Growth and Nb-doping of MoS$_2$ towards novel 2D/3D heterojunction bipolar transistors

DISSERTATION

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By

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Abstract

Molybdenum disulfide (MoS$_2$) is a member of a group of layered materials called transition metal dichalcogenides (TMDs) characterized by monolayers consisting of a transition metal atom (Mo or W for example) sandwiched between chalcogen atoms (S, Se, Te) on either side. The monolayers have no out-of-plane bonds and bulk TMDs consist of many monolayers stacked and held together weakly by van der Waals forces. Bulk MoS$_2$ exhibits an indirect band gap of 1.2 eV, but monolayer films exhibit a direct gap of 1.8 eV. MoS$_2$ has been studied for a wide range of applications, many by utilizing micromechanically exfoliated, micron-scale flakes to study its material properties. Study of these flakes points to scaling limitations, and many groups have explored large-area growth methods to produce high-quality, continuous films. This work aims to demonstrate traditional device engineering based on MoS$_2$ including growth, doping, heterostructure study and device design.

We demonstrate single crystal growth of MoS$_2$ by depositing Mo on sapphire substrates and sulfurizing the samples in a chemical vapor transport process. The growth process is robust, and reasonably could be scaled up to wafer-scale processing. The films
exhibited excellent structural qualities, and electrical measurements showed high space-
charge mobility. The MoS$_2$ films were also doped with Nb in order to achieve p-type
mobility. Degenerate doping of the films was demonstrated and confirmed by low
temperature Hall measurement, and film conductivity increased by four orders of
magnitude over unintentionally doped films. The degenerately doped films were shown
to exhibit a Hall mobility of approximately $10\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Heterojunction diodes were formed between degenerately doped p-MoS$_2$ and n-
doped SiC and GaN by direct growth and film transfer, respectively, to form 2D/3D
heterojunctions. Electrical measurements were utilized to extract the conduction band
offsets in MoS$_2$/SiC ($\Delta E_C = 1.6$ eV) and MoS$_2$/GaN ($\Delta E_C = 0.2$ eV) junctions.
Characterization of the heterostructures showed that traditional 3D semiconductor
methods are sufficient to characterize the 2D materials despite the van der Waals gaps
between each MoS$_2$ monolayer. The MoS$_2$/GaN heterojunction was used as the
base/collector junction for a tunneling heterojunction bipolar transistor (THBT) for which
the emitter was atomic layer deposited Al$_2$O$_3$. THBTs showed small common base gain
corresponding with positive transconductance in the common emitter configuration. As
such, the MoS$_2$/GaN heterojunction shows significant promise for future HBT
applications.
Dedication

Dedicated to my mother, father and brother who inspire me.
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# Table of Contents

Abstract .......................................................................................................................... ii

Dedication ...................................................................................................................... iv

Acknowledgments .......................................................................................................... v

Vita .................................................................................................................................... viii

List of Figures .................................................................................................................. xvi

1. Introduction ...................................................................................................................... 1

1.1 Motivation ..................................................................................................................... 3

1.1.1 CVT growth of single crystal MoS₂ ................................................................. 3
1.1.2 P-type doping of MoS₂ with Nb ..................................................................... 4
1.1.3 2D/3D Heterojunctions .................................................................................. 4
1.1.4 MoS₂/GaN-based Tunneling Heterojunction Bipolar Transistor (THBT) ....... 5
1.2 Overview of the thesis ................................................................................................................. 6

2. Chemical vapor transport growth of single crystal MoS₂ .......................................................... 8

2.1 Introduction ................................................................................................................................. 8

2.2 MoS₂ growth with elemental sulfur .......................................................................................... 9

2.2.1 Growth method ....................................................................................................................... 9

2.2.2 Material characterization of vapor-solid grown MoS₂ .......................................................... 11

2.3 MoS₂ growth with MoS₂ powder as sulfur precursor ............................................................... 17

2.3.1 Growth method ..................................................................................................................... 17

2.3.2 Material characterization ........................................................................................................ 18

2.4 Electrical characterization of MoS₂ .......................................................................................... 22

2.4.1 Space-Charge-Limited Transport in MoS₂ ............................................................................ 22

2.4.2 Surface passivation of MoS₂ ............................................................................................... 25

2.5 MoS₂ Photoconductivity .......................................................................................................... 26

2.5.1 Experimental Configuration of Optical Characterization .................................................. 26

2.5.2 Detector Measurements and Persistent Photoconductivity .............................................. 28

2.5.3 Responsivity of MoS₂ Detectors ......................................................................................... 29

2.6 Summary and Conclusion ......................................................................................................... 32

3. P-type doping of MoS₂ with Nb ............................................................................................... 34

3.1 Introduction ................................................................................................................................. 34

3.2 Growth and Characterization of p-MoS₂ ................................................................................. 35

3.2.1 Growth of p-MoS₂ with Layered Metal Precursor ............................................................ 35

3.2.2 Material Characterization of p-MoS₂ with Layered Metal Precursor ............................... 36

3.2.3 p-MoS₂ with Alloyed Metal Precursor ............................................................................... 41

3.3 Electrical characterization of p-MoS₂ ...................................................................................... 43
3.3.1 Hall Measurements ................................................................. 43
3.3.2 Film thickness dependence of Hall mobility ................................. 46
3.3.3 TLM Analysis ........................................................................... 47
3.4 Optical Characterization ............................................................... 48
3.4 Summary and Conclusion .............................................................. 51

4. MoS_2-based 2D/3D Heterojunctions .................................................. 53
4.1 Introduction ................................................................................. 53
4.2 p-MoS_2 on 4H-SiC ..................................................................... 55
  4.2.1 Growth of MoS_2/SiC Heterojunctions ..................................... 55
  4.2.2 MoS_2/SiC Material Characterization ..................................... 56
4.3 Electrical characterization of MoS_2/SiC PN diodes .......................... 58
  4.3.1 Vertical and lateral I-V characteristics .................................... 58
  4.3.2 2D/3D heterojunction transport ............................................ 61
  4.3.3 MoS_2/SiC conduction band offset extraction .......................... 62
4.4 p-MoS_2 on GaN .......................................................................... 65
  4.4.1 Film transfer process for MoS_2/GaN heterojunction ............... 65
  4.4.2 Electrical and optical characterization of MoS_2/GaN heterojunction .... 69
4.5 Summary and Conclusion .............................................................. 76

5. 2D/3D Tunneling Heterojunction Bipolar Transistor ............................ 78
5.1 Introduction ................................................................................. 78
5.2 Emitter/base junction: Al_2O_3/MoS_2 MOS diode ............................ 80
  5.2.1 Al_2O_3/MoS_2 by direct deposition ......................................... 81
  5.2.2 Al_2O_3/MoS_2 with AlO_x transition layer ............................... 82
  5.2.3 Al_2O_3/MoS_2 with MoO_x transition layer .............................. 83
5.3 Base/Collector Junction ................................................................................. 88
  5.3.1 MoS$_2$/SiC and MoS$_2$/GaN Base collector........................................ 88
5.4 2D/3D THBTs .................................................................................................. 89
  5.4.1 Al$_2$O$_3$/p-MoS$_2$/n-SiC THBT ............................................................... 89
  5.4.2 Al$_2$O$_3$/p-MoS$_2$/n-GaN THBT ............................................................ 93
  5.4.3 Al$_2$O$_3$/p-MoS$_2$/n-GaN THBT with device engineering ................. 98
5.5 Summary and Conclusion .............................................................................. 102

6. Conclusions and Future Work .......................................................................... 104
  6.1 Conclusion ..................................................................................................... 104
  6.2 Future Work .................................................................................................. 106
    6.2.1 van der Waals epitaxy of 2D/3D heterojunctions .......................... 106
    6.2.2 GaN/MoS$_2$/GaN HBT .................................................................. 107
    6.2.3 van der Waals epitaxy of other 2D/2D and 2D/3D Heterojunctions .... 107
Bibliography ........................................................................................................... 110
List of Figures

Figure 2.1: Growth schematic for large-area, continuous MoS₂. ............................................... 10
Figure 2.2: AFM images of samples A-D showing temperature evolution of MoS₂ films grown by sulfurization of electron beam evaporated Mo metal. ................................. 12
Figure 2.3: Visualization of the characteristic vibrational modes of MoS₂ observed by Raman spectroscopy. .............................................................................................................. 13
Figure 2.4: Temperature evolution of Raman spectra ................................................................. 14
Figure 2.5: Temperature evolution of MoS₂ on-axis X-Ray diffraction spectra.................... 15
Figure 2.6: High resolution TEM image of the MoS₂/sapphire interface.............................. 17
Figure 2.7: Comparison of MoS₂ films grown with (a) MoS₂ powder and (b) elemental sulfur as the sulfur precursor................................................................. 19
Figure 2.8: Off-axis XRD spectra revealing epitaxial relationship between MoS₂ and sapphire............................................................................................................... 20
Figure 2.9: Epitaxial relationship between MoS₂ and sapphire.................................................. 21
Figure 2.10: (a) Raman spectra of single crystal MoS₂. (b) STEM image of [0001] oriented, single crystal MoS₂ with pristine interface. ......................................................... 22
Figure 2.11: I-V characteristic for sulfur-grown films exhibiting space-charge-limited transport. ...................................................................................................................... 24
Figure 2.12: I-V characteristic for MoS₂ powder-grown films exhibiting space-charge-limited transport. ........................................................................................................ 25
Figure 2.13: Temperature dependent I-V of MoS₂ after surface passivation with Al₂O₃. 26
Figure 2.14: (a) Visualization of active device area for MoS$_2$ photodetectors. (b) Incident power spectra for MoS$_2$ photoconductivity measurements.................................................. 27
Figure 2.15: (a) Photocurrent shows an onset at incident light energy of approximately 1.8 eV. (b) Persistent photoconductivity in MoS$_2$. ................................................................. 29
Figure 2.16: Responsivity of MoS$_2$ photodetectors; blue points are multilayer detectors while red points are monolayer films. Stars represent large-are detectors. ......................... 31
Figure 2.17: Responsivity and effective responsivity of MoS$_2$. ..................................................... 32
Figure 3.1: Growth schematic for p-type MoS$_2$ by adding Nb to the metal precursor.... 36
Figure 3.2: XRD Spectra for heavily doped p-MoS$_2$ compared with UID MoS$_2$......... 37
Figure 3.3: Raman Spectra for heavily doped p-MoS$_2$, compared with UID MoS$_2$.... 39
Figure 3.4: AFM of degenerately doped MoS$_2$ with rms roughness of 1.3 nm............. 40
Figure 3.5: Z-contrast STEM image of p-MoS$_2$ grown on sapphire with layers oriented in the [0001] direction.......................................................... 41
Figure 3.6: (a) Off-axis XRD spectra of p-MoS$_2$ grown from alloyed precursor exhibiting six-fold symmetry indicative of single-crystal MoS$_2$. (b) AFM image (5 µm X 5 µm, height scale: 5 nm) of p-MoS$_2$ with rms roughness of 0.5 nm. ................................................. 42
Figure 3.7: Temperature dependent Hall measurements confirming degenerate p-doping in MoS$_2$. ................................................................................................. 44
Figure 3.8: Summary of p-type Hall measurement results. (a) Hall mobility as a function of doping concentration for p-type samples grown with 5 nm Mo/Nb precursors. (b) Sheet resistance as a function of doping concentration. (c) Hall mobility as a function of sheet resistance........................................................................ 47
Figure 3.9: TLM analysis for degenerately doped p-type MoS$_2$ ............................................. 48
Figure 3.10: Experimental setup for absorbance measurements on MoS$_2$ films .......... 49
Figure 3.11: Absorbance spectra of samples A-C showing onset at 1.8 eV consistent with the direct transition at the K-point of the MoS$_2$ Brillouin zone. .............................. 51
Figure 4.1: AFM image (5 µm X 5 µm, height scale: 12 nm) of p-MoS$_2$ grown on n-type 4H-SiC with rms roughness of 1.66 nm......................................................... 57
Figure 4.2: XRD spectra of p-MoS$_2$/n-SiC heterojunction exhibiting the (002) family of peaks for MoS$_2$ and the (004) peak of SiC. ................................................................. 57
Figure 4.3: Raman spectra of MoS2/SiC heterojunction .............................................. 58
Figure 4.4: Lateral I-V characteristics of p-MoS2 grown on SiC confirming Ohmic contact; (a) TLM measurement (b) Lateral I-V ................................................................. 59
Figure 4.5: Temperature dependent vertical I-V characteristic of MoS2/SiC PN junction with device structure included in the inset................................................................. 60
Figure 4.6: Transport analysis confirming multi-step recombination tunneling as the transport mechanism in the low forward bias region of the MoS2/SiC heterojunction. (a) Temperature-dependent J-V characteristic. (b) Ln(J)-V characteristic. ......................... 62
Figure 4.7: C-V characteristic of MoS2/SiC diode with linear 1/C2 plot from which a built-in potential of 2.2 V is extracted .......................................................... 63
Figure 4.8: Band diagram of the MoS2/SiC heterojunction ........................................ 65
Figure 4.9: Film transfer process for fabricating MoS2/GaN heterojunction diodes....... 66
Figure 4.10: AFM images of (a) GaN after growth of the moderately doped layer (5 µm X 5 µm, height scale: 5 nm) and (b) p-MoS2 after film transfer. ......................... 68
Figure 4.11: XRD spectra of p-MoS2 transferred to GaN ............................................ 68
Figure 4.12: Micrograph of MoS2 devices after transfer to GaN ................................. 69
Figure 4.13: MoS2/GaN PN diode device configuration and epitaxial stack. .................. 70
Figure 4.14: J-V characteristic of the MoS2/GaN PN diode depicted in Figure 4.13a. .... 71
Figure 4.15: Vertical J-V characteristic of the MoS2/GaN PN diode exhibiting 9 orders of magnitude rectification at +/- 2 V ......................................................... 72
Figure 4.16: C-V characteristic of MoS2/GaN diode with linear 1/C2 plot from which a built-in potential of 1.5 V is extracted ...................................................... 73
Figure 4.17: Photo-yield extracted from IPE measurements of MoS2/GaN diodes. ....... 75
Figure 4.18: MoS2/GaN band diagram determined by electrical and optical analysis. .... 76
Figure 5.1: (a) Emitter/base junction device configuration. (b) Emitter/base I-V characteristic with Al2O3 deposited on MoS2 without a seeding layer ....................... 82
Figure 5.2: Oxidation of top monolayer of MoS2 to facilitate high quality Al2O3 deposition by ALD .......................................................... 83
Figure 5.3: AFM image (5 µm X 5 µm, height scale: 5 nm) of ALD Al2O3 deposited on MoS2 with MoOx interfacial layer with rms roughness of 1.15 nm.... 84
Figure 5.4: (a) & (c) MOS diode I-V characteristic exhibiting Fowler-Nordheim tunneling due to the use of a MoO$_x$ transition layer for 20 nm and 15 nm oxide thickness, respectively. (b) & (d) C-V characteristic confirms emitter thicknesses................................. 86

Figure 5.5: Confirmation of Fowler Nordheim tunneling in Al$_2$O$_3$/MoS$_2$ MOS diodes with oxide thicknesses (a) 15 nm and (b) 20 nm. ................................................................. 88

Figure 5.6: (a) Top view of vertical THBT devices. (b) THBT device cross section. ..... 89

