the evaporation rate of sulfur in our setup. Another question raised at this stage was the amount of sulfur that we should put in the quartz boat, to guarantee a sufficient sulfur for each sulfurization process, which may differ in temperature and time.

5S sulfurization process is a two-zone process. The 3M Mo sample was sulfurized. The grown sample was labeled 3M5S. We inserted the sulfur-loaded boat in the middle of zone I. We inserted the Mo/sapphire sample in in the middle of zone II. Argon flow rate was 24 sccm/min. First, we have increased zone I temperature to 115 °C at a rate of 10 °C/min. After zone I temperature reach 115 °C we have increased zone II temperature to 900 °C at a rate of 20 °C/min. After zone II temperature reaches 900 °C we kept both zones at their final temperatures for an hour. Then we decreased zone II temperature from 900 °C to room temperature at a rate of 10 °C/min. Meanwhile, we kept zone I temperature at 115
 Cuando la temperatura en el zón II alcanzó 237 °C, apagamos el horno del zón I y lo dejamos enfriar naturalmente. El flujo de argón se mantuvo hasta que la temperatura de crecimiento alcanzó la temperatura ambiente, para evitar la oxidación. El propósito de este experimento fue verificar la reproducibilidad de nuestros muestras y observar más detenidamente el experimento. La muestra 3M5S MoS$_2$ color de malla fue gris oscuro.

El proceso de sulfurización de 6S, es un proceso de dos zonas. La muestra Mo de 3M fue sulfurizada. La muestra crecida fue etiquetada como 3M6S. Insertamos el barco de sulfuro en el medio del zón I. Insertamos el sample Mo/sapphire en el medio del zón II. El flujo de argón fue de 24 sccm/min. En primer lugar, aumentamos la temperatura del zón I de la temperatura ambiente a 115 °C a una tasa de 10 °C/min. Después de que la temperatura del zón I alcanza 115 °C, aumentamos la temperatura del zón II a 900 °C a una tasa de 20 °C/min. Después de que la temperatura del zón II alcanza 900 °C, mantenemos ambas zonas a sus temperaturas finales durante una hora y 40 minutos. Después, disminuimos la temperatura del zón II de 900 °C a la temperatura ambiente a una tasa de 10 °C/min. Mientras, mantenemos la temperatura del zón I a 115 °C. Cuando la temperatura del zón II alcanzó 254 °C, disminuimos la temperatura del zón I de 115 °C a la temperatura ambiente a una tasa de 10 °C/min. El flujo de argón se mantuvo hasta que la temperatura del crecimiento alcanzó la temperatura ambiente, para evitar la oxidación. La motivación detrás de este experimento fue verificar la reproducibilidad del experimento. Como veremos más tarde, la causa de este color oscuro puede ser las características dome-like en la superficie.

El proceso de sulfurización de 7S, es un proceso de dos zonas. La muestra 3M6S fue sulfurizada nuevamente. La muestra crecida fue etiquetada como 3M6S7S. Insertamos el barco de sulfuro en el medio del zón I. Insertamos el sample Mo/sapphire en el medio del zón II. El flujo de argón fue de 24 sccm/min. En primer lugar, aumentamos la temperatura del zón I de la temperatura ambiente a 115 °C a una tasa de 10 °C/min. Después de que la temperatura del zón I alcanza 115 °C, aumentamos la temperatura del zón II a 900 °C a una tasa de 20 °C/min. Después de que la temperatura del zón II alcanza 900 °C, mantenemos ambas zonas a sus temperaturas finales durante una hora y 40 minutos. Después, disminuimos la temperatura del zón II de 900 °C a la temperatura ambiente a una tasa de 10 °C/min. Mientras, mantenemos la temperatura del zón I a 115 °C. Cuando la temperatura del zón II alcanzó 254 °C, disminuimos la temperatura del zón I de 115 °C a la temperatura ambiente a una tasa de 10 °C/min. El flujo de argón se mantuvo hasta que la temperatura del crecimiento alcanzó la temperatura ambiente, para evitar la oxidación. La motivación detrás de este experimento fue verificar la reproducibilidad del experimento. Como veremos más tarde, la causa de este color oscuro puede ser las características dome-like en la superficie.
of zone I. We inserted the 3M6S sample in the middle of zone II. Argon flow rate was 24 sccm/min. First, we have increased zone we temperature to 150 °C at a rate of 10 °C/min. After zone I temperature reach 150 °C we have increased zone II temperature to 900 °C at a rate of 20 °C/min. After zone II temperature reaches 900 °C we kept both zones at their final temperatures for an hour. Then we decreased zone II temperature from 900 °C to room temperature at a rate of 10 °C/min. Meanwhile we kept zone I temperature at 150°C. When zone II temperature reached 254 °C, we decreased zone I temperature from 115 °C to room temperature at a rate of 10 °C/min. Argon flow was maintained till growth zone temperature reaches room temperature, to avoid oxidation. The weight of the sulfur-loaded boat before and after the sulfurization process was 18.573 and 18.2528 g, respectively. This means the consumed sulfur during the entire process was 0.3202 g. At this point, we realized the need for a detailed study on the evaporation rate of sulfur at different temperatures so we can optimize sulfurization process based on this information. Also, we wanted to know the maximum and minimum boundaries for the sulfur evaporation rate. For this sake, we have performed the following sulfurization processes.

13S and 14S are two zone sulfurization processes. We increased Zone I temperature to 225 °C and 200 °C for 13S and 14S processes respectively at a rate of 10 °C/min. We increased zone II temperature to 1100 °C at a rate of 20 °C/min. Once zone II temperature reaches 1100 °C we cool it down to 700 °C at a rate of 5 °C/min, then we cool it down to room temperature at a rate of 10 °C/min. We cooled down zone I to room temperature at a rate of 10 °C/min., when zone II temperature reaches 225 °C and 700 °C for 13S and 14S
processes, respectively. Argon was flowing at a rate was 81 sccm until the CVD chamber reaches room temperature.

### 3.2.3 Sulfur Evaporation Rate at Atmospheric Pressure

The aim of this study was to know the sulfur evaporation rate under different experimental conditions and to determine the minimum amount of sulfur needed in each case to minimize the waste. The knowledge of the amount of sulfur needed for each experimental condition is important to maintain adequate sulfur vapor concentration in the growth zone during the entire sulfurization process. We have calculated the average sulfur evaporation rate as a function sulfur zone temperature (zone I), at atmospheric pressure and different argon flow rates. As shown in figure 3.5, in the case of argon flow rate of 48 sccm, the average evaporation rate of sulfur increases from 5.6 mg/min. to 28.9 mg/min. as sulfur zone temperature increase from 200 °C to 250 °C. The increase in the average evaporation rate is not linear and depends on the carrier gas flow rate. Higher carrier gas flow rate will increase the evaporation rate and will dilute the concentration of sulfur vapor in the growth zone. The time of sulfurization used in these calculations is the time between turning on and turning off the power to the sulfur-furnace (zone I). The weight of the evaporated sulfur was calculated by weighing sulfur-loaded boat before and after each sulfurization process. In each sulfurization process, we started with a fresh sulfur powder. The details of the sulfurization processes are given in table 3.1.
Figure 3.5: Average sulfur evaporation rate as a function of sulfur zone temperature, at two different flow rates of 48 and 81 sccm.

Table 3.1
Sulfur evaporation rate experimental details.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sulfur temp. (°C)</th>
<th>Argon flow rate (sccm)</th>
<th>Weight of evaporated Sulfur</th>
<th>Time of sulfurization process (hr)</th>
<th>Evaporation rate (mg/min.)</th>
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</thead>
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<tr>
<td>SE001</td>
<td>200</td>
<td>48</td>
<td>0.6739 g</td>
<td>2</td>
<td>5.6</td>
</tr>
<tr>
<td>SE005</td>
<td>200</td>
<td>81</td>
<td>1.1692 g</td>
<td>2.78</td>
<td>7.0</td>
</tr>
<tr>
<td>SE004</td>
<td>225</td>
<td>48</td>
<td>1.2046 g</td>
<td>1.73</td>
<td>11.58</td>
</tr>
<tr>
<td>SE004(2)</td>
<td>225</td>
<td>81</td>
<td>2.9602 g</td>
<td>1.38</td>
<td>11.26</td>
</tr>
<tr>
<td>SE002</td>
<td>250</td>
<td>48</td>
<td>2.7109 g</td>
<td>2.15</td>
<td>21.0</td>
</tr>
<tr>
<td>SE003</td>
<td>250</td>
<td>48</td>
<td>2.9745 g</td>
<td>1.72</td>
<td>28.9</td>
</tr>
</tbody>
</table>

We have designed a procedure to study the change in evaporation rate of sulfur with temperature. No Mo samples were used in this study, but the growth zone (zone II) temperature was maintained at 900 °C during the experiment to match the conditions of a typical sulfurization process. The only variable that we changed is zone I temperature. The
limits of zone I temperature in this experiment was based on the melting and evaporation temperatures of sulfur, which are 115 and 400 respectively. That means just after the melting point temperature we will have little evaporation and as the temperature increases up to the evaporation temperature the evaporation rate will increase. The selected temperatures at which we have conducted this experiment were 150, 200, 250, and 300 °C.

The details of the process were as follows. We turn on the digital scale to warm up at least 30 minutes before the experiment. Then we clean the quartz boat and load it with the required amount of sulfur after weighing it on the scale. Then we weigh the boat loaded with sulfur. Then we put the quartz boat loaded with Sulfur in the middle of zone I. Then we open the main argon cylinder valve and adjust the valve on the regulator to the required pressure. Then we adjust the rotameter to regulate argon gas flow. We purge the CVD chamber first at high argon flow rate (~ 500 sccm/min.), then we decrease the flow rate to the required value. Then we increase the temperature of zone I to the required temperature. Then we increase the temperature of zone II to the required temperature. Then we maintain the temperature for specific times. Then we cool down the zone II to room temperature. When zone II temperature reaches a specific temperature, we turn off the power of zone I to stop sulfur evaporation. Argon gas is flowing until the temperatures both zones reach room temperature. The evaporation rate was calculated as follows:

\[
\text{Evaporation rate (mg/min.)} = \frac{\text{Weight of evaporated Sulfur (mg)}}{\text{Time of sulfurization process (min.)}}
\]  

(3.6)
3.2.4 Characterization Techniques

A PANalytical X'Pert® MRD X-ray diffractometer with a five-axis cradle and using a hybrid monochromator source, operating at 45 kV and 40 mA. Raman spectroscopy was carried out using a Renishaw inVia micro-Raman spectrometer system. The excitation light is a 532 nm laser, with a laser spot size of 1-2 μm and a maximum laser power of 100 mW. 100% laser power was used for all measurements in the present work. The average collection time for a single spectrum varied from 30 to 84 s per point. The incident and scattered beams were focused with a microscope having a 100x objective lens, which allowed keeping a laser spot as low as 1–2 μm. All measurements were performed at room temperature. The Raman spectrum was calibrated using the 520 cm⁻¹ peak of Silicon as a reference.

3.3 Results and Discussion

We have observed that Mo films deposited on unheated sapphire wafers resulted in smooth films with poor adhesion to the substrate, to the extent that if we wash it by a deionized water from a wash bottle, it will peel off. Washing it by methanol, isopropanol or acetone will result in a film peeling too. Therefore, the substrate should be diced to the required size if no heat treatment will be performed after deposition. Otherwise, heat treatment or heating of the substrate holder during the deposition should be done. On the other hand, films which have been deposited on heated sapphire wafers at ~ 700 °C resulted in specular films with good adhesion. Therefore, we can wash it with any of the above-mentioned solutions without worrying about damaging the film.
3.3.1 X-ray Diffraction

Figure 3.6 shows XRD for sample 4M of Mo/sapphire. Two peaks of Mo corresponding to the two parallel planes (110) and (220) were observed. This result matches the epitaxy reported earlier for a Mo film on a heated sapphire substrate above 600 °C [86]. A peak corresponds to (006) plane of sapphire exists and dominates due to sapphire crystallinity and thickness which causes higher x-ray reflection signal.

Figure 3.6: Symmetric Out-of-plane XRD patterns for sample 4M of Mo/sapphire and reference XRD pattern of Mo, where Mo peaks are labeled in red and sapphire peak are labeled in blue.

Figure 3.7 shows XRD for sample 5M of Mo/sapphire. Venting the deposition chamber fast while the deposited Mo film is still hot results in the formation of oxide phase on top of the Mo film. After a few days, cracks in the top oxide layer developed which was obvious in SEM images. We did not use these films to grow MoS₂.
Figure 3.7: Symmetric Out-of-plane XRD patterns for sample 5M of Mo/sapphire, where Mo peaks are labeled in blue and MoO$_2$ phase peaks are labeled in green.

Figure 3.8 shows out-of-plane x-ray diffraction patterns of samples 3M4S and 3M1S of MoS$_2$. The six observed diffraction peaks are identified as the (002), (004), (100), (006), (110) and (008) peaks of MoS$_2$. The presence of peaks corresponds to unparallelled planes confirms the polycrystalline nature of the film. The location of these peaks matches well the XRD card PDF # 00-37-1492. Two diffraction peaks (006) and (0 0 12) from the sapphire substrate are also observed (PDF # 01-070-5679). The relative strength of the (002) peak indicates preferred orientation such that the (002) plane of MoS$_2$ is parallel to the (006) plane of the sapphire substrate.
Figure 3.8: Symmetric Out-of-plane XRD patterns of (a) sample 3M4S, (b) sample 3M1S and (c) reference XRD pattern of MoS$_2$, where MoS$_2$ peaks are labeled in red and sapphire peaks are labeled in blue.

### 3.3.2 Raman Spectroscopy

Figure 3.9 compares Raman spectra of two MoS$_2$-on-sapphire samples (A and B) to a reference spectrum of c-plane sapphire. The reference spectrum has five peaks located at 378, 417, 449, 576 and 750 cm$^{-1}$, which match published [89] values of 378, 418, 451, 578, and 751 cm$^{-1}$. A sixth previously reported peak at 432 cm$^{-1}$ [89] is an unresolved shoulder in our spectrum. The MoS$_2$ samples have identical Raman spectra comprising four peaks located at 283, 379, 406 and 450 cm$^{-1}$ in agreement with expectations for 2H-MoS$_2$, which has first-order Raman-active modes $E_{1g}$, $B_{2g}^1$, and $A_{1g}$ [90]. All four frequencies are in good
agreement with published values for 2H-MoS$_2$ crystal [91] (see table 3.2). They are also in good agreement with other studies [90, 92-93], although the peaks are slightly red-shifted and broadened, as expected for polycrystalline materials in comparison with single crystals [93].

Figure 3.9: Raman spectra of MoS$_2$-on-sapphire for samples 3M4S, 3M1S, and blank c-plane sapphire wafer.

The Raman spectrum from the dome and flat spots on the surface of sample 3M4S of MoS$_2$ were identical as shown in Figure 3.10.
Figure 3.10: Raman spectra from the dome and flat spots on the surface of sample 3M4S of the MoS$_2$ thin film.

Table 3.2
Comparison of observed Raman modes of MoS$_2$ in our work and earlier reports.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{1g}$ (cm$^{-1}$)</th>
<th>$E_{2g}$ (cm$^{-1}$)</th>
<th>$A_{1g}$ (cm$^{-1}$)</th>
<th>$2\times$LA(M) (cm$^{-1}$)</th>
<th>Incident laser wavelength (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our samples</td>
<td>283</td>
<td>379</td>
<td>406</td>
<td>450</td>
<td>532</td>
<td>-</td>
</tr>
<tr>
<td>Natural 2H-MoS$_2$ crystal</td>
<td>287</td>
<td>383</td>
<td>409</td>
<td>-</td>
<td>514.5</td>
<td>[94]</td>
</tr>
<tr>
<td>2H-MoS$_2$ crystal</td>
<td>286</td>
<td>383</td>
<td>408</td>
<td>450</td>
<td>514.5</td>
<td>[91]</td>
</tr>
<tr>
<td>2H-MoS$_2$ powder</td>
<td>-</td>
<td>383</td>
<td>409</td>
<td>-</td>
<td>530.9</td>
<td>[92]</td>
</tr>
<tr>
<td>Bulk MoS$_2$ platelet</td>
<td>-</td>
<td>382</td>
<td>407</td>
<td>465</td>
<td>632.8</td>
<td>[93]</td>
</tr>
<tr>
<td>Bulk MoS$_2$</td>
<td>-</td>
<td>381</td>
<td>408</td>
<td>455</td>
<td>632.8</td>
<td>[93]</td>
</tr>
<tr>
<td>1 layer - MoS$_2$</td>
<td>-</td>
<td>384.3</td>
<td>403</td>
<td>-</td>
<td>514.5</td>
<td>[90]</td>
</tr>
</tbody>
</table>
3.3.3 Electron Microscopy and EDX

E-beam evaporation of Mo without substrate heating results in poor film adhesion. Even washing these films with water, methanol or acetone can peel the film easily.

Figure 3.11: SEM images of (a-b) 4M Mo film (heated substrate) (c-f) 5M Mo film (unheated substrate) suffered oxidation.
It was reported earlier that heating the sapphire substrate above 600 °C will result in a good film adhesion and epitaxial growth. Figure 3.11 shows SEM images of the surface of 4M Mo films (heated substrate) and 5M Mo film (unheated substrate) at different magnifications. The 4M Mo films surface is smooth with a needle and square features on top of it. The 4M Mo film surface does not change over time, while 5M Mo film surface cracks.

The reason behind these cracks is oxidation, which developed because of taking the film out of the evaporator before completely cooling it down. Although usually, we leave the evaporated Mo films overnight under vacuum to cool down, in only sample 5M we did not. Figure 3.11(c-f) shows SEM images of the surface of 5M Mo films taken fast out of the chamber without appropriate cooling time. Although the surface was shiny at the beginning, it became diffusive gradually in a few days. This happened because the formed oxide layer on top of the Mo film suffered a lot of cracks due to lattice mismatch. Then the unconnected edges of the oxide layer bent upside to give this diffusive effect as if the surface contains very small tiny mirrors when seen by naked eyes.

Figure 3.12 shows SEM images of sample 3M4S of MoS$_2$ at different magnifications using a secondary electron detector located inside the final lens, which commonly called “In-lens detector” [95]. Microdomes of MoS$_2$ were observed on a smooth film of MoS$_2$. Figure 3.12(a) and (b) shows the randomness and dispersion of the microdomes on the film surface. Figure 3.12(c) and (d) reveals the large surface area of these domes.
microdomes surface resembles flower petals as shown in Figure 3.12(f), which make these films potentially attractive for sensing applications, due to its large surface area.

