

**Investigation of Intrinsic and Tunable Properties of Two-Dimensional
Transition-Metal Dichalcogenides for Optical Applications**

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Ellen Sarah Reifler

B.S., Physics, University of Virginia

M.S., Materials Science and Engineering, Carnegie Mellon University

Carnegie Mellon University
Pittsburgh, PA

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ABSTRACT

Since the scotch-tape isolation of graphene, two-dimensional (2D) materials have been studied with increasing enthusiasm. Two-dimensional transition-metal dichalcogenides are of particular interest as atomically thin semiconductors. These materials are naturally transparent in their few-layer form, have direct band gaps in their monolayer form, exhibit extraordinary absorption, and demonstrate unique physics, making them promising for efficient and novel optical devices.

Due to the two-dimensional nature of the materials, their properties are highly susceptible to the environment above and below the 2D films. It is critical to understand the influences of this environment on the properties of 2D materials and on the performance parameters of devices made with the materials. For transparent optical devices requiring electrical contacts and gates, the effect of transparent conducting oxides on the optical properties of 2D semiconductors is of particular importance. The ability to tune the optical properties of 2D transition-metal dichalcogenides could allow for improved control of the emission or absorption wavelength of optical devices made with the materials. Continuously tuning the optical properties of these materials would be advantageous for variable wavelength devices such as photodetectors or light emitters.

This thesis systematically investigates the intrinsic structural and optical properties of two-dimensional transition-metal dichalcogenide films, the effect of substrate-based optical interference on the optical emission properties of the materials, and demonstrates methods to controllably tune the luminescence emission of the materials for future optical applications. This thesis advances the study of these materials toward integration in future efficient and novel optical devices. The specific transition-

metal dichalcogenides investigated here are molybdenum disulfide (MoS_2), molybdenum diselenide (MoSe_2), tungsten disulfide (WS_2), and tungsten diselenide (WSe_2). The thickness-dependence of the intrinsic in-plane crystal structure of these materials is elucidated with high-resolution transmission electron microscopy; thickness-dependent optical properties are studied using Raman and photoluminescence spectroscopies.

This thesis investigates the optical interference effects from substrates with transparent conducting oxide layers on the optical properties of few-layer MoS_2 films. An understanding of these effects is critical for integrating MoS_2 into efficient optical devices. We predict contributions of optical interference effects to the luminescence emission of few-layer MoS_2 films. The predictions are experimentally verified. We also demonstrate the use of optical interference effects to tune the wavelength and intensity of the luminescence emission of few-layer MoS_2 .

This thesis explores the use of electric fields applied perpendicular to the films to continuously and reversibly tune the band gap of few-layer MoS_2 for future variable wavelength devices. To facilitate integration into devices, we demonstrate electric field-induced band gap tuning by applying electric fields with a pair of transparent or semi-transparent conducting layers, and without the need for direct electrical contact to the MoS_2 films. The observed band gap tuning is attributed to the Stark Effect. We discuss challenges to maximizing the effect of electric field-induced band gap tuning. We demonstrate that optical interference effects do not prevent observation of band gap tuning via applied electric fields. We successfully combine two luminescence emission tuning methods: optical interference effects and electric field effects.

TABLE OF CONTENTS

Chapter 1. Introduction	1
1.1 Optical Interference Effects	3
1.2 Methods to Tune the Optical Properties of Two-Dimensional Transition-Metal Dichalcogenides.....	5
1.3 Thesis Objectives and Contribution.....	8
1.4 Thesis Structure	10
Chapter 2. Crystal Structure.....	12
2.1 Crystal Structure	12
2.1.1 Hexagonal Brillouin Zone.....	14
Chapter 3. Intrinsic Structural Properties of Two-Dimensional Transition-Metal Dichalcogenides.....	15
3.1 Measurement of the Out-of-plane Lattice Parameter for MoS ₂	15
3.2 Measurement of In-plane Lattice Parameters for MoS ₂ , MoSe ₂ , WSe ₂ , and WS ₂ .	17
3.3 Observation of Crystal Symmetry	27
3.4 Summary	30
Chapter 4. Intrinsic Optical Properties of Two-Dimensional Transition-Metal Dichalcogenides.....	32
4.1 Raman Spectroscopy.....	34
4.1.1 Observation of the A _{1g} and E _{2g} ¹ Vibrational Modes.....	35
4.1.2 Determination of Crystal Thickness	37
4.2 Photoluminescence Spectroscopy	40
4.2.1 Band Gaps of MoS ₂ , MoSe ₂ , WS ₂ , and WSe ₂	41

4.2.2 Indirect to Direct Band Gap Transition	44
4.2.3 Dependence of Luminescence Emission on MoS ₂ Film Thickness.....	46
4.2.4 Evidence of Spin-Orbit Coupling	48
4.3 Summary	51
Chapter 5. Optical Interference Effects	52
5.1 Introduction.....	53
5.2 Derivation of Interference Factor $I(\lambda)$	55
5.3 Cavity Model	62
5.4 Photoluminescence Prediction Process Using Interference Factor $I(\lambda)$	66
5.5 Predicted Photoluminescence of Mono- and Bilayer MoS ₂ on SiO ₂ /Si, Al ₂ O ₃ /ITO/SiO ₂ /Si, Al ₂ O ₃ /AZO/SiO ₂ /Si, and Al ₂ O ₃ /SiO ₂ /Si Substrates	67
5.6 Experimental Photoluminescence of Mono- and Bilayer MoS ₂ on SiO ₂ /Si, Al ₂ O ₃ /ITO/SiO ₂ /Si, Al ₂ O ₃ /AZO/SiO ₂ /Si, and Al ₂ O ₃ /SiO ₂ /Si Substrates	70
5.7 Discussion of Other Substrate-Based Effects	73
5.8 Predicted Photoluminescence of Monolayer MoS ₂ on SiO ₂ /Si and Al ₂ O ₃ /ITO/SiO ₂ /Si Substrates with Varied Substrate Material Parameters	74
5.9 Summary	81
Chapter 6. Effect of External Electric Field on the Band Gap of Few-Layer MoS ₂	83
6.1 Motivation.....	85
6.2 Effect of External Electric Field on Few-Layer MoS ₂	87
6.3 Optical Interference Effects and Electric Field Induced Band Gap Tuning	95
6.4 Summary	97
Chapter 7. Summary and Future Work	98