Figure 5.7: MoS$_2$/SiC THBT Junction characteristics (a) Base Ohmic pads; (b) Emitter/base junction; (c) Base/collector junction................................................................. 90

Figure 5.8: (a) Common base characteristic for MoS$_2$/SiC THBT with $\alpha = 0$. (b) Band diagram depicting cause of relaxation of all electrons in the base when device measured in common base configuration................................................................. 92

Figure 5.9: (a) Cross-section of MoS$_2$/GaN based THBT. (b) Base/collector I-V characteristic. (c) Emitter/base I-V characteristic................................................................. 95

Figure 5.10: (a) Gummel plot depicting slight increase in collector current. (b) Common base gain showing an increase beginning at $V_{BE} = 1.2$ V. (c) Common emitter measurements dominated by base/collector leakage. ................................................................. 97

Figure 5.11: Band diagram of the Al$_2$O$_3$/MoS$_2$/GaN THBT depicting electrons reaching the collector in common base configuration................................................................. 98

Figure 5.12: (a) Device stack for MoS$_2$/GaN THBT with collector/subcollector device design. (b) Band diagram of THBT. ................................................................. 99

Figure 5.13: (a) Base/collector I-V with suppressed band-to-band tunneling leakage in reverse bias. (b) Emitter/base I-V exhibiting high leakage current due to poor interface created by the transfer process................................................................. 100

Figure 5.14: (a) Gummel plot consistent with $\alpha \approx 0.01\%$, where gain is observed above $V_{BE} = 1.2$ V. (b) Common emitter characteristic exhibiting positive transconductance. 101

Figure 6.1: 2D/3D band line ups, providing insight on the study of future 2D/3D heterojunctions................................................................. 109
Chapter 1

Introduction

Molybdenum disulfide (MoS$_2$) is a two-dimensional (2D) layered, semiconductor in the transition metal dichalcogenide (TMDs) family of materials. The TMDs include those layered compounds of the chemical form MX$_2$, where M represents a transition metal (Mo, W, etc.) and X refers to one of the chalcogen atoms (S, Se, Te). Each monolayer consists of a sheet of transition metal atoms, in which each metal atom is bonded to a chalcogen atom in both out-of-plane directions, respectively. These monolayers are typically 0.65 nm (6.5 Å) thick and do not have out-of-plane bonds. Bulk TMDs consist of many of these vertically stacked layers held together weakly by van der Waals forces.
Although early reports on the properties and bandstructure of MoS$_2$ and other TMDs date back to the 1960s, recent interest in these materials was sparked by the isolation of free-standing atomic 2D crystals by micromechanical exfoliation and the subsequent study of the excellent electronic properties of MoS$_2$. MoS$_2$ has a non-zero band gap near that of silicon in bulk, making it a favorable candidate for the fabrication of low-power electronics. Bulk MoS$_2$ has been shown to exhibit an indirect band gap of 1.2 eV while monolayer films exhibit a direct band gap of 1.8 eV. The thickness dependence of the band gap is a characteristic of quantum confinement in layered, d-electron materials.

Much of the early device work on MoS$_2$ focused on devices based on thin films that were micromechanically exfoliated by scotch tape method from geological samples. Mechanical exfoliation results in a minority of the wafer surface being covered with TMD flakes of varying size and thickness. This method is not viable for producing scalable device technologies although transistors fabricated based on these flakes have demonstrated large on/off ratio ($10^8$), relatively high field effect mobility (200 cm$^2$/Vs), and current densities on the order of milliamps per millimeter. These flakes have also been used to demonstrate transistors, sensors, photodetectors, transparent and flexible electronics, and other devices.

Growth of MoS$_2$ by chemical vapor deposition (CVD) in order to achieve large, uniform layers has been reported using a wide range of precursors including MoO$_2$, MoO$_3$, Mo, sulfur powder and other sulfur compounds.
Many of these growths were also performed on non-epitaxial substrates like silicon wafers with approximately 300 nm SiO$_2$ layers. While these growth methods typically produce flakes of larger area and greater uniformity than those obtained by mechanical exfoliation, they do not produce continuous, large-area, single crystal films. For example, chemical vapor deposition (CVD) growth of MoS$_2$ that uses MoO$_3$ as a Mo precursor produces MoS$_2$ triangles on the order of hundreds of microns in length. Although these individual triangles have been shown to be single-crystal, their coalescence results in large-area, polycrystalline films with many grain boundaries which inevitably degrade lateral conduction.

This thesis aims to elucidate methods used to mature MoS$_2$ device technology in order to demonstrate its viability as a platform for potential next generation devices. We demonstrate large-area growth of single-crystal MoS$_2$, p-type doping with Nb to tune film conductivity, formation and electronic and optical study of heterojunctions formed between MoS$_2$ and wide band gap semiconductors. Each of these contributes to the demonstration of tunneling heterojunction bipolar transistors (THBTs) based on the heterojunction formed between MoS$_2$ and GaN.

1.1 Motivation

1.1.1 CVT growth of single crystal MoS$_2$

Many reports have focused on devices based on MoS$_2$ flakes mechanically exfoliated from geological samples. While these studies are useful in their demonstration of the material properties of MoS$_2$, device engineering is significantly limited by the inability to control film thickness and size of mechanically exfoliated flakes. Growth of continuous, wafer-scale films provides flexibility toward achieving a wide range of
devices that can better assess the viability of MoS$_2$ for novel, high-performance device technologies.

1.1.2 P-type doping of MoS$_2$ with Nb

Controllable doping is a key parameter for semiconductor device design. In order to assess the viability of MoS$_2$ for scalable device technologies, stable, substitutional n- and p-type dopants must be identified. Both mechanically exfoliated flakes and CVD-grown MoS$_2$ films have been shown to naturally exhibit n-type conductivity that can be attributed to sulfur vacancies. [34] [35] [36] Doping of MoS$_2$ flakes by selective area plasma treatment, single crystal growth of doped-MoS$_2$ based on stoichiometric mixtures of elements and doping via dielectric screening have all been demonstrated. However, each of these methods are not stable and substitutional, limiting their viability to a wide range of device designs. Furthermore, these doping methods have not been demonstrated for large-area, high quality MoS$_2$ films which would be necessary for industrially viable technologies. Nb has been identified as a p-type dopant for TMDs in several previous studies. [1] [37] [38] [39] However, high crystalline quality, large-area, p-type films must be achieved to facilitate the production of bipolar devices with MoS$_2$.

1.1.3 2D/3D Heterojunctions

Forming heterojunctions between dissimilar materials is typically limited by the inability to grow high crystalline quality material on certain substrates due to lattice mismatch. However, TMDs do not have out-of-plane bonds, allowing them to circumvent the lattice mismatch issue. Growth and film transfer of MoS$_2$ and other TMDs to traditional so-called “3D” semiconductors could extend the current technology toward novel device topologies that cannot be otherwise obtained without 2D materials. There
have been several reports of these 2D/3D heterojunctions, particularly the MoS$_2$/Si heterojunction.

An example of an area of opportunity for 2D/3D heterojunctions is bipolar devices in wide band gap materials. Wide band gap semiconductors like SiC, GaN, AlN, and ZnO suffer from prohibitively large hole activation energy, which often precludes these semiconductors from achieving high doping concentrations. [40] [41] This issue makes the implementation of high performance, wide band gap semiconductor devices challenging. TMDs with p-type conductivity may provide a way to circumvent these challenges in order to achieve high performance devices.

1.1.4 MoS$_2$/GaN-based Tunneling Heterojunction Bipolar Transistor (THBT)

The performance of GaN-based bipolar junction transistors (BJTs) has been limited by poor p-type GaN. [42] This requires integration of a low sheet resistance, p-type layer on GaN could enable GaN heterojunction bipolar transistors (HBTs) to circumvent large hole activation energy and poor hole mobility in p-GaN. However, fabrication of heterojunction bipolar transistors (HBTs) is limited by the ability to grow high quality p-type material on GaN due to lattice mismatch. To overcome the lattice mismatch problem, wafer-fused devices combining GaAs and InGaAs with GaN have been demonstrated to exploit the high breakdown field of GaN and achieve devices with better power/frequency performance than those utilizing just GaAs. [43] The process of wafer fusing itself limits the performance of these devices due to poor electronic interfaces.

The demonstration of high-quality MoS$_2$/GaN heterojunction diodes highlights their viability as the base/collector junction of a heterojunction bipolar transistor.
Furthermore, the specific contact resistance and resistivity achieved with p-MoS$_2$ compares favorably with that achievable in p-doped GaN with non-annealed contacts.

1.2 Overview of the thesis

This thesis is organized as follows: in chapter two, the growth of single-crystal, unintentionally doped (UID) MoS$_2$ is shown via a metal sulfurization (chemical vapor transport, CVT) technique. Material characterization of the large-area MoS$_2$ demonstrated by Raman spectroscopy, X-ray diffraction (XRD), scanning transmission electron microscopy (STEM) and atomic force microscopy (AFM), and the single-crystallinity of the films was confirmed. The electrical and optical properties of MoS$_2$ were explored, confirming the semiconductor nature of our films. [44] [45]

In Chapter 3, the p-type doping of MoS$_2$ with Nb will is discussed. Nb is shown to be an efficient substitutional dopant, and even at very high doping concentrations, MoS$_2$ maintains its semiconductor properties. It is also shown that the reduction of Nb concentration by alloying the metal precursor decreases the doping concentration of p-MoS$_2$ films. This reduced Nb concentration also results in improvement of the crystalline quality of the films, and single-crystal, large-area, p-doped MoS$_2$ is demonstrated. [46]

In chapter 4, the electrical properties of 2D/3D heterojunctions formed by direct growth (MoS$_2$/SiC) and film transfer (MoS$_2$/GaN) are discussed. Nb-doped MoS$_2$ is grown on n-doped SiC (4H polytype) with a 4° miscut. Current-voltage (I-V) and capacitance-voltage (C-V) characteristics are used to determine the conduction band offset between MoS$_2$ and SiC. Furthermore, the conduction mechanisms in this MoS$_2$/SiC heterojunction diode are explored. MoS$_2$/GaN heterojunctions are formed by film transfer
and the band line up between the materials is determined by C-V measurement and internal photoemission (IPE). [47] [48]

Chapter 5 discusses tunneling heterojunction bipolar transistors (HET) formed with and atomic layer deposited (ALD) dielectric emitter, a p-MoS$_2$ base and SiC and GaN collector layers. Emitter/base and base/collector junction engineering was used to optimize the device. As a result of this device optimization, positive transconductance was is shown in the 2D/3D transistor, confirmed by the common base and common emitter configuration characteristics.
Chapter 2

Chemical vapor transport growth of single crystal MoS$_2$

2.1 Introduction

This chapter details the growth process developed to produce large-area, single crystalline MoS$_2$. During recent increased interest in MoS$_2$, properties such as on/off ratio, mobility and high current density were demonstrated using micromechanically exfoliated flakes obtained by the scotch tape method. In these cases, the flakes were exfoliated onto insulating substrates after which contacts were evaporated onto the MoS$_2$. [49] [9] [50] [51] [11] [52] These reports demonstrate the viability of MoS$_2$ based on demonstrable material properties, but MoS$_2$ flakes cannot be extended for exploring significant device topologies.

The mechanical exfoliation process results in a large number of flakes that cover a minority of the surface of the substrate onto which they are transferred. The flakes also
vary significantly in size and thickness. In order to overcome the lack of uniformity innate to the mechanical exfoliation process, growth of large-area MoS$_2$ has been explored using several growth methods and precursors. While methods such as seeding layers, [53] liquid and chemical exfoliation, [54] [55] and powder synthesis were all utilized to produce large-area MoS$_2$, chemical vapor deposition is the most widely reported method for growth of large-area MoS$_2$. A variety of precursors used to synthesize MoS$_2$ have been reported including Mo, [29] MoCl$_5$, [56] [57] MoO$_2$, [24] MoO$_3$, [33][58][59][60] and (NH$_4$)MoS$_2$. [61] While these growth methods have resulted in single-crystal material, micron and centimeter scale MoS$_2$, and controlled growth of monolayer MoS$_2$ (~7 Å thick), none of these reports resulted in continuous films of excellent crystalline quality.

In this chapter, the growth method for producing continuous MoS$_2$ is discussed as well as the growth method used to improve the film quality from polycrystalline to single crystal MoS$_2$. The temperature and substrate dependence of the film quality will be discussed, and material characterization of these continuous MoS$_2$ films will be presented. Finally, electrical characterization of the unintentionally doped MoS$_2$ films revealed space charge limited transport.

2.2 MoS$_2$ growth with elemental sulfur

2.2.1 Growth method

A metal-first growth method was chosen in order to facilitate large-area MoS$_2$ growth on target substrates. [44] Initially, sapphire substrates were cleaned using acetone, isopropanol (IPA) and deionized (DI) water with ultrasonic agitation. Mo (5 nm thickness) was deposited onto the clean sapphire substrates by electron beam evaporation
in a CHA Solution System E-Gun Evaporator. The metalized substrates were loaded into a quartz tube with 20 mg of elemental sulfur. The quartz tubes were pumped down and sealed by torch. The tubes were then heated, causing sulfur to become vaporized and react with the Mo on the substrate surface. The growth schematic described above is summarized in Figure 2.1.

Identically Mo-covered sapphire substrates were sulfurized at 500°C, 700°C, 900°C and 1100°C (referred to as samples A-D, respectively) for 12 hours to demonstrate the temperature dependence of the film morphology. (It was later determined that identical growth results could be achieved by using a 30-minute growth time.) Each of
the sample surfaces were inspected optically by microscope after growth, and no unreacted metal was evident on the sample surface, i.e. the surface was entirely reflective without dark spots.

2.2.2 Material characterization of vapor-solid grown MoS₂

Atomic force microscopy was used to illustrate the temperature dependence of surface morphology for samples A-D (Figure 2.2). Sample A exhibited a smooth surface with root mean square (RMS) roughness of 0.30 nm. However, the feature size in the AFM was very small, indicative of polycrystalline material. The increase in growth temperature for sample B resulted in both an increase in feature size and RMS roughness (3.5 nm).

The 900°C growth temperature used for sample C is the first temperature in the experiment at which hexagonal features in the MoS₂ commensurate with its hexagonal basal plane were observed in the AFM image (Figure 2.2c). The appearance of hexagonal features indicates that the MoS₂ films grown here are oriented in the (0001) direction. The feature size at 900°C is also significantly larger than that at lower temperatures, (Figure 2.2c is a 25 µm² image while Figures 2.2a and 2.2b are 1 µm²) and the films were again found to be continuous.

The increased growth temperature on sample D increased the mobility of Mo atoms on the sapphire surface, evidenced by the large hexagonal structures shown in Figure 2.2d. The hexagonal crystallites appear to be oriented along the step edges of the sapphires substrates, indicating epitaxial growth. Only the MoS₂ grown at 1100°C was found to be non-continuous. It is evident that Mo atom mobility during growth increases
with increased growth temperature due to both the constant increase of feature size with temperature and the height of the largest features in the AFM images.

Figure 2.2: AFM images of samples A-D showing temperature evolution of MoS$_2$ films grown by sulfurization of electron beam evaporated Mo metal.