Figure 3.12: SEM images of Sample 3M4S of MoS$_2$ (a-d) using Inlens detector at different magnifications, (e) using Everhart-Thornley type detector, and (f) using energy selective backscattered (ESB) detector.
Figure 3.12(e) shows a SEM image of the surface of sample 3M4S of MoS$_2$ taken by Everhart-Thornley type detector. The relatively large microdomes are obvious, the finer details observed in Figure 3.12(d) is canceled out, as expected from this detector. Also since this detector is at an angle with respect to the film surface the topography of the domes is well revealed, as it is clear from the shadows. We compared the dome to the flat regions by composition-sensitive techniques. Raman spectra from small selected flat spot and dome spot were identical. Figure 3.12(f) shows SEM image taken by energy selective backscattered (ESB) detector reveals that the composition is almost the same, where the slight difference, in contrast, is due to variation in height, which affects the collected signal.

Figure 3.13 shows EDX data over an area of sample 3M4S equivalent to the field of view of figure 3.12(e), which includes both flat regions and domes, gives S/Mo ratio of 1.96. This means the film is almost stoichiometric, which matches well the Raman and XRD results. A reasonable explanation of the cause of the formation of these microdomes is the small thickness of the Mo thin film and coefficient of thermal expansion mismatch between the sapphire substrate (7.3×10$^{-6}$/°C ) and the grown MoS$_2$ (10.7×10$^{-6}$/°C ) [96-97].
3.3.4 Electrical Properties

Figure 3.14 shows the spreading resistance as a function of 1 hr anneals in Ar for sample 4M14S of MoS$_2$ in a sequence of annealing temperatures 200, 400, and 600 °C (so that after the highest temperature anneal the sample has received a cumulative 3 hours of heat treatment). Also, shown in figure 3.14 is the result of a single 1 hour anneal of sample 4M13S of MoS$_2$ at 800 °C, where the total resistance change is less than for the 3-hour cumulative annealing of sample 4M14S at lower temperatures. This suggests that total integrated annealing time is more important than annealing temperature. The decrease in spreading resistance could be due to many reasons including oxidation, loss of sulfur and grain growth. More investigation is needed to identify the cause. Spreading resistance was measured by a two Tungsten carbide probes (SP4-62045TBJ- SIGNATONE, USA). The probe tip radius is 0.254 mm, and the distance between the two probes is 1.5875 mm.
Figure 3.14: Spreading resistance of samples 4M13S and 4M14S of MoS$_2$ before and after annealing.

The spreading resistance, $R_s$ is related to resistivity $\rho$ by the well-known formula [98]:

$$ R_s = \frac{\rho F}{2a} \quad (3.7) $$

Where $a$ is the probe tip radius and $F$ is a correction factor for finite sample dimensions.

For thin film samples ($t < a$), where $t$ is the thin film thickness, the correction factor is given by:

$$ F = \frac{2a}{\pi t} \ln \left( \frac{s}{a} \right) \quad (3.8) $$

And the spreading resistance is given by:

$$ R_s = \frac{\rho}{\pi t} \ln \left( \frac{s}{a} \right) = \frac{R_{sh}}{\pi} \ln \left( \frac{s}{a} \right) \quad (3.9) $$
Where \( R_{sh} \) is the sheet resistance. We cannot use this equation to determine the resistivity since experimentally the relation is not linear, but we can use the spreading resistance as a semi-qualitative technique for the change of resistivity.

### 3.3.5 Optical Properties

The transmittance of sample 3M4S of MoS\(_2\) compared to the spectral irradiance from the sun indicates an excellent absorption across the visible spectrum. The reflectance from these films is almost half the reflectance of a smooth film as will be shown in detail experimentally and theoretically in the following chapter.

![Figure 3.15: Transmittance of sample 3M4S of MoS\(_2\) (right axis) compared to the spectral irradiance from the sun (left axis).](image-url)
3.4 Conclusion

The pure phase of MoS$_2$ has been grown by atmospheric pressure chemical vapor deposition. X-ray diffraction and Raman measurements confirmed the polycrystalline nature of the grown films. Scanning images of the grown films revealed the formation of microdomes of MoS$_2$ on top of the smooth film. These microdomes are very promising for light harvesting applications, as confirmed by the almost zero transmittance over the visible region. The spreading resistance of these films is greater than 10 M$\Omega$, which is relatively high.
CHAPTER 4: ANTIREFLECTION STRUCTURES OF MoS₂

4.1 Introduction

Light harvesting of incident light on solar cells is critical for boosting their efficiency. A 33% reflectance means we lose one-third of the incident light energy. Minimizing this reflectance to zero would increase the efficiency by 50% if all the absorbed photons generate hole-electron pairs that are collected. Two techniques are known to reduce reflections. The first is smooth antireflection coatings, which strongly reduce reflectance at a specific wavelength and for a narrow range of light incident angles by destructive interference [99-101]. The second is engineered micro- or nanostructures on the front surface of solar cells [102-104], which advantageously feature broad spectral range and omnidirectionality in comparison with the smooth coatings [103-107].

Three main geometries of these antireflection structures have been studied earlier, namely pyramids [104, 108-112], domes [103, 106-107, 113-115], and pillar [116-120]. Nanotips, nanocones, and nanowires can be considered special cases of the basic shapes by considering elongation in one direction. The usual Fresnel reflection due to the sudden refractive index discontinuity is decreased or almost eliminated by the surface structures, which gradually change the effective refractive index between the two media [121]. Inspiration comes from the dome structures on the corneal surface of moths’ eyes, which efficiently suppress reflectance for better light-harvesting and night vision [113, 115, 121-124]. The optimum structure geometries depend on the materials considered, while ease of fabrication depends strongly on the specific shapes. Thus, experimentally optimizing for
structure shape is impractical. Simulating these structures using rigorous three-dimensional finite difference time domain (3D-FDTD) method facilitates the study and optimization of structures geometries.

MoS$_2$ is one of the promising materials for solar cells due to its favorable optical, electrical, chemical, and mechanical properties [5-6, 125]. MoS$_2$ absorption coefficient $> 10^4$ cm$^{-1}$ exceeds that of silicon [6, 125], potentially allowing thinner, lighter, and cheaper solar cells. The bandgap of MoS$_2$ is 1.3 eV, which matches well the solar spectrum. The predicted high mobility (410 cm$^2$ V$^{-1}$ s$^{-1}$), mechanical flexibility and the chemical inertness to most acids of MoS$_2$ have attracted the attention [16]. On the other hand, MoS$_2$ has high refractive index $\sim 3.5$ which causes 31% reflection loss for light normally incident on its smooth surface [81]. Therefore front-surface antireflection structures are essential to maximize light harvesting and minimize losses [106].

Here we investigate different anti-reflection structure geometries on a smooth film of MoS$_2$ for solar cell applications. This study is relevant to MoS$_2$ films with microdome texture, which we grew by atmospheric pressure chemical vapor deposition. The microdomes which appear spontaneously without any lithographic processing are shown to be effective as an omnidirectional light trap. The demonstrated method of growth has significance for MoS$_2$-based solar cells and other optical and optoelectronic applications.
4.2 Simulation

Microdomes of MoS\(_2\) on a smooth film of MoS\(_2\) supported by sapphire substrate were simulated and analyzed using the 3D-FDTD method to determine the best structure geometry and arrangement that results in minimum reflectance at different angles and broad spectrum. The incident light source was a plane wave with either S or P polarization. To simulate an unpolarized beam or plane wave source, we need to perform two simulations with orthogonally polarized beams. The fields from each simulation can then be added incoherently according to the equation:

\[
\langle |E|^2 \rangle = \frac{1}{2} |\vec{E}_s|^2 + \frac{1}{2} |\vec{E}_p|^2
\]  \hspace{1cm} (4.1)

In practice, this means that we simulate a beam with a polarization angle of 0° and then a beam with a polarization angle of 90°. Where \(\langle |E|^2 \rangle\) represents the time-averaged electric field intensity of an unpolarized beam light source. \(|\vec{E}_s|^2\) and \(|\vec{E}_p|^2\) represents the reflectance from S and P polarized light source respectively.

The derivation of equation (4.1) is as follows:

To calculate the response of a system to an unpolarized beam, we need to average over all possible input polarizations:

\[
\langle |E|^2 \rangle = \frac{1}{2\pi} \int_0^{2\pi} |\vec{E}(\theta)|^2 \, d\theta
\]  \hspace{1cm} (4.2)
Due to the linearity of Maxwell's equations, we can represent the electric field of an arbitrarily polarized incoming beam as a sum of two orthogonal polarizations:

\[ E(\theta) = E_s \sin \theta + E_p \cos \theta \]  \hspace{1cm} (4.3)

Therefore, the integral can be computed as follows:

\[ \langle |E|^2 \rangle = \frac{1}{2\pi} \int_0^{2\pi} |E(\theta)|^2 \, d\theta \]  \hspace{1cm} (4.4)

\[ \langle |E|^2 \rangle = \frac{1}{2\pi} \int_0^{2\pi} |E_s \sin \theta + E_p \cos \theta|^2 \, d\theta \]  \hspace{1cm} (4.5)

\[ \langle |E|^2 \rangle = \frac{1}{2\pi} \int_0^{2\pi} \left( |E_s|^2 \sin^2 \theta + |E_p|^2 \cos^2 \theta + 2|E_s E_p| \sin \theta \cos \theta \right) \, d\theta \]  \hspace{1cm} (4.6)

\[ \langle |E|^2 \rangle = \frac{|E_s|^2}{2\pi} \int_0^{2\pi} \sin^2 \theta \, d\theta + \frac{|E_p|^2}{2\pi} \int_0^{2\pi} \cos^2 \theta \, d\theta + \frac{2|E_s E_p|}{2\pi} \int_0^{2\pi} \cos \theta \sin \theta \, d\theta \]  \hspace{1cm} (4.7)

\[ \langle |E|^2 \rangle = \frac{1}{2} \left( |E_s|^2 + |E_p|^2 \right) \]  \hspace{1cm} (4.8)

The following identities were used to simplify the above integral:

\[ \int_0^{2\pi} \sin^2 \phi \, d\phi = \pi \]  \hspace{1cm} (4.9)

\[ \int_0^{2\pi} \cos^2 \phi \, d\phi = \pi \]  \hspace{1cm} (4.10)

\[ \int_0^{2\pi} \cos \phi \sin \phi \, d\phi = 0 \]  \hspace{1cm} (4.11)
Bloch boundaries were used vertically and perfectly matched layers (PML) boundaries were used horizontally above the domes and below the substrate. The wavelength dependence of refractive index and extinction coefficient of the domes, the film, and the substrate was considered in the simulation. We used the FDTD software (Lumerical Solutions, Inc.) to calculate total reflectance (specular plus diffuse) for different shapes and geometries.

Parameters that affect reflectance include dome base diameter, height, and spatial distribution on the surface. We first investigated the effect of different base diameters on reflectance using monochromatic incident light with 500 nm wavelength, which corresponds to the peak of the solar spectrum [106]. The best base diameter that minimized reflectance was then considered in simulations at different wavelengths from 300 to 1200 nm. The effect of height and distribution have been investigated as well.

4.3 Results and Discussion

4.3.1 Domes with Different Base Diameters

Figure 4.1 shows the total reflectance of parabolic domes with different base diameters. The square array of domes is on a 2.5-μm-thick smooth film of MoS₂ supported by a sapphire substrate. Each reflectance point in the plot represents the average reflectance overall light incident angles from 0° to 80°. This demonstrates the omnidirectionality of these structures. The dome height is half the base diameter. The incident light wavelength is 500 nm.
The reflectance decreases from 33.6% to 12.2% with increasing the base diameter from 0 to 0.5 µm. Then the reflectance slightly increases to 18.5% with increasing the base diameter from 0.5 µm to 2 µm. Therefore we chose the 0.5 µm diameter for further studies over a broad range of wavelengths. As shown in figure 4.1 the most effective base diameter equals the incident wavelength, but we next demonstrate that the same base diameter is nearly equally effective at all relevant wavelengths.

**4.3.2 Broadband Nature of Antireflection Structures**

Figure 4.2 shows a comparison between the reflectance of a smooth film and a square array of 0.5 µm diameter domes over a broad range of wavelengths from 300 nm to 1200 nm. Each reflectance point in the plot represents the average reflectance overall light incident angles from 0° to 80°. The reflectance decreased by 51% over the full range. This demonstrates the broad spectral range for the effectiveness of these structures.
The wavelength independence of reflectance reinforces the effective medium theory [126] and shows that the antireflection effect is due the gradual change of effective refractive index rather than scattering.

![Figure 4.2: The reflectance of a square array of MoS\textsubscript{2} domes with 0.5 µm base diameter compared to that of a smooth film.](image)

4.3.3 Omnidirectionality of Antireflection Structures

Figure 4.3 shows the reflectance of square arrays of parabolic domes with different heights but constant 0.5 µm base diameter. The total (specular plus diffuse) reflectance averaged over all the incident angles from 0° to 80° decreased from 12.18% to 4.22% as the height of the dome increased from 0.25 µm to 2 µm. Importantly, the average reflectance of square arrays of parabolic domes with heights of 1 µm and 2 µm is practically zero over all the incident light angles from 0° to 50°.
4.3.4 Comparison of Different Geometrical Antireflection Structures

Figure 4.4 shows the reflectance averaged over incident angles from 0° to 80° for different spatial distributions of domes and monochromatic incident light with 500 nm wavelength. The hexagonal array of parabolic domes with 0.5 μm base diameter and 0.25 μm height reduces the reflectance more efficiently than a square array of these domes, but this effect is less than the difference in fill factor. For a square array of parabolic domes, the fill factor is 39%, while for a hexagonal array it's 45%. In addition, we compared the former two arrays to hexagonal arrays of pyramids, cones, and hemispherical domes of the same base area and height. The average reflectance of the pyramids was the highest while the average reflectance of a hexagonal array of parabolic domes was lowest. Cones had the second
highest reflectance after the pyramids. Thus, smooth structures such as domes are better than faceted structures such as pyramids.

Figure 4.4: The total reflectance of arrays of different structures and spatial arrangements.

4.3.5 Reflectance Measurement and Simulation

Figure 4.4 compares the experimentally measured total reflectance (specular plus diffuse) spectrum of MoS₂, sample 3M4S, with that simulated for a square array of parabolic domes (2 µm in diameter and 1 µm in height) with a period of 2.2 µm. The simulation of an area of a few microns requires large computing resources, therefore we chose to simulate a periodic spatial distribution with a Bloch boundary condition. Although the regular distribution of simulated domes differs from the random arrangement on the actual sample, it nevertheless demonstrates a strong reduction in reflectance that agrees well with experiment. Based on experimental measurement and simulation domes with 2 µm base
diameter could reduce the reflectance by 45% which consequently improves light harvesting and solar cell efficiency.

![Graph showing reflectance of MoS2-on-sapphire sample 3M4S compared to simulation for parabolic domes with 2 µm base diameter.](image)

**Figure 4.5:** The reflectance of MoS2-on-sapphire sample 3M4S in comparison with simulation for parabolic domes with 2 µm base diameter.

### 4.4 Conclusion

Different structures and geometries have been studied and analyzed by FDTD method to assess their performance for antireflection applications. A comparison between cones, pyramids, parabolic and spherical domes of the same base area and height showed that parabolic domes are the best antireflection structures. A parabolic dome of 0.5µm base diameter and 2µm height can reduce reflectance to almost zero for all incident angles from 0° to 50°. These antireflection structures can boost MoS2-based solar cells efficiency by almost 50%. MoS2 films with microdome texture were grown by APCVD. SEM images revealed the uniform random distribution of these microdomes. Stoichiometric
composition and structure of MoS$_2$ have been confirmed by EDX, Raman spectroscopy, and x-ray diffraction. Based on experimental measurement and simulation domes with 2 µm base diameter and 1 µm height could reduce the reflectance by 45%.
CHAPTER 5: GROWTH OF MoS$_2$ BY LPCVD

5.1 Introduction

Doping of MoS$_2$ by diffusion requires high processing temperatures which cause sulfur loss and changes the stoichiometry. We optimized a process to grow MoS$_2$ thin films such that the growth zone can reach elevated temperatures up to 1000 °C, under sulfur vapor flow. In this chapter, we optimized a process to grow undoped MoS$_2$. This process is doping compatible, and pave the way to the growth of doped MoS$_2$ which is very important for the fabrication of electronic and optoelectronic devices. MoS$_2$ was grown by sulfurization of electron-beam evaporated Mo thin film. To inhibit sulfur loss and to enhance thermodynamic stability of the grown phase of MoS$_2$, we maintain sulfur vapor flow during the cooling cycle.

The critical temperature required to grow a pure phase of MoS$_2$ was determined by turning off sulfur vapor flow during the cooling cycle at different temperatures namely 1000, 900, 800, and 700 °C. The structure, electrical and optical properties of the grown films were investigated and compared to reported results in the literature. The critical temperature is between 900 °C and 800 °C. The electrical properties of grown MoS$_2$ in terms of mobility is superior to earlier reports. The mobility increases upon heating. We rigorously calculated the optical constants of the grown films, which vary from a report to another. For example, the ordinary refractive index values in literature are in the range 2.6 to 4.3 [73, 127]. This difference is quite large and makes optical and optoelectronic devices design cumbersome.
5.2 Experiment

MoS$_2$ was grown on a sapphire substrate (2 inches, c-plane, 430 µm thick) in two steps. First, Mo thin film was electron-beam evaporated at a rate of 2 Å/s on a pre-cleaned substrate. The substrate holder temperature raised to ~750 °C before the evaporation of the Mo using quartz lamps above the substrate holder. The holder was rotating during the evaporation to achieve uniform heating. The film thickness from the thickness monitor attached to the E-beam evaporator was 500 nm. The substrate was cleaned by rinsing it with acetone, methanol and deionized water, and then blown dry with ultra-high purity nitrogen. We diced the wafer after Mo evaporation to small pieces namely 6 mm × 6 mm and ~ 20 mm × 20 mm pieces.

Second, we sulfurized the Mo thin films in a two-zone low pressure chemical vapor deposition (LPCVD) setup to grow MoS$_2$ as shown in figure 5.1. The sulfur powder (Sigma-Aldrich purum ≥ 99.5%) was loaded in a quartz boat in the zone I (upstream), and the Mo/sapphire was supported by another quartz boat in zone II (growth zone, downstream). We purged the CVD chamber by Ultrahigh pure argon at a high rate (>500 sccm/min) for 5 minutes, then decreased the flow rate to 37 sccm/min to achieve 1 Torr vacuum pressure. Then we raised the temperature of zone I and zone II to 100 °C and 1000 °C at a rate of 10 °C/min and 20 °C/min respectively. Then we cooled down zone II at a rate of 2 °C/min to room temperature. We turned off sulfur vapor flow (zone I) during the cooling cycle of the growth zone at different temperatures namely 1000, 900, 800, and 700
61 °C, and the grown samples labeled A, B, C, and D respectively. We maintained argon gas flow during the growth until the CVD chamber temperature reaches room temperature.