7.1 Summary	98
7.2 Future Work	100
References	101
Appendix: Methods	110
Exfoliation Process	110
Layered Substrate Fabrication Process	111
Capacitor Fabrication Process	112
Photoluminescence Spectroscopy Measurement	114
Raman Spectroscopy Measurement	115
Measurement Setup for Photoluminescence Spectroscopy with Applied Electric Field	116
Density Functional Theory Calculations	117

LIST OF FIGURES

Figure 2-1. 2H crystal structure of transition-metal dichalcogenides MX_2	13
Figure 2-2. Three-dimensional hexagonal Brillouin zone	14
Figure 3-1. AFM micrograph of monolayer MoS_2	16
Figure 3-2. High-resolution TEM sample preparation method	18
Figure 3-3. High-resolution TEM micrograph of bulk MoS_2	19
Figure 3-4. Simulation of MoS_2 high-resolution TEM micrographs as a function of MoS_2 thickness.....	20
Figure 3-5. High-resolution TEM micrograph of bulk MoS_2 with lattice parameter measurement	21
Figure 3-6. High-resolution TEM micrograph of bilayer MoS_2	22
Figure 3-7. High-resolution TEM micrograph of bilayer MoSe_2	24
Figure 3-8. High-resolution TEM micrograph of four-layer WSe_2	24
Figure 3-9. High-resolution TEM micrograph of bilayer WS_2	25
Figure 3-10. High-resolution TEM micrographs of few-layer MoS_2 , MoSe_2 , WSe_2 , and WS_2 highlighting mirror symmetry	29
Figure 3-11. High-resolution TEM micrographs of few-layer MoS_2 , MoSe_2 , WSe_2 , and WS_2 highlighting screw axis symmetry	30
Figure 4-1. Optical microscope images of monolayer, bilayer, and trilayer MoS_2	33
Figure 4-2. Allowed Raman active modes in transition-metal dichalcogenide films.....	35
Figure 4-3. Raman spectra of monolayer, few-layer, and bulk MoS_2 , MoSe_2 , WSe_2 , and WS_2	36

Figure 4-4. The difference between the frequency for the MoS ₂ A _{1g} and E _{2g} ¹ Raman modes as a function of MoS ₂ film thickness.....	39
Figure 4-5. The vibrational frequency difference between the A _{1g} and the E _{2g} ¹ Raman modes for MoS ₂ as a function of number of layers in the MoS ₂ crystal.....	40
Figure 4-6. Electronic band structures of monolayer, bilayer, and bulk MoS ₂ , MoSe ₂ , WS ₂ , and WSe ₂	42
Figure 4-7. Photoluminescence spectra of monolayer MoS ₂ , MoSe ₂ , WS ₂ , and WSe ₂	43
Figure 4-8. Photoluminescence spectra of monolayer MoS ₂ , MoSe ₂ , WS ₂ , and WSe ₂ compared with <i>ab initio</i> band gap energies	44
Figure 4-9. Photoluminescence spectra of monolayer, few-layer, and bulk MoS ₂ , MoSe ₂ , WS ₂ , and WSe ₂	45
Figure 4-10. Photoluminescence spectral peak energy of MoS ₂ as a function of MoS ₂ film thickness.....	47
Figure 4-11. Photoluminescence spectra of monolayer, bilayer, and trilayer MoS ₂ highlighting the indirect band gap emission	48
Figure 4-12. Photoluminescence spectra of MoS ₂ correlated with spin-orbit coupling band structure.....	49
Figure 5-1. Schematic of transition-metal dichalcogenide films on a four-layer substrate; multiple reflections within a substrate layer	56
Figure 5-2. Multiple reflections of light absorbed and emitted by transition-metal dichalcogenide films	56
Figure 5-3. Schematic of the cavity model and its corresponding parts in the thin oxide/TMD/substrate structure	63

Figure 5-4. Schematic of 2D MoS ₂ film modeled as a point emitter in a cavity	65
Figure 5-5. Photoluminescence spectrum of monolayer MoS ₂ on SiO ₂ /Si substrate, predicted photoluminescence spectrum of monolayer MoS ₂ on Al ₂ O ₃ /SiO ₂ /Si substrate, optical interference factors of MoS ₂ on SiO ₂ /Si and Al ₂ O ₃ /SiO ₂ /Si.....	67
Figure 5-6. Schematic of MoS ₂ on layered substrates: SiO ₂ /Si, Al ₂ O ₃ /ITO/SiO ₂ /Si, Al ₂ O ₃ /AZO/SiO ₂ /Si, and Al ₂ O ₃ /SiO ₂ /Si	68
Figure 5-7. Interference factors of monolayer and bilayer MoS ₂ on SiO ₂ /Si, Al ₂ O ₃ /ITO/SiO ₂ /Si, Al ₂ O ₃ /AZO/SiO ₂ /Si, and Al ₂ O ₃ /SiO ₂ /Si substrates.....	69
Figure 5-8. Predicted photoluminescence spectra of monolayer MoS ₂ on Al ₂ O ₃ /ITO/SiO ₂ /Si, Al ₂ O ₃ /AZO/SiO ₂ /Si, and Al ₂ O ₃ /SiO ₂ /Si substrates; experimental photoluminescence spectra of monolayer MoS ₂ on SiO ₂ /Si.....	70
Figure 5-9. Experimental photoluminescence spectra of monolayer MoS ₂ on Al ₂ O ₃ /ITO/SiO ₂ /Si, Al ₂ O ₃ /AZO/SiO ₂ /Si, and Al ₂ O ₃ /SiO ₂ /Si substrates.....	72
Figure 5-10. Photoluminescence peak wavelength and intensity of monolayer and bilayer MoS ₂ on Al ₂ O ₃ /ITO/SiO ₂ /Si, Al ₂ O ₃ /AZO/SiO ₂ /Si, and Al ₂ O ₃ /SiO ₂ /Si substrates.....	73
Figure 5-11. Predicted photoluminescence spectra of monolayer MoS ₂ on SiO ₂ /Si when the thickness and refractive index of SiO ₂ are systematically varied	76
Figure 5-12. Predicted photoluminescence spectra of monolayer MoS ₂ on Al ₂ O ₃ /ITO/SiO ₂ /Si when the thicknesses of Al ₂ O ₃ , ITO, and SiO ₂ are systematically varied.....	77
Figure 5-13. Predicted photoluminescence spectra of monolayer MoS ₂ on Al ₂ O ₃ /ITO/SiO ₂ /Si when the real refractive indices (n) of Al ₂ O ₃ , ITO, and SiO ₂ are systematically varied.....	78