Raman spectroscopy was also used to characterize the crystalline quality of the films grown by this method. The characteristic vibrational modes most often utilized to characterize the crystalline quality of MoS$_2$ in literature are the A$_{1g}$ and E$^{1g}$ modes. [62] The A$_{1g}$ mode is associated with the out-of-plane vibration of the sulfur atoms in opposite directions. The in-plane vibrational mode, E$^{1g}$, is associated with the directionally opposite vibrations of the sulfur atoms and Mo atom comprising MoS$_2$, respectively. [63] [64] [65] Figure 2.3 illustrates the vibrational modes for clarity.
Raman spectra for samples A-C were measured using a Renishaw Spectral Analyzer (514 nm laser, 60 mW power). Geological MoS\(_2\) (SPI supplies) was also measured using with the same system in order to compare the crystalline quality of grown MoS\(_2\) with naturally occurring material.

The Raman spectra of samples A and B were compared directly in Figure 2.4a. The characteristic vibrational modes of MoS\(_2\) (\(E^{1}_{2g}\) at 382 cm\(^{-1}\) and \(A_{1g}\) at 407 cm\(^{-1}\)) are evident in the spectra of both samples. The increased temperature (from 500\(^\circ\)C to 700\(^\circ\)C) resulted in an increase of the peak intensity ratio (\(E^{1}_{2g}:A_{1g}\)). Figure 2.4b compares the Raman spectra of sample C with that of geological MoS\(_2\). Both scans exhibit similar peak intensity ratio and peak intensity. Thus, MoS\(_2\) films grown at 900\(^\circ\)C achieve crystalline quality comparable with naturally occurring, bulk MoS\(_2\). As such, we correlate a Raman
peak intensity ratio greater than unity as consistent with improved crystalline quality of the vapor-solid grown MoS$_2$.

Figure 2.4: Temperature evolution of Raman spectra

X-ray diffraction (XRD) was also used to characterize the crystalline quality of samples A-D. Geological MoS$_2$ was measured using high resolution $\omega$-2$\theta$ scans, and its spectra exhibited the (002) family of diffraction peaks including higher order peaks up to (0010) peak. The XRD spectra of sample A showed a small peak at $2\theta = 14.5^\circ$ ($\omega = 7.25^\circ$) consistent with the (002) peak, but no higher order peaks were evident. The (002) diffraction peak measured in the spectra for sample B increased in intensity as compared to sample A. However, the higher order peaks are not evident until the growth temperature is increased to 900$^\circ$C (sample C). At this temperature the XRD spectra most closely resembles that of the geological MoS$_2$, and this result is consistent with the temperature evolution observed for the Raman spectra.
The spectra for sample D (growth temperature of 1100°C) also exhibits the (002) family of diffraction peaks, including all those present in the spectra of the geological sample. However, the increased temperature results in more narrow diffraction peaks without thickness fringes present in the scan of sample C. Figure 2.5 summarizes the temperature evolution of the on-axis XRD spectra.

![Temperature evolution of MoS$_2$ on-axis X-Ray diffraction spectra.](image)
The substrate growth dependence of MoS\textsubscript{2} was elucidated by using an identical sample preparation process with SiO\textsubscript{2}/Si as the target substrate. The growth of MoS\textsubscript{2} was confirmed on these substrates by Raman spectra, optical inspection and scratch test (MoS\textsubscript{2} films should easily be scratched off the substrates on which they were grown with a gentle stroke of the edge of a tweezer due to the lack of out-of-plane bonds). However, XRD spectra of MoS\textsubscript{2} on SiO\textsubscript{2}/Si showed no diffraction peaks. This suggests that the films were either polycrystalline or amorphous, and the substrate dependence of this growth method points to an epitaxial relationship between MoS\textsubscript{2} and target substrates. It should be noted that sapphire and MoS\textsubscript{2} are both hexagonal basal plane structures. Several other reports have shown substrate dependence of MoS\textsubscript{2} growths. [66] [67]

Transmission electron microscopy (TEM) was also used to characterize MoS\textsubscript{2}. Figure 2.6 shows the TEM image detailing the cross-section of the MoS\textsubscript{2}/sapphire interface (sample C). The layered structure of MoS\textsubscript{2} is clear as layers were (0001)-oriented, consistent with Raman and XRD analysis. Close inspection of the MoS\textsubscript{2} region in the TEM image shows some isolated regions that are slightly rotated from the (0001) direction. Furthermore, there exists some interfacial layer between MoS\textsubscript{2} and sapphire.
MoS$_2$ grown using Mo metal and elemental sulfur as material precursors has been demonstrated to result in high crystalline quality, large area, continuous (0001)-oriented MoS$_2$. However, the material is not single-crystal, as revealed by TEM characterization, and the lack of in plane symmetry that might be evidenced by off-axis XRD spectra. The growth diagram for MoS$_2$ shows a large window for growth of the 2H polytype of MoS$_2$. By utilizing 20 mg of elemental sulfur, the sealed quartz tubes contain a supersaturation of sulfur during growth. Reducing the supersaturation of sulfur in the tubes during growth could result in less nucleation sites during growth, thus improving the crystalline quality of MoS$_2$.

2.3 MoS$_2$ growth with MoS$_2$ powder as sulfur precursor

2.3.1 Growth method

Reducing the supersaturation of sulfur within the quartz tubes is not as simple as reducing the mass of sulfur used for growth because it is difficult to control the amount
sulfur in the tube at high temperatures. To reduce the sulfur pressure during growth, the sulfur source was changed to MoS$_2$ powder (obtained from Sigma Aldrich). At high growth temperature, the MoS$_2$ powder decomposes, releasing sulfur that reacts with the Mo metal deposited on the sapphire substrates. The reaction is summarized by the following:

$$\text{MoS}_2\text{ powder} \rightarrow \text{MoS}_x (x < 2) + \frac{2-x}{2} \text{S}_2$$

$$\text{Mo (on sapphire)} + \text{S}_2 \rightarrow \text{MoS}_2(\text{on sapphire}).$$ [45]

The films were grown at 1100°C for 4.5 hours (refer to the growth schematic in Figure 2.1). The growth temperature was selected both because it falls within the 2H-MoS$_2$ growth window and it is the temperature at which the equilibrium between MoS$_2$ powder and sulfur would result in a sulfur vapor pressure which is the lowest that produces pure MoS$_2$.

2.3.2 Material characterization

Optical inspection of the films showed that MoS$_2$ grown by this method resulted in continuous films (Figure 2.7a). AFM of MoS$_2$ grown by this new method showed continuous films with low RMS roughness of 0.5 nm (Figure 2.7b). AFMs of MoS$_2$ powder grown films show similar roughness and film morphology compared to the best MoS$_2$ achieved by the previous growth method (sample C grown at 900°C, Figure 2.2c).
On-axis XRD spectra (ω-2θ scan) exhibited the (002) family of diffraction peaks including all high order peaks observed in geological samples. The (002) peak showed thickness fringes, likely due to the improvement of the MoS$_2$/sapphire interface. An off-axis (φ scan) of the (103) peak of MoS$_2$ was used to characterize the in-plane order of the films. The 360° φ-scan showed six-fold symmetry consistent with the hexagonal structure of MoS$_2$. This six-fold symmetry definitively indicates that the sapphire precursor change, resulted in single-crystal, large area MoS$_2$.

The φ-scan of the (01-12) peak of sapphire substrate was measured with the sample identically positioned. It revealed the three-fold symmetry of the single crystal substrates. Plotting the scans together revealed that the basal plane of MoS$_2$ was rotated by 30° with respect to the sapphire basal plane. Figure 2.8 shows the off-axis XRD spectra detailing the rotation between MoS$_2$ and sapphire.
Figure 2.8: Off-axis XRD spectra revealing epitaxial relationship between MoS$_2$ and sapphire.

The rotation observed between basal planes observed in the off-axis XRD implies that MoS$_2$ indeed grows epitaxially on sapphire, despite the lack of out-of-plane bonds in MoS$_2$ films. The basal planes are found to be rotationally commensurate as the 30° rotation relative to each other minimizes the in-plane lattice mismatch between MoS$_2$ and sapphire. The rotation reduces the MoS$_2$/sapphire lattice mismatch from 50.5% to 13.0%. In fact, with this 30° rotation, the length 7 MoS$_2$ unit cells is equal to that of 8 sapphire unit cells. Figure 2.9 shows the visualization of the atomic structure of MoS$_2$ and sapphire overlayed with the rotation.
Raman spectra was again used to characterize the characteristic vibrational modes of MoS$_2$. Figure 2.10a shows the characteristic $E^{1\,2g}$ and $A_{1g}$ peaks with the peak intensity ratio indicative of good structural quality, as detailed in section 2.1.2. TEM was again used to analyze the MoS$_2$/sapphire cross section. Figure 2.10b shows MoS$_2$ oriented in the [0001] direction. Unlike the TEM image of MoS$_2$ grown with elemental sulfur, the MoS$_2$ shows no regions of rotation and the MoS$_2$/sapphire interface was abrupt and pristine.
2.4 Electrical characterization of MoS$_2$

The repeatable growth of large area MoS$_2$ allows standard optical lithography techniques to be adopted for device processing. Transfer length method (TLM) patterns were fabricated using both contact lithography (EV Group 620 Advanced Contact Aligner) and stepper lithography (GCA 6100 Stepper (i-line)). The fabrication of large structures on MoS$_2$ (TLM structures were approximately 22,500 $\mu$m$^2$) demonstrates the viability of this growth method for scalable processing on MoS$_2$.

2.4.1 Space-Charge-Limited Transport in MoS$_2$

Ti/Au contacts were evaporated by electron beam onto elemental sulfur-grown MoS$_2$ to form an Ohmic contact. The current-voltage (I-V) characteristics for the TLM patterns were measured (Agilent B1500 parameter analyzer). In the measurements of TLM pads with 2 $\mu$m, 3 $\mu$m and 4 $\mu$m spacing (Figure 2.11), resistance did not scale linearly. In fact, I-V characteristics were found to exhibit two conduction regimes. The

Figure 2.10: (a) Raman spectra of single crystal MoS$_2$. (b) STEM image of [0001] oriented, single crystal MoS$_2$ with pristine interface.
first, low-bias regime, current exhibited a linear dependence on applied voltage. The second regime exhibited a quadratic relationship between current and voltage. This current-voltage relationship is indicative of space-charge limited transport. It can be inferred that MoS$_2$ has a low background carrier concentration, and transport is dictated by injection of carriers from the Ohmic contacts. [68]

The Mott-Gurney equation, which describes space-charge limited transport in thin films, is given by

$$I = \frac{qn \mu L}{d} V + \frac{2 \varepsilon_s \mu L}{\pi d} V^2$$

(1)

where $q$ is the elementary charge of an electron, $n$ is the background carrier concentration, $\mu$ is the electron mobility, $L$ is the width of the TLM pads, $\varepsilon_s$ is the dielectric constant of MoS$_2$ and $d$ is the contact spacing of the pads. Material parameters were extracted from a polynomial fit ($I = BV + CV^2$) of the measured I-V characteristic. Sulfur-grown MoS$_2$ was found to exhibit a carrier concentration of $3.5 \times 10^{16}$ cm$^{-3}$ and a space-charge mobility of approximately $12(\pm 2)$ cm$^2$/Vs from fitting parameters for the high field (quadratic) regime.
I-V characteristics were also measured for MoS$_2$ powder-grown films, and the two characteristic conduction regimes were observed. Improved crystalline quality resulted in a two order of magnitude increase in current density over sulfur grown films. The electron mobility and background concentration extracted from fitting parameters in the high field regime were 120(±20) cm$^2$/Vs and 2.8 x 10$^{17}$ cm$^{-3}$, respectively. Figure 2.12 shows the I-V characteristics for contact spacings of 2, 3 and 4 µm and the corresponding data fits.
Figure 2.12: I-V characteristic for MoS$_2$ powder-grown films exhibiting space-charge-limited transport.

TLM structures oriented orthogonally (in-plane) were found to exhibit a significantly lower electron mobility (65 cm$^2$/Vs). This anisotropic mobility corresponds with the anisotropic electron effective mass described for bulk films by Peelaers and Van de Walle. [69] The electron mobilities in the $\Lambda_{\text{min}}$ and perpendicular to the $\Lambda_{\text{min}}$ direction are 0.53$m_0$ and 0.73$m_0$, respectively.

2.4.2 Surface passivation of MoS$_2$

A 20 nm layer of Al$_2$O$_3$ was deposited on MoS$_2$ powder-grown MoS$_2$ by atomic layer deposition (ALD) (Picosun SUNALE R-150B Atomic Layer Deposition Tool) in order to passivate surface charge and subsequently reduce Coulombic scattering. [70] I-Vs continued to exhibit space charge limited transport, but the room temperature mobility increased to 192 cm$^2$/Vs with surface passivation from ALD. I-Vs exhibited weak temperature dependence, as shown in Figure 2.13.
2.5 MoS$_2$ Photoconductivity

2.5.1 Experimental Configuration of Optical Characterization

The photoconductivity of MoS$_2$ powder-grown MoS$_2$ was characterized using the previously discussed TLM structures. A monochrometer was used to sweep the incident light wavelength from 700 nm to 400 nm. Long pass filters (400 nm filter for incident light wavelengths ranging from 700 nm to 475 nm and 280 nm filter for incident light wavelengths ranging from 450 nm to 400 nm) were used to remove integer multiple wavelengths from the light source, ensuring monochromaticity. Current-voltage (I-V) characteristics were measured with a measurement protocol designed in LabView.
An optical power meter was used to determine the incident power, $P$, from the light source. The area of the spot size of the incident light source, $A_1$, was larger than that of the active area of the devices, $A_2$. The power measured from the optical power meter was scaled by a factor $A_2/A_1$ to account for this (Figure 2.14a). The incident power spectra, shown in Figure 2.14b, was determined by the relationship,

$$P_{inc} = \frac{A_2}{A_1} \cdot P = 0.091 \cdot P$$

(2)

where $P_{inc}$ is the optical power incident on the device at each wavelength.

Figure 2.14: (a) Visualization of active device area for MoS$_2$ photodetectors. (b) Incident power spectra for MoS$_2$ photoconductivity measurements.
Photocurrent, $I_{ph}$, was determined by calculating the difference between current measured with the light source on and that measured with the light source off. Dark current was measured prior to the device being exposed to light from the monochrometer. After the initial dark current measurement, the light source was turned on with the device being exposed to 700 nm wavelength light. After two minutes, another I-V was measured to determine the light current. The light source was then turned off for two minutes before measuring the dark current after illumination while the light wavelength was decreased by 25 nm. This sequence was repeated for all measurements as the wavelength of incident light was swept from 700 nm to 400 nm.

2.5.2 Detector Measurements and Persistent Photoconductivity

The I-V characteristics for the photodetector were found to be Ohmic. Figure 2.15b shows the dark current used to calculate the photocurrent at each incident wavelength. The increase in dark current as incident light wavelength decreased was attributed to persistent photoconductivity (PPC) and was consistently observed in our device measurements. Similar PPC was discussed by Wu et al., who attributed the phenomenon to extrinsic factors like adsorbates on the substrate surface. [71] Although the persistent photoconductivity can significantly decrease the calculated photocurrent, light current measured at each wavelength exceeds dark current.
Figure 2.15: (a) Photocurrent shows an onset at incident light energy of approximately 1.8 eV. (b) Persistent photoconductivity in MoS$_2$.