![Figure 5.1: A schematic illustration of a two-zone LPCVD setup.](image)

Room-temperature Raman spectroscopy was performed using a Renishaw inVia micro-Raman spectrometer system with 532 nm 100 mW laser excitation. The laser spot size was 1–2 μm. Out-of-plane symmetric x-ray diffraction (XRD) was performed using a PANalytical Empyrean X-ray diffractometer with a hybrid monochromator source. The surface morphology of MoS₂ thin films was characterized by a Zeiss ULTRA-55 FEG scanning electron microscope (FEG-SEM). The film thickness measured by cross-sectional scanning electron microscopy. The concentration profiles of Mo and S across the film thickness were determined using secondary ion mass spectroscopy (Physical Electronics ADEPT 1010 quadrupole SIMS). The primary 3 keV Cs⁺ ions were rastered over a 300 μm
× 300 μm area at 45° incidences with 40 nA beam current. A 20% electronic gating was used to collect the ejected ions from only the center region of the sputtered area, to reduce the crater sidewall effects. Hall-Effect measurements, in the Van der Pauw geometry, were performed using a commercial system from MMR Technologies (Mountain View, California, USA). Four electrodes of Ti/Au (50 nm/150 nm) were deposited at the corners of 6 mm × 6 mm samples, using a shadow mask. The majority carrier type and concentration, mobility, Hall coefficient and mean free path were determined. The UV-vis-NIR measurements were performed using LABSPHERE integrating sphere attached to a CARRY 500 spectrophotometer.

5.3 Results and Discussion

5.3.1 Sulfur Evaporation Rate at Low Pressure

We have calculated the average sulfur evaporation rate as a function sulfurization times, at a constant pressure of 1 Torr and sulfur zone temperature of 100 °C. As shown in figure 5.2 the average evaporation rate of sulfur decreases from 22.8 mg/min. to 13.2 mg/min. as sulfurization time increase from 42 min. to 200 min. The decrease in the average evaporation rate can be explained by the decrease in the quantity of sulfur remaining in the sulfur zone. The time of sulfurization used in these calculations is the time between turning on and turning off the power to the sulfur zone (zone I).
Figure 5.2 The average sulfur evaporation rate as a function sulfurization times.

The weight of the evaporated sulfur was calculated by weighing sulfur-loaded quartz boat before and after each process. In each sulfurization process, we started with a fresh sulfur powder. The details of the sulfurization processes are given in table 5.1.

Table 5.1
The average sulfur evaporation rate as a function sulfurization times.

<table>
<thead>
<tr>
<th>Sulfur zone temperature (°C)</th>
<th>Time of sulfurization (min.)</th>
<th>Average evaporation rate (mg/sec)</th>
<th>Weight of evaporated sulfur (g)</th>
<th>Pressure (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>42</td>
<td>0.38</td>
<td>0.9584</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>98</td>
<td>0.29</td>
<td>1.6983</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>149</td>
<td>0.22</td>
<td>1.9696</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>200</td>
<td>0.22</td>
<td>2.5964</td>
<td>1</td>
</tr>
</tbody>
</table>
5.3.2 Structural Characterization

Figure 5.3 shows Raman spectra of samples A, B, C and D. The spectrum of sample A (1000 °C) consists of several peaks located at 124, 196, 222, 351, 488, 562, 730 cm\(^{-1}\), in agreement with reported values for MoO\(_{3-x}\) (or equivalently MoO\(_{2+x}\)) \[128\], while MoS\(_2\) peaks were completely absent in sample A. The unavoidable presence of a small oxygen concentration in the argon flowing gas (due to the unavoidable vacuum leaks) leads to the growth of MoO\(_{3-x}\) as the main phase forming the top layer of the film. XRD results (as will be shown later) indicated that MoS\(_2\) exists underneath the top MoO\(_{3-x}\) layer, but the Raman-excitation laser does not penetrate to this depth so that only the MoO\(_{3-x}\) Raman peaks were observed in this sample. In contrast, the spectrum of sample B (900 °C) is dominated by MoS\(_2\) peaks located at 282, 376, 403 and 450 cm\(^{-1}\). The peaks positions and their relative intensities agree with earlier reports \[5, 90, 92-93\].

The first three peaks correspond to \(E_{1g}\), \(E_{2g}^1\), and \(A_{1g}\) first order Raman-active modes and the fourth peak corresponds to the second order Raman-active mode respectively \[90-91, 93\]. Just three peaks of MoO\(_{3-x}\) located at 196, 222, and 488 cm\(^{-1}\) remain in sample B spectrum. Since we turned off sulfur vapor flow, in sample B, at a lower temperature (900 °C), the growth of MoS\(_2\) become dominant, due to the thermodynamic stability of MoS\(_2\) achieved by the presence of sulfur vapor till this temperature even in the presence of small oxygen partial pressure. When we turn off sulfur vapor flow at even lower temperatures such as 800 and 700 °C, we observe only MoS\(_2\) peaks, while MoO\(_{3-x}\) peaks completely disappear, which indicates the growth of a pure phase of MoS\(_2\).
Figure 5.4 shows symmetric out-of-plane x-ray diffraction patterns of samples A, B, C, and D respectively. The pattern of sample A (1000 °C) comprises eight diffraction peaks, which correspond to (002), (006) and (008) planes of MoS₂, (006) and (0012) planes of Sapphire, and (-111), (-211) and (-312) planes of MoO₂. The position of MoS₂, Sapphire, and MoO₂ peaks matches well the XRD cards PDF # 00-37-1492, 01-070-5679 and 00-032-0671 respectively. The formation of MoO₂ but not MoO₃ phase indicates that the excess oxygen, as determined by Raman signature of MoO₃₋ₓ, was not high enough to form MoO₃. The intensity of the (-111) peak of MoO₂ is stronger than the intensity of the (002) peak of MoS₂, which indicates that the main phase present in this sample is MoO₂. The presence of MoS₂ peaks in XRD indicates that this phase exists under the surface oxide layer, though it was inaccessible in Raman characterization of sample A, due to limited penetration.
Turning off sulfur vapor flow at 1000 °C facilitated the oxidation of the film by the small concentration of oxygen exist due to unavoidable vacuum leaks. The XRD-pattern of sample B (900 °C) consists of nine diffraction peaks, which correspond to (002), (004), (006), (008) and (0010) planes of MoS₂, (006) and (0012) planes of Sapphire, and (-111) and (-211) planes of MoO₂. The MoO₂ peaks intensities become relatively weaker, which agrees with Raman data. The intensity of the (002) peak of MoS₂ is stronger in sample B than the intensity of the (-111) peak of MoO₂ since MoS₂ is the main phase.

Figure 5.4: Symmetric out-of-plane XRD patterns of samples A, B, C, D, where MoS₂ peaks are labeled in green, sapphire peaks are labeled in black and MoO₂ are labeled in red.
The XRD pattern of sample C (800 °C) comprises a somewhat different collection of eight diffraction peaks. Six diffraction peaks correspond to (002), (004), (006), (110), (008) and (0010) planes of MoS$_2$. The other two diffraction peaks correspond to (006) and (0012) planes of Sapphire. No diffraction peaks from MoO$_2$ phase were observed in sample C. The intensity of MoO$_2$ peaks observed in sample A, decreased upon letting sulfur vapor to continue flow at a lower temperature (900 °C sample B) and completely disappeared upon letting sulfur vapor to flow to a further lower temperature (800 °C sample C). The XRD pattern of sample D (700 °C) consists of seven peaks, which correspond to (002), (004), (006), (008) and (0010) planes of MoS$_2$, and (006) and (0012) planes of Sapphire. The disappearance of (110) peak of MoS$_2$ and the presence of the other parallel planes (002), (004), (006), (008) and (0010) indicate epitaxial growth with the (002) plane of MoS$_2$ parallel to the (006) plane of sapphire.

The improvement in crystallinity after letting sulfur vapor flow to lower temperatures is due to the thermodynamic stability of the grown phase of MoS$_2$ under the presence of high concentration of sulfur vapor flow. The sulfur loss due to sulfur concentration difference between sulfur in MoS$_2$ solid phase and the sulfur vapor inside the growth chamber can be eliminated by increasing the sulfur vapor concentration in the chamber. In other words, the improvement of crystallinity is due to the prevention of sulfur element volatilization, and subsequently the prevention of formation of structural defects. Equation 1 describes a possible desulfurization reaction:

$$\text{MoS}_2(s) \rightleftharpoons \text{Mo(s)} + 2\text{S(g)} \quad (5.1)$$
The presence of sulfur partial pressure will push the equilibrium to the left and prevent sulfur loss and consequently suppress the formation of lattice defects, which we can notice as an improvement in crystallinity [129]. It is worth to note here that we should turn off sulfur vapor flow before the growth zone (zone II) reach the boiling point of sulfur; otherwise, we will end up with a thin film of sulfur on top of the MoS$_2$ thin film, which is undesirable. The boiling point of sulfur is 444.6 °C at 1 atmospheric pressure, and it will be lower at 1 Torr [130]. Sulfur vapor flow is critical for crystallinity and growth of stoichiometric and pure phase of MoS$_2$.

Figure 5.5 shows SEM images of samples A, B, C, and D. Figure 5.5(a) shows the surface morphology of sample A. The MoO$_x$ grains has the form of elongated irregular rods. In addition, some voids exist. Figure 5.5(b) shows the surface morphology of sample B, which is mainly MoS$_2$. The layered structure of MoS$_2$ is observable and the film is dense. Figure 5.5(c) shows the surface morphology of sample C. The film is dense and the layers of MoS$_2$ layers is very noticeable. Figure 5.5(d) shows the surface morphology of Sample D. The film is dense and the grains are bigger which matches the XRD and Raman results.
Figure 5.5: SEM images of samples (a) A, (b) B, (c) C, and (d) D.

Figure 5.6 shows the concentration of S and Mo in sample D as a function of sputtering time as measured by secondary ion mass spectroscopy (SIMS). The sulfur concentration is constant over the whole thickness of sample D, which indicates a complete sulfurization of the Mo film, and the formation of a stoichiometric MoS$_2$ film. This result supports the sulfur compensation hypothesis claimed earlier in this work. This developed process is very useful for doping by diffusion, which requires elevated temperatures, without sacrificing stoichiometry or structure quality.
Figure 5.6: SIMS depth profile for sample D of MoS$_2$.

5.3.3 Electrical Characterization

The electrical properties of the grown films were investigated by Hall effect measurements. The Hall effect calculations’ algorithm as implemented by the software of the commercial Hall-effect system from MMR Technologies (Mountain View, California, USA) was as follows: First, the resistivity measured by van der Pauw method without any magnetic field. The current reversed and eight measurements have been performed and averaged. The resistance between any two contacts calculated as follows:

$$ R = \frac{V_2 - V_1}{I_2 - I_1} $$

(5.2)

The ratio of the resistances of all sides was then calculated:
\[ x = \frac{R_{12,34}^1}{R_{23,41}} \]  \hspace{1cm} (5.3)

Then the form factor, \( F \) is calculated using the equation:

\[ F = \frac{-2 \ln 2}{\ln a + \ln(1-a)} \]  \hspace{1cm} (5.4)

Where \( a \) satisfies \( a^z = 1 - a \) where \( z = x \) if \( x \leq 1 \) or \( z = 1/x \) if \( x > 1 \). The resistivity is then calculated using the equation:

\[ \rho = \frac{\pi t F(R_{12,34} + R_{23,41})}{2 \ln 2} \]  \hspace{1cm} (5.5)

Where \( t \) is the film thickness, \( R_{ij,kl} \) is the resistance such that the current is probed between \( i \) and \( j \), while voltage is measured between \( k \) and \( l \). Magnetic field and current reversed, during Hall effect measurements to cancel the undesired thermoelectric effects. The Hall coefficient calculated using the equation:

\[ R_{\text{Hall}} = \frac{10^8 (\Delta R_{12,34} + \Delta R_{24,31}) t}{2 \Delta B} \]  \hspace{1cm} (5.6)

Where \( t \) is the film thickness and \( \Delta R_{12,34} \) and \( \Delta R_{24,31} \) represent the change of resistance caused by the change in the magnetic field, \( \Delta B \). The mobility calculated from the equation

\[ \mu = \frac{R_{\text{Hall}}}{\rho} \]  \hspace{1cm} (5.7)

The number of majority carrier concentration, \( \eta \), calculated using the equation:
\( \eta = \frac{1}{\rho \mu e} \) \hspace{1cm} (5.8)

Where \( e \) is the electron charge. The type of carriers was determined from the Hall voltage sign and confirmed by hot probe measurements. The mean free path, \( l \), for a nondegenerate semiconductor, calculated using the equation [131]:

\[
l = \frac{3}{4} \frac{\mu}{e} \left(2\pi m_e kT\right)^{1/2}
\] \hspace{1cm} (5.9)

Figure 5.7 shows the resistivity, sheet resistance, carrier concentration and mobility of samples A, B, C, and D measured by Hall effect at 300 K. Sample A, which is mainly MoO\(_x\), showed n-type conductivity according to Hall effect and thermoprobe measurements, which agrees with the previously reported n-type conductivity of MoO\(_2\) [132-134]. Sample A has a very low resistivity and very high carriers concentration, therefore it is a degenerate semiconductor which can be used as a contact as proposed in earlier reports [135]. The mobility of sample A is relatively high by considering its high carrier concentration. As the structure of MoO\(_2\) did not distort dramatically as XRD implied, the excess oxygen atoms behave as dopants. Since oxygen has two valence electrons, it acts as a donor in this case, which explains the n-type conductivity. This explanation is consistent with the basic theory of doping in semiconductors.

Sample B, which is mainly MoS\(_2\), has a resistivity of 6 \( \Omega \)-cm which is in the range 3-100 \( \Omega \)-cm reported for MoS\(_2\) earlier [71]. The MoS\(_2\) dominated Samples B, C, and D showed p-type conductivity, which matches the type of the majority carriers of natural and
synthetic samples grown by sulfurization of Mo film reported earlier [4, 136]. The majority carrier type was verified by thermoprobe measurements for all samples. These results cast doubts on the claimed Schottky junction between MoS₂ and gold reported earlier [5]. The Schottky junction was claimed to be the main reason behind the observed photovoltaic effect, although the MoS₂ film used in the fabrication of this solar cell was grown by sulfurization of Mo film too, which means it had p-type conductivity [4, 28]. Therefore, Au contacts should make an ohmic contact with a p-type MoS₂.

Figure 5.7: Resistivity, sheet resistance, carrier concentration, and mobility of samples A, B, C, and D.
The increase in mobility in MoS$_2$ (B, C, and D) dominated samples with turning off sulfur vapor flow at lower temperatures is correlated with the relative improvement in crystallinity of MoS$_2$ as indicated by XRD and SEM images where sample D has the strongest XRD peaks and biggest grains, respectively. Also, the other factor behind the increase in mobility is the decrease of carrier concentration. The mobility of sample D is 20 cm$^2$/Vs, which is twice the highest Hall effect mobility reported recently for synthetic MoS$_2$ [137]. The resistivity $\rho$ depends on mobility $\mu$ and carrier concentration $\eta$ according to the relation:

$$\rho = \frac{1}{\eta \mu e}$$

Where $e$ is the electron charge. The resistivity first increased upon turning off sulfur vapor flow at lower temperatures as in samples B (900 °C) and C (800 °C). In sample B, the increase in resistivity is due to the decrease of both the mobility and carrier concentrations, but in sample C, mobility increased but carrier concentration decreased with a faster rate. Then the resistivity decreased upon turning off sulfur vapor flow at a lower temperature (sample D 700 °C). In sample D, resistivity decreased due to the increase in mobility and the stability of carrier concentration. The increase in mobility with sulfur vapor flow to lower temperatures agrees with earlier results [138] where annealing under Ar + S improved the mobility significantly in comparison with annealing under argon alone. This is due to thermodynamically stability in terms of structure and composition of MoS$_2$, under sulfur vapor flow.
A perfect stoichiometric MoS$_2$ should not p- or n-type, but since there is no such perfect material in the real world, we observe a tendency of a compound semiconductor toward one type of conductivity or another. The origin of the p- and n-type conductivity in MoS$_2$ is under debate [27-29, 139]. The deficiency or excessive concentration of sulfur is partly a reasonable explanation of the n- or p-type conductivity, respectively. A sulfur concentration between 1.6 and 2.1 (it should be 2 for stoichiometric MoS$_2$) has been reported and was determined by XPS spectra analysis [28]. The concentrations of carbon and oxygen impurities, in this earlier study, were high enough to be detected by XPS in MoS$_2$ [28]. In addition, a considerable concentrations of other impurities were detected by inductively coupled plasma mass spectrometry (ICPMS) such as Al, Ag, As, Ba, Bi, Ca, Cd, Cu, Fe, K, Sb, Pb, Ti and W in geological sample of MoS$_2$ as well as in synthetic samples, which was grown from pure elements in an evacuated ampoules [28]. Therefore, the type of conductivity we observe is a result of the effect of different dopants each introduces a donor or an acceptor level in the band gap of MoS$_2$. The net effect is that the holes will be compensated by electrons and we will have effective n-type doping or vice versa.

The resistivity of p-type natural crystals reported earlier [136] was in the range 0.2-111 $\Omega$ cm, and the carrier concentration of the natural crystal with the highest mobility was $2 \times 10^{17}$ cm$^{-3}$ at room temperature. This value of carrier concentration is higher than sample D, which has a lower carrier concentration of $3.76 \times 10^{16}$ cm$^{-3}$. This indicates a lower concentration of impurities in our sample D. The mobility values of p-type natural
crystals determined from Hall coefficient were in the range 5-147 cm$^2$/Vs. It is worth to note that synthetic MoS$_2$ which were grown by vapor phase transport from pure elements had p-type conductivity [140]. In that earlier work [140], the carrier concentration was $1.6 \times 10^{17}$ cm$^{-3}$, while the resistivity and mobility were 2 Ω-cm and 20 cm$^2$/Vs respectively. This means our film quality is very close to the synthetic single crystal of MoS$_2$, which is the main objective of this work. The slightly lower value of resistivity (2 Ω cm) of the single crystal than our best sample D (8.3 Ω cm) is due to their higher carrier concentrations ($1.6 \times 10^{17}$ cm$^{-3}$) which is higher than sample D carrier concentration ($3.76 \times 10^{16}$ cm$^{-3}$). Their higher carrier concentration may be due to traces of the transporting agent. Earlier work of sulfurization of Mo thin films in an evacuated ampoule resulted in p-type MoS$_2$ films with Hall mobility typically between 0.1 and 20 cm$^2$/Vs [141].

![Figure 5.8: Resistivity and mobility of holes in sample D as a function of temperature.](image)
Sample D is the best in terms of structure and electrical transport properties. Therefore, we further studied its electrical transport by Hall Effect as a function of temperature from 300 K to 600 K. We performed Ohm’s law check at each temperature during the measurement of resistivity with no applied magnetic field to check if Ohm's law is obeyed. Figure 5.8 shows the resistivity and the hole mobility of sample D as a function of temperature. The temperature dependence of resistivity is characteristic of the extrinsic range, in which the resistivity decreases with increasing the temperature. On the other hand, in the intrinsic range, we expect an increase in resistivity with increasing the temperature, due to the scattering by lattice vibrations (phonons).