Figure 5-14. Predicted photoluminescence spectra of monolayer MoS ₂ on Al ₂ O ₃ /ITO/SiO ₂ /Si when the imaginary refractive indices (k) of Al ₂ O ₃ , ITO, and SiO ₂ are systematically varied.....	79
Figure 6-1. Parallel plate capacitor structure used to apply electric fields across MoS ₂	88
Figure 6-2. Photoluminescence spectra of monolayer, bilayer, and trilayer MoS ₂ with electric fields applied	90
Figure 6-3. Average change in photoluminescence peak energy of monolayer, bilayer, and trilayer MoS ₂ as a result of applied electric fields	91
Figure 6-4. Photoluminescence spectra of bilayer MoS ₂ before and after dielectric breakdown.....	95

LIST OF TABLES

Table 3-1. In-plane lattice parameters of bulk and few-layer transition-metal dichalcogenide films	25
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Chapter 1. Introduction

The isolation of few-layer graphene by Geim and Novoselov^{1,2} in 2004 ushered in an era of great interest in two-dimensional (2D) materials. Two-dimensional materials are layered films whose thickness in the out-of-plane direction is on the order of angstroms. Different types of two-dimensional materials, that include conductors (graphene^{1,2}), semiconductors (transition-metal dichalcogenides^{3,4}), and insulators (hexagonal boron nitride) have been investigated. Use of 2D films has been demonstrated in applications such as photodetectors⁵⁻⁷, transistors⁸, and light emitters⁹⁻¹¹. This thesis focuses on transition-metal dichalcogenide (TMD) 2D materials, which are two-dimensional semiconductors with band gaps that range from the infrared to the visible. Specific TMDs of interest are molybdenum disulfide (MoS_2), molybdenum diselenide (MoSe_2), tungsten disulfide (WS_2), and tungsten diselenide (WSe_2).

Due to their unique properties, transition-metal dichalcogenides have gained interest as semiconducting two-dimensional materials. The 2D transition-metal dichalcogenides are direct band gap materials when pared down to a single layer^{3,4}. Absorption in a monolayer is predicted to be up to ~5-10 %, which is exceptional for a film that is <1 nm thick¹². Coupling of light to certain electron spins or conduction band valleys has opened up new directions for spin and valley physics¹³⁻¹⁶, with possible applications in spintronics and valleytronics. Strong photoluminescence^{3,4} and electroluminescence¹⁷ emission from monolayer transition-metal dichalcogenides have been demonstrated. These materials have been successfully integrated into devices such as transistors⁸, photodetectors⁵, light emitters⁹⁻¹¹, and phototransistors¹⁸. Their unique

optical and structural properties make them highly attractive for a variety of optical applications. The exotic physics of these materials and their potential for integration in future novel and efficient device applications is a primary motivation for their continued study.

Although progress has been made in understanding the materials, there are still aspects that are not fully understood. Profitable application of two-dimensional semiconductors in optical devices is only possible with a thorough understanding of their properties. A systematic investigation of the structural and optical properties of monolayer, few-layer, and bulk MoS₂, MoSe₂, WS₂, and WSe₂ can inform their integration into future devices.

It is important to understand how the materials properties and the performance parameters of optical devices made from the materials are affected by external influences. In order to integrate few-layer films into any optical or electronic device, other materials must be incorporated above and/or below the 2D films. Due to their atomic scale thinness, the 2D films are highly susceptible to influence by any other materials adjacent to them. It has previously been shown that the environment surrounding few-layer transition-metal dichalcogenides can alter their optical properties, specifically through dielectric screening¹⁹, strain^{20–22}, optical interference^{23–26}, and doping/charge transfer^{27–31}. For optical devices that require electrical Ohmic contacts or gates, understanding the effects of the contact films is vitally important.

The ability to control and manipulate the emission spectrum of 2D transition-metal dichalcogenide films could potentially expand the functionality of devices made from these materials. Controllably tuning the emission wavelength of the materials

means that their use is not limited by the intrinsic band gap energies available in MoS₂, MoSe₂, WS₂, and WSe₂. Tunable emission or absorption can potentially expand the application space of the materials in devices with operational energies outside of the intrinsic band gap. This could allow for engineered devices with specific performance parameters. Continuous and reversible tuning could be promising for variable wavelength detectors and light emitters. For these reasons, tuning the optical properties of these materials is highly desirable.

This thesis will advance the study of two-dimensional transition-metal dichalcogenide materials and accelerate their adoption in the realization of future efficient and novel optical devices. We approach this goal by systematically examining the intrinsic structural and optical properties of the materials and investigating the effect of optical interference from substrates on the emission spectra of few-layer MoS₂ (particularly from substrates with transparent conducting oxides). In addition, we demonstrate the ability to tune the optical properties of few-layer MoS₂ using optical interference effects and external electric fields.