Photocurrent at an applied bias of 5 V was plotted as a function of incident light energy in Figure 2.15a, and showed an onset of approximately 1.8 eV. This corresponds with the direct transition between the valence and conduction band extrema at the K point of the MoS$_2$ Brillouin zone. Simulation results (density functional theorem) [69] [72] and experimental absorbance spectra in other reports showed that this direct transition exists in bulk MoS$_2$ despite the lowest energy transition for bulk MoS$_2$ of 1.2 eV ($\Gamma$-$\Lambda_{min}$). [46] [73] The photocurrent versus light energy plot also showed photocurrent saturation for light energy above 2.8 eV.

### 2.5.3 Responsivity of MoS$_2$ Detectors

Responsivity is the measurement of the input-output gain of a photodetector, and is given by

\[ R = \frac{I_{ph}}{P_{inc}} \]  

(3)
in units of $\text{AW}^{-1}$. While the maximum value for photoresponsivity for these MoS$_2$ photodetectors were measured at an incident light wavelength of 400 nm, we report the figure-of-merit for incident light wavelength of 600 nm and applied bias of 5 V in order to facilitate direct comparison to the high-sensitivity MoS$_2$ detectors found in literature. [74], [75] The applied bias for the figures reported here was equivalent to or less than those reported for other MoS$_2$ photodetectors (PDs) in order to limit enhancement of the merit figures due to larger drift current. The MoS$_2$ photodetector yielded photoresponsivity of 311.8 $\text{AW}^{-1}$ under these measurement conditions.

The photoresponsivity reported here is the highest reported value for large-area MoS$_2$ photodetectors to date (Figure 2.16). [76] [77] [78] [79] [80] [81] While these did not represent records for MoS$_2$ PDs in general, these devices illustrate the viability of high-quality, large-area, single-crystal MoS$_2$ for photodetector applications. The two mechanically exfoliated MoS$_2$ photodetector studies which reported greater merit figures obtained those for incident light power less than that which is reported here, enhancing the responsivity of their devices. Unlike other high-sensitivity MoS$_2$ PDs, our devices do not require dark current suppression techniques in order to exhibit high sensitivity. In fact, the responsivity of our devices compares favorably with merit figures reported for when those figures are compared for similar incident light power and incident wavelength. [74] [75]
Figure 2.16: Responsivity of MoS\textsubscript{2} photodetectors; blue points are multilayer detectors while red points are monolayer films. Stars represent large-area detectors.

The persistent photoconductivity found in our films limited the sensitivity of our large-area MoS\textsubscript{2} photodetectors. If the time between the measurement of light current and the subsequent dark current measurement was increased significantly, all photoexcited carriers would recombine, and the initial dark current would be universal for all measurements. Using the initial dark current, we determined an effective value of photoresponsivity, \( R_{\text{eff}} = 505 \text{ AW}^{-1} \), shown in Figure 2.17. These measurements further show that our single-crystal, large-area MoS\textsubscript{2} is optimal for low-cost photodetection applications.
Figure 2.17: Responsivity and effective responsivity of MoS$_2$.

2.6 Summary and Conclusion

In conclusion, we grew large-area, single crystal, unintentionally doped MoS$_2$ on sapphire substrates using a metal sulfurization process. The MoS$_2$ films were found to exhibit excellent structural quality and an epitaxial relationship with sapphire in which the 30° rotation between the material basal planes minimized lattice mismatch. Raman spectra and TEM show excellent structural quality and highly oriented layers for the CVT grown MoS$_2$. The films were shown to exhibit space-charge limited transport due to their low doping concentration, and high space charge mobility up to 192 cm$^2$V$^{-1}$s$^{-1}$. Optical measurements indicate an onset of 1.8 eV, confirming the semiconductor behavior of the single crystal films. The films also exhibited high photoresponsivity without the use of dark current suppression techniques.

While large-area films provide a pathway towards scaling up device production using MoS$_2$ films, subsequent device design requires the ability to tune the conductivity
of films by doping. Although both mechanically exfoliated and CVD-grown MoS$_2$ films have been shown to exhibit n-type conductivity, an \textit{in situ} method for producing doped films (n-type or p-type) is required for achieving bipolar devices and exploring the functionality of MoS$_2$. 


Chapter 3

P-type doping of MoS$_2$ with Nb

3.1 Introduction

This chapter introduces the efficient doping of MoS$_2$, utilizing niobium as an acceptor. Niobium was originally reported to act as an acceptor the transition metal dichalcogenides MoS$_2$ and WSe$_2$ in the late 1960s and early 1970s. Nb has been predicted to act as an acceptor in MoS2 by density functional theorem (DFT) calculations, besides its position on the periodic table with respect to Mo, hence having one less valence electron than Mo.

MoS$_2$ doping has previously been demonstrated by several methods. Reports have used liquid gating techniques to dope MoS$_2$ electrostatically. [82] Doping by MoS$_2$ has been demonstrated stable selective area plasma treatment and other surface treatments.
Other groups have used stoichiometric amounts of Mo, S and Re or Fe (n-type doping) to grow doped bulk MoS$_2$ crystals. Others have used electrostatic doping with back-gating and doping by dielectric encapsulation. While these techniques are effective in tuning the conductivity of MoS$_2$, however none of these techniques are stable, substitutional and in situ. These drawbacks preclude the previously mentioned doping methods from being used to produce large area, uniformly doped films.

This work represents the first report of large-area, uniform doping of MoS$_2$ films. Subsequently, this chapter will detail the growth of p-type MoS$_2$, characterization of the degenerately doped films, and the transport effects of tuning of doping concentration by reducing the Nb:Mo ration in the metal precursor.

3.2 Growth and Characterization of p-MoS$_2$

3.2.1 Growth of p-MoS$_2$ with Layered Metal Precursor

The metal first approach for growth of unintentionally doped (UID) MoS$_2$ that was introduced in chapter 2 is again used for growth of p-type films. Sapphire substrates are cleaned with acetone, isopropanol and deionized water in an ultrasonic bath. The substrates are dried at 120°C for five minutes on a hotplate before being loaded into the AJA Orion RF/DC Sputter tool. While the metal precursor for UID MoS$_2$ includes 5 nm of Mo, the p-type metal precursor includes a thin layer of Nb (0.2 – 0.3 nm) sandwiched between 2.5 nm Mo layers. The sapphire substrates are diced into 10 mm x 8 mm pieces and loaded into quartz tubes with 80 mg of MoS$_2$ powder utilized as the sulfur precursor. The tubes are pumped down on a vacuum line and torch sealed. After sealing, the quartz tubes are loaded into a furnace and heated to 1100°C for 4.5 hours. They are then cooled
at a rate of 0.5°C/min until they can be manually removed. A simple schematic of the p-
MoS$_2$ growth is shown in Figure 3.1.

![Growth schematic for p-type MoS$_2$ by adding Nb to the metal precursor.](image)

**Figure 3.1:** Growth schematic for p-type MoS$_2$ by adding Nb to the metal precursor.

In order to demonstrate the effect of the addition of the Nb dopant layer to the
metal precursor on the structural properties and conductivity of MoS$_2$, we compare three
samples: two samples using the p-type doping stack (samples A and B), and an UID
sample as a control (sample C). Sample A is doped using a 3 Å layer of Nb while sample
B’s doping layer was 2 Å. The samples’ XRD spectra, Raman spectra, Hall mobility, and
absorbance spectra are compared.

### 3.2.2 Material Characterization of p-MoS$_2$ with Layered Metal Precursor

Each of the samples was characterized by high-resolution, on-axis XRD. The
spectra for the three samples are shown in Figure 3.2. Sample C shows the typical on-axis
spectra that is discussed in Chapter 2 (Figure 2.5). While the spectra for Sample A, the
heavily doped sample with a carrier concentration of $1.5 \times 10^{21}$ cm$^{-3}$ (equivalent carrier
density of $2 \times 10^{15}$ cm$^{-2}$), exhibits a clear (002) peak, its intensity is lower than that of
sample C and the higher order peaks (i.e. (006) diffraction peak) are not evident in the
scan. This is indicative of degradation in film quality due to lattice distortion from the large concentration of Nb atoms. The XRD spectra for sample B compares more favorably to the control sample. While still degenerately doped, with a carrier concentration of $3.1 \times 10^{20} \text{ cm}^{-3}$ (equivalent carrier density of $4 \times 10^{14} \text{ cm}^{-2}$), the intensity of the (002) peak is strong and the presence of the higher order (006) peak shows improved crystalline quality over sample A.

![XRD Spectra](image)

Figure 3.2: XRD Spectra for heavily doped p-MoS$_2$ compared with UID MoS$_2$.

Off-axis XRD scans of the (103) peak of UID films like sample C exhibit six-fold symmetry and epitaxial registry with the sapphire substrates on which they are grown, indicating the single-crystalline nature of our UID MoS$_2$ (section 2.3.2). Identical off-axis scans were performed on sample B to assess whether this degenerate p-type material was
single crystal. However, the off-axis scans of sample B showed no peaks. This suggests that even this reduced concentration of Nb, as compared to sample A, results in film degradation. The degenerately doped, p-type MoS\(_2\) in sample B is not single crystal.

Raman spectra of the three samples was compared to further assess the effect of Nb dopants on the crystalline structure of MoS\(_2\). The samples were measured with identical laser power in order to ensure measurement uniformity. Figure 3.3 shows the typical Raman spectra for each of the three samples. The UID MoS\(_2\) from sample C showed a peak intensity ratio, E\(^{1}\)\(_{2g}\):A\(_{1g}\), greater than one, indicating excellent film quality as previously discussed. For this measurement, the peak positions for the E\(^{1}\)\(_{2g}\) and A\(_{1g}\) peaks were 381 and 407 cm\(^{-1}\), respectively. The spectra for samples A and B indicated no shift in peak position, and the consistent peak separation shows that each of the films were the same thickness. The Raman spectra of sample A was consistent with its XRD; the peak intensity ratio for the degenerately doped MoS\(_2\) was less than one, owing to the degradation of structural properties from the high doping. Although sample B was also degenerately doped, its peak intensity ratio was similar to sample C.
The AFM scan of sample B is shown in Figure 3.4. While the scan area is 4 $\mu$m$^2$, all scans of the surface exhibited full surface coverage indicative of a continuous film. The RMS roughness of the p-doped film was found to be 1.3 nm, and the degenerately p-doped samples are typically rougher than typical UID films, likely due to lattice distortion from heavy niobium doping. The general morphology of the films, however, remains consistent with Nb dopants added. The height scale of the image was 8 nm.

Figure 3.5 shows the Z-contrast STEM image of the cross-section of the Nb-doped MoS$_2$. The STEM measurements were completed on an aberration-corrected Nion.
UltraSTEM 100™ electron microscope (acceleration voltage of 60 kV). The atomic-scale image shows the highly-oriented layered structure of the film oriented in the [0001] direction. The STEM image also indicates that there is an abrupt, clean interface between the sapphire substrate and the MoS\textsubscript{2} film.

Figure 3.4: AFM of degenerately doped MoS\textsubscript{2} with rms roughness of 1.3 nm.
3.2.3 p-MoS$_2$ with Alloyed Metal Precursor

The sputter chamber used to deposit the metal precursor for p-type MoS$_2$ has cannot controllably deposit less than 2 Å of Nb. This constraint does not allow a doping concentration less than $3 \times 10^{20}$ cm$^{-3}$ to be achieved. To circumvent this issue, we utilized Mo:Nb alloyed sputter targets from Kurt J. Lesker Company. The target utilized for this experiment was designed for a Nb to Mo ratio of 0.01%. It should be noted that the atomic percentage of the sample B precursor was 3.4% (hand calculation).

Sample preparation for the alloyed precursor followed the same growth recipe as that demonstrated for UID MoS$_2$. 5 nm thick layers of the alloys were sputtered onto clean sapphire substrates, and p-MoS$_2$ was grown. Sample D (0.01% alloy) was characterized by XRD, Raman and AFM.

The on-axis XRD spectra of Sample D showed the typical (002) family of diffraction peaks. The peak intensities and thickness fringes observed in the spectra
resemble that of the single-crystal, UID MoS$_2$ discussed previously. Off-axis scans of the (105) peak of MoS$_2$ were measured with tilt angle, $\chi = 42^\circ$. Unlike the degenerately doped p-type samples, sample D showed the six-fold symmetry indicative of single-crystal material. This shows that the decrease in Nb doping concentration leads to less degradation of the crystalline structure and thus single crystal, p-type MoS$_2$ was achieved. The off-axis XRD spectra of sample D and the corresponding AFM are shown in Figure 3.6a and 3.6b, respectively.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure36.png}
\caption{(a) Off-axis XRD spectra of p-MoS$_2$ grown from alloyed precursor exhibiting six-fold symmetry indicative of single-crystal MoS$_2$. (b) AFM image (5 µm X 5 µm, height scale: 5 nm) of p-MoS$_2$ with rms roughness of 0.5 nm.}
\end{figure}

The Raman spectra of the alloyed precursor grown p-MoS$_2$ was measured as well. While the $E_{2g}^{1}$:$A_{1g}$ peak intensity ratio has been shown to be consistently greater than unity for all growths reported in this work, a line scan of the Raman spectra was utilized
for sample D to exhibit the uniformity of the p-type films. Figure 3.8 shows a 40-μm line scan of the Raman spectra of MoS$_2$. The peak intensity ration is greater than unity over the length of the scan, asserting the uniformity and crystalline quality of the low-doped p-MoS$_2$.

The material characterization of Nb-doped MoS$_2$ shows that we can dope the films with Nb and maintain the crystalline order. By utilizing alloyed precursor metals, the Nb concentration was decreased significantly, allowing us to achieve single crystal p-MoS$_2$. In the next section, we discuss the electrical characterization of these p-doped films.

3.3 **Electrical characterization of p-MoS$_2$**

3.3.1 **Hall Measurements**

van der Pauw structures used for Hall measurements were fabricated on samples A and B using standard contact lithography. Ohmic contacts for the p-MoS$_2$ were comprised of a Ni/Au/Ni metal stack. The structures were isolated using 30 W of RIE power and BCl$_3$/Ar chemistry. Hall measurements were not performed on sample C due to the high sheet resistance of the UID films.

Room temperature Hall measurements indicate that sample A exhibited a hole mobility of 0.5 cm$^2$/Vs and a sheet carrier density of $2 \times 10^{15}$ cm$^{-2}$. The reduction of the Nb thickness by 1 Å for the p-doped MoS$_2$ of sample B exhibited a hole mobility of 8.5 cm$^2$/Vs with a sheet carrier density of $4 \times 10^{14}$ cm$^{-2}$. Sample C exhibited n-type conductivity, as discussed in Chapter 2. It is clear from analysis of the Hall measurements that the addition of Nb causes MoS$_2$ to exhibit p-type conductivity. Thus, Nb acts as an acceptor in MoS$_2$. 

43
Degenerately doped semiconductors do not undergo carrier freeze out at low temperature due to the formation of impurity bands. Temperature-dependent Hall measurements of sample A exhibit this degenerately doped semiconductor behavior (Figure 3.8). While the mobility of holes decreases slightly at temperatures as low as 20 K, the carrier concentration remained temperature invariant.