The hole mobility increased from 20 cm$^2$/Vs at 300 K to 29 cm$^2$/Vs at 550 K. The same behavior has been observed in two different natural p-type MoS$_2$ crystals, where the hole mobility was 22 at room temperature and increased as temperature increased [136]. An increase in mobility with an increase in temperature has been reported earlier for synthetic p-type MoS$_2$ up to 300 K [142]. The shift in the mobility peak to a higher temperature is due to unintentional doping or defects. This phenomenon is very promising for enhancing real devices performance such as solar cells and transistors. The temperature of these devices increases under normal operation, and consequently, the mobility will increase which will result in faster transport and performance.

There are two main types of scattering, which significantly affect the carrier mobility [143]. Ionized impurity scattering, which dominates at low temperatures, and phonon scattering, which dominates at high temperatures [143]. At intermediate temperatures, both effects are
relatively weak and mobility reaches its maximum [143]. The general trend is an increase in mobility with temperature until it reaches a maximum value, then the mobility decreases upon a further increase in temperature. A shift in the maximum value of mobility and conductivity to higher temperatures with increasing the carrier concentrations in Ge has been reported earlier [144]. All these results indicate that higher carrier concentrations and consequently ionized impurities may lead to this phenomenon. In addition, the polycrystalline nature of our sample and consequently additional scattering centers may have enhanced this behavior.

A Semiconductor can be degenerate or non-degenerate based on carrier concentration and temperature. At high carrier concentration and low temperature, the semiconductor is degenerate, where Fermi-Dirac statistics must be followed [131]. On the other hand, for a non-degenerate semiconductor Boltzmann statistics can be used. For a specific carrier concentration (e.g. holes, P) we can determine the degeneracy temperature, $T_o$, such that if the semiconductor temperature $T \gg T_o$ we treat the semiconductor as non-degenerate semiconductor and if the semiconductor temperature $T \ll T_o$ we treat the semiconductor as a degenerate semiconductor [131]. We calculated the degeneracy temperature, $T_o$, for sample D according to the following equation:

$$T_o = \frac{\hbar^2}{8k_m} \left( \frac{3}{\pi} \right)^{2/3} p^{2/3}$$  \hspace{1cm} (5.11)

Where $\hbar$ is Planck's constant, $k$ is Boltzmann's constant, $m$ is the mass of electron in free space, and $p$ is the concentration of holes. Figure 5.9(b) shows the concentration of holes
for sample D of MoS$_2$ as a function of temperature. The degeneracy temperature, $T_0$, as a function of concentration is plotted as a reference. It is obvious from the graph that our sample is non-degenerate since $T \gg T_0$ at any concentration within the 300-600 K range of temperatures [131]. The logarithm of carrier concentration increases linearly with temperature in the extrinsic range from 300-575 K as shown in figure 5.9(a) [131].

Figure 5.9: (a) The logarithm of the carrier concentration of sample D as a function of temperature and (b) concentration of holes in sample D as a function of temperature. $T_0$ is the degeneracy temperature. The solid blue line is a theoretical fit to the experimental red circles.

To excite electrons across the band gap, sufficient thermal energy should be supplied to the sample. The intrinsic range of MoS$_2$ is above 600 K as reported earlier [145]. In a p-type semiconductor the law of mass action which govern the concentration of holes, p, electrons, n, acceptors, $N_A$, and donors, $N_D$ is given by [131]:

$$K_h = \frac{p(p+N_D)}{N_A-N_D-p}$$  \hspace{1cm} (5.12)
Where, \( K_h \), is the equilibrium constant, \( h \) subscript refer to holes, which can be determined from the following equation [146]:

\[
K_h = 2g \left( \frac{\pi m_h k T}{\hbar^2} \right)^{3/2} e^{-E_A/kT}
\] (5.13)

Where \( g \) is a degeneracy factor, \( m_h \) is hole effective mass, \( E_A \) is ionization energy, the energy required to excite an electron from the valence band to fill an acceptor level, \( h \) is Planck's constant, \( k \) is Boltzmann's constant, \( T \) is the absolute temperature. A theoretical fitting for hole concentration dependence on temperature (which has been determined experimentally from Hall effect measurements) was performed in the 300-550 K range of temperatures using the following equation [146]:

\[
\frac{p (p+N_D)}{N_A-N_D-p} = 2g \left( \frac{\pi m_h k T}{\hbar^2} \right)^{3/2} e^{-E_A/kT}
\] (5.14)

Or [146]

\[
p \propto T^{3/2} e^{-E_A/kT}
\] (5.15)

Figure 5.10 shows the temperature dependence of the holes’ mean free path for sample D as a function of temperature. In the impurity scattering range (at low temperatures), the mean free path increases with increasing the temperature [131]. On the other hand, in the intrinsic range, (not shown in the figure) where scattering by lattice vibrations dominates (at high temperatures) the mean free path will decrease as the temperature increase [131].
5.3.4 Optical Characterization

The optical constants of as-grown films were determined from the measured transmittance and reflectance using the matrix method [147]. In this rigorous method, Maxwell’s equations relating the amplitudes of the electric and magnetic fields at the boundary between each two different media is written using matrix form [147]. Four medium structure air/thin film/substrate/air, as shown in figure 5.11, were considered, which represents the true physical case, rather than the three medium approximation Air/thin film/semi-infinite substrate which ignores the reflection from the last substrate-air interface [147-148].
Figure 5.11: A schematic of four media structure consisting of thin film/substrate layers surrounded by air from both sides.

An absorbing film of thickness $d_1$ and refractive index $n_1-ik_1$ on a transparent substrate (in the wavelength range of interest) of thickness $d_2$ and refractive index $n_2$, immersed in air medium with $n_0$ refractive index, is shown in figure 5.11. For the case of normal incidence, such that the light is incident from the air layer on the thin film layer, the three boundary conditions in a matrix form are given as follows [147-148]:

\[
\begin{align*}
\begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} &= \frac{1}{t_1} \begin{pmatrix} 1 & r_1 \\ r_1 & 1 \end{pmatrix} \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix} = \left( \frac{c_1}{t_1} \right) \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix} \\

\begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix} &= \frac{1}{t_2} \begin{pmatrix} e^{i\delta_1} & r_2 e^{i\delta_1} \\ r_2 e^{-i\delta_1} & e^{-i\delta_1} \end{pmatrix} \begin{pmatrix} E_2^+ \\ E_2^- \end{pmatrix} = \left( \frac{c_2}{t_2} \right) \begin{pmatrix} E_2^+ \\ E_2^- \end{pmatrix} \\

\begin{pmatrix} E_2^+ \\ E_2^- \end{pmatrix} &= \frac{1}{t_3} \begin{pmatrix} e^{i\delta_2} & r_3 e^{i\delta_2} \\ r_3 e^{-i\delta_2} & e^{-i\delta_2} \end{pmatrix} \begin{pmatrix} E_3^+ \\ E_3^- \end{pmatrix} = \left( \frac{c_3}{t_3} \right) \begin{pmatrix} E_3^+ \\ E_3^- \end{pmatrix}
\end{align*}
\]
Where $E_{m}^{+}$ and $E_{m}^{-}$ represent the incident and reflected electric field amplitudes of the waves travelling in the $m$th layer respectively, where $m = 1, 2, \text{ or } 3$ [147, 149]. The Fresnel reflection and transmission coefficients are given by:

\[ r_1 = \frac{E_0^-}{E_0^+} = \frac{N_0 - N_1}{N_0 + N_1} \]  \hspace{1cm} (5.19)

\[ t_1 = \frac{E_1^+}{E_0^+} = \frac{2N_0}{N_0 + N_1} \]  \hspace{1cm} (5.20)

\[ r_2 = \frac{E_1^-}{E_1^+} = \frac{N_1 - N_2}{N_1 + N_2} \]  \hspace{1cm} (5.21)

\[ t_2 = \frac{E_2^+}{E_1^+} = \frac{2N_1}{N_1 + N_2} \]  \hspace{1cm} (5.22)

\[ r_3 = \frac{E_2^-}{E_2^+} = \frac{N_2 - N_3}{N_2 + N_3} \]  \hspace{1cm} (5.23)

\[ t_3 = \frac{E_3^+}{E_2^+} = \frac{2N_2}{N_2 + N_3} \]  \hspace{1cm} (5.24)

Where

\[ N_1 = n_0 \]  \hspace{1cm} (5.25)

\[ N_1 = n_1 - ik_1 \]  \hspace{1cm} (5.26)

\[ N_2 = n_2 \]  \hspace{1cm} (5.27)

\[ N_3 = n_0 \]  \hspace{1cm} (5.28)
The factor $i\delta_1$ and $i\delta_2$ can be written in terms of attenuation and phase factors as follows:

\[ i\delta_1 = a_1 + i\gamma_1 \]  \hspace{1cm} (5.29)

\[ i\delta_2 = a_2 + i\gamma_2 \]  \hspace{1cm} (5.30)

Where

\[ a_1 = \frac{2\pi}{\lambda} k_1 d_1 \]  \hspace{1cm} (5.31)

\[ a_2 = \frac{2\pi}{\lambda} k_2 d_2 \]  \hspace{1cm} (5.32)

\[ \gamma_1 = \frac{2\pi}{\lambda} n_1 d_1 \]  \hspace{1cm} (5.33)

\[ \gamma_2 = \frac{2\pi}{\lambda} n_2 d_2 \]  \hspace{1cm} (5.34)

The relationship between the first medium and the last one can be determined as follows:

\[
\begin{pmatrix}
E_0^+ \\
E_0^-
\end{pmatrix} = \begin{pmatrix}
c_1 & c_2 & c_3 \\
t_1 t_2 t_3 & 0 & 0
\end{pmatrix} \begin{pmatrix}
E_0^+ \\
0
\end{pmatrix} = \frac{1}{t_1 t_2 t_3} \begin{pmatrix}
a & b \\
c & d
\end{pmatrix} \begin{pmatrix}
E_3^+ \\
0
\end{pmatrix}
\]  \hspace{1cm} (5.35)

It is worth to note that we assume no negative-going wave in the 3\textsuperscript{rd} medium (air), and therefore $E_3^- = 0$. Consequently, the reflection and transmission amplitudes will be given by:
\[ R = \frac{E_0^*}{E_0^+} = \frac{c}{a} \quad (5.36) \]

\[ T = \frac{E_0^+}{E_0^*} = \frac{t_1t_2t_3}{a} \quad (5.37) \]

The reflectance and transmittance, are given by:

\[ R = RR^* = \frac{c c^*}{a a^*} \quad (5.38) \]

\[ T = \frac{n_3}{n_0} T T^* = \frac{n_3 (t_1t_2t_3) (t_1^* t_2^* t_3^*)}{n_0 a a^*} \quad (5.39) \]

The film thickness was determined by SEM-cross section, and the substrate thickness is known too. In addition, we determined the substrate refractive index experimentally across the whole wavelength from 250 nm to 2500 nm. The only two unknowns in equations (5.38) and (5.39) are \( n_1 \) and \( k_1 \), which were determined from the measured reflectance and transmittance numerically. To get initial values of \( n_1 \) and \( k_1 \), the following approximate relation was used to calculate the absorption coefficient, \( \alpha \).

\[ T = \frac{(1-R)^2 e^{-\alpha d_1}}{(1-R^2) e^{-2\alpha d_1}} \quad (5.40) \]

Where \( T \) is the measured transmittance, \( R \) is the measured reflectance, \( d_1 \) is the film thickness and \( \alpha \) is the absorption coefficient, which is related to extinction coefficient by the following equation:

\[ \alpha = 4\pi k_1/\lambda \quad (5.41) \]
An approximate value for the refractive index, $n_1$, is then calculated using the following equation:

$$ R = \frac{(n_1-1)^2+k_1^2}{(n_1+1)^2+k_1^2} $$

(5.42)

Figure 5.12 shows the UV-VIS-NIR transmittance and reflectance of samples A, B, C, and D. The transmittance increases with the decrease of turning off temperature of sulfur vapor flow. This can be correlated with major carrier density since the carrier density decrease from samples A to D. The transmittance of sample D is between 10-20% in the range of 1000-2500 nm and 1-10% in the range of 700-1000 nm. Since MoS$_2$ is a semiconductor with 1.3 eV indirect band gap [15], we expect a weak absorption at a wavelength below 950 nm and consequently lower transmittance. In addition, MoS$_2$ has a direct band gap of 1.8 eV [70], which results in strong absorption below 680 nm and consequently almost no transmittance. Samples C and D of MoS$_2$ show relatively high reflectance 30-40% over the investigated range of 250-2500 nm.
Figure 5.13 shows the absorption coefficient of samples A, B, C and D at room temperature. The optical absorption coefficient, $\alpha$, calculated from the relation:

$$\alpha = \frac{4\pi k_1}{\lambda} \quad (5.43)$$

Two knees at 1.8 eV and 1.3 eV corresponding to MoS$_2$ direct and indirect band gaps respectively. The absorption coefficient of Sample D is higher than $1.6 \times 10^4 \text{cm}^{-1}$ in the high-energy range above 1.8 eV. A rapid decrease in the absorption coefficient at 1.8 eV, from $1.6 \times 10^4 \text{cm}^{-1}$ to $8 \times 10^3 \text{cm}^{-1}$ is due to the direct band gap transition. A second relatively gradual decrease in the absorption coefficient at 1.3 eV is due to the indirect band gap transition. Samples C and D shows four exciton peaks (obvious on a linear scale, but not shown here), located at 1.913 eV, 2.119 eV, 3.024 eV, and 3.735 eV which labeled A, B, D, and $\alpha$ respectively [30, 150]. Since our grown films of MoS$_2$ have preferred orientation such that the c-plane is parallel to the substrate, the calculated absorption
coefficient is comparable to those of single crystals calculated such that the electric vector of the incident light is perpendicular to the c-axis of the crystals ($E \perp c$). The presence of the strong exciton peaks is a good indication of the high quality of the structure [72]. In earlier report, a MoS$_2$ film, which was grown by sulfurization of Mo film in an evacuated ampule at 500 °C, did not show any exciton peaks. The absence of the exciton peaks was explained by the poor quality of the grown film structure [72].

Figure 5.13: The absorption coefficient of samples A, B, C, and D.

Figure 5.14 shows the refractive index and extinction coefficient of samples A, B, C, and D. The refractive index of samples C and D (pure MoS$_2$) is between 3.5 and 5 over the range of 250-2500 nm, which agrees well with recent and old reported values [76, 81]. The high values of refractive index indicate high reflectance which should be managed well in the process of designing a device by antireflection layer(s) and/or antireflection structures. Interestingly, we can tune the refractive index of the grown film by changing the
temperature at which we turn off the sulfur vapor flow, which is very useful for obtaining a material with a specific refractive index at a specific wavelength.

Figure 5.14: (a) Refractive index and (b) extinction coefficient of samples A, B, C, and D.

The real and imaginary parts of the dielectric constant ($\varepsilon'_r$ and $\varepsilon''_r$ respectively) as a function of wavelength (figure 5.15) were calculated using the following equations:

$$\varepsilon'_r(\omega) = n^2(\omega) - k^2(\omega)$$

(5.44)

$$\varepsilon''_r(\omega) = 2 \, n(\omega) \, k(\omega),$$

(5.45)
Figure 5.15: (a) Real and (b) Imaginary parts of the dielectric constant of samples A, B, C, and D.

The real part of the dielectric constant of samples C and D extrapolate to high values in the range of $\varepsilon(0) \sim 13 - 16$, which are reasonable values by considering the small band gap of MoS$_2$ [76]. These values agrees well with the results of a natural MoS$_2$ [76]. The real part of the dielectric constant of samples C and D consists of seven peaks located at 1.34 eV, 1.79 eV, 1.84 eV, 2 eV, 2.77 eV, 3.18 eV and 3.86 eV. The absorption coefficient and imaginary part of dielectric constant values are one order of magnitude less when calculated from both transmittance and reflectance than when calculated from reflectance only using Kramers-Kronig analysis [75-76]. The imaginary part of the dielectric constant of samples C and D consists of three peaks located at 1.8 eV, 2 eV, and 2.7 eV. The maxima located at 2.7 eV matches exactly the value obtained for 2H-MoS$_2$ natural crystal. The strong resolved peaks observed here are excitons as explained in more details in earlier [76, 78, 150].
5.4 Conclusion

In summary, we optimized a process to grow MoS$_2$ that is suitable for doping by diffusion at high temperatures up to 1000 °C. To successfully grow a pure phase of MoS$_2$, sulfur vapor flow should be maintained during cooling cycle below the critical temperature (between 900 °C and 800 °C). The mobility of the grown MoS$_2$ thin films was 20 cm$^2$/Vs at room temperature and increase to 27 cm$^2$/Vs at 226 °C, which is a very interesting useful property. Absorption coefficients of the grown films were in the range of 10$^4$ cm$^{-1}$. The optical constants of the grown films were calculated rigorously using the matrix theory. The knowledge of the fundamental electrical and optical properties of the grown MoS$_2$ have a significant importance in devices design.
CHAPTER 6: Ti-DOPED MoS$_2$

Doping of MoS$_2$ is essential for the fabrication of many electronic and optoelectronic devices. Ti-doped MoS$_2$ was grown by low pressure chemical vapor deposition (LPCVD). Different growth temperatures from 1000 °C to 700 °C were studied. No other phases except 2H-MoS$_2$ were detected by x-ray diffraction and Raman spectroscopy for the films grown at 1000 °C. The films grown at a lower temperature, namely 900 °C, and shorter time have Ti$_2$S phase. Hall effect and hot probe measurements demonstrated p-type conductivity in the films grown at 1000 °C with a mobility of 0.85 cm$^2$/Vs at 300 K. Decrease in carrier concentration upon doping of MoS$_2$ with Ti indicates n-type doping. Secondary ion mass spectroscopy (SIMS) revealed the Gaussian diffusion of Ti in MoS$_2$ sample grown at 1000 °C. Optical properties of the grown films have been studied as well across the UV-vis-NIR spectrum.

6.1 Introduction

MoS$_2$ is a semiconductor which has attracted the attention for its fascinating properties. It is layered structure guarantee it is chemical inertness down to a monolayer which is very promising for different electronic and optoelectronic applications. In addition, its high mobility, band gap tunability, and high absorption coefficient are very useful. N- and p-type of conduction has been reported for natural and synthetic MoS$_2$ according to the concentration of unintentional dopants exist in it [27]. Doping of MoS$_2$ was achieved in evacuated ampoules earlier [151-152]. This technique is expensive and not scalable. The
doping by diffusion in an open system, on the other hand, is challenging due to the problem of sulfur loss which is incompatible with the elevated temperature required for dopants diffusion.

6.2 Ti-doping Calculations

The Ti-doping will be achieved by depositing three layers of Mo/Ti/Mo, which will be sulfurized in the CVD chamber (figure 6.1).