1.1 Optical Interference Effects

Optical interference effects due to the environment surrounding few-layer transition-metal dichalcogenides affects the emission spectra of the 2D films. An understanding of these effects is critical for successfully integrating few-layer TMDs into future optical devices. Light incident on or emitted from 2D films undergoes multiple reflections at the interfaces between stacked layers in a substrate and between the substrate and the 2D

film(s). The constructive and destructive interference of these reflections alters the emission spectrum from the 2D film/substrate structure.

Several studies have explored the effect of substrate-based optical interference on the optical emission intensity from 2D materials on said substrates. The 2D materials in the studies include graphene^{25,32} and TMDs such as MoS₂, MoSe₂, WS₂, and WSe₂^{23,24,26,33,34}. These previous studies have focused on the effect of optical interference on the intensity of Raman and photoluminescence emission. Due to optical interference effects, changes to the 2D film thickness or SiO₂ thickness affect the Raman or photoluminescence emission intensity from monolayer graphene, MoS₂, and WSe₂ on the standard SiO₂/Si substrates^{24–26}. There has been very little discussion of how optical interference affects emission wavelength.

The contribution to an emission spectrum from interference effects can be removed through a normalization process^{23,34}. This allows one to isolate the optical interference effects from other substrate-based effects; this approach has been used for substrates such as hexagonal boron nitride²³, mica²³, LaAlO₃³⁴ and SrTiO₃³⁴.

The current knowledge base still lacks results from an exploration of optical interference effects in structures that include transparent conducting oxide layers. So far the optical devices that have been made from few-layer MoS₂ include photodetectors⁵ and phototransistors/transparent transistors^{18,35–40}. Transparent gates are required in these devices; however, until now the impact of optical interference effects from those gates on device performance has not been addressed. Understanding optical interference effects from substrates or superstrates with transparent conducting oxide films is critical for future devices that require use of optically transparent conductors.

1.2 Methods to Tune the Optical Properties of Two-Dimensional Transition-Metal Dichalcogenides

When using external perturbations to tune the luminescence emission and band gap of two-dimensional semiconductors, larger tuning ranges will provide wider applicability of the materials in devices. However, tuning range is not the only important parameter to consider. Other issues germane to successfully integrating the tuning method into functional devices must also be considered. For optical devices in general, transparent auxiliary film structures and room temperature operation are important. Depending on the application, it may be imperative to tune the emission intensity, emission wavelength, or both. For wavelength-tunable light emitters and detectors, the ability to reversibly and continuously tune emission or absorption is required. It is within this framework that several methods for tuning optical emission properties of two-dimensional transition-metal dichalcogenides are discussed.

The optical properties of two-dimensional films are easily influenced by the foreign films above and below them due to a combination of dielectric screening¹⁹, optical interference effects^{23–26}, and charge transfer effects^{23,29–31,34}. Dielectric screening¹⁹ and charge transfer²³ can tune the emission wavelength of few-layer MoS₂ by as much as 5 nm (15 meV) and 13 nm (36 meV), respectively. In the past, optical interference effects have primarily been demonstrated to affect the MoS₂ emission spectral intensity, not wavelength. Environment-based tuning methods (dielectric screening and optical interference effects) are advantageous due to the relative ease of integration into devices. Although implementing these methods is not trivial (some

deposition or fabrication processes may damage 2D films), fabrication of substrates or superstrates with 2D films has been realized for numerous substrates/superstrates. Optical interference is a more versatile tuning method than dielectric screening because it provides more variables that can be adjusted to tune optical emission. Optical interference effects depend on the thickness and dielectric constants of all the foreign films above and below the 2D materials; dielectric screening is only effective for the foreign films directly adjacent to the 2D materials.

The realization of a continuously tunable emission from 2D transition-metal dichalcogenides would open up the possibility of using these materials in future wavelength-tunable optical devices. Two tuning methods: strain^{20-22,41} and external electric field⁴²⁻⁴⁴ have been shown to continuously and reversibly tune emission from few-layer MoS₂. Uniaxial tensile strain can tune the band gap of monolayer and bilayer MoS₂. When 1 % tensile strain is applied to the 2D film, the material is distorted such that its lattice parameter becomes ~ 1.01 times its original value. For such a strain, the band gaps of monolayer and bilayer MoS₂ films are shifted by 50-70 meV^{20,22}. Compressive strain tunes the band gap of trilayer MoS₂ by 300 meV due to 1 % lattice strain⁴¹.

Despite promising results from straining MoS₂, continuous band gap tuning via electric field is a more advantageous method. It is easier to apply electric field than strain in a device application. Optical devices often require electric gating such that no additional fabrication steps are needed to apply an electric field. On the other hand, integration of strain-based band gap tuning requires devices with mechanically moving parts. One could use a piezoelectric substrate to strain the 2D materials⁴¹, but that

severely limits the substrate options and therefore limits the versatility of strain-based tuning in devices. Piezoelectric materials also may not be optically transparent. In addition, straining MoS₂ introduces the possibility of structurally damaging the 2D film.

For these reasons, external electric field is a far more feasible method to continuously and reversibly tune the luminescence emission of 2D transition-metal dichalcogenide films. Theoretical results predict that an external electric field applied perpendicular to bilayers of TMDs can reduce the band gap of these materials. With large enough electric fields ($\sim 1.5\text{-}3$ V/nm), the band gaps of the bilayer films are predicted to close, rendering the materials metallic⁴⁴. Further theoretical studies have confirmed these predictions in MoS₂ and other TMDs⁴⁵⁻⁴⁹. Experimental confirmation of band gap reduction in bilayer^{42,43} and few-layer⁴³ MoS₂ via external electric field has been demonstrated, with the band gap of bilayer MoS₂ reduced by up to ~ 300 meV when 1.2 V/nm is applied.