![Figure 3.7: Temperature dependent Hall measurements confirming degenerate p-doping in MoS2.](image)

Identical van der Pauw structures were fabricated on sample D. Hall measurements indicated extracted a sheet carrier density of $6 \times 10^{11}$ cm$^{-2}$, demonstrating that the alloyed precursor resulted in a three order of magnitude reduction in carrier concentration. The Hall measurements also indicated p-type conductivity, but the Hall mobility for sample D was 9 cm$^2$/Vs. Sample D showed virtually no increase in mobility when compared to samples A and B, despite a significant reduction in doping.
concentration. The mobility of the p-MoS$_2$ films exhibits weak dependence on carrier concentration. This suggests that ionized impurity scattering is not the dominant scattering mechanism affecting these p-type films. The results of the Hall measurements on samples A-D are summarized in Table 1. It should be noted that the mobility extracted from sample C is space charge mobility (Chapter 2), and is noted in Table 3.1 in italics.

Analysis of the Hall data shows that Nb acts as an efficient, substitutional acceptor in MoS$_2$. While Nb-doped films were consistently found to be p-type, sample-to-sample variation in doping concentration was observed. This variation could be attributed to experimental error or varying deposition conditions. As such, it is difficult to definitively ascertain the efficiency of Nb acceptors in MoS$_2$. However, hand calculations determined the lower bound for Nb-dopant efficiency in these films was approximately 26%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nb thickness (nm)</th>
<th>Type</th>
<th>Carrier Density (cm$^{-2}$)</th>
<th>Mobility (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.3</td>
<td>p</td>
<td>$2 \times 10^{15}$</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>0.2</td>
<td>p</td>
<td>$4 \times 10^{14}$</td>
<td>8.5</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>n</td>
<td>$2 \times 10^{11}$</td>
<td>192*</td>
</tr>
<tr>
<td>D</td>
<td>Alloy (0.01%)</td>
<td>p</td>
<td>$6 \times 10^{11}$</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 3.1: Hall mobility of p-type films compared to UID films. Note: The UID MoS$_2$ mobility is space charge mobility.
3.3.2 Film thickness dependence of Hall mobility

Subsequent growths of p-MoS$_2$ continues to exhibit an upper bound of about 10 cm$^2$/Vs for hole mobility, while typical mobility of these films ranged from approximately 1-10 cm$^2$/Vs. Figure 3.8a shows a chart of carrier concentration vs. Hall mobility for many samples. While Figure 3.8b indicates a general decrease in sheet resistance with increased doping concentration, sheet resistance and hole mobility also did not exhibit any correlation (Figure 3.8c).

Any dominant scattering mechanisms that could contribute to the consistent upper limit for the mobility despite the change in Nb dopant concentration would have to be a result of a material property present in all films. As mentioned previously, the lack of correlation between doping concentration and Hall mobility suggests that ionized impurity scattering is unlikely to be the dominant scattering mechanism influencing carriers in MoS$_2$. It is unlikely that the scattering mechanism responsible for this limited mobility is remote impurity scattering because the sapphire substrates used to grow MoS$_2$ were insulating. Also, the lack of out-of-plane bonds in MoS$_2$ limits the possibility of the scattering contribution of charged surface states.
Figure 3.8: Summary of p-type Hall measurement results. (a) Hall mobility as a function of doping concentration for p-type samples grown with 5 nm Mo/Nb precursors. (b) Sheet resistance as a function of doping concentration. (c) Hall mobility as a function of sheet resistance.

All MoS₂ samples reported in this work were grown on identical sapphire substrates. The MoS₂/sapphire interface and the MoS₂ surface are consistent amongst all samples on which Hall mobility data was collected. To determine the contribution of the substrate/film interface to the mobility, thicker MoS₂ was grown. Nb-doped MoS₂ samples were prepared by the same growth method, but the metal precursor thickness was doubled (Mo/Nb/Mo, 5 nm/0.4 nm/5 nm). Hall measurements performed on the samples exhibited increased hole mobility up to 27 cm²V⁻¹s⁻¹. Sheet resistance was 14 kΩ/square. Assuming a film thickness of 20 nm, the doping concentration was found to be 8 x 10¹⁸ cm⁻³. While the origin of this mobility increase with increased film thickness is not clear, the MoS₂/sapphire interface may act as a scattering center due to interface roughness or the material quality may improve as the film thickness increases.

3.3.3 TLM Analysis

Transfer length method measurements (TLM) were performed on sample B to characterize sheet resistance and contact resistance of the films. The Ni/Au/Ni contacts
were found to be Ohmic by the TLM measurements, as the film resistance scaled linearly with contact length. The sheet resistance extracted from the measurement was 1.9 kΩ/□ (resistivity of approximately 19 mΩ-cm). It should be noted that this value matched that determined by Hall measurement. The contact resistance was 0.6 Ω-mm. Figure 3.9 shows both the TLM structure fabricated on sample B (inset) and the results of the TLM measurement.

![Figure 3.9: TLM analysis for degenerately doped p-type MoS$_2$.](image)

### 3.4 Optical Characterization

Optical absorbance measurements were used to confirm that Nb-doped MoS$_2$ is a semiconductor and has not become metallic as a result of degenerate doping by measuring the band gap. [91] The absorbance spectra for samples A, B and C were measured to determine the semiconductor nature of MoS$_2$ and demonstrate the effects of
Nb-doping on the material band structure. A broad UV-VIS-NIR deuterim-tungsten-halogen white light source was utilized for the measurements and the incident light was swept from 310 nm to 825 nm (light energy: 1.5 – 4.0 eV). The light transmitted through the samples was then collected by a monochromator. The schematic for the measurement is shown in Figure 3.10.

![Schematic diagram of the measurement setup](image)

**Figure 3.10:** Experimental setup for absorbance measurements on MoS₂ films.

The sapphire substrate on which the MoS₂ films were grown was used to measure the reference intensity for the absorbance measurements, given by I₀(λ). This reference intensity is the light collected by the monochromator after it was transmitted through the...
sapphire. After the reference intensity is determined, the intensity after transmission through each sample (A-C) was measured and was given by \( I(\lambda) \). The absorbance spectra for each sample was then calculated by,

\[
A = \frac{I(\lambda)}{I_0(\lambda)}.
\]  

(1)

Figure 3.12 shows the absorbance spectra determined by equation 1 for samples A, B and C. It is clear that each of the spectra exhibits an onset at approximately 1.8 eV, consistent with the direct band transition associated with the band edge at the K-point of the Brillouin zone. The films in samples A-C were all multilayer (bulk) samples which exhibit an indirect, lowest energy transition of 1.2 eV. However, DFT calculations indicate that the 1.8 eV direct gap transition is still present in bulk MoS\(_2\).
The absorbance spectra from sample C exhibited a sharp onset at 1.8 eV. The degenerately p-doped samples (A and B) do not exhibit onsets as sharp at 1.8 eV. The shoulders observed in the absorbance spectra of samples A and B are indicative of band tailing due to the large concentration of holes. This measurement shows that the degenerately doped p-MoS$_2$ is not metallic, and is another demonstration of the efficient incorporation of Nb into the MoS$_2$ lattice.

3.4 Summary and Conclusion
In conclusion, we demonstrated the first in situ, substitutional p-doping of large-area MoS$_2$ films by adding Nb to the metal precursor stack. Degenerately doped films were first achieved using this method, and degenerate doping was confirmed by low temperature Hall measurement. While the degenerately doped films exhibited the (002) family of diffraction peaks consistent with 2H-MoS$_2$, degenerate doping reduced the structural quality of MoS$_2$ such that off-axis scans did not exhibit six-fold symmetry. The utilization of an alloy metal precursor lowered the doping significantly, and single-crystal, p-type MoS$_2$ was demonstrated. Absorbance measurements indicated that doping did not alter the semiconductor nature of MoS$_2$ as samples of all doping levels exhibited onsets commensurate with the direct gap transition at the K-point of the Brillouin zone.

While controllable n-type doping of MoS$_2$ has not yet been demonstrated, p-type films are transferrable (due to the lack of out-of-plane bonds) and could be grown on conductive substrates, facilitating the study of the band alignment between MoS$_2$ and traditional 3D semiconductors. The study of these 2D/3D heterojunctions could lead to unique bipolar device topologies that circumvent issues with poor p-type performance experienced by wide band gap semiconductors.
Chapter 4

MoS$_2$-based 2D/3D Heterojunctions

4.1 Introduction

This chapter details the analysis of the 2D/3D heterojunctions formed between MoS$_2$ and the wide band gap semiconductors, SiC and GaN. These heterojunction devices are formed by direct growth (MoS$_2$/SiC) and film transfer (MoS$_2$/GaN) in order to form high quality heterojunction PN diodes.

Wide band gap (WBG) semiconductors have been exploited for a number of applications including high power devices due to their large breakdown field, and high speed and high frequency applications, specifically in the case of III-nitride wide band gap semiconductors. GaN benefits from high saturation velocity and low effective mass and thus can be utilized for high frequency applications. These and other wide band gap
semiconductors however, suffer from large hole activation energy, which leads to p-type material with large sheet resistance and low hole mobility. As such, NPN heterojunction bipolar transistors are limited by base resistance. Table 2.1 displays the electron and hole activation energies for several wide band gap semiconductors, and their prohibitively large hole activation energy.

<table>
<thead>
<tr>
<th></th>
<th>GaN</th>
<th>SiC</th>
<th>Ga₂O₃</th>
<th>AlN</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_g) (eV)</td>
<td>3.4</td>
<td>3.3</td>
<td>4.9</td>
<td>6.1</td>
<td>3.4</td>
</tr>
<tr>
<td>(E_a) (eV) Holes</td>
<td>0.16</td>
<td>0.20</td>
<td>N/A</td>
<td>0.50</td>
<td>0.18</td>
</tr>
<tr>
<td>(E_d) (eV) Electrons</td>
<td>0.015</td>
<td>0.085</td>
<td>0.060</td>
<td>0.063</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 4.1: Activation energy of wide band gap semiconductors

It is possible to circumvent the hole activation energy constraint by growing dissimilar materials on these wide band gap semiconductors in order to combine the high breakdown field of WBG semiconductors with the improved sheet resistance and hole mobility of a smaller band gap semiconductor. However, growing these heterointerfaces requires that the materials have similar basal planes and are lattice matched in order to improve material quality by mitigating interfacial strain that can induce dislocations in the grown material.

Transition metal dichalcogenides lack out-of-plane bonds, and as such can be integrated with a large range of epitaxial substrates without consideration for lattice
mismatch as a growth constraint. [92] [93] This is presents an opportunity for the extension of WBG semiconductor device technology, specifically integrating Nb-doped, p-type MoS$_2$ to form high quality heterojunctions that circumvent the issue of poor p-type conductivity as a barrier to high performance bipolar WBG devices.

The following details the characterization of the electronic properties of 2D/3D heterojunctions formed by both direct growth and by film transfer.

4.2 p-MoS$_2$ on 4H-SiC

4.2.1 Growth of MoS$_2$/SiC Heterojunctions

MoS$_2$ and 4H-SiC are both hexagonal basal plane semiconductors, allowing for direct growth of high quality Nb-doped MoS$_2$ films on SiC. The SiC substrates used in this study had a 4° miscut and were nitrogen doped with n-type carrier concentration of approximately $8.6 \times 10^{18}$ cm$^{-3}$. This carrier concentration was confirmed by capacitance-voltage measurement, which will be detailed in the following discussion.

Before MoS$_2$ growth, C-face SiC substrates were cleaned using acetone, isopropanol and deionized water, each with ultrasonic agitation. The substrates were dried for 5 minutes at 120°C. The degenerate, p-type metal precursor stack (Mo/Nb/Mo, 25 Å/2 Å/25 Å) was sputtered onto the substrates using an AJA Orion Radio Frequency/Direct Current (RF/DC) Sputter Deposition Tool. The metalized samples were then placed in quartz tubes with 90 mg of MoS$_2$ powder as the sulfur source. The quartz tubes were evacuated and sealed. The tubes were heated to 1100°C for 4.5 hours and then cooled to room temperature at a rate of 0.5°C/min. It should be noted that the growth process used to produce these films was optimized for growth on sapphire substrates and simply adapted for growth on SiC.
4.2.2 MoS$_2$/SiC Material Characterization

The resulting p-MoS$_2$ films were large area, and represent the first growth of high quality MoS$_2$ films on conductive substrates forming a high quality heterojunction. Figure 4.1 shows a 25 $\mu$m$^2$ atomic force microscopy (AFM) image of p-MoS$_2$ grown on SiC. The rms roughness of the films was found to be 1.66 nm (12 nm height scale). On-axis XRD spectra (Figure 4.2) exhibited the (002) family of diffraction peaks associated with 2H-MoS$_2$. The presence of large area, high quality MoS$_2$ was confirmed by Raman spectra (Figure 4.3). The Raman spectra showed the characteristic E$_{2g}^{1}$ and A$_{1g}$ peaks associated with the in-plane and out-of-plane vibrational modes of MoS$_2$. The peak intensity ratio of the vibrational modes, E$_{2g}^{1}$:A$_{1g}$, is greater than unity, indicating that high quality MoS$_2$ has been grown on 4H-SiC. The Raman spectra also shows a peak 203 cm$^{-1}$, which is the E$_2$ transverse acoustic mode for 4H-SiC. [94]
Figure 4.1: AFM image (5 µm X 5 µm, height scale: 12 nm) of p-MoS₂ grown on n-type 4H-SiC with rms roughness of 1.66 nm.

Figure 4.2: XRD spectra of p-MoS₂/n-SiC heterojunction exhibiting the (002) family of peaks for MoS₂ and the (004) peak of SiC.
4.3 Electrical characterization of MoS$_2$/SiC PN diodes

4.3.1 Vertical and lateral I-V characteristics

Ohmic contacts were patterned on p-MoS$_2$/n-SiC samples by ultraviolet stepper lithography (i-line), and the Ni/Au/Ni metal stack was deposited by electron beam evaporation. The device mesas for the vertical devices were etched using reactive ion etching with BCl$_3$/Ar chemistry (30 W RIE power). Contact to n-type SiC was made by scratching the substrate with a diamond scribe and applying an indium dot to the scratched area.

Lateral transport was measured between Ohmic pads on a mesa were characterized. Transfer length method, shown in Figure 4.4a, was used to characterize the Ohmic contact and sheet resistance. Contact resistance was found to be 0.8 $\Omega$-mm with a specific resistivity of $3.6 \times 10^{-6} \Omega\cdot\text{cm}^2$. The sheet resistance measured was 1.7 k$\Omega$/square.
corresponding with a resistivity of 1.7 m$\Omega$-cm. Lateral I-V characteristics were measured between Ohmic contacts on MoS$_2$, and the isolated films exhibited a current density of approximately 3 A/mm at 5 V (Figure 4.4b). While Hall measurements were not performed on p-MoS$_2$ grown on SiC, the metal stack precursor corresponds with a carrier concentration of 3.1 x 10$^{20}$ cm$^{-3}$ and hole mobility of 8.5 cm$^2$/V-s.

![Figure 4.4: Lateral I-V characteristics of p-MoS$_2$ grown on SiC confirming Ohmic contact; (a) TLM measurement (b) Lateral I-V.](image)

The vertical I-V characteristics of p-MoS$_2$/n-SiC heterojunction diodes were measured by applying bias between the Ohmic contacts to p-MoS2 and the backside In contact to the conductive SiC substrate. The room temperature I-V is shown in Figure 4.5. The inset of this figure shows the device configuration for the heterojunction PN diodes. The room temperature I-V characteristics of the diodes exhibited six orders of magnitude rectification at +/- 2 V with a forward current density greater than 100 A/cm$^2$. 

at 5 V. The p-MoS$_2$/n-SiC diodes were found to exhibit an ideality factor slightly greater than 2 at room temperature.