![Figure 6.1: A schematic of the growth of Ti-doped MoS2.](image)

Densities of Mo and Ti are given by:

\[ \rho_{\text{Mo}} = 10.28 \text{ g/cm}^3 \]

\[ \rho_{\text{Ti}} = 4.506 \text{ g/cm}^3 \]

Atomic weights of Mo and Ti are given by:

\[ A_{\text{Mo}} = 95.95 \text{ g/mole} \]
The one atomic percent (at%) of Ti, and 99 at% of Mo were converted to their corresponding weight percent (wt%) using the following equations [153]:

\[
C_{Ti} = \frac{C_{Ti}'}{C_{Ti}' A_{Ti} + C_{Mo} A_{Mo}} = 5.01386992 \times 10^{-3} \text{ wt%}
\]

\[
C_{Mo} = \frac{C_{Mo}' A_{Mo}}{C_{Mo}' A_{Mo} + C_{Ti}' A_{Ti}} = 0.994986130 \text{ wt%}
\]

Where \( C \) and \( C' \) refer to the weight and atomic percent, respectively. To determine the required thickness of Ti and Mo, we had to figure out the relation between thickness and weight percent of each element. The weight percent of each element is given by the weight of this element divided by the total weight of both elements as follows:

\[
C_{Ti} = \frac{m_{Ti}}{m_{Ti} + m_{Mo}} \times 100
\]

\[
C_{Mo} = \frac{m_{Mo}}{m_{Mo} + m_{Ti}} \times 100
\]

Where \( m_{Mo} \) and \( m_{Ti} \) are the masses of a thin film of Mo and Ti respectively. Any of the former two equations can be used to get the relation between the mass of Ti as a function of the mass of Mo and weight percent of any element of them. Using the second equation we can write it as follows [153]:
\[ m_{\text{Ti}} = \frac{m_{\text{Mo}} (1 - C_{\text{Mo}}/100)}{C_{\text{Mo}}/100} \]

The relation between mass, \( m \), and thickness, \( t \), of a thin film is given by:

\[ m = \rho V = \rho A \cdot t \]

Where \( \rho \) is the density and \( A \) is the thin film area, and since both films (M and Ti) will have the same area on the substrate, we will consider the case of unit area, \( A= 1 \text{ cm}^2 \). The equation can be rewritten as follows:

\[ t_{\text{Ti}} = \frac{t_{\text{Mo}} (1 - C_{\text{Mo}}/100)}{C_{\text{Mo}}/100} \]

Since we determined \( C_{\text{Mo}} \), we have only two unknowns. By deciding the thickness of any of the thin films (Mo or Ti), we will be able to determine the other directly using the above equation. In this Work, we decided that the combined thickness will be 200 nm \( (t_{\text{Mo}} + t_{\text{Ti}} = 200 \text{ nm}) \). We determined the thickness of each film numerically. The Mo and Ti thin films thicknesses were 197.7 nm and 2.3 nm respectively.

6.3 Experiment

In this work, we doped MoS\(_2\) by Ti in a CVD chamber rather than an evacuated ampoule. This work is based on the doping compatible process we developed earlier to grow undoped MoS\(_2\) at high temperatures and following the triple layers doping technique demonstrated in earlier reports [151]. The structures of the grown films were studied by Raman...
spectroscopy and x-ray diffraction (XRD). The surface of the grown films and its cross-section were investigated using scanning electron microscopy (SEM). The concentration profiles of Mo, S, and Ti were determined using secondary ion mass spectroscopy (Physical Electronics ADEPT 1010 quadrupole SIMS). The primary 3 keV Cs$^+$ ions were rastered over 200 μm × 200 μm area at 45° incidence with beam current 40 nA. To reduce the crater side wall effects, a 20% electronic gating was used to collect the ejected ions from just the center region. The depth scale was generated by measuring the crater depth with a stylus profilometer (Dektak3). Electrical properties of the grown films were investigated using Hall effect and hot probe techniques. Finally, the optical constants were determined from the transmittance and reflectance in the range of 250 – 2500 nm.

Four different sample of MoS$_2$ were grown at different growth temperatures. Mo (100 nm)/Ti (2.3 nm)/Mo (97.7 nm) thin films were e-beam evaporated on a pre-cleaned c-plane sapphire substrate. This thickness of Ti leads to the deposition of 1 at% of Ti according to theoretical calculations. The substrate holder temperature raised to ~750 °C before the deposition and kept at this temperature during the whole evaporation time to improve the adhesion of Mo thin films to the sapphire substrate. The sapphire/Mo/Ti/Mo was diced to small pieces 20×20 mm$^2$ and 7×7 mm$^2$. The stack was sulfurized in a two-zone chamber. The sulfur powder was in a quartz boat upstream in the first zone (zone I), while Sapphire/Mo/Ti/Mo samples were supported by another quartz boat downstream in the second zone (zone II). We raised the temperature of zone I to 100 °C at a rate of 10 °C/min. Almost at the same time we raised zone II (growth zone) temperature to the desired
temperature at a rate of 20 °C/min. Four growth temperatures were studied, namely 1000 (sample A), 900 (sample B), 800 (sample C), and 700 °C (sample D). After zone II reach the desired growth temperature we cool it down at a rate of 2 °C/min. When zone II temperature reaches 700 °C, we turn off sulfur vapor flow by shutting down the power of zone I. Argon gas flow at a rate of 37 sccm/min was maintained during growth time until the CVD chamber cools down to the room ambient temperature. The CVD chamber pressure was 1 Torr for all the four samples.

6.4 Results and Discussion

6.4.1 X-ray Diffraction

The structure of the grown films was studied by out-of-plane symmetric x-ray diffraction, which indicated the polycrystalline nature of the grown films. Figure 6.2 shows the XRD pattern of sample A (1000 °C). Four diffraction peaks corresponding to the (100), (110), (200), and (1011) planes of MoS2 were observed. Sample A has a preferred orientation such that the (110) plane of MoS2 is parallel to (006) plane of the sapphire substrate. Therefore, the inclusion of Ti has altered the (002) preferred orientation of undoped MoS2 grown under the same conditions of sample A. No other phases except MoS2 and sapphire were observed in XRD pattern of sample A, which indicate the complete sulfurization of Mo and diffusion of the Ti layer.
Figure 6.2: Symmetric Out-of-plane XRD patterns of samples A (1000 °C), B (900 °C), C (800 °C), and D (700 °C), where MoS$_2$ peaks are labeled in magenta, sapphire peaks are labeled in green, Ti$_2$S peaks are labeled in orange, and Mo peaks are labeled in red.

Figure 6.2 shows the XRD pattern of sample B (900 °C). Three diffraction peaks corresponding to the (100), (110), and (1011) planes of MoS$_2$ were observed. A peak corresponding to (430) plane of dititanium sulfide (Ti$_2$S) was observed, indicating the presence of a second phase. The short drive-in time rather than the relatively lower temperature (900 °C) probably is the reason behind the formation of this second phase.

Figure 6.2 shows XRD pattern of sample C (800 °C). We observed that the shorter growth time and lower temperature resulted in even incomplete sulfurization since we can observe clearly a peak corresponds to (110) plane of Mo. In addition, in sample C, we can observe
strong peaks corresponding to (130), (141), and (711) planes of Ti$_2$S. Two diffraction peaks corresponding to the (100), and (110) planes of MoS$_2$ were observed in sample C. Figure 6.2 shows XRD pattern of sample D (700 °C). The Peak corresponding the (110) plane of Mo is the strongest in sample D, which indicate an incomplete sulfurization of the bulk of the film. More time is required for complete sulfurization at relatively low temperatures. The positions of MoS$_2$, sapphire, and Ti$_2$S peaks match well the XRD cards PDF # 00-37-1492, 01-070-5679 and 01-076-5873 respectively.

6.4.2 Raman Spectroscopy

Figure 6.3 shows Raman spectra of samples A, B, C and D. The spectra of all samples consist of four peaks located at 283, 379, 404, and 450 cm$^{-1}$ where the first three peaks correspond to $E_{1g}$, $E_{2g}^1$, and $A_{1g}$ first order Raman-active modes and the fourth peak corresponds to a second order Raman-active mode [90-91, 93]. The slight shift in the peaks towards a lower wave number in comparison with a single crystal is expected due to the polycrystalline structure of the grown thin films [154]. The undoped MoS$_2$ grown under the same conditions of sample A has a four Raman peaks located at 282, 376, 403 and 450 cm$^{-1}$. Therefore, a slight decrease in the frequency of the $E_{1g}$, $E_{2g}^1$, and $A_{1g}$ peaks, is observed after Ti-doping. Only the MoS$_2$ peaks are detectable in samples B, C, and D, Although, the presence of Ti$_2$S phase under the top MoS$_2$ layer since the Raman technique has limited penetration depth. On the other hand, Mo is Raman inactive and no peaks are expected.
Figure 6.3: Raman spectra of samples A, B, C, and D.

6.4.3 Scanning Electron Microscopy

Figure 6.4 shows SEM images of the surface of samples A, B, C, and D. The presence of dome features on the surface was observed in sample A at the high growth temperature (1000 °C). We observed these domes too in APCVD grown MoS$_2$ which was explained by the small thickness of the Mo film and the difference in thermal expansion coefficient between the grown film and substrate. At a lower growth temperature of 900 °C, the domes were relatively shorter in height and the film is smoother. The domes disappeared completely at 800 °C and 700 °C growth temperatures. The explanation of the domes disappearance at lower growth temperature require further analysis, and the incomplete sulfurization of these films should be considered.
Figure 6.4: SEM images of the surface of samples (a) A (1000 °C) (b) B (900 °C) (c) C (800 °C) (d) D (700 °C).

Figure 6.5 shows SEM cross-section images of samples A, B, C, and D. The top layer is a metal layer which we have deposited to improve the contrast of the image. The cross-section was cleaned by focused ion beam before imaging. The cross-section of samples A (1000 °C) and B (900 °C) indicating the growth of a single layer. On the other hand, samples C (800 °C) and D (700 °C) shows distinctive two layers, where the top layer is the layer which is sulfurized, and the bottom layer is the remaining Mo layer. The Mo layer in sample B is smaller in thickness than the Mo layer in sample D which agrees well with 101
XRD results. These results indicate the dependence of the kinetics of reaction on the growth temperature and/or the reaction time.

Figure 6.5: SEM cross-section images of the surface of samples A (1000 °C), B (900 °C), C (800 °C), and D (700 °C).

### 6.4.4 Secondary Ion Mass Spectroscopy (SIMS)

The diffusion behavior of Ti and S in Mo have been studied. SIMS depth profiles of Mo, S, Ti, Al, and O at different growth temperatures and using different polarities of secondary ions captured. In the positive polarity mode, the Mo, Al, and Ti positive ions signal will be more intense, while in the negative polarity mode the S and O negative ions intensity will be more intense. To evaluate the profile of Ti we should consider the signal interference
between one atom of 48Ti (which have an atomic mass of 48) and three atoms of 16O which will be at 48 too on the mass spectrum. Using the positive secondary mode for this purpose when the oxygen signal is minimum and the Ti signal is maximum is the right procedure, if there is no other interference. We evaluate first possible interference by acquiring a broad range mass spectrum.

(a)  
(b)  
(c)  
(d)  

Figure 6.6: SIMS depth profiles of Ti-doped MoS2 samples (a, b) A and (c, d) B.
Figure 6.6(a, b) shows SIMS depth profile of sample A using positive and negative modes respectively. From the negative mode, the concentration of sulfur is constant across the whole thickness. On the other hand, from the negative mode, the Ti concentration have a Gaussian peak which characteristic of limited-source gaussian diffusion. SIMS depth profile of Ti in sample B is similar to sample A, which indicate a good diffusion at 900 ℃ (figure 6.6(c, d)). Obviously, the Mo depth profile of sample B has a peak close to the MoS2/sapphire interface, which may indicate the presence of very thin Mo layer which is not sulfurized. A corresponding small decrease in sulfur signal was observed too, which reinforce this conclusion.

Figure 6.7(a, b) shows SIMS depth profile of sample C (800 ℃). In sample C, however, the concentration of sulfur was constant across 62% of the thickness. The sulfur concentration then decreases and the Mo concentration increases, indicating incomplete sulfurization. The Ti depth profile in sample C has a narrow quasi-Gaussian shape, indicating a relatively slower diffusion at 800 ℃. Figure 6.7(c, d) shows SIMS depth profile of sample D (700 ℃). The sulfurization of sample D is incomplete too. In sample D, the concentration of sulfur was constant across 22% of the thickness. The Ti depth profile in sample D has a triangle peak indicating the weak diffusion of Ti at this temperature. These results match well XRD and SEM cross-section results. The change of the Mo signal in an analogous manner with Ti signal (figure 6.7) indicates the reaction between Ti and Mo before sulfurization.
6.4.5 Electrical and Optical Properties

Hall effect measurements of sample A at 300 K indicated a p-type conductivity. Its resistivity, carrier concentration, and mobility were 209.6 Ω-cm, $3.5\times10^{16}$ cm$^{-3}$, and 0.85 cm$^2$/Vs, respectively. The decrease in carrier concentration of Ti-doped MoS$_2$ in comparison with undoped MoS$_2$ indicates that Ti acts as a donor in MoS$_2$. 

Figure 6.7: SIMS depth profiles of Ti-doped MoS$_2$ samples (a, b) C and (c, d) D.
Figure 6.8: Transmittance and reflectance spectra of Samples A, B, C, and D.

Figure 6.8 presents UV to near-IR transmittance and reflectance spectra of samples A, B, C, and D. The transmittance of sample A is high in comparison with the other samples because this is the only sample which undergone complete sulfurization. This result provides a straightforward way to check the completion of sulfurization process by measuring the transmittance.
Figure 6.9: Absorption coefficient of Ti-doped MoS$_2$ in comparison with undoped MoS$_2$.

Figure 6.9 shows the absorption coefficient of Ti-doped MoS$_2$ in comparison with undoped MoS$_2$. The absorption coefficient of Ti-doped MoS$_2$ ($\sim 6 \times 10^4$ cm$^{-1}$) is about four times larger than the absorption coefficient of undoped MoS$_2$. Ti-doping increased the steepness of the absorption edge. Ti-doped MoS$_2$ has preferred orientation such that the c-plane is perpendicular to the substrate. Therefore, this should be considered when Ti-doped MoS$_2$ properties are compared with other films, where the c-plane is parallel to substrate.

Figure 6.10 shows refractive index, extinction coefficient, real and imaginary parts of the dielectric constant of samples A. The optical constants are very important for optical and optoelectronic devices design.
Figure 6.10: Optical constants of sample A. (a) Refractive index and extinction coefficient. (b) Real and imaginary parts of the dielectric constant.

6.5 Conclusion

Ti-doped MoS$_2$ have been grown by low pressure chemical vapor deposition (LPCVD). X-ray diffraction and Raman spectroscopy confirmed the growth of polycrystalline MoS$_2$ at 1000 °C. Ti$_2$S phase was observed in the films grown at a lower temperature (900 °C). N-type doping was achieved in MoS$_2$ using Ti. The mobility of the films grown at 1000 °C was 0.85 cm$^2$/Vs at 300 K. Secondary ion mass spectroscopy (SIMS) revealed the Gaussian diffusion of Ti in MoS$_2$ sample grown at 1000 °C. The optical properties of the grown material were studied in the range from 250-2500 nm. The optical constants of sample A were determined across the whole investigated range of wavelengths.
CHAPTER 7: FLUORINE-DOPED TIN OXIDE

7.1 Introduction

Fluorine-doped tin oxide (FTO) is a transparent conductive semiconductor which has significant applications including solar cells and thin film transistors. The growth of FTO thin films by a cheap aqueous-spray-based method is very promising for large-scale applications. The control of fluorine dopants atoms in the grown films has significant effects on its electrical and optical properties. The aim of this study is to correlate the concentration of fluorine in the solution to the actual concentration in the grown films.

7.2 Experiment

7.2.1 Growth of FTO

FTO films were grown by a streaming process for electrodeless electrochemical deposition (SPEED) [155]. The Precursors include 0.4 M stannic chloride (SnCl₄) and ammonium fluoride (NH₄F) dissolved in a mixture of deionized water (20%) and organic solvents (80%). The organic solvents ethanol, isopropanol, and methyl propanol are the complexing agents for Sn ions. The proposed chemical reactions sequence is as follows:

First, the adsorbed hydroxyl group on the hydrophilic substrate will react with tin-ligands, [SnLₙ]ⁿ⁺(₄⁺) to form tin hydroxide, SnOH³⁺, while the ligands will decompose and evaporate.

\[
\text{OH}^- + [\text{SnL}_n]^{n+}(\text{₄⁺}) \rightarrow \text{SnOH}^{3+} + L_n \uparrow
\]  (7.1)
where \( L \) represents the ligands, \( p \) is the valence of the ligand \( L \), and \( n \) is the number of ligands attached to \( Sn \). The tin hydroxide, \( SnOH^{3+} \) will react further with hydroxyl groups to form a tin oxide on the substrate and water, which will evaporate.

\[
SnOH^{3+} + 3OH^- \rightarrow SnO_2 + 2H_2O \uparrow \tag{7.2}
\]

The tin hydroxide, \( SnOH^{3+} \) will react also with ammonium fluoride in addition to the hydroxyl group to form \( SnF_4 \) as follows:

\[
SnOH^{3+} + 4NH_4F + 3OH^- \rightarrow SnF_4 + 4H_2O \uparrow + 4NH_3 \uparrow \tag{7.3}
\]

Three groups of samples have been grown for this study. The first group, labeled A, was grown at 450°C on borosilicate glass substrates. The second group, labeled B, was grown at 480°C on borosilicate glass substrates. The third group, labeled C, was grown at 480°C on \( SiO_2/Si \) wafers. Higher temperatures of substrates’ top-surface have been achieved by increasing the growth temperature or using thinner substrates with higher thermal conductivity (\( SiO_2/Si \) wafers). The grown samples labels and their nominal fluorine concentrations (concentration in the precursor solution) are listed in table 7.1.