Incorporation of electric field effects into functional optical devices remains to be seen. Before realization of such a device, several steps need to be taken. Previous experimental demonstrations of electric field induced band gap tuning have used opaque silicon as the back electrical gate; transparent top and back gate contacts must be used for fully transparent optical devices. Although an electrically tunable band gap in a bilayer MoS₂ film has been demonstrated at room temperature⁴², analogous band gap tuning in few-layer films at room temperature has not yet been reported. In order to apply an electric field across 2D transition-metal dichalcogenide films, the films must be embedded within a structure of other materials. It is critical that the other materials do

not inhibit the electric-field induced band gap change in the TMD films. The effects of optical interference from the foreign structural layers have not yet been investigated.

In addition to tuning the optical properties of few-layer TMDs with a singular method, it may be necessary to combine more than one tuning method to achieve optimal device performance. Theoretical studies that combine tuning methods, such as electric field and strain⁵⁰ have been reported; as of now, the experimental combination of tuning methods has not been realized.

1.3 Thesis Objectives and Contribution

The objective of this thesis is to investigate two-dimensional transition-metal dichalcogenide (TMD) films for future optical device applications. We achieve this by studying the properties of the materials, the effect of extrinsic factors on those properties, and discussing approaches to controllably tune the properties. The particular transition-metal dichalcogenide films of interest in this work are molybdenum disulfide (MoS_2), molybdenum diselenide (MoSe_2), tungsten disulfide (WS_2), and tungsten diselenide (WSe_2).

A key contribution of this thesis is predicting the influence of optical interference effects from substrates on which few-layer TMD films are placed. We focus on optical interference effects from substrates formed from stacks of transparent conducting oxide layers because of the importance of transparent conductors in optical devices.

A second contribution of this thesis is the investigation of methods to controllably tune emission from two-dimensional transition-metal dichalcogenide films. Tuning the optical properties of these materials would facilitate their incorporation in optical devices

with engineered performance parameters, thus expanding the possible uses of these materials.

Two primary tuning methods are employed: optical interference effects and external electric fields. These methods are chosen due to the relative ease with which they can be integrated in optical devices, and for their potential to continuously tune the band gap of the materials. We predict and experimentally confirm the use of engineered substrates to tune the luminescence spectrum of few-layer MoS₂ through optical interference effects. We demonstrate tunable emission from few-layer MoS₂ when external electric fields are applied using a parallel plate capacitor configuration with transparent electrical contact layers at room temperature; tuning is attributed to the Stark Effect. We also discuss challenges to maximizing the magnitude of band gap tuning from externally applied electric field, and demonstrate that optical interference effects do not inhibit electric field based tuning. The two tuning methods are combined to expand the luminescence tuning range beyond what is observed from either method alone. These results advance the study of electric field effects in 2D materials such as MoS₂ to guide the use of electrically tunable band gaps in future wavelength-tunable devices.

The final goal of the thesis is to enhance the understanding of intrinsic structural and optical properties of two-dimensional transition-metal dichalcogenide films; this is approached through a systematic study of the films. The in-plane structural properties of bulk and few-layer TMDs are extracted from high-resolution transmission electron micrographs. We contribute experimental evidence of the thickness independent in-plane lattice structure of TMD films. Thickness-dependent optical properties are explored

using Raman and photoluminescence spectroscopies and are correlated with in-plane lattice structure.

1.4 Thesis Structure

The structure of this thesis is as follows. An introductory Chapter provides the motivation, background, thesis objectives and contributions, and the thesis document outline. Chapter 2 provides a more detailed background on the crystal structure of transition-metal dichalcogenide films. Information provided in Chapter 2 facilitates understanding of the results in subsequent Chapters.

The intrinsic properties of four transition-metal dichalcogenide films (MoS_2 , MoSe_2 , WS_2 , and WSe_2) are investigated in Chapters 3 and 4. The intrinsic crystal structure properties of the TMD films are studied in Chapter 3; a systematic study of the in-plane lattice structure of few-layer MoS_2 , MoSe_2 , WS_2 , and WSe_2 is presented. The in-plane lattice structure is elucidated using high-resolution transmission electron microscopy and micrograph simulations. Conclusions are drawn from the correlation of experimental and simulated micrographs, and from comparison of in-plane structures of different few-layer and bulk TMD films.

In Chapter 4, the intrinsic optical properties of the transition-metal dichalcogenide films are experimentally investigated using photoluminescence and Raman spectroscopies. The photoluminescence measurements are correlated with *ab initio* band structure calculations to provide an understanding of the spectral emission. As with the structural properties in Chapter 3, a systematic study of the optical properties in Chapter 4 allows for the direct comparison of TMDs with varying thicknesses and compositions.

This Chapter provides a necessary baseline from which to investigate luminescence emission tuning methods in the remainder of the thesis.

The next two Chapters examine the effect of external influences on the optical properties of two-dimensional transition-metal dichalcogenide films. In Chapter 5, the effect of optical interference from transparent conducting oxide based substrate structures on emission spectra of few-layer MoS₂ is investigated. A method to predict the optical interference effects from any stacked substrate underneath a 2D TMD film is presented; predictions are experimentally verified. The results of this chapter demonstrate the ability to tune both the wavelength and intensity of luminescence emission from few-layer MoS₂ using optical interference effects.

Chapter 6 employs the transparent conducting oxide based substrates examined in Chapter 5 in a device to apply electric field across few-layer MoS₂ and investigate the effect of electric field on the optical properties of the material. We find that externally applied electric fields tune the band gap of few-layer MoS₂ via the Stark Effect. Limitations to the electric field induced band gap tuning are presented. Chapter 6 demonstrates the successful combination of two wavelength tuning methods (optical interference effects and electric field effects), and establishes that optical interference effects do not hinder luminescence tuning via electric field.

Chapter 7 summarizes the results and contributions of this thesis, and suggests directions for future study. Details of experimental methods are provided in the Appendix.