Low-temperature I-V characteristics were measured on the heterojunction diodes to further characterize the dominant transport mechanism in the low forward bias region. It should be noted that at applied bias greater than 1 V, conduction in the diode is resistance limited. The sample was cooled to 6.9 K by liquid helium, and I-Vs are measured up to room temperature. The slope of the I-V characteristics in the exponential region was maintained for each temperature, which suggests that the transport does not follow the diode current equation, since the ideality factor increases outside its specified range.

Figure 4.5: Temperature dependent vertical I-V characteristic of MoS$_2$/SiC PN junction with device structure included in the inset.
4.3.2 2D/3D heterojunction transport

Current density in the low-forward bias region of the MoS\textsubscript{2}/SiC heterojunction diode I-V characteristic was found to exhibit an exponential dependence on both applied bias and temperature. The heterojunction diode current can be expressed as

\[ J = B \exp(A_I V + \gamma T) \]  

(1)

where \( B \) is a constant dependent on tunneling probability, \( A_I \) is a temperature independent constant and \( \gamma \) is the temperature dependence of the bandgap. This transport mechanism is referred to as multi-step recombination tunneling and was reported by Riben and Feutch [95] and Marsal \textit{et al.} [96] In this case, electrons in the conduction band of SiC and holes in the valence band recombine via mid-gap states in the depletion region of SiC. To demonstrate this, diode current in the low forward bias range (0.55 V – 1.0 V) is plotted as a function of temperature (Figure 4.6a) and as a function of voltage (Figure 4.6b). In Figure 4.6a, each plot represents the diode current measured at a given bias for temperatures ranging from 6.9 K to 240 K. The diode current is shown to exhibit an exponential dependence on temperature, and the dependence is consistent for biases throughout the exponential region. The voltage dependence of the current is shown in Figure 4.6b. The natural logarithm of the current in the low bias region is plotted for each temperature, and the slope of the ln(J)-V characteristics is constant for all temperatures. This is consistent with the temperature independent \( A_I \) factor included in the voltage dependent part of the multi-step recombination tunneling equation.
Figure 4.6: Transport analysis confirming multi-step recombination tunneling as the transport mechanism in the low forward bias region of the MoS$_2$/SiC heterojunction. (a) Temperature-dependent J-V characteristic. (b) Ln(J)-V characteristic.

4.3.3 MoS$_2$/SiC conduction band offset extraction

The MoS$_2$/SiC heterojunction diodes were also characterized with capacitance-voltage (C-V) measurements. The C-V characteristic, shown in Figure 4.7, was typical for a reverse-biased PN junction. The inset of figure 4.7 shows the $\frac{1}{C^2}$ dependence on applied bias is linear, indicating a uniformly doped junction from which the built-in potential of the junction can be extracted. The built-in potential is given by the equation

$$V_{bi} = \frac{q\varepsilon_s N_D}{2C_Z^2} + \frac{kT}{q}$$  \hspace{1cm} (2)
where \( \epsilon_s \) and \( N_D \) are the dielectric constant and doping concentration of SiC, respectively, and \( C_{ZB} \) is the zero-bias capacitance. The built-in potential for the MoS\(_2\)/SiC heterojunction was found to be 2.2 eV. This value was also verified by the extrapolated voltage axis intercept of the \( \frac{1}{C^2} \) plot.

Figure 4.7: C-V characteristic of MoS\(_2\)/SiC diode with linear \( 1/C^2 \) plot from which a built-in potential of 2.2 V is extracted.

To determine the conduction band offset between MoS\(_2\) and SiC, we utilize the method of balancing the energy values to reach the Fermi level on either side of the junction. This given by the equation

\[
\Delta E_C = qV_{bi} - E_{g,MoS_2} - \Phi_p + \Phi_n
\]  

(3)
where $\Delta E_C$ is the conduction band offset and $\Phi_p$ and $\Phi_n$ are the energy difference between the valence band and the Fermi level on the MoS$_2$ side and that between the conduction band and the Fermi level on the SiC side, respectively. Due to the degenerate doping of p-MoS$_2$, it is expected that band tailing will result in bang gap narrowing. Band gap narrowing of MoS$_2$ has not been investigated and is beyond the scope of this work. To approximate the gap narrowing, we use that data reported for Si. This approximation is based on the similar band gap between Si and bulk MoS$_2$ as well as their similar hole effective mass. According to Ref. [97], we estimate a gap narrowing of approximately 250 meV. The approximate band gap of MoS$_2$ used for the conduction band offset is 0.95 eV. We calculated the values of $\Phi_n$ and $\Phi_p$ using the Joyce-Dixon approximation due to the degenerate doping of both MoS$_2$ and SiC. While the Fermi level approximately overlaps the conduction band in SiC ($\Phi_n \approx 0$ eV), $\Phi_p$ was 0.34 eV. These values correspond with a conduction band offset of 1.6 eV.
Figure 4.8: Band diagram of the MoS2/SiC heterojunction.

4.4 p-MoS2 on GaN

4.4.1 Film transfer process for MoS2/GaN heterojunction

The lack of out-of-plane bonds allows for TMDs to be transferred to other substrates. We form heterojunction diodes by transferring our degenerately doped MoS2 to GaN substrates to form heterojunction MoS2/GaN diodes.

The GaN templates onto which MoS2 was to be transferred were n-type doped from Lumilog \((N_D = 3 \times 10^{18} \text{ cm}^{-3})\). MoS2/GaN diodes were processed with as-received GaN templates and those on which an additional 200 nm of moderately doped GaN \((N_D = 7 \times 10^{17} \text{ cm}^{-3})\) was grown by molecular beam epitaxy. The electrical characteristics of both diodes will be detailed in section 4.5.

The transfer process depicted in Figure 4.9 is explained here. (1) Nb-doped MoS2 was grown on sapphire substrates as previously detailed. (2) Ohmic contacts were patterned on p-MoS2 using stepper lithography and (3) isolation mesas were patterned
using BCl$_3$/Ar RIE recipe that was previously detailed. In order to transfer the previously isolated devices to the GaN substrates, polymethylmethacrylate (PMMA) was used as a carrier polymer. (4) PMMA was spun onto samples with MoS$_2$ mesas and baked at 50°C. A solution containing NH$_4$OH, H$_2$O$_2$, and deionized water was prepared (1:1:3) and heated to 80°C in a process adapted from Ref. [98]. (5) Oxygen bubbles are formed in the solution when it is heated, and when the PMMA coated sample is submerged in the solution, the O$_2$ bubbles permeate the edges of the PMMA/MoS$_2$ film, lifting it off of the substrate. The PMMA/MoS$_2$ is removed from the solution and rinsed in a DI water bath. The GaN substrate is then used to fish out the detached film from the DI water bath, and the film is dried on the surface overnight. The film is then baked for 25 minutes at 125°C to remove any water remaining at the MoS$_2$/GaN interface. (6) The transferred films are soaked in NMP for 20 minutes, and then washed in acetone, IPA and DI water.

Figure 4.9: Film transfer process for fabricating MoS$_2$/GaN heterojunction diodes.
An AFM image of the MBE grown, moderately doped GaN layer is shown in Figure 4.10a. The 5 µm x 5 µm scan had an RMS roughness of 0.63 nm and the height scale for the image is 5 nm. Figure 4.10b shows the AFM image of the MoS$_2$ film after it is transferred to a GaN substrate. The 2 µm x 2 µm scan exhibited a RMS roughness of 1.95 nm with a height scale of 15 nm. The films were also characterized with XRD after being transferred to GaN. The on-axis scan of the MoS$_2$/GaN stack is shown in Figure 4.11, and exhibits the (002) family of diffraction peaks associated with MoS$_2$. The XRD scan also shows the (002) peak of GaN and the (006) peak of sapphire associated with the Lumilog templates. It should be noted that the intensity of the (002) and (006) diffraction peaks associated with MoS$_2$ decreased in comparison to as-grown MoS$_2$. The (004) peak is not exhibited, likely due to some film degradation, its structure factor is the weakest among the family of peaks. Figure 4.12 shows a micrograph of the devices after transfer and PMMA removal. It should be noted that the devices are not wrinkled or folded after the transfer process. The remaining flakes in the field between devices was from the material not removed by dry etching.
Figure 4.10: AFM images of (a) GaN after growth of the moderately doped layer (5 µm X 5 µm, height scale: 5 nm) and (b) p-MoS₂ after film transfer (2 µm X 2 µm, height scale: 15 nm).

Figure 4.11: XRD spectra of p-MoS₂ transferred to GaN
4.4.2 Electrical and optical characterization of MoS$_2$/GaN heterojunction

The MoS$_2$/GaN PN diodes were measured using an Agilent B1500 Parameter Analyzer. Contact to the GaN substrate was made by indium dot. Figure 4.13 shows the device schematics for the two MoS$_2$/GaN diodes discussed in this section.
Figure 4.13: MoS$_2$/GaN PN diode device configuration and epitaxial stack.

The vertical J-V characteristic for the diode described by Figure 4.13a is shown in Figure 4.14. The diode exhibited one order of magnitude rectification at +/− 2V. We attributed the large current in reverse bias to band-to-band tunneling due to the large doping concentration of p-MoS$_2$ and n-GaN, respectively. This large reverse current precluded us from measuring the C-V characteristic of the junction to determine more information about the band lineup of the MoS$_2$/GaN heterojunction.
We reduce the reverse leakage by growing a 200 nm moderately doped layer ($N_D = 5 \times 10^{17} \text{ cm}^{-3}$) of GaN on the Lumilog templates to increase the depletion width between MoS$_2$ and GaN, suppressing band-to-band tunneling in reverse bias. The device schematic is shown in Figure 4.13b. The J-V characteristic of this junction is shown in Figure 4.15. This diode showed a significant reduction in reverse biased current, as the rectification at +/- 2 V has increased to 9 orders of magnitude. The diode also exhibited an ideality factor of approximately 2 in the exponential region of the J-V characteristic before series resistance became dominant. This is consistent with recombination dominant conduction mechanism. The inset of Figure 4.15 shows the linear J-V characteristic.
Capacitance-voltage measurements were performed on the MoS$_2$/GaN diodes to determine the heterojunction band lineup. The C-V characteristic (Figure 4.16) showed low loss, and was consistent with that of a reverse-biased PN junction. The $\frac{1}{\varepsilon}$ plot was linear with respect to applied bias, and a built-in potential of 1.5 V was extracted from the intercept with the voltage axis. The assumptions for band gap narrowing in degenerately doped p-MoS$_2$ and Fermi level position are the same as those discussed in Section 4.3. Using Equation (3) and the data extracted from the C-V, we determine a conduction band offset of 230 meV.
Figure 4.16: C-V characteristic of MoS$_2$/GaN diode with linear $1/C^2$ plot from which a built-in potential of 1.5 V is extracted.

The MoS$_2$/GaN heterojunction was also characterized optically by internal photoemission (IPE) measurements. This measurement characterizes the conduction band offset between MoS$_2$ and GaN by optically exciting electrons from the valence band of MoS$_2$ over the barrier between MoS$_2$ and GaN. A Xe lamp was utilized for the optical excitation, and the incident photon energy was swept from 1.2 eV to 2.5 eV. The photocurrent was measured with an electrometer, and it was normalized to the flux variation of the lamp in order to ensure that the measured onset was not shifted by contributions of the lamp. Finally, no bias was applied to the junction for the measurement. [48] Fowler’s hypothesis [99] and Ref. [100] assert that photocurrent associated with electron excitation from the valence band of an indirect semiconductor and the subsequent emission of those photoexcited carriers over a potential barrier
exhibits a quadratic dependence on incident photon energy. This photo-yield, \( Y \), is given by

\[
Y = A(h\nu - E)^2
\]  

(4)

where \( A \) is a constant, \( h\nu \) is the energy of the incident photon and \( E \) is the total energy needed to excite an electron from the valence band of MoS\(_2\) to the conduction band of GaN. Figure 4.17 shows the square root of the photo-yield as a function of incident photon energy extracted from the IPE spectra for the MoS\(_2\)/GaN heterojunction diode. An onset 1.46 eV was extracted from the linear region.

The conduction band offset for MoS\(_2\)/GaN was extracted from the optical measurements using the equation

\[
\Delta E_C = E_0(E_{g,MoS_2} + \Phi_p)
\]  

(5)

where \( E_0 \) is the energy threshold determined by the IPE measurement and \( \Phi_p \) is the Fermi level position in MoS\(_2\). Based on this calculation, the IPE measurement determined a conduction band offset of 170 meV. The measurement apparatus introduced an error of approximately 50 meV.
The electrical and optical characterization of the conduction band offset between MoS$_2$ and GaN exhibit satisfactory agreement. Figure 4.18 shows the band diagram of the MoS$_2$/GaN heterojunction. The diagram shows the offset determined by electrical measurements (0.23 eV).
The small conduction band offset between MoS$_2$/GaN allows for efficient electron injection from MoS$_2$ to GaN while blocking hole injection. These characteristics make this heterojunction ideal for the emitter-base and/or base-collector junctions in a heterojunction bipolar transistor. This work also demonstrates that 2D/3D heterojunctions can be treated electrically using theory developed for traditional heterojunctions, in spite of their unique layered structure. In chapter 3, Nb-doped, p-type MoS$_2$ was shown to achieve specific contact resistance and resistivity that compare favorably with p-GaN. The following chapter details transistors that utilize MoS$_2$/GaN as the base-collector junction of a hot electron transistor, and we evaluate the potential of its high frequency performance to achieve a cutoff frequency that exceeds that which can be produced by GaN-based electronics.

4.5 Summary and Conclusion
2D/3D heterojunction diodes utilizing MoS₂ and wide band gap semiconductors were demonstrated both by direct growth (MoS₂/SiC) and by film transfer (MoS₂/GaN). Both diode I-V characteristics exhibited rectification, and the C-V characteristics were used to extract the conduction band offsets in both cases. Internal photoemission measurements were also used to confirm the conduction band offset between MoS₂ and GaN. The small conduction band offset between MoS₂ and GaN (ΔE_C = 0.2 eV) makes the heterojunction an ideal candidate for the base/collector junction in a heterojunction bipolar transistor.

Due to constraints in the growth recipe in this work, growing a semiconductor emitter on MoS₂ is outside the scope of this work. However, tunneling heterojunction bipolar transistors could be achieved by utilizing Al₂O₃ as a tunneling layer for an emitter.
Chapter 5

2D/3D Tunneling Heterojunction Bipolar Transistor

5.1 Introduction

Heterojunctions formed between 2D materials and 3D semiconductors have been discussed for several device applications in literature. These 2D/3D heterojunctions benefit from the ability to use 2D materials to circumvent lattice mismatch when integrating dissimilar material systems, as detailed in chapter 4. Several reports have presented devices based on the integration of TMDCs with traditional semiconductors.