Depth profiles of \( Sn, O, F \) and \( Cl \) were determined using secondary ion mass spectroscopy (Physical Electronics ADEPT 1010 quadrupole SIMS). The primary 3 keV \( Cs^+ \) ions were rastered over a 300 μm × 300 μm area at 45 deg incidence with beam current 20 nA. To reduce the crater side wall effects, a 20% electronic gating was used to collect the ejected ions from just the center region.
Table 7.1
FTO samples labels and their corresponding nominal concentrations.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Growth temperature (℃)</th>
<th>Substrate</th>
<th>Fluorine concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0.5</td>
<td>450</td>
<td>glass</td>
<td>0.5</td>
</tr>
<tr>
<td>A5</td>
<td>450</td>
<td>glass</td>
<td>5</td>
</tr>
<tr>
<td>A15</td>
<td>450</td>
<td>glass</td>
<td>15</td>
</tr>
<tr>
<td>B0.1</td>
<td>480</td>
<td>glass</td>
<td>0.1</td>
</tr>
<tr>
<td>B0.2</td>
<td>480</td>
<td>glass</td>
<td>0.2</td>
</tr>
<tr>
<td>B0.5</td>
<td>480</td>
<td>glass</td>
<td>0.5</td>
</tr>
<tr>
<td>B1</td>
<td>480</td>
<td>glass</td>
<td>1</td>
</tr>
<tr>
<td>B2</td>
<td>480</td>
<td>glass</td>
<td>2</td>
</tr>
<tr>
<td>B5</td>
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<td>glass</td>
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</tr>
<tr>
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</tr>
<tr>
<td>B20</td>
<td>480</td>
<td>glass</td>
<td>20</td>
</tr>
<tr>
<td>C10</td>
<td>480</td>
<td>Si/SiO2</td>
<td>10</td>
</tr>
<tr>
<td>C15</td>
<td>480</td>
<td>Si/SiO2</td>
<td>15</td>
</tr>
<tr>
<td>C20</td>
<td>480</td>
<td>Si/SiO2</td>
<td>20</td>
</tr>
</tbody>
</table>

7.2.2 Calibration Standard by Ion Implantation

To determine the concentration of fluorine in the grown films we need a calibration standard with a known concentration of fluorine. To get reliable results, the matrix material of the sample in question should have the same structure as the matrix material of the standard calibration. Therefore, we synthesized a calibration standard using undoped SnO$_2$ thin film grown on a glass substrate by SPEED method. Then we implanted this undoped thin film with a known dose of fluorine to make our calibration standard.

The SRIM/TRIM (acronyms for stopping and range of ions in matter /Transport of Ions in Matter) software was used to simulate the implantation process, to determine the dose of fluorine ions required to implant the SnO$_2$ thin film, and the required implantation energy to achieve specific concentration at a specific depth.
The peak concentration depth (projected range) below the SnO₂ film surface and the fluorine concentration should be decided before the simulation. We decided that the target fluorine concentration in the SnO₂ matrix is 1%, and the peak concentration depth is about 200 nm. The following step was to determine the ion implantation energy needed to achieve the 200 nm peak concentration depth. We will use the SRIM 2013 software to generate stopping and range table based on the dopant (fluorine) and matrix (SnO₂) density. The generated table will include broad ranges of ion energies and the corresponding projected range. According to the table, 180 Kev ion energy results in 201.7 nm projected range. The determined ion energy of 180 KeV will be used to perform the TRIM simulation.

Next, we will calculate the number of fluorine atoms/cm³ (peak concentration) equivalent to the 1% atomic concentration in SnO₂. The atomic percent of SnO₂ is 99 at%. The fluorine weight percent (wt%) is given by:

\[
C_F = \frac{C_F^'}{A_F + C_{SnO2}^' A_{SnO2}} \times 100 \tag{7.4}
\]

\[
C_F = \frac{1}{1 + 18.9984} \times 100 = 0.127170716 \text{ wt%} \tag{7.5}
\]

Where \(C_F\) is the fluorine weight percent, \(C_F'\) and \(C_{SnO2}'\) are the fluorine and SnO₂ atomic percent, respectively. \(A_F\) and \(A_{SnO2}\) are the atomic weights (molar masses) of fluorine and SnO₂, respectively. The number of fluorine atoms/cm³, \(N_F\), equivalent to 1 at% doping can be calculated using the following equation:
\[ N_F = \frac{N_A C_F}{\frac{c_F A_F}{\rho_F} + \frac{A_F}{\rho_{SnO_2}} (100 - C_F)} \quad (7.6) \]

\[ N_F = \frac{(6.022 \times 10^{23}) \times 0.12717}{0.12717 \times (18.9984)} + \frac{18.9984}{6.95} (100 - 0.12717) = 2.78293429 \times 10^{20} \text{ atoms/cm}^3 \quad (7.7) \]

Where \( N_A \) is Avogadro's number. \( \rho_F \) and \( \rho_{SnO_2} \) are the fluorine and SnO\(_2\) density, respectively. The density of fluorine, \( \rho_F = 1.1111 \) is the value stored in SRIM 2013 software. We have used slightly different value of fluorine concentration, equation (7.8), due to the adoption of different density value. The new concentration of fluorine is 1.01 at\%.

\[ N_F = 2.81313996 \times 10^{20} \text{ atom/cm}^3 \quad (7.8) \]

The TRIM simulation will produce ion ranges plot represents the distribution of fluorine ions (180 KeV) building up in the SnO\(_2\) target. The y-axis units are in \((\text{atoms/cm}^3)/(\text{atoms/cm}^2)\). From this plot, we can determine the implantation dose \((\text{ions/cm}^2)\) by dividing the calculated fluorine peak concentration \((\text{atoms/cm}^3)\) over the peak value on the y-axis \((\text{atoms/cm}^3)/(\text{atoms/cm}^2)\). From the ion range plot, the peak value was:

\[ 5 \times 10^4 \frac{\text{atoms/cm}^3}{\text{atoms/cm}^2} \quad (7.9) \]

Therefore, the implantation dose was as follows:
\[
\text{Implantation dose} = \frac{2.8131396 \times 10^{20} \text{ atom/cm}^3}{5 \times 10^4 \text{ atoms/cm}^3} \times 10^{20} \text{ atoms/cm}^3
\]

\[
\text{Implantation dose} = 5.62627992 \times 10^{15} \text{ Ions/cm}^2
\]

TRIM simulation indicates that the dopant concentration peak (from ion range plot) occurs at a depth of 206.1 nm, but SIMS data as will be shown below for the implanted SnO\(_2\) thin film shows a peak at a depth of 237 nm. Based on the above results, the calibration standard was synthesized by implanting fluorine ions dose of 5.626 \times 10^{15} ions/cm\(^2\) into an undoped SnO\(_2\) thin film at 180 keV energy (Leonard Kroko, Inc.).

7.3 Results and Discussion

7.3.1 Sputtering Rate & Normalization

The concentration profile of F in the calibration standard and the grown films were determined using secondary ion mass spectroscopy (SIMS). The crater-depth for the calibration standard sample was measured using stylus profiler. The depth was 522.3 nm and 517.5 nm across two different paths, and the average is 519.9 nm. The sputtering rate of 0.636 nm/s was determined by entering the average depth value in the SIMetric software (the instrument control program) which used to compute the sputtering rate based on the total sputtering time and crater depth. This rate was considered constant for all the grown samples. Recorded intensities for fluorine I\(_F\) were normalized with respect to Sn intensity I\(_{Sn}\) which represent the matrix.
7.3.2 Relative Sensitivity Factor

The relative sensitivity factor (RSF) was calculated using implanted fluorine ion dose using SIMetric software (the instrument control program). The software places three cursors on the interactive display define integration limits and background. The relative sensitivity factor (RSF) of the calibration standard sample is \(5.58 \times 10^{18}\) atoms/cm\(^3\). The concentration of fluorine based on ion dose quantification at the peak is \(3.1109\times10^{20}\) atoms/cm\(^3\) as shown in figure 7.1. Fluorine weight percent, \(C_F = 0.14227\) wt\%, calculated using equation (7.6) and the experimentally determined concentration of fluorine. Therefore, fluorine atomic percent was \(C'_{SnO_2} = 1.12\) at\%.

![SIMS depth profiles of 1.12 At% of Fluorine in SnO\(_2\) on a glass substrate.](image)

Figure 7.1: SIMS depth profiles of 1.12 At% of Fluorine in SnO\(_2\) on a glass substrate.
Next, we will calculate the number of SnO\textsubscript{2} atoms/cm\textsuperscript{3} equivalent to the 98.88 at\%. The SnO\textsubscript{2} weight percent is given by:

\[
C_{\text{SnO}_2} = \frac{C'_F A_{\text{SnO}_2}}{C'_F A_{\text{SnO}_2} + C'_S A_{\text{SnO}_2}} \times 100
\]

\[
C_{\text{SnO}_2} = \frac{98.88 \times (150.71)}{98.88 \times (150.71) + 1.12 \times (18.984)} \times 100 = 99.85773 \text{ wt\%} \quad (7.13)
\]

Where \(C_{\text{SnO}_2}\) is the SnO\textsubscript{2} weight percent, \(C'_F\) and \(C'_S\) are the fluorine and SnO\textsubscript{2} atomic percent, respectively. \(A_F\) and \(A_{\text{SnO}_2}\) are the atomic weights (molar masses) of fluorine and SnO\textsubscript{2}, respectively. The number of SnO\textsubscript{2} atoms/cm\textsuperscript{3}, \(N_{\text{SnO}_2}\), equivalent to 99.85 wt\% can be calculated using the following equation:

\[
N_{\text{SnO}_2} = \frac{N_A C_{\text{SnO}_2}}{\rho_{\text{SnO}_2} + \frac{A_{\text{SnO}_2}}{\rho_F} (100 - C_{\text{SnO}_2})} \quad (7.14)
\]

\[
N_{\text{SnO}_2} = \frac{(6.022 \times 10^{23}) \times 99.85773}{99.85773 \times (150.71) + 6.95 \times (100 - 99.85773)} = 2.75251891 \times 10^{22} \text{ atoms/cm}^3 \quad (7.15)
\]

Where \(N_A\) is Avogadro’s number. \(\rho_F\) and \(\rho_{\text{SnO}_2}\) are densities of fluorine and SnO\textsubscript{2} atomic percent, respectively.

The experimental fluorine concentration is close to the theoretical value of 1.01 at\%. The difference could be due to an experimental error. The difference between experimental and theoretical concentration is given by:

\[
\text{Difference} = \frac{1.12 - 1.01}{1.01} = 10.9\% \quad (7.16)
\]

116
It is worth to note that the number of SnO₂ molecule/cm³ (or equivalently Sn atoms/cm³) based on 100 at% SnO₂ is not strictly accurate.

\[
N_{\text{SnO}_2} = \text{density} \left( \frac{g}{cm^3} \right) \frac{1}{\text{Molar mass} \left( \frac{\text{mole}}{g} \right)} \text{Avogadro's number} \left( \frac{\text{atoms}}{\text{mole}} \right)
\]  

(7.17)

\[
N_{\text{SnO}_2} = \frac{6.95 \times 6.022 \times 10^{23}}{150.71} = 2.777048636 \times 10^{22} \text{ molecule/cm}^3
\]  

(7.18)

The number of F atoms/cm³ based on 100 at% F is given by:

\[
N_F = \frac{1.1111 \times 6.022 \times 10^{23}}{18.998} = 3.522 \times 10^{22} \text{ molecule/cm}^3
\]  

(7.19)

The experimental dopant concentration peak for the implanted standard is located at a depth of 237 nm, which is deeper than the theoretical value of 206.1 nm determined from the ion range plot.

### 7.3.3 Quantification of Fluorine in the Grown Samples

The fluorine in the grown samples was quantified based on the RSF calculated using the calibrated standard and by normalization with respect to the Sn intensity I_{Sn} which represent the matrix. The fluorine concentration of the grown samples was determined using the following equation:

\[
C_F = \frac{I_F}{I_{\text{Sn}}}
\]  

(7.20)
Where $C_F$ is the concentration of fluorine in atoms/cm$^2$, $I_F$ is the recorded intensity of fluorine signal measured in units of counts/S, $I_m$ is the recorded intensity of Sn signal measured in units of counts/s.

![SIMS depth profiles of FTO/glass grown at 450 C](image)

Figure 7.2: SIMS depth profiles of FTO/glass grown at 450 with nominal F/Sn atomic concentration of (a) 0.5% (b) 5% and (c) 15%.

Figure 7.2 shows the concentration of Sn, O, F and Cl in FTO/glass grown at 450 C (group A). The F concentration in sample A.5 is consistent with group B results. The F concentrations in samples A5 and A15 are not uniform across the thickness of the film.
The F concentration of samples A.5, A5, and A15 are 0.007, 0.7, and 0.5 at% respectively. The ratio between nominal and actual concentrations of fluorine is 71, 71, and 30 respectively.

Figure 7.3: SIMS depth profiles of FTO/glass grown at 480 °C with nominal F/Sn atomic concentration of (a) 0.1%, (b) 0.2%, (c) 0.5%, and (d) 1%.

Figure 7.3 shows the concentration of Sn, O, F and Cl in FTO/glass grown at 480 C with nominal F/Sn atomic concentration of 0.1%, 0.2%, 0.5%, and 1% (group B). The films with nominal F/Sn concentrations below 0.5% have lower thicknesses. The F concentration increase on average as the nominal concentrations increase from 0.1 at% nominal concentration of F/Sn to 20 at% nominal concentration of F/Sn. Higher concentration of
fluorine near the substrate has been observed in samples B.5 and B1. The F concentration of samples B.1, B.2, B.5 and B1 are 0.005, 0.07, 0.04 and 0.007 at% respectively. The ratio between nominal and actual concentrations of fluorine is 20, 3, 13 and 143 respectively.

Figure 7.4 shows the concentration of Sn, O, F and Cl in FTO/glass grown at 480 C with nominal F/Sn atomic concentration of 2%, 5%, 10%, and 20% (group B). The fluorine concentration is uniform on average across the thickness of most of the samples except sample B20. The F concentration of samples B2, B5, B10 and B20 are 0.08, 0.4, 0.5 and 0.5 at% respectively. The ratio between nominal and actual concentrations of fluorine is 25, 13, 20 and 40 respectively.
Figure 7.4: SIMS depth profiles of FTO/glass grown at 480 °C with nominal F/Sn atomic concentration of (a) 2%, (b) 5%, (c) 10%, and (d) 20%.

Figure 7.5 shows the concentration of Sn, O, F and Cl in FTO/SiO$_2$/Si grown at 480 C (group C). The F concentration of samples C10, C15, and C20 are 1.3, 1.5, and 2.4 at% respectively. The ratio between nominal and actual concentrations of fluorine is 8, 10, and 8 respectively.
Fluorine-doped tin oxide (FTO) thin films on glass and SiO₂/Si wafer at different temperatures were grown aqueous-spray-based method. A comparison between the concentration of fluorine in the aqueous solution and the grown film was performed using secondary ion mass spectroscopy (SIMS). The concentration of fluorine in the grown films is proportional to the concentration in the aqueous solution. A nominal to the actual ratio between 8-10 was determined for samples of group A. The ratio was higher for group A.
and B. Further work is required to fully understand the cause of the difference between the ratios.
CHAPTER 8: CONCLUSION

We have successfully grown MoS$_2$ thin films by atmospheric pressure chemical vapor deposition and low pressure chemical vapor deposition. The MoS$_2$ thin films grown by both methods were polycrystalline in nature. Microdomes of MoS$_2$ were observed on the surface of the grown films at 1000 $^\circ$C if the Mo film thickness is small (~ 200 nm), due to thermal coefficient mismatch. No microdomes will be observed if the Mo film thickness is about 500 nm. Diffusion of sulfur in Molybdenum is temperature dependent.

At a growth temperature of 1000 $^\circ$C and sulfur vapor flow rate of 37 sccm/min. The sulfur diffusion in 200 nm of Mo is complete without dwelling time at the growth temperature. Increasing the temperature at a rate of 20 $^\circ$C/min. then cooling down immediately to room temperature is sufficient for complete sulfurization. On the other hand, at a growth temperature of 700 $^\circ$C, a partial sulfurization will occur at the same sulfur vapor flow and heating rate. The sulfur vapor flow is one of the very important parameters that can affect the quality of the grown MoS$_2$. Especially at elevated temperatures (> 800 $^\circ$C) where the oxidation process can compete well with the sulfurization process. Sulfur vapor flow should be maintained during the cooling cycle till 700 $^\circ$C to avoid surface oxidation.

The microdomes structures of MoS$_2$ are very interesting since it can reduce the reflectance over a wide range of wavelengths and incident angles. The antireflection properties of these microdomes were studied by finite difference time domain (FDTD) method to rigorously solve Maxwell’s equations in three dimensions and calculate the reflectance. Parabolic
domes of 0.5 µm base diameter and 1 µm height reduce the reflectance to almost zero for all incident angles from 0° to 50° by gradually changing the effective refractive index, which consequently improves light harvesting. Different geometries, including pyramids, spherical domes, and cones were compared to parabolic domes of the same base area and height. Parabolic domes were the most effective antireflection structure overall light incident angles from 0° to 80°.

We optimized a process to grow MoS₂ thin films by low pressure chemical vapor deposition such that the growth zone can reach elevated temperatures up to 1000 °C, under sulfur vapor flow. This process is compatible with doping by diffusion. The critical temperature required to grow a pure phase of MoS₂ was determined by turning off sulfur vapor flow during the cooling cycle at different temperatures namely 1000, 900, 800, and 700 °C. The critical temperature is between 900 °C and 800 °C. Turning off sulfur vapor flow at 700 °C leads to the growth of highly textured MoS₂ with the highest Hall mobility and the best crystallinity as determined by x-ray diffraction and Raman measurements. On the other hand, turning off sulfur vapor flow at 1000 °C leads to the growth of MoO₃-x phase in addition to MoS₂ phase due to the unavoidable presence of oxygen (due to vacuum leaks), the absence of sulfur vapor, and the relatively high thermodynamic stability of MoO₃-x phase at elevated temperatures. The as-grown MoS₂ has p-type conductivity. The origin of the majority carrier is unintentional dopants. Both n- and p-type natural crystals of MoS₂ have been reported earlier which supports our claim [27]. The mobility of the grown film increases with improvements in crystallinity. The highest Hall mobility was 20
cm²/Vs. The carrier concentration was on the order of 10¹⁷ cm⁻³. The mobility of MoS₂ increases by 35% as the temperature rises from 26.85 °C to 276.85 °C, which is very useful for electronic devices which become hot under normal operation, such as transistors. The absorption coefficients of the grown films were on the order of ~ 10⁴ cm⁻¹. The refractive index, extinction coefficient, real and imaginary part of the dielectric constant of the grown films have been determined in the 250-2500 nm range.

Doping of MoS₂ is essential for the fabrication of electronic and optoelectronic devices. Ti-doped MoS₂ was grown by LPCVD process we developed in this work. Different growth temperatures were studied. The gown films at 1000 °C were pure MoS₂ as indicated from x-ray diffraction and Raman measurements. The films grown at a lower temperature, namely 900 °C (shorter time) have Ti₂S phase. Hall effect and hot probe measurements demonstrated p-type conductivity in the films grown at 1000 °C with a mobility of 0.85 cm²/Vs at 300 K. The carrier concentration was 3.5×10^{16} cm⁻³.