Chapter 2. Crystal Structure

This Chapter presents a more in-depth discussion of the structural properties of two-dimensional transition-metal dichalcogenide materials. The crystal structure of transition-metal dichalcogenide materials is experimentally investigated in Chapter 3; the background information presented in Section 2.1 will enable understanding of these results.

2.1 Crystal Structure

Transition-metal dichalcogenides share the layered hexagonal crystal structure of other two-dimensional materials such as graphene and hexagonal boron nitride. These materials are strongly bonded in the plane (within a layer) with covalent bonds. In the out of plane direction, layers of the materials are held together with weak van der Waals bonds. A monolayer of transition-metal dichalcogenide material consists of a layer of transition-metal atoms sandwiched by two layers of chalcogen atoms. The stacking structure of chalcogen atoms within a layer and the orientation of the layers on top of one another determine the polytype of the crystal.

Several polytypes of the transition-metal dichalcogenide materials exist including 1T, 1H, 2H, and 3R. This naming convention follows the Ramsdell notation⁵¹ and is commonly used for the TMD materials. Each polytype signifies a different layer stacking structure. The polytype name is determined by the crystal symmetry of the stacking structure: the number (1, 2, or 3) indicates the number of layers in a unit cell of the given polytype, and the letter indicates the crystal system of the structure (Trigonal, Hexagonal, or Rhombohedral for TMD materials). Only the 2H (bulk and few-layer) and 1H (single-

layer) polytypes are discussed here because they are the most common naturally occurring polytypes. The layers in a 2H crystal are stacked such that the chalcogen atoms in one layer are vertically aligned with the transition-metal atoms in adjacent layers. The stacking configuration of the 2H polytype is shown in Figure 2-1(b). With this stacking, bulk 2H-MoS₂, MoSe₂, WSe₂, and WS₂ belong to the $P_{6/3}mmc$ space group and the D_{6h} point group. The symmetry operations in this group include a 6_3 screw rotation about the [0001] axis. This creates a hexagonal structure when the crystal is viewed along this axis, as shown in Figure 2-1(a).

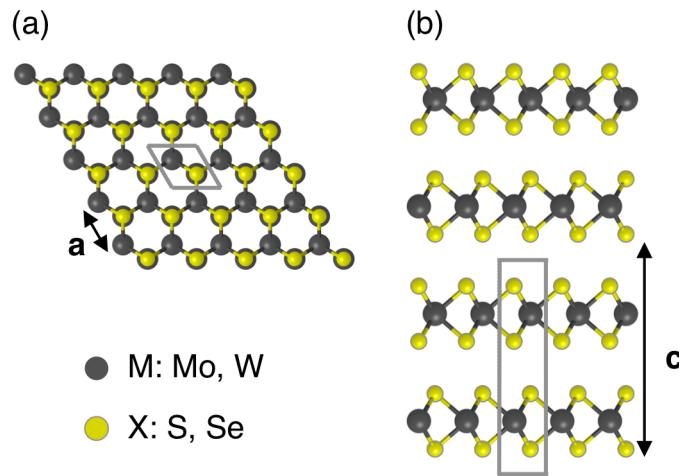


Figure 2-1: The 2H crystal structure of transition-metal dichalcogenide films, MX₂. Metal (chalcogen) atoms are shown in grey (yellow). The light grey lines outline a single unit cell. In-plane (a) and out-of-plane (c) lattice constants are defined. (a) Plan view of the crystal viewed along the [0001] direction, showing the hexagonal character of the lattice. (b) Side view of the crystal, which is viewed along the $[2\bar{1}\bar{1}0]$ direction. This shows the 2H stacking structure. Four layers are shown.

When pared down to a single-layer or a few layers, the films show the same hexagonal rotational symmetry as seen in the bulk. The key difference is that in few-layer films (approximately ten layers or less), one must separate the films into two

symmetry classes: one for films with an odd number of layers and the other for films with an even number of layers. The inversion symmetry in bulk materials and in films with an even number of layers is broken in few-layer films with an odd number of layers. The lack of inversion symmetry in the odd-layered films places them in the space group $P\bar{6}m2$ and the point group D_{3h} . These designations affect the naming conventions of the Raman vibrational modes of the films, which is discussed in Chapter 4.

2.1.1 Hexagonal Brillouin Zone

The three-dimensional hexagonal Brillouin zone of transition-metal dichalcogenides is shown in Figure 2-2. Note that, while identical in a fully six-fold symmetric crystal, the K and K' points differ in this crystal as a result of the 6_3 screw axis. Observation of the crystal structure of the materials (Figure 1(a)) reveals that the atom at each hexagonal corner alternates between a transition-metal and chalcogen. As a result, the K and K' points are inequivalent.

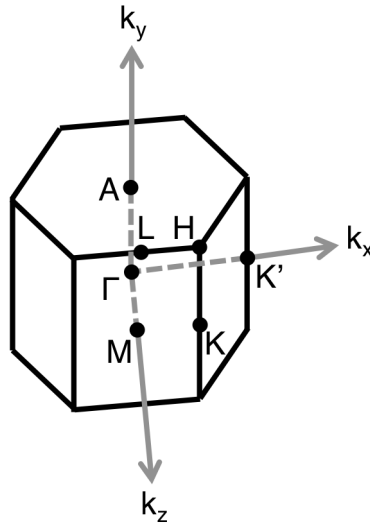


Figure 2-2: Three-dimensional hexagonal Brillouin Zone. Points of high symmetry are labeled.