Solar cells, photodetectors and heterojunction diodes based on MoS$_2$/Si heterojunctions have been explored in several reports, with photodetectors exhibiting excellent photoresponsivity and specific detectivity. [101] [102] [103] [104] [105] [106] [107] [108] [109] [110] MoS$_2$/InP solar cells [111] and MoS$_2$/GaAs solar cells [112] and photodetectors [113], and other devices have also been reported demonstrating the
versatility of MoS$_2$ in being transferred, exfoliated and grown on a wide range of substrates. [114] [115] [116] Sarkar et. al. demonstrated a tunnel field-effect transistor with sub-thermionic threshold slope based on the MoS$_2$/Ge heterojunction. [117] While studies of the band alignment between TMDCs and other semiconductor materials is important for evaluating what material combinations lend themselves well toward different device configurations, demonstration of devices is critical to the evaluation of the viability of 2D/3D heterojunctions for future electronics.

This chapter details the development of a tunneling heterojunction bipolar transistor (THBT) utilizing atomic layer deposited Al$_2$O$_3$ as an emitter layer, p-type MoS$_2$ as the base layer and n-type wide band gap semiconductors (SiC and GaN) as the collector. It has been shown that performance of wide bandgap, homojunction BJTs is degraded significantly by poor p-type material, and integration of p-type MoS$_2$ into these devices could significantly improve their performance by reducing the total intrinsic delay.

Intrinsic delay is given by,

\[ \tau = q \frac{t_{base}^2}{2\mu kT} + \frac{kT \varepsilon}{qI_c} (C_{je} + C_{jc}) + \frac{W_{depl}}{2v_{sat}} + R_{base} C_{jc} \]  

(1)

where $t_{base}$ is the base layer thickness, $\mu$ is the mobility, $I_c$ is the collector current, $C_{je}$ and $C_{jc}$ are the emitter/base and base/collector capacitances, respectively, $W_{depl}$ is the base/collector depletion width, $v_{sat}$ is the saturation velocity, and $R_{base}$ is the base resistance. [118] Base resistance becomes a critical limiting factor for GaN-based HBTs.
due to low hole mobility and large acceptor ionization energy. [119] [120] The reduction in base resistance by using p-MoS$_2$ instead of p-type wide band gap materials provides a pathway toward high frequency operation HBTs. Using digital etching to thin the base layer [121] and increasing the collector current through device engineering are other ways to reduce this delay.

A semiconductor material, particularly n-doped GaN, would be preferable as MBE growth of GaN on MoS$_2$ has been demonstrated previously [122] and the GaN MoS$_2$ junction would provide significant injection of electrons from GaN into MoS$_2$ (~1 kA/cm$^2$, Chapter 4) and large valence band offset for excellent emitter injection efficiency. However, development of the growth of high quality GaN on our large-area, single crystal MoS$_2$ is beyond the scope of this work. A GaN/MoS$_2$/GaN npn-HBT would likely also be ideal for maximizing current injection and approaching THz cutoff frequency. However, this chapter aims to demonstrate the potential of the MoS$_2$/wide bandgap semiconductor base/collector junction for providing pathways toward high performance 2D/3D HBTs.

The concept of current injection using ALD MoS$_2$ has been explored by Di Lecce et al. [123] This work showed that Fowler-Nordheim tunneling injection was achieved in Al$_2$O$_3$/GaN MOS diodes. Utilizing an Al$_2$O$_3$ emitter and tunneling, we inject electrons into the base. It should be noted that the Al$_2$O$_3$/p-MoS$_2$ junction is utilized as the base/emitter junction in all device configurations discussed in this chapter.

5.2 Emitter/base junction: Al$_2$O$_3$/MoS$_2$ MOS diode
5.2.1 Al$_2$O$_3$/MoS$_2$ by direct deposition

A 20 nm Al$_2$O$_3$ emitter was deposited on MoS$_2$ by atomic layer deposition at 250ºC using trimethyl aluminum (TMA) and water as precursors (TMA first). After deposition, emitter pads were patterned by stepper lithography (i-line) and a Ti/Au/Ni metal stack was evaporated on Al$_2$O$_3$ to serve as the emitter contact. Windows were opened in the Al$_2$O$_3$ layer with by dry etching (ICP/RIE, BCl$_3$ chemistry) so that Ohmic contacts could be evaporated on p-MoS$_2$ (Ni/Au/Ni). The device configuration for the Al$_2$O$_3$/p-MoS$_2$ metal-oxide-semiconductor (MOS) diode is shown in Figure 5.1a. Figure 5.1b shows the I-V characteristic of the junction with significant leakage current at low emitter bias. This is indicative a poor emitter/base interface. The I-V is approximately symmetric between emitter biases of ±5 V. As the magnitude of negative bias applied to the emitter increases beyond 5 V, the tunneling current becomes dominant and the I-V ceases to be symmetric. The injection current at $V_E = -10$ V was approximately $10^{-4}$ A/cm$^2$, which is extremely low compared to those achieved for wide band gap homojunction BJTs.
5.2.2 Al$_2$O$_3$/MoS$_2$ with AlO$_x$ transition layer

A thin layer of AlO$_x$ was used as a transition layer to promote the conformal deposition of Al$_2$O$_3$ by ALD and subsequently improve the Al$_2$O$_3$/MoS$_2$ interface. 2.5 nm of Al was evaporated on degenerately doped p-MoS$_2$ (CHA Evaporator), and the Al layer was oxidized in low power O$_2$ plasma (Diener Pico Oxygen Plasma Asher) to produce a thin layer of AlO$_x$. After Al oxidation, 20 nm of Al$_2$O$_3$ was deposited by ALD at 250°C. Typical MOS diode I-V characteristics showed approximately an order of magnitude rectification for electron injection from Al$_2$O$_3$ to MoS$_2$. While increased current density
was observed (on the order of 1 A/cm² at $V_E = -5$ V), I-Vs were extremely leaky compared to direct deposition of Al₂O₃ on MoS₂.

5.2.3 Al₂O₃/MoS₂ with MoOₓ transition layer

It is clear that achieving high quality interfaces between Al₂O₃ and MoS₂ is challenging due to the lack of out of plane bonds in MoS₂. When the interface is not pristine, low-energy leakage paths exist likely due to pinholes in the Al₂O₃ or states at the Al₂O₃/MoS₂ interface due to processing steps or the introduction of a non-native transition layer.

Lee et al. showed that the top monolayer of MoS₂ can be oxidized with low power O₂ plasma. [121] This process provides a native MoOₓ transition layer that facilitates conformal Al₂O₃ deposition, producing a high quality oxide-semiconductor interface. [124] A visualization of this oxidation step is shown in Figure 5.2.

![Figure 5.2: Oxidation of top monolayer of MoS₂ to facilitate high quality Al₂O₃ deposition by ALD.](image)
The top monolayer of degenerately doped p-MoS\textsubscript{2} samples was oxidized in low power O\textsubscript{2} plasma for 30 minutes to produce MoO\textsubscript{x} on the surface. A 20 nm thick layer of Al\textsubscript{2}O\textsubscript{3} was then deposited on p-MoS\textsubscript{2} by ALD at 250\textdegree C. A 5 \textmu m X 5 \textmu m AFM scan of the sample surface after atomic layer deposition (shown in Figure 5.3) features consistent with previously discussed MoS\textsubscript{2} morphology with low RMS roughness (1.1 nm), indicative of conformal Al\textsubscript{2}O\textsubscript{3} deposition.

![AFM image](image)

**Figure 5.3:** AFM image (5 \textmu m X 5 \textmu m, height scale: 5 nm) of ALD Al\textsubscript{2}O\textsubscript{3} deposited on MoS\textsubscript{2} with MoO\textsubscript{x} interfacial layer with rms roughness of 1.15 nm.

MOS diodes were fabricated using the process described in Section 5.2.1. I-V characteristics of the 20 nm Al\textsubscript{2}O\textsubscript{3} MOS diodes showed suppressed leakage in the low-
bias regime, with current below the noise floor of our measurement apparatus. This suggests that the native MoO\textsubscript{x} transition layer has removed low energy leakage paths promoting tunneling as the exclusive conduction mechanism through the oxide layer. Figure 5.4a shows the typical I-V for the MOS diodes produced with the MoO\textsubscript{x} transition layer. When compared directly to the I-V characteristic from the MOS diode discussed in Section 5.2.1, it is clear that tunneling becomes the dominant conduction mechanism at approximately the same applied field. Also, the current density at \( V_E = -10 \) V has increased by two orders of magnitude. The C-V characteristic for the MOS diode was constant over a 6 V sweep with negligible loss (Figure 5.4b). C-V analysis also confirmed the Al\textsubscript{2}O\textsubscript{3} thickness. The 20 nm ALD samples were dry etched (5 nm in BCl\textsubscript{3} plasma) to fabricate 15 nm diodes which also exhibited suppression of low energy leakage paths and Fowler-Nordheim tunneling onset (I-V and C-V shown in Figure 5.4c and 5.4d, respectively).
The work function of titanium (the emitter contact) is approximately 4.3 eV. The electron affinity of MoS$_2$ is 4.1 eV. Considering the position of the Fermi level in our degenerately doped p-MoS$_2$ ($E_V - E_F = 0.34$ eV), the work function of p-MoS$_2$ is approximately 5.3 eV. From the work function difference, we can infer that the total potential drop across the oxide layer of these MOS diodes is about 1 V, equivalent to the work function difference between p-MoS$_2$ and Ti.
Typical MOS diodes with 20 nm and 15 nm oxide layers exhibited tunneling onsets at approximately $V_E = -6.6$ V and $V_E = -3.3$ V, respectively. The field in the oxide, $F_{ox}$, at the onset of tunneling is given by

$$F_{ox} = \frac{V_{on} + V_{FB}}{t_{ox}}$$

(2)

where $V_{on}$ is the applied bias corresponding with the tunneling onset, $V_{FB}$ is the flat band voltage and $t_{ox}$ is the thickness of the oxide. The onset for the 20 nm MOS diodes corresponds with a oxide field of 3.8 MV/cm, while the onset of the 15 nm diodes corresponded with $F_{ox} = 2.8$ MV/cm. While the difference in the onset field could be attributed to charged states at the metal/oxide interface introduced by the dry etching process, the tunneling onset for the 20 nm MOS diode could occur at bias below the detection limit of the parameter analyzer.

Tunneling current begins to flow when electrons injected from the emitter contact see a triangular barrier in the oxide layer. Fowler-Nordheim tunneling current is given by

$$J_{FN} = A \times F_{ox}^2 \times \exp\left(-\frac{4}{3hqF_{ox}} \sqrt{2m^*\Phi_{Barr}^3}\right)$$

(3)

where $m^*$ is the tunneling effective mass, $\Phi_{Barr}$ is the barrier seen by electrons, $h$ is Planck’s constant and $A$ is a parameter dependent on $m^*$ and $\Phi_{Barr}$. [123] [125] [126] Fowler-Nordheim tunneling was confirmed in both the 20 nm and 15 nm Al$_2$O$_3$ MOS
diodes by extracting the linear region in Figure 5.5, for which the onset of the tunneling current corresponds with the previously mentioned onsets.

Figure 5.5: Confirmation of Fowler Nordheim tunneling in Al_{2}O_{3}/MoS_{2} MOS diodes with oxide thicknesses (a) 15 nm and (b) 20 nm.

Using the MoO_{x} transition layer leads to the optimal Al_{2}O_{3}/MoS_{2} emitter/base junction for the 2D/3D THBTs. This native transition layer minimizes leakage in the base/emitter I-V characteristics by eliminating the introduction of interface states that may promote low-energy leakage paths.

5.3 Base/Collector Junction

5.3.1 MoS_{2}/SiC and MoS_{2}/GaN Base collector

Recall from Chapter 4 the band line up between MoS_{2} and SiC and MoS_{2} and GaN, respectively. These 2D/3D junctions are the base/collector junctions for the 2D/3D THBTs. Forward-active operation of the transistors requires the base collector junction
operate in reverse bias, facilitating the collection of electrons that have diffused across the base after being injected from the emitter.

The following sections discuss the characterization of the THBTs based on the previously reported 2D/3D heterojunctions.

5.4 2D/3D THBTs

5.4.1 Al₂O₃/p-MoS₂/n-SiC THBT

Degenerately doped MoS₂ was grown directly on 4H-SiC templates as discussed in Section 4.2. A 5 nm Al₂O₃ emitter was deposited without a transition layer at 250°C. Transistors were fabricated using stepper lithography and using Ti/Au/Ni and Ni/Au/Ni metal stacks for the emitter and base contacts, respectively. The collector contact was made by scratching the substrate on the backside and applying an indium dot. Figure 5.6a and 5.6b show the top view and cross-section of typical 2D/3D THBT devices, respectively.

Figure 5.6: (a) Top view of vertical THBT devices. (b) THBT device cross section.
Ohmic base contacts were confirmed from the linear I-V characteristics between contacts to p-MoS$_2$. The base/collector junction I-V exhibited seven orders of magnitude rectification at ±2 V and emitter injection was consistent with the leakage previously discussed for the emitter layer deposited without a transition layer. Figure 5.7 summarizes the junction characteristics.

![Figure 5.7: MoS$_2$/SiC THBT Junction characteristics (a) Base Ohmic pads; (b) Emitter/base junction; (c) Base/collector junction.](image)

THBT devices were characterized by common base configuration. Per this configuration, the base was connected to the common terminal of the B1500 parameter analyzer while the collector bias was held at zero bias. Negative bias was applied to the emitter to inject electrons into the base. The common base current gain, $\alpha$, is given by

$$\alpha = \frac{I_C}{I_E}$$  \hspace{1cm} (4)
which defines the amount of collectors injected from the emitter that reach the collector. Optimally, all electrons injected from the emitter reach the collector and $\alpha = 1$. In the case of the MoS$_2$/SiC based THBT, however the common base characteristic exhibits $\alpha = 0$, as zero collector current is observed. Figure 5.8a shows the common base characteristic for this device.

The large conduction band offset between MoS$_2$ and SiC ($\Delta E_C = 1.6$ eV) is the most likely cause for the poor device performance. Electrons injected into the base from the emitter must diffuse across about 10 nm of degenerately doped MoS$_2$. It is likely that some of these minority carriers recombine in the base as they diffuse through MoS$_2$. Should any electrons reach the MoS$_2$/SiC interface, they see a large barrier corresponding with the conduction band offset. These carriers likely are reflected at the barrier and recombine in the base. Figure 5.8b depicts this process.
Due to the large conduction band offset between MoS\textsubscript{2} and SiC, this 2D/3D heterojunction is not suitable for THBT devices. We have previously shown that the conduction band offset between MoS\textsubscript{2} and GaN is negligible by comparison, and explore this junction as a potential base/collector.
5.4.2 Al₂O₃/p-MoS₂/n-GaN THBT

MoS₂/GaN junctions were fabricated utilizing PMMA as a carrier polymer and chemical bubbling to transfer the films from sapphire to GaN as was described previously in Chapter 4. After transfer, the sample was dried in a N₂ desiccator overnight, followed by removal of PMMA before subsequent device processing.

This transfer process ensures that the MoS₂ surface is not pristine. Section 5.2 detailed the importance of a high quality Al₂O₃/MoS₂ interface for the emitter/base junction of the 2D/3D THBTs. However, the carrier polymer introduces residue on the MoS₂ surface that cannot be removed and promotes leakage in the junction. A benign transfer method using deionized water and utilizing the difference in surface energies of MoS₂ and the sapphire substrates on which the films were grown was used to transfer large area, single crystal MoS₂ from sapphire to other substrates has been demonstrated previously. [127] This process was not suitable for degenerately doped MoS₂, as the non-single crystal films broke up into very small flakes upon being separated from the sapphire substrates by DI water. These small flakes made stepper lithography extremely difficult.