The decrease in carrier concentration of Ti-doped MoS₂ in comparison with undoped MoS₂ indicates that Ti acts as a donor in MoS₂. Secondary ion mass spectroscopy (SIMS) revealed a Gaussian diffusion of Ti in MoS₂ sample grown at 1000 °C and 900 °C, which is expected for limited source diffusion. The absorption coefficient of sample A of Ti-doped MoS₂ was on the order of ~ 10⁴ cm⁻¹, but four-times greater than the absorption coefficient of undoped MoS₂. The refractive index, extinction coefficient, real and imaginary part of the dielectric constant of sample A of Ti-doped MoS₂ have been determined in the 250-2500 nm range.
Fluorine-doped tin oxide (FTO) was grown by a cheap aqueous-spray-based method. This method is very promising for large-scale applications. The control of fluorine dopants atoms in the grown films has significant effects on its electrical and optical properties. The aim of this study was to correlate the concentration of fluorine atoms in the solution to the actual concentration in the grown films. A wide range of F nominal concentrations from 0.1 to 20 at% has been studied. Three groups of samples labeled A, B, and C was studied. Group C was the best in terms of conductivity and fluorine concentration uniformity across the thickness.
APPENDIX A:
GAS FLOW CALCULATIONS
Flowmeters are a very important component in a chemical vapor deposition system, without the complete knowledge of their working principles, and how to properly use them in different pressure conditions, researchers will not be able to reproduce the published results. Therefore, here we will give the essential information needed to properly use variable area flowmeters (Rotameters). Rotameters are very popular flowmeters because they are relatively cheap, do not require a power supply, and can be made from different materials which allow their usage in diverse applications.

A.1 The Physical Description of a Rotameter

Rotameter is a tapered tube (usually from borosilicate glass, but it can be made from other materials depending on the application), where the bottom area of this tube (inlet) is smaller than the top area (outlet). Inside this tube, there is a float, which can be made from different materials and shapes according to the application. We consider here that the tube is set up vertically (this is a must for the rotameter to work properly if the float is not confined to the center by a spring or any other way) and the float is free to move inside the tube. As fluid flow upward, it pushes the float upward by the action of buoyancy force and drag force, on the other hand, the weight of the float acting downward [156]. At equilibrium, the total upward forces cancel the downward force, and this position indicates the flow rate [156]. Rotameters are variable area flowmeters because the area through which the fluid flow increase as the flow rate increase [156]. The principle on which rotameters are based is that the differential pressure across the tube is constant, by increasing the area through which the gas flow as the flow rate increases.
There are two common types of rotameters, direct reading, and correlated reading rotameters. A direct reading rotameters can be used for specific gas, and we can read the flow rate directly from the position of the float in the tube in the units indicated on the tube or as indicated by the manufacturer. A correlated reading rotameter can be used to measure the flow rate of a variety of gases. Common tube scales are 65mm and 150mm. A reading on this scale is correlated to the standard flow rate of a specific gas. Correlation tables for specific gases are provided by the manufacturers. The 150mm scale is better than the 65mm scale because it results in more resolution.

Many factors can affect the reliability of readings such as viscosity variation, and changes in fluid density. We can design rotameters which can handle viscosity variation over a wide range, while it can handle changes in fluid density over a smaller range [156].

A.2 Corrections for the Metered Gas Type

It is important to note that, we may have correlation tables for air (which is the commonly available tables), but we want to measure the standard flow rate of other gas such as argon or nitrogen. In this case, we should use an equation to calculate the correct standard flow for this metered gas, under the condition that the temperature and pressure in the lab are the same as the standard temperature and pressure:

\[
Q_{\text{gas}} = \frac{Q_{\text{air}}}{\sqrt{G}}
\]  

(A.1)
Where $Q_{gas}$ is the corrected standard flow for the metered gas, $Q_{air}$ is the correlated standard flow for the air which we get from the table, and $G$ is the specific gravity of the metered gas.

Where specific gravity is the ratio of the density of a gas to the density of air, at standard temperature (70 F) and pressure (14.7 psia). By noting that the density of air, at standard conditions, is given by:

$$
\rho_{air} = 1.225 \text{ kg/m}^3 = 0.001225 \text{ gm/ml (gm/cm}^3) \quad (A.2)
$$

We can rewrite the last equation as:

$$
Q_{gas} = \frac{Q_{air}}{\sqrt{G}} = Q_{air} \times \frac{\rho_{air}}{\rho_{gas}} = Q_{air} \times \sqrt{\frac{0.001225}{\rho_{gas}}} \quad (A.3)
$$

Where $\rho_{gas}$ is the density of the metered gas, at standard conditions in gm/ml (gm/cm$^3$) units. Or more generally we can determine the standard Flow of other gas, $Q_2$ if we know the standard flow of first gas, $Q_1$ (by looking it up from the table), and their densities according to the following general equation:

$$
Q_2 = Q_1 \times \sqrt{\frac{\rho_1}{\rho_2}} \quad (A.4)
$$

Where $Q_2$ is the corrected standard flow for the metered gas, $Q_1$ is the correlated standard flow for the gas which we have its correlated table, $\rho_2$ is the density of the metered gas, $\rho_1$ is the density of the gas which we have its correlated table.
A.3 Corrections for the Metered Gas Temperature and Pressure

Most of the time the temperature and the working pressure in the lab are not the same as the standard temperature and pressure. In this case, we need to correct for that deviation by using the following equation:

\[ Q_{gc} = Q_{gt} \times \sqrt{\frac{T_s}{T}} \times \frac{P}{P_s} \]  

(A.5)

Where \( Q_{gc} \) is the corrected standard flow for the metered gas, \( Q_{gt} \) is the correlated standard flow for the metered gas which we get from the table, \( T_s \) and \( P_s \) are the standard Absolute temperature (530 R (70°F) or 294 K (21°C)) and pressure (14.7 psia), and \( T \) and \( P \) are the temperature in the lab at the time of measurements and the working pressure. Note the pressure, \( P \) is the local pressure plus the gauge pressure. For example, if the local pressure is 14.8 psia, and the gauge pressure is 20 psig, then \( P \) is given by:

\[ P = 14.8 + 20 = 34.8 \text{ psia} \]  

(A.6)

Also, the use of Rankine units for temperature is widely used. The temperature of 459.67 R is equal to 0 F, and one Rankine degree is exactly equal to one Fahrenheit degree. Practically 0 F is rounded to 460 R, Therefore:

\[ T_s = 460 \text{ R} + 70 \text{ °F} = 530 \text{ R} \]  

(A.7)
And $T$ is given by adding the temperature in the lab at the time of measurements to 460 R. For example, if the temperature in the lab at the time of measurements is 72 °F, then $T$ is given by:

$$T = 460 \text{ R} + 72 \text{ °F} = 532 \text{ R}$$ (A.8)

A.4 Corrections for the Metered Gas Type, Temperature, and Pressure

We can do the three last corrections, in one step using the following equation:

$$Q_2 = Q_1 \times \sqrt{\frac{\rho_1 T_s P}{\rho_2 T P_s}}$$ (A.9)

Where $Q_2$ is the corrected standard flow for the metered gas, $Q_1$ is the correlated standard flow for the gas which we have its correlated table, $\rho_2$ is the density of the metered gas, $\rho_1$ is the density of the gas which we have its correlated table, $T_s$ and $P_s$ are the standard Absolute temperature (530 R (70°F) or 294 K (21°C)) and pressure (14.7 psia), and $T$ and $P$ are the Absolute temperature in the lab at the time of measurements and working pressure. In the case, we have a correlated table of air we can rewrite the last equation as:

$$Q_{\text{gas}} = Q_{\text{air}} \times \sqrt{\frac{\rho_{\text{air}} T_s P}{\rho_{\text{gas}} T P_s}} = Q_{\text{air}} \times \sqrt{\frac{0.001225 T_s P}{\rho_{\text{gas}} T P_s}} = Q_{\text{air}} \times \sqrt{\frac{T_s P}{G T P_s}}$$ (A.10)

Where $Q_{\text{gas}}$ is the corrected standard flow for the metered gas, $Q_{\text{air}}$ is the correlated standard flow for the air which we get from the table, $G$ is the specific gravity of the metered gas, $\rho_{\text{gas}}$ is the density of the metered gas, at standard conditions in
gm/ml \( (\text{gm/cm}^3) \) units, \( T_s \) and \( P_s \) are the standard absolute temperature (530 R \( (70^\circ F) \) or 294 K \( (21^\circ C) \)) and pressure (14.7 psia), and \( T \) and \( P \) are the absolute temperature in the lab at the time of measurements and the working pressure.

A.5 Working Pressure

Working pressure or operating pressure is the pressure inside the rotameter tube if we ignore the pressure drop across the tube. It is important to recognize that we will have different situations depending on the application. For example, if the outlet of the rotameter is connected to a chamber at atmospheric pressure the situation will be totally different than if the chamber is under vacuum. The working pressure is the pressure at the output of the rotameter. It is important to note that, the needle valve at the inlet of the rotameter screen the pressure from the output of the gas cylinder. The location of the needle valve is very important when dealing with gases, due to its compressible property. The point is that pressure changes result in gas compression and consequently changes in gas density which affects the upward force and the accuracy of the readings. Let us now discuss that for different situations.

A.5.1 Chamber at Atmospheric Pressure

If the chamber is at atmospheric pressure as shown in figure A.1(a), it is better to have the needle valve which always included in the rotameter at the inlet, because that way the working pressure will be the atmospheric pressure which is relatively very stable. The
needle valve will screen the pressure at the output of the gas cylinder from the rotameter inlet.

Figure 8.1: The position of the needle valve must be (a) at the inlet of rotameter if the chamber is at atmospheric pressure or (b) at the outlet if the chamber is under vacuum.

A.5.2 Chamber at Vacuum Pressure

If the chamber is under vacuum as shown in figure A.1(b), it is better to have the needle valve at the rotameter outlet. If the valve was at the rotameter inlet originally, the rotameter should be dismantled and the tube inverted, then sealed tight again. The working pressure,
in this case, is the pressure at the output of the gas cylinder since there is nothing screen this pressure from the inlet of the rotameter and consequently its output. Also, the needle valve at the outlet will screen the rotameter tube from the vacuum pressure.

A.5.3 No Needle Valve at All

In this case, the pressure at the output of the rotameter will be considered the operating pressure. Note the pressure drop across the tube is negligible.

A.5.4 Two Needle Valves at the Inlet and Outlet of the Rotameter

In this case, the operating pressure will be the pressure at the output of the rotameter and before the needle valve. In this dissertation, the float was a stainless-steel bead, and we took the readings by looking horizontally at the same level of the bead, such that the marker on the tube at the center of the float. The flowmeters used in this dissertation are correlated flowmeters, such that the reading we get does not represent the actual reading of fluid flow of any kind, but we use tables provided by the manufacturers which correlate these readings to the actual flow of specific fluid. In the case of APCVD experiments, the needle valve was at the inlet of the rotameter, while in the case of LPCVD experiments the needle valve was at the outlet of the rotameter.
APPENDIX B:
XRD CALCULATIONS
The relation between the crystallographic planes is essential to perform advanced x-ray diffraction experiments, which require the rotation of the investigated sample in three dimensions. The angle between two different crystallographic planes \((h_1k_1l_1)\) and \((h_2k_2l_2)\), can be calculated by using the following equation [157]:

\[
\cos \theta = \frac{\mathbf{r}_{H_1} \cdot \mathbf{r}_{H_2}}{\mathbf{r}_{H_1} \cdot \mathbf{r}_{H_2}} = \frac{d_{H_1} d_{H_2}}{} \mathbf{r}_{H_1} \cdot \mathbf{r}_{H_2} \tag{B.1}
\]

Where \(\mathbf{r}^* = ha^* + kb^* + lc^*\) is a vector in the reciprocal space, which is normal to the \((hkl)\) family of lattice planes [157]. The spacing between these \((hkl)\) planes in the direct lattice is given by:

\[
d_H = \frac{1}{r^*} \tag{B.2}
\]

We can compute the scalar product of \(\mathbf{r}_{H_1}^*\) and \(\mathbf{r}_{H_2}^*\) by using the metric tensor, \(G^*\) for the reciprocal lattice (also called the metric matrix) [157].

\[
G^* = \begin{pmatrix}
a^* \cdot a^* & a^* \cdot b^* & a^* \cdot c^* \\
b^* \cdot a^* & b^* \cdot b^* & b^* \cdot c^* \\
c^* \cdot a^* & c^* \cdot b^* & c^* \cdot c^*
\end{pmatrix} \tag{B.3}
\]

Therefore:

\[
\mathbf{r}_{H_1}^* \cdot \mathbf{r}_{H_2}^* = H_1 G^* H_2 \tag{B.4}
\]

\[
\mathbf{r}_{H_1}^* = h_1a^* + k_1b^* + l_1c^* \tag{B.5}
\]

\[
\mathbf{r}_{H_2}^* = h_2a^* + k_2b^* + l_2c^* \tag{B.6}
\]
The angles between the base vectors in the reciprocal space are $\gamma^*$, $\alpha^*$, and $\beta^*$. Where $\gamma^*$ is the angle between $a^*$ and $b^*$, $\alpha^*$ is the angle between $b^*$ and $c^*$, and $\beta^*$ is the angle between $a^*$ and $c^*$.

$$r_{H_1}^* = (h_1 \ k_1 \ l_1) \begin{pmatrix} a^* \cdot a^* & a^* \cdot b^* & a^* \cdot c^* \\ b^* \cdot a^* & b^* \cdot b^* & b^* \cdot c^* \\ c^* \cdot a^* & c^* \cdot b^* & c^* \cdot c^* \end{pmatrix} \begin{pmatrix} h_2 \\ k_2 \\ l_2 \end{pmatrix}$$  \hspace{0.5cm} (B.7)

The relation between direct lattice and the reciprocal lattice is different from a crystal system to another. For the cubic system, the relation is as follows:

$$a^* \parallel a \quad b^* \parallel b \quad c^* \parallel c$$  \hspace{0.5cm} (B.11)

$$a^* = \frac{1}{a} \quad b^* = \frac{1}{b} \quad c^* = \frac{1}{c}$$  \hspace{0.5cm} (B.12)

$$\gamma^* = \alpha^* = \beta^* = \frac{\pi}{2}$$  \hspace{0.5cm} (B.13)
Therefore, the metric tensor, $G^*$ reduces to:

$$G^* = \begin{pmatrix} a^*^2 & 0 & 0 \\ 0 & b^*^2 & 0 \\ 0 & 0 & c^*^2 \end{pmatrix}$$  \hspace{1cm} (B.14)

For the hexagonal and trigonal (P) system, $c^* \parallel c$ while $a^* \ & b^*$ are in the (a, b) plane.

$$a^* = b^* = \frac{2}{a\sqrt{3}} \quad c^* = \frac{1}{c} \hspace{1cm} (B.15)$$

$$\gamma^* = \frac{\pi}{3} \quad \alpha^* = \beta^* = \frac{\pi}{2} \hspace{1cm} (B.16)$$

Therefore, the metric tensor, $G^*$ reduces to:

$$G^* = \begin{pmatrix} a^*^2 & a^*b^*/2 & 0 \\ a^*b^*/2 & b^*^2 & 0 \\ 0 & 0 & c^*^2 \end{pmatrix}$$  \hspace{1cm} (B.17)

Consequently, the spacing between adjacent (hkl) planes in the direct lattice for the cubic system is given by:

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2} \hspace{1cm} (B.18)$$

And for the hexagonal and trigonal (P) system is given by:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2} (h^2 + k^2 + hk) + \frac{l^2}{c^2} \hspace{1cm} (B.19)$$
The angle between two different crystallographic planes \((h_1k_1l_1)\) and \((h_2k_2l_2)\) for the cubic system is given by [158]:

\[
\cos \theta = \frac{h_1h_2+k_1k_2+l_1l_2}{\sqrt{(h_1^2+k_1^2+l_1^2)(h_2^2+k_2^2+l_2^2)}} \tag{B.20}
\]

And for the hexagonal system is given by:

\[
\cos \theta = \frac{h_1h_2+k_1k_2+\frac{1}{3}(h_1k_2+h_2k_1)+\frac{3}{4}a^2c^2l_2}{\sqrt{(h_1^2+k_1^2+h_1k_1+\frac{3}{4}a^2c^2l_1^2)(h_2^2+k_2^2+h_2k_2+\frac{3}{4}a^2c^2l_2^2)}} \tag{B.21}
\]

Crystal structure of Mo unit cell is shown in figure B.1. The angles between the (110) plane of Molybdenum and the other planes have been calculated using a MATLAB code and listed in table B.1.
Table B.1. The angle between different planes and the (110) plane of Molybdenum (PDF# 00-004-0809), in addition to the complementary angle, which is the tilt angle to get a diffraction in a phi-scan.

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<th>Angle between the first and second plane ($^\circ$)</th>
<th>Complementary angle (°) Which is the tilt angle $\chi$ with respect to the first plane</th>
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The following figures show the angles between the (110) plane of Molybdenum and the other planes graphically.

Figure B.2. (a) (110) plane of Mo, (b) (200) plane of Mo and (c) (110) and (200) planes of Mo.
Figure B.3. (a) (110) plane of Mo, (b) (211) plane of Mo and (c) (110) and (211) planes of Mo.

Figure B.4. (a) (110) plane of Mo, (b) (220) plane of Mo and (c) (110) and (220) planes of Mo.
Figure B.5. (a) (110) plane of Mo, (b) (310) plane of Mo and (c) (110) and (310) planes of Mo.

Figure B.6. (a) (110) plane of Mo, (b) (222) plane of Mo and (c) (110) and (222) planes of Mo.
(a) (110) the plane of Mo

(b) (321) the plane of Mo

(c) (110) and (321) planes of Mo

Figure B.7. (a) (110) plane of Mo, (b) (321) plane of Mo and (c) (110) and (321) planes of Mo.

Figure B.8. A schematic of the sample rotation, to measure the x-ray diffraction from the (200) and (321) planes of Mo.
Figure B.8 shows a schematic of the sample rotation, to measure the x-ray diffraction from the (200) and (321) planes of Mo. The crystal structure of a sapphire unit cell is shown in figure B.9. The (006) plane is highlighted in magenta.

![Figure B.9. A unit cell of sapphire. The (006) plane is highlighted in magenta.](image)

Table B.2 lists the angles between the (006) plane of sapphire and all other planes of sapphire, while table B.3 lists the angle between the (002) plane of MoS$_2$ and all other planes of MoS$_2$.