Chapter 3. Intrinsic Structural Properties of Two-Dimensional Transition-Metal Dichalcogenides

This Chapter presents experimental observations of the crystalline structure of transition-metal dichalcogenides, including the determination of the lattice parameters of two-dimensional molybdenum disulfide, molybdenum diselenide, tungsten disulfide, and tungsten diselenide. The in-plane lattice parameters of these materials are intrinsic properties of the materials. Although the lattice parameters for bulk MoS_2 , MoSe_2 , WS_2 , and WSe_2 are well-known^{52–54}, the parameters of few-layer TMDs have not been systematically studied. Here, atomically thin films of these materials are examined with high-resolution transmission electron microscopy (TEM). The results are analyzed to extract the lattice parameters and some symmetry elements of the materials. A fuller understanding of the structure of these materials enhances the study and future use of them in device applications. Comparing the extracted lattice parameters of bulk and few-layer TMDs has implications for thickness-dependent optical properties of the materials.

3.1 Measurement of the Out-of-plane Lattice Parameter for MoS_2

The investigation of the crystal structure begins with topographic measurements of the surface of MoS_2 on a SiO_2/Si substrate with an atomic force microscope (AFM). The AFM used in this work is an NT-MDT Solver Next instrument operating in semicontact mode. A cross-sectional map of the surface allows one to measure the height difference between a bare substrate and a monolayer film on it. Knowing the number of layers in the film together with the height difference between the film and the substrate allows one to

determine the approximate out-of-plane lattice parameter. Such a topographic map for a monolayer of MoS₂ on SiO₂/Si is shown in Figure 3-1. A cross-section of the height was taken along the line labeled “1” in the figure. We measure the height difference between the substrate and the monolayer of MoS₂ to be $\sim 9.7 \text{ \AA}$. However, we expect this value to be $\sim 6.15 \text{ \AA}$ ^{52,55} because the thickness of a monolayer of MoS₂ should be half of the out-of-plane lattice parameter, $c/2 = (12.3 \text{ \AA})/2 \approx 6.15 \text{ \AA}$ (since the unit cell of MoS₂ consists of a bilayer). Therefore, the measured value is larger than expected for a monolayer film. This measured value of $\sim 9.7 \text{ \AA}$ is still within the range of previously obtained values. The height of a single layer of MoS₂ acquired with AFM, when measured in reference to a SiO₂/Si substrate, has been found to vary from 0.6-1.0 nm⁵⁶⁻⁶⁰. The variations and larger than expected height measurements may be caused by the presence of adsorbates below the MoS₂ layers^{58,60} or by substrate surface roughness^{56,58}. A more accurate single layer height measurement may be obtained by measuring the height between monolayer and bilayer MoS₂ instead of the height between monolayer MoS₂ and the substrate^{58,60}.

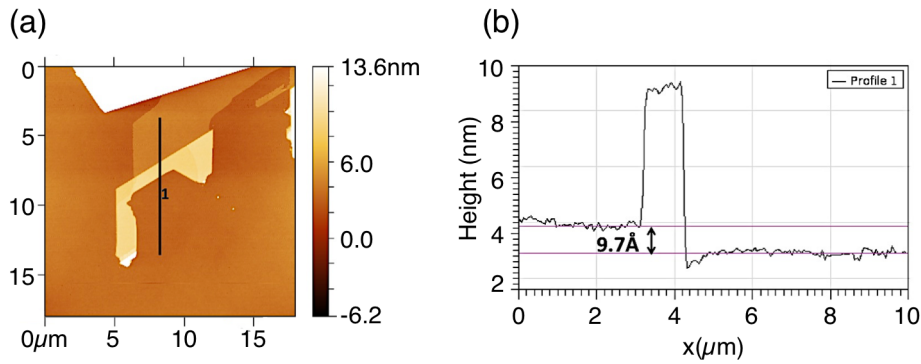


Figure 3-1: (a) AFM micrograph of monolayer MoS₂ on SiO₂/Si. (b) The height of the monolayer MoS₂ is measured (along line 1 in (a)) to be $\approx 9.7 \text{ \AA}$.

3.2 Measurement of In-plane Lattice Parameters for MoS₂, MoSe₂, WSe₂, and WS₂

Transmission electron microscopy has been widely used to image two-dimensional materials. In particular, this tool has been successfully used to study few-layer TMD grain boundaries^{61,62}, TMD point defects⁶³, ripples in MoS₂⁶⁴, and damage mechanisms^{65,66}. However, a systematic study of the intrinsic structure of high-quality, few-layer TMDs has yet to be presented. This section uses high-resolution transmission electron microscopy to investigate the in-plane structure of few-layer MoS₂, MoSe₂, WSe₂, and WS₂. The results of this work have been presented at several conferences⁶⁷⁻⁶⁹.

The weak van der Waals interaction between layers of the materials was exploited to create few-layer samples on holey carbon TEM grids (Ted Pella holey carbon film on 3mm grid). This direct sample preparation method minimizes introduction of defects that might be formed by other TEM preparation methods that require dry or wet transfer of 2D materials from separate substrates onto a TEM grid. In the method used in this work, a thin bulk TMD crystal is placed on a glass slide. A drop of isopropyl alcohol is put on top of the TMD followed by the holey carbon TEM grid. Surface tension of the alcohol pulls the TMD and the grid together. After the alcohol dries, the TEM grid is slowly pulled away from the TMD and glass slide. Some TMD material remains on the TEM grid due to van der Waals attraction between the grid and the TMD. This process may be repeated several times. If needed, the TEM grid can be gently moved across the top of the TMD on the glass slide to promote van der Waals peeling. Not all the TMD material left on the grid is a mono- or few-layer film, but regions of monolayer or few-layer material can be found. This sample preparation process and a microscale image of a WS₂ sample on the TEM grid are shown in Figure 3-2. We use an aberration-corrected FEI

Titan G2 80-300 transmission electron microscope operating at 300 kV for imaging; this instrument is capable of a resolution on the order of tenths of angstroms.