Growth of GaN on MoS₂ was previously demonstrated by Yamada et al. and MoS₂ growth on GaN could provide a pristine MoS₂ surface for THBT fabrication. [122] However, the growth process used to produce large-area, Nb-doped MoS₂ introduced constraints precluding the use of GaN templates due to decomposition during direct growth of MoS₂ on GaN. The MBE growth of MoS₂ on GaN is being explored, but is outside the scope of this work. Due to these constraints, bubbling transfer was necessary.
to maximize the area of p-MoS$_2$ transferred to GaN in order to facilitate device fabrication.

For the first iteration of the 2D/3D Al$_2$O$_3$/MoS$_2$/GaN THBTs, p-MoS$_2$ was transferred to Lumilog GaN templates with doping concentration $N_D = 3 \times 10^{18}$ cm$^{-3}$, by chemical bubbling. A 20 nm layer of Al$_2$O$_3$ was deposited on the samples by atomic layer deposition. The device cross section is detailed in Figure 5.9a. The base collector I-V (Figure 5.9b) showed significant reverse-bias current due to band-to-band tunneling as a result of the highly doped base and collector. Figure 5.9c shows the emitter/base I-V with high leakage due to the poor interface achieved without a MoO$_x$ transition layer. Transistors were subsequently measured in both common base and common emitter configurations.
Figure 5.9: (a) Cross-section of MoS$_2$/GaN based THBT. (b) Base/collector I-V characteristic. (c) Emitter/base I-V characteristic.

The common base current gain was 2.3%, showing that the reduction of the conduction band offset at the base/collector junction allowed electrons injected from the emitter to reach the collector (Figure 5.10b). Figure 5.11 shows the band diagram of the common base configuration of the MoS$_2$/GaN THBT, showing that without a barrier at the base/collector junction, electrons that diffuse to the interface may reach the collector. The low gain could be attributed to significant minority carrier relaxation in the base and recombination at the interfaces. It is important to note that electrons injected into the base from the emitter at applied emitter bias below approximately 1.2 V could not be injected into the conduction band of MoS$_2$, and thus could not diffuse to the base collector interface. Figure 5.10a shows the Gummel plot for the device. Most of the electrons
injected from the emitter relaxed in this case, but the plot of the common base current gain showed gain above $V_{BE} = 1.2$ V, reflected by the slight increase in $I_C$ in the Gummel plot, and more clearly observed in the plot of the common base gain as a function of emitter bias (Figure 5.10c).

The device was also measured in common emitter configuration (Figure 5.10c). Positive bias was applied to the collector ($V_C = 2.5$ V) to reverse bias the base/collector junction. The emitter was the common terminal while holes were injected into the base by applying positive bias to that terminal. At $V_{BE} = 0$ V, the reverse current due to band-to-band tunneling gives a non-zero collector current. As the base was swept in the positive direction, electrons were injected from the emitter. Positive transconductance should be apparent as an increase in the collector current as $V_{BE}$ is increased beyond the band gap of MoS$_2$. However, as shown in the common base configuration, a small amount of electrons injected from the emitter can reach the base at this low bias. Once the emitter/base bias at which the common base gain is approximately 1% ($V_{BE} = 4$) is reached, the base/collector junction is forward biased, and the collector current decreased.
Figure 5.10: (a) Gummel plot depicting slight increase in collector current. (b) Common base gain showing an increase beginning at $V_{BE} = 1.2$ V. (c) Common emitter measurements dominated by base/collector leakage.
Figure 5.11: Band diagram of the $\text{Al}_2\text{O}_3$/MoS$_2$/GaN THBT depicting electrons reaching the collector in common base configuration.

In order to demonstrate positive transconductance, the current due to Zener tunneling in the MoS$_2$/GaN diode was suppressed by device engineering. The following section discusses the device design changes that enabled positive transconductance in MoS$_2$/GaN based 2D/3D THBTs.

5.4.3 $\text{Al}_2\text{O}_3$/p-MoS$_2$/n-GaN THBT with device engineering

While the previous iteration of the MoS$_2$/GaN 2D/3D THBT used as-received Lumilog GaN templates as the collector, a collector/subcollector device stack was used to reduce the band-to-band tunneling in the base/collector. The collector layer was comprised of a 50 nm unintentionally doped GaN collector on 200 nm, n-doped GaN ($N_D = 1 \times 10^{19} \text{ cm}^{-3}$) subcollector on the Lumilog templates, grown by MBE (Veeco). The UID GaN collector served to increase the tunneling barrier and due to the constant field
drop across the UID material, any electrons reaching GaN should be swept into the subcollector. Figure 5.12a shows the MoS$_2$/GaN THBT device stack while 5.12b shows the corresponding band diagram for the device.

![Device stack and band diagram for MoS$_2$/GaN THBT](image)

Figure 5.12: (a) Device stack for MoS$_2$/GaN THBT with collector/subcollector device design. (b) Band diagram of THBT.

p-MoS$_2$ was again transferred to GaN, but in order to minimize the residual PMMA on the p-MoS$_2$ surface after film transfer, the samples were soaked in heated NMP for one hour before the standard PMMA removal process. After removal, the MoS$_2$/GaN samples were oxidized in O$_2$ plasma for 30 minutes to produce the MoO$_x$ transition layer. A 5 nm layer of Al$_2$O$_3$ was then deposited at 250°C. Subsequent device processing was consistent with the previously discussed THBT processing recipe.

Despite the extensive efforts to clean the MoS$_2$ surface before MoO$_x$ transition layer oxidation, the use of the carrier polymer for transfer introduces interface states that
were reflected in the emitter/base I-V characteristic by low-bias leakage. As stated previously, this problem could not be circumvented within the scope of this work.

Figure 5.13 details the junction characteristics of the MoS$_2$/GaN THBT. The base/collector junction exhibits improved rectification as a result of the collector/subcollector design (Figure 5.13a). Reverse-bias current in the base/collector diode is below the noise floor for collector bias, $V_C < 2$ V. Figure 5.14b shows the emitter/base characteristic with high leakage due to the compromised surface obtained by using a carrier polymer in the chemical bubbling transfer process.

Figure 5.13: (a) Base/collector I-V with suppressed band-to-band tunneling leakage in reverse bias. (b) Emitter/base I-V exhibiting high leakage current due to poor interface created by the transfer process.

The THBT was again characterized in common base (Figure 5.14a) and common emitter (Figure 5.14b) configurations. Common base analysis showed that despite the large base emitter leakage, electrons injected as the emitter was swept negatively diffuse
through the base and reach the collector beginning at $V_{BE} \approx 1.2$ V, as was the case for the previously discussed device configuration. The common base current gain, $\alpha$, was approximately 0.01%. In common emitter, the collector was held at 2 V while the base potential was swept positively. The non-zero collector current at zero-bias in common emitter was due to the current in the reverse-biased base/collector diode. The positive sweep on the base terminal caused electrons to be injected from the emitter, and once $V_{BE}$ was greater than the band gap of MoS$_2$, the collector current increased. This increase in collector current shows positive transconductance.

Figure 5.14: (a) Gummel plot consistent with $\alpha \approx 0.01\%$, where gain is observed above $V_{BE} = 1.2$ V. (b) Common emitter characteristic exhibiting positive transconductance.

While the 2D/3D THBT exhibits proper operation, common base gain is much too low for high performance devices. The common base gain $\alpha$ is given by [118]
\[ \alpha = \Gamma \alpha_T M \] (5)

where \( \Gamma \) is the emitter injection efficiency, \( \alpha_T \) is the base transport factor and \( M \) is the avalanche multiplication coefficient. [118] The emitter injection efficiency would likely be improved by achieving a pristine MoS\(_2\) surface on GaN by direct growth. \( \alpha_T \) depends on the amount of the electrons injected in the base that reach the collector. As the amount of electrons that relax in the base increases, the base transport factor decreases, ultimately reducing the common base gain. The base transport factor could be enhanced by thinning the base layer. [121]

This demonstration of positive transconductance and the correlation between common base and common emitter configuration measurements of the 2D/3D MoS\(_2\)/GaN THBT show that the integration of wide band gap semiconductors holds promise for achieving high performance devices through the integration of 2D TMDCs and wide band gap semiconductors.

5.5 Summary and Conclusion

Al\(_2\)O\(_3\)/MoS\(_2\)/GaN tunneling heterojunction bipolar transistors were shown to exhibit positive transconductance and common base gain of 0.01%. The gain is likely low due to a combination of low base transport factor and emitter injection efficiency. However, the transistor shows gain in both common base and common emitter configurations, ensuring that hole injection into the base layer leads to an increase in electrons that reach the collector.
THBT gain could be improved by improving the Al$_2$O$_3$/MoS$_2$ interface to reduce leakage and subsequently improve the emitter injection efficiency. In order to achieve this pristine interface, p-doped MoS$_2$ must be grown directly on GaN.
Chapter 6

Conclusions and Future Work

6.1 Conclusion

This thesis has explored growth and doping techniques for MoS$_2$ films that provided pathways toward producing 2D/3D heterojunction bipolar transistors.

Large-area, single crystal MoS$_2$ was achieved by CVT growth utilizing Mo metal sputtered onto sapphire substrates and MoS$_2$ powder as the Mo and S precursors, respectively. The films were approximately 10 nm thick and were characterized by AFM, XRD, Raman spectroscopy and TEM. These characterization methods showed that our films were continuous and smooth-surfaced, exhibited excellent crystalline quality and epitaxial registry with sapphire substrates, and pristine orientation. Electrical measurements showed that transport was space-charge limited and space-charge mobility as high as 192 cm$^2$V$^{-1}$s$^{-1}$ was observed. Photoconductive measurements exhibited an
optical onset at incident wavelength consistent with the direct band gap of MoS$_2$ (1.8 eV). Photodetectors based on MoS$_2$ showed persistent photoconductivity and high photoresponsivity without dark current suppression techniques.

The first stable, substitutional doping of large-area, continuous MoS$_2$ was demonstrated by adding Nb to the metal precursor. Nb acts as a p-type dopant, and the typical degenerately doped p-MoS$_2$ films exhibit a resistivity of 10 mΩ-cm. Degenerately doped films were found to exhibit Hall mobility of approximately 10 cm$^2$V$^{-1}$s$^{-1}$. Material characterization showed that degenerate doping precluded the films from achieving the single crystallinity achieved for unintentionally doped MoS$_2$, while optical absorbance measurements showed that the films maintained semiconductor characteristics despite high doping. Alloyed precursors were used to lower the doping of p-MoS$_2$, and single-crystal p-type MoS$_2$ was demonstrated.

Heterojunction diodes formed between 2D p-MoS$_2$ and 3D, wide band gap, n-type semiconductors were studied to extract their band line up and to assess the viability of the heterojunctions for different device technologies. MoS$_2$/SiC heterojunctions were formed by direct growth, while a film transfer process was used to achieve MoS$_2$/GaN heterojunction diodes. Capacitance-voltage measurements were used to extract the conduction band offsets in both 2D/3D heterojunctions. MoS$_2$/SiC was found to exhibit a large barrier in the conduction band ($\Delta E_C = 1.6$ eV) while MoS$_2$/GaN had a conduction band offset of 0.2 eV. The offset in MoS$_2$/GaN was also confirmed by internal photoemission measurements. The analysis of these vertical 2D/3D heterojunctions shows that despite the van der Waals gaps between individual MoS$_2$ monolayers in bulk,
traditional semiconductor device physics is relevant for understanding transport in these junctions.

Finally, tunneling heterojunction bipolar transistors were demonstrated with electrons injected into the p-MoS$_2$ base from the Al$_2$O$_3$ emitter via Fowler-Nordheim tunneling. n-GaN was utilized as the collector. Fowler-Nordheim tunneling was confirmed in the MOS diode comprised by the emitter/base junction, and common base measurement of the THBT showed that electrons injected from the emitter diffused across the base to reach the collector. Common emitter measurements demonstrate similar gain, and show that hole injection into the base can dictate the operation of the device.

**6.2 Future Work**

**6.2.1 van der Waals epitaxy of 2D/3D heterojunctions**

We have shown that transistors based on 2D/3D heterojunctions can be developed with proper device engineering (collector/subcollector design) and by improving the junctions (MoO$_x$ transition layer for the emitter/base junction) to ensure a pristine interface and improve transport.

Van der Waals epitaxy refers to the growth of 2D materials like TMDs onto 3D substrates on which the dangling bonds are terminated. [128] [129] The lattice mismatch constraints usually present for growth of highly dissimilar materials are relaxed with van der Waals epitaxy, and as such, many target substrates can be explored for growth of 2D TMDs like MoS$_2$ and MoSe$_2$. [130]

This growth method would be ideal for improving the operation of the THBT discussed in Section 5.4.3. Direct growth onto GaN would eliminate the film transfer
process, ensuring a pristine emitter/base junction and subsequently improving emitter injection efficiency. While a recent report has demonstrated CVD growth of micron-scale MoS$_2$ on GaN, large-area, continuous MoS$_2$ growth remains critical for exploring device applications. [131]

6.2.2 GaN/MoS$_2$/GaN HBT

MBE growth of GaN on MoS$_2$ has been previously demonstrated. [122] In chapter 5, we demonstrated the importance of optimizing the emitter/base junction in order to improve device operation. Utilizing n-type GaN as an emitter has the potential to increase the emitter current density, while the large valence band offset, $\Delta E_v$, between MoS$_2$ and GaN could still allow for high emitter injection efficiency, leading to an improved common base gain. The growth of high quality n-GaN on MoS$_2$ by molecular beam epitaxy must be developed to achieve these junctions. This increased current density, combined with the low resistivity of the p-MoS$_2$ base could pave the way for demonstration of heterojunction bipolar transistors based on 2D/3D heterojunctions with higher cutoff frequencies than those that could be achieved previously with wide band gap materials.

6.2.3 van der Waals epitaxy of other 2D/2D and 2D/3D Heterojunctions

Cataloging the band line ups of a wide range of heterojunctions by growing them via van der Waals epitaxy could lead to significant insight on the viability of these materials for many devices. MBE growth of these materials allows for a wide range of material combinations to be explored. Utilizing Nb as a p-type dopant and n-type MoSe$_2$ provides a pathway toward 2D/2D PN junctions that could be useful for photodetector applications and other device topologies. [132] [133] [134] [135] [136]
Figure 6.1 shows the band line ups of MoS$_2$/Gan and MoS$_2$/SiC as determined by the studies in this thesis. [137] [138] Other semiconductors, both 2D and 3D, are included based on their electron affinity. The band line ups for other 2D/3D heterojunctions such as MoS$_2$/Ga$_2$O$_3$, MoSe$_2$/GaN and MoS$_2$/ZnO can provide useful insight toward new device topologies. A thorough extraction of the band line ups of these heterojunctions by electrical and optical measurements can be facilitated by MBE growth of TMDs on these substrates to determine their viability for transistors, tunnel junctions, photodetectors and other devices. An example of this 2D/3D growth has been demonstrated with the GaSe/GaN heterojunction. [139]
Figure 6.1: 2D/3D band line ups, providing insight on the study of future 2D/3D heterojunctions.
Bibliography


113