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<th>Angle between the first and second plane (°)</th>
<th>Complementary angle (°) Which is the tilt angle χ with respect to the first plane</th>
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APPENDIX C:
ELECTRICAL TRANSPORT CALCULATIONS
C.1 Van der Pauw Technique: Sheet Resistance

In this section, we will explain the Van der Pauw technique for sheet resistance measurement. Figure C.1 shows a schematic representation of a sample with four square contacts labeled 1, 2, 3, and 4. Here we consider no magnetic field is applied externally. We force current through two contacts and measure the voltage between the other two contacts. \( R_{12,34} \) and \( R_{23,41} \) can be determined from direct experimental measurements as follows:

\[
R_{12,34} = \frac{V_{34}}{I_{12}}
\]  

(C.1)

\[
R_{41,23} = \frac{V_{23}}{I_{41}}
\]  

(C.2)

Then the sheet resistance \( R_s \) and/or the resistivity \( \rho \) can be determined from the following equations by a numerical iteration:
$e^{-\frac{\pi}{R_s}R_{12,34}} + e^{-\frac{\pi}{R_s}R_{41,23}} = 1$ \hspace{1cm} (C.3)

$e^{-\frac{\pi t}{\rho}R_{12,34}} + e^{-\frac{\pi t}{\rho}R_{41,23}} = 1$ \hspace{1cm} (C.4)

Where $t$ is the sample thickness. In the case of symmetry (such as square samples) $R_{12,34} = R_{41,23} = \frac{V}{I}$ and the last equation will be simplified to:

$2 e^{-\frac{\pi}{R_s}R_{12,34}} = 1$ \hspace{1cm} (C.5)

$R_{12,34} = \frac{\pi}{R_s} \ln 2$ \hspace{1cm} (C.6)

And the sheet resistance and the resistivity are given by:

$R_s = \frac{\pi V}{\ln 2 I}$ \hspace{1cm} (C.7)

$\rho = \frac{\pi V}{\ln 2 I t}$ \hspace{1cm} (C.8)

$R_s = \frac{\rho}{t}$ \hspace{1cm} (C.9)

Figure C.2: A van der Pauw sample of arbitrary shape.
The derivation of the transcendental equation $e^{-\frac{\pi t}{\rho} R_{12,34}} + e^{-\frac{\pi t}{\rho} R_{14,32}} = 1$ is as follows. First, we should show that this equation holds for a particular shape of the sample. Second, we should show that if this holds for a particular shape, it should hold for any shape (figure C.2). We will show the derivation of the first part only here. For our particular shape, we choose a semi-infinite plane (figure C.3) with contacts $M$, $N$, $O$, and $P$ along its boundary, spread at distances $a$, $b$, and $c$ respectively.

![Semi-infinite half-plane diagram](image)

**Figure C.3:** A van der Pauw sample of semi-infinite plane shape.

First, we will solve the current pattern of one contact of the four contacts. Imagine a cylinder with height $t$, where $t$, is the thickness of the sample as shown in figure C.4. The current density and the electric field are given by:

$$J = \frac{I}{A} = \frac{1}{\pi r t} = \sigma E$$  \hspace{1cm} (C.10)

$$E = \frac{1}{\pi r t \sigma} = \frac{I}{\pi r t} = -\nabla V$$  \hspace{1cm} (C.11)
The voltage is given by:

\[ V = - \int_{r_o}^{r} E \, dr = - \int_{r_o}^{r} \frac{I \rho}{\pi r t} \, dr \]  (C.12)

Where \( r_o \) is a point far enough from the source such that \( V(r_o) = 0 \) (a reference point).

\[ V = V(r) - V(r_o) = -\frac{I \rho}{\pi t} \int_{r_o}^{r} \frac{1}{r} \, dr = -\frac{I \rho}{\pi t} \ln \left( \frac{r}{r_o} \right) \]  (C.13)

\[ V(r) - V(r_o) = -\frac{I \rho}{\pi t} \int_{r_o}^{r} \frac{1}{r} \, dr = -\frac{I \rho}{\pi t} \ln \left( \frac{r}{r_o} \right) \]  (C.14)

Here we force current such that it enters at M contact and come out from N contact. We measure the voltage difference between O and P contacts (figure C.3). To calculate this voltage difference, first, we will calculate the contribution from contact M at both contacts O and P.

\[ V(P) = -\frac{I \rho}{\pi t} \ln \left( \frac{a+b+c}{r_o} \right) \]  (C.15)
\[ V(O) = -\frac{1}{\pi t} \ln \left( \frac{a+b}{r_o} \right) \]  
\[ (C.16) \]

\[ V_{PO} = -\frac{1}{\pi t} \left[ \ln \left( \frac{a+b+c}{r_o} \right) - \ln \left( \frac{a+b}{r_o} \right) \right] = -\frac{1}{\pi t} \left[ \ln \left( \frac{a+b+c}{r_o} \right) \right] \]  
\[ (C.17) \]

\[ V_{PO} = -\frac{1}{\pi t} \ln \left( \frac{a+b+c}{a+b} \right) \]  
\[ (C.18) \]

Similarly, the contribution from contact N at both contacts O and P is given by.

\[ V'_{PO} = +\frac{1}{\pi t} \ln \left( \frac{b+c}{b} \right) \]  
\[ (C.19) \]

\[ R_{MN,OP} = \frac{V_{PO} + V'_{PO}}{t} = -\frac{\rho}{\pi t} \ln \left( \frac{a+b+c}{a+b} \right) + \frac{\rho}{\pi t} \ln \left( \frac{b+c}{b} \right) \]  
\[ (C.20) \]

\[ R_{MN,OP} = +\frac{\rho}{\pi t} \ln \left( \frac{a+b}{a+b+c} \right) + \frac{\rho}{\pi t} \ln \left( \frac{b+c}{b} \right) = +\frac{\rho}{\pi t} \ln \left( \frac{(a+b)(b+c)}{b(a+b+c)} \right) \]  
\[ (C.21) \]

Similarly:

\[ R_{NO,PM} = +\frac{\rho}{\pi t} \ln \left( \frac{(a+b)(b+c)}{ac} \right) \]  
\[ (C.22) \]

\[ \frac{\pi t R_{MN,OP}}{\rho} = \ln \left( \frac{(a+b)(b+c)}{b(a+b+c)} \right) \]  
\[ (C.23) \]

\[ \frac{\pi t R_{NO,PM}}{\rho} = \ln \left( \frac{(a+b)(b+c)}{ac} \right) \]  
\[ (C.24) \]

\[ e^{-\frac{\pi t}{\rho} R_{MN,OP}} = \frac{b(a+b+c)}{(a+b)(b+c)} \]  
\[ (C.25) \]

\[ e^{-\frac{\pi t}{\rho} R_{NO,PM}} = \frac{ac}{(a+b)(b+c)} \]  
\[ (C.26) \]
By using the following equation:

\[(a + b)(b + c) = ab + ac + bb + bc = b(a + b + c) + ac\]  \hspace{1cm} (C.27)

\[e^{-\frac{\pi t}{\rho}R_{MN,OP}} + e^{-\frac{\pi t}{\rho}R_{NO,PM}} = \frac{b(a+b+c)}{(a+b)(b+c)} + \frac{ac}{(a+b)(b+c)} = \frac{b(a+b+c)+ac}{(a+b)(b+c)}\]  \hspace{1cm} (C.28)

\[e^{-\frac{\pi t}{\rho}R_{MN,OP}} + e^{-\frac{\pi t}{\rho}R_{NO,PM}} = 1\]  \hspace{1cm} (C.29)

This is the end of the derivation for a specific shape.

C.2 Precise Measurement of Sheet Resistance

A precise measurement of sheet resistance can be performed by taking several reciprocal measurements and averaging them (up to 8). The following equation lists the equations for these measurements.

\[R_{14,23} = \frac{V_{23}}{I_{14}}\]  \hspace{1cm} (C.30)

\[R_{41,32} = \frac{V_{32}}{I_{41}}\]  \hspace{1cm} (C.31)

\[R_{23,14} = \frac{V_{14}}{I_{23}}\]  \hspace{1cm} (C.32)

\[R_{32,41} = \frac{V_{41}}{I_{32}}\]  \hspace{1cm} (C.33)

\[R_{43,12} = \frac{V_{12}}{I_{43}}\]  \hspace{1cm} (C.34)
\[ R_{34,21} = \frac{V_{21}}{I_{34}} \]  

(C.35)

\[ R_{12,43} = \frac{V_{43}}{I_{12}} \]  

(C.36)

\[ R_{21,34} = \frac{V_{34}}{I_{21}} \]  

(C.37)

Then we average these measurements using the following equation:

\[ R_A = \frac{(R_{14,23} + R_{41,32} + R_{23,14} + R_{32,41})}{4} \]  

(C.38)

\[ R_B = \frac{(R_{43,12} + R_{34,21} + R_{12,43} + R_{21,34})}{4} \]  

(C.39)

By solving the following equation by a numerical method such as Newton-Raphson method, we can determine the sheet resistance.

\[ e^{-\frac{\pi}{R_s} R_A} + e^{-\frac{\pi}{R_s} R_B} = 1 \]  

(C.40)

C.3 Newton-Raphson Method

Following the algorithm of the national institute of standards and technology (NIST) we can determine the sheet resistance numerically. We will define \( Z_i \) as follows:

\[ R_s = \frac{1}{Z_i} \]  

(C.41)

Where \( R_s \) is the sheet resistance. Then we will calculate an initial value of \( Z_i \), (which we will call \( Z_0 \)) as follows:
\[ Z_0 = \frac{2 \ln 2}{\pi (R_A + R_B)} \]  \hspace{1cm} (C.42)

Then we will calculate the \( i \)th iteration of \( y_i \), as follows:

\[ y_i = e^{-\pi Z_{i-1} R_A} + e^{-\pi Z_{i-1} R_B} \]  \hspace{1cm} (C.43)

Then we will calculate the \( i \)th iteration of \( Z_i \), as follows:

\[ Z_i = Z_{i-1} - \frac{(1 - y_i)}{\pi (R_A e^{-\pi Z_{i-1} R_A} + R_B e^{-\pi Z_{i-1} R_B})} \]  \hspace{1cm} (C.44)

We will repeat the last two calculations (manually or using software) until

\[ \frac{Z_i - Z_{i-1}}{Z_i} < \delta \]  \hspace{1cm} (C.45)

Where \( \delta \) is the error limit which we can set it to a small number such as \( \delta = 0.0005 \), which corresponding to an error of 0.05%.

C.4 Hall Effect Measurements

Hall effect measurement is one of the very important techniques to determine the electrical properties of semiconductor materials. We will consider the sample is prepared as shown in figure C.5.
Figure C.5: A schematic representation of Van der Pauw sample. The direction of current, Hall voltage and magnetic field for Hall effect measurement are illustrated.

By considering a p-type semiconductor material, where the conductivity $\sigma \sim \sigma_p$ because the number of holes is higher than the number of electrons $p \gg n$. The conductivity is given by:

$$\sigma = \sigma_p = q_p \mu_p$$  \hspace{1cm} (C.46)

By applying the current in the x-direction, the current density is given by:

$$J_x = \frac{l_x}{w t} = \sigma E_x \sim \sigma_p E_x = q_p \mu_p E_x$$  \hspace{1cm} (C.47)
The average hole drift velocity is given by:

\[ v_x = \mu_p E_x = \frac{j_x}{q_p} \]  \hspace{1cm} (C.48)

In the y-direction, we will have two forces, the magnetic field and the electric force from charge pile up in the y-direction.

\[ F_B = q v_x \times B_z \]  \hspace{1cm} (C.49)

\[ F_E = q E_y \]  \hspace{1cm} (C.50)

These forces balance each other as follows:

\[ q E_y = q v_x \times B_z \]  \hspace{1cm} (C.51)

By substituting equation (C.48) into (C.51) we get:

\[ E_y = \frac{j_x}{q_p} B_z \]  \hspace{1cm} (C.52)

We define the Hall coefficient as follows:

\[ R_H \equiv \frac{1}{q_p} \]  \hspace{1cm} (C.53)

\[ E_y = R_H j_x B_z \]  \hspace{1cm} (C.54)

The Hall voltage is given by:

\[ V_H = E_y w \]  \hspace{1cm} (C.55)
By substituting equation (C.54) in (C.55) we get:

\[ V_H = R_H J_x B_z w \]  
(C.56)

Or explicitly:

\[ V_H = \frac{1}{q \, p} J_x B_z w \]  
(C.57)

\[ J_x = \frac{I_x}{w \, t} \]  
(C.58)

\[ V_H = \frac{1}{q \, p} \frac{I_x}{t} B_z \]  
(C.59)

The carrier concentration can be calculated as follows:

\[ p = \frac{I_x B_z}{q \, t \, V_H} \]  
(C.58)

Similarly:

\[ R_H \equiv \frac{1}{q \, p} = \frac{t \, V_H}{I_x \, B_z} \]  
(C.59)

By using equation (C.46) and (C.59) we can determine the mobility as follows:

\[ \mu_p = \frac{\sigma_p}{q \, p} = R_H \sigma_p = \frac{R_H}{\rho} = \frac{t \, V_H}{\rho \, I_x \, B_z} \]  
(C.60)
The sign of the Hall voltage is what determines the type of majority carrier in a semiconductor. Since this experiment has many variables including magnetic field direction, current direction, contacts order (clockwise vs. counterclockwise), it would be better if these variables were analyzed before doing the experiment. The expected signs of the Hall voltages of n-type material under different magnetic field polarities and different current polarities are shown in figures C.6 and C.7. The electrons move against current direction (from negative terminal to positive terminal). The numbers of the contacts are ordered clockwise as in the MMR software schematics. Source + is where we apply current and source − is the ground. Meter + is where we sense the voltage and meter − is the ground.
Figure C.6: A schematic representation of Hall voltage polarity of an n-type semiconductor, using two opposite current polarities. The magnetic field direction is out of the page.
Figure C.7: A schematic representation of Hall voltage polarity of an n-type semiconductor, using two opposite current polarities. The magnetic field direction is in the page.
The optical constants can be determined from the measurements of transmittance and reflectance using the matrix method [147]. In this rigorous method, Maxwell’s equations relating the amplitudes of the electric field and magnetic field at the interface between each two-different media is written using matrix form [147].

Figure D.1: A schematic of N-layers structure consisting of different media.
For the case of normal incidence, the boundary conditions between any two-different media, such that the light is incident from the m-1th layer on the mth layer as shown in figure D.1, can be written in matrix form as follows [147-148]:

\[
\begin{pmatrix}
E_{m-1}^+ \\
E_{m-1}^-
\end{pmatrix} = \frac{1}{t_m} \begin{pmatrix}
e^{i\delta_{m-1}} & r_m e^{i\delta_{m-1}} \\
r_m e^{-i\delta_{m-1}} & e^{-i\delta_{m-1}}
\end{pmatrix}
\begin{pmatrix}
E_m^+ \\
E_m^-
\end{pmatrix}
\]

(D.1)

Which can be written in a simpler form as follows:

\[
\begin{pmatrix}
E_{m-1}^+ \\
E_{m-1}^-
\end{pmatrix} = \frac{1}{t_m} \left( C_m \right)
\begin{pmatrix}
E_m^+ \\
E_m^-
\end{pmatrix}
\]

(D.2)

Where \(C_m\) is given by:

\[
\left( C_m \right) = \begin{pmatrix}
e^{i\delta_{m-1}} & r_m e^{i\delta_{m-1}} \\
r_m e^{-i\delta_{m-1}} & e^{-i\delta_{m-1}}
\end{pmatrix}
\]

(D.3)

Where \(E_m^+\) and \(E_m^-\) represent the incident and reflected electric field amplitudes of the waves travelling in the mth layer respectively [149]. Similarly \(E_{m-1}^+\) and \(E_{m-1}^-\) represent the incident and reflected electric field amplitudes of the waves travelling in the m-1th layer respectively [147]. \(r_m\) and \(t_m\) and are the Fresnel reflection and transmission coefficient respectively, given by:

\[
r_m = \frac{E_{m-1}^-}{E_{m-1}^+} = \frac{N_{m-1} - N_m}{N_{m-1} + N_m}
\]

(D.4)

\[
t_m = \frac{E_m^+}{E_{m-1}^-} = \frac{2N_{m-1}}{N_{m-1} + N_m}
\]

(D.5)
Where \( N_m \) and \( N_{m-1} \) are the complex refractive index of the \( m^{th} \) and \( m-1^{th} \) layer respectively. The factor \( i\delta_{m-1} \) can be written as follows:

\[
i\delta_{m-1} = i \frac{2\pi}{\lambda} (n_{m-1} - ik_{m-1}) d_{m-1}
\]  

(D.6)

Which can be rewritten in terms of the attenuation and phase factors as follows:

\[
i\delta_{m-1} = a_{m-1} + i\gamma_{m-1}
\]  

(D.7)

\[
a_{m-1} = \frac{2\pi}{\lambda} k_{m-1} d_{m-1}
\]  

(D.8)

\[
\gamma_{m-1} = \frac{2\pi}{\lambda} n_{m-1} d_{m-1}
\]  

(D.9)

For a system of \( N \) layers, we should determine the relationship between the incident amplitude \( E_0^+ \) and the transmitted amplitude \( E_{N+1}^+ \) to determine the transmission coefficient, \( t_N \), and the relation between the incident amplitude \( E_0^+ \) and the reflected amplitude \( E_0^- \) to determine the reflection coefficient \( r_N \). If we determined the relation between each successive layers (media), we can determine the relation between the first medium and the last one by the following relation:

\[
\begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} = \frac{(c_1)(c_2) \ldots (c_{N+1})}{t_1 t_2 \ldots t_{N+1}} \begin{pmatrix} E_{N+1}^+ \\ E_{N+1}^- \end{pmatrix}
\]  

(D.10)

It is worth to note that we assume no negative-going wave in the \( N+1^{th} \) medium, and therefore \( E_{N+1}^- = 0 \). We can rewrite the matrix product as follows:

168
\[(C_1)(C_2) \ldots (C_{N+1}) = \begin{pmatrix} a & b \\ c & d \end{pmatrix}\]  
(D.11)

\[
\begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} = \frac{1}{t_1 t_2 \ldots \ldots t_{N+1}} \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} E_{N+1}^+ \\ 0 \end{pmatrix} = \frac{1}{t_1 t_2 \ldots \ldots t_{m+1}} \begin{pmatrix} a E_{N+1}^+ \\ c E_{N+1}^+ \end{pmatrix}
\]  
(D.12)

\[E_0^+ = \frac{a E_{N+1}^+}{t_1 t_2 \ldots \ldots t_{N+1}}\]  
(D.13)

\[E_0^- = \frac{c E_{N+1}^+}{t_1 t_2 \ldots \ldots t_{N+1}}\]  
(D.14)

Consequently, the reflection and transmission amplitudes will be given by:

\[R = \frac{E_0^-}{E_0^+} = \frac{c}{a}\]  
(D.15)

\[T = \frac{E_{N+1}^+}{E_0^+} = \frac{t_1 t_2 \ldots \ldots t_{N+1}}{a}\]  
(D.16)

The reflectance, transmittance, and absorptance are given by:

\[R = RR^* = \frac{c c^*}{a a^*}\]  
(D.17)

\[T = \frac{n_{N+1}}{n_0} TT^* = \frac{n_{N+1}}{n_0} \frac{(t_1 t_2 \ldots \ldots t_{N+1})(t_1^* t_2^* \ldots \ldots t_{N+1}^*)}{a a^*}\]  
(D.18)

\[A = 1 - R - T\]  
(D.19)


LIST OF REFERENCES


[129] Y. Zhang, S. Ouyang, Q. Yu, P. Li and J. Ye, Modulation of sulfur partial pressure in sulfurization to significantly improve the photoelectrochemical performance over the Cu2ZnSnS4 photocathode, Chemical Communications (Cambridge), (2015), 51, 74, 14057-14059.