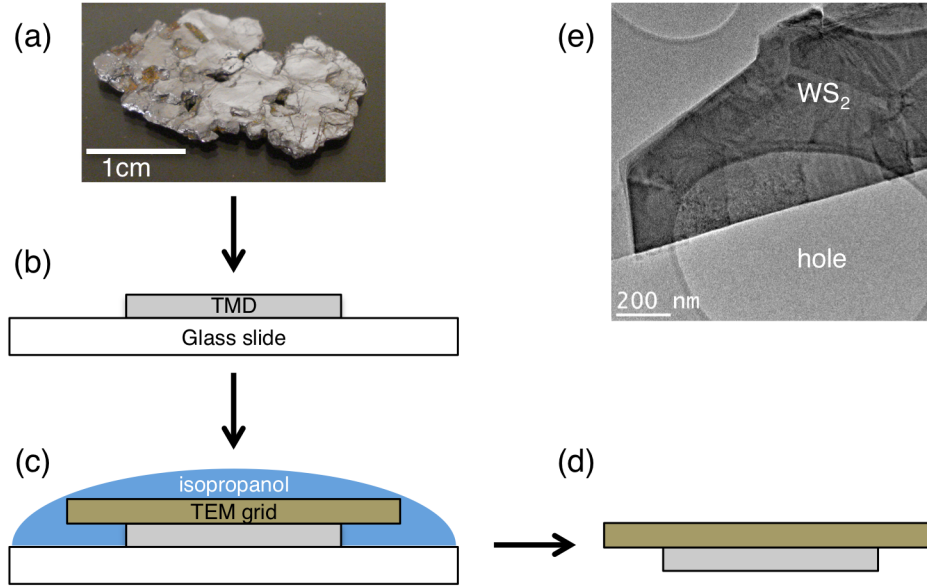


Figure 3-2: (a) TEM sample preparation method. Begin with a bulk piece of TMD material. (b) Using tweezers, peel a thinner bulk piece away from the large bulk piece. Place the thinner bulk TMD on a clean glass slide. (c) Put a few drops of isopropyl alcohol on top of the TMD/glass slide, followed by the TEM grid. (d) Allow the isopropyl alcohol to dry, then slowly pull the TEM grid away from the glass slide. Some flakes of the TMD will be adhered to the TEM grid. (e) Prepared WS₂ flake on the holey carbon TEM grid.

We first consider a micrograph of bulk MoS₂. Comparison of our experimental in-plane lattice parameter of bulk MoS₂ with the well-known value of 3.16 Å⁵² confirms the validity of our method. The high-resolution TEM micrograph of bulk MoS₂ is shown in Figure 3-3. This image is correlated with a simulated image. Since high-resolution TEM images are not directly interpretable, simulations are necessary to fully understand experimental micrographs. A simulation helps determine the location of the atomic columns in an experimental micrograph. In other words, the simulation is used to resolve

the question of whether the atomic columns are the dark or light areas in the grayscale micrograph.

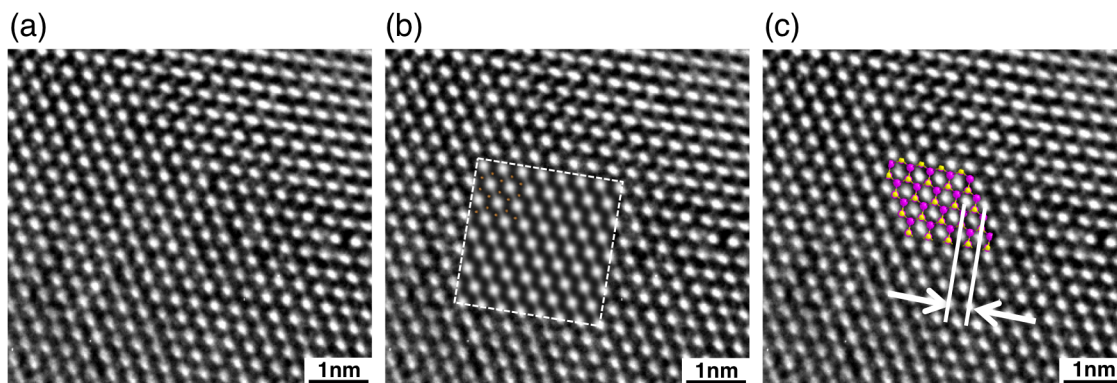


Figure 3-3: (a) High-resolution TEM micrograph of bulk MoS₂. (b) High-resolution TEM micrograph of bulk MoS₂ with simulation overlay. The simulation is outlined by a white box. The orange dots in the upper left part of the simulated image indicate the locations of the atomic columns. (c) High-resolution TEM micrograph of bulk MoS₂ with [0001] lattice plane overlay, indicating the atomic locations. The in-plane lattice parameter is indicated by the two solid white lines, and measured to be ~ 3.15 Å using the process outlined in Figure 3-5.

The simulations in this work were performed using the multislice method⁷⁰ in the Java Electron Microscopy Simulation (JEMS) software package⁷¹. All simulations were performed along the [0001] axis. The simulated image is obtained using the same microscope parameters that were used in the experiment. Several unknown parameters (sample thickness, defocus, image contrast, image brightness) are adjusted until the simulated image matches the experimental micrograph. An example of a series of simulated images with varying sample thickness is shown in Figure 3-4. Once a simulated image is matched to the experimental image, the thickness of the film imaged in the experimental micrograph is taken to be the thickness of the simulated material. In this way, the thickness of the sample in the experimental micrograph can be

approximately determined. This is the best method for determining the thickness of the TEM samples, since the areas are laterally too small ($<1\ \mu\text{m}$) to observe with other 2D TMD thickness measurement techniques such as Raman spectroscopy or atomic force microscopy. The JEMS software can only simulate images for samples with thicknesses that are integer multiples of unit cells. Since the unit cell of 2H-MoS₂, MoSe₂, WS₂, and WSe₂ is two layers thick (bilayer), the JEMS software can only simulate images of these materials with an even number of layers (bilayer, four-layer, six-layer, etc...). Therefore, the difference between a monolayer, bilayer, and trilayer image cannot be simulated. All identified few-layer micrographs shown in this Chapter were matched to simulated bilayer or four-layer images.

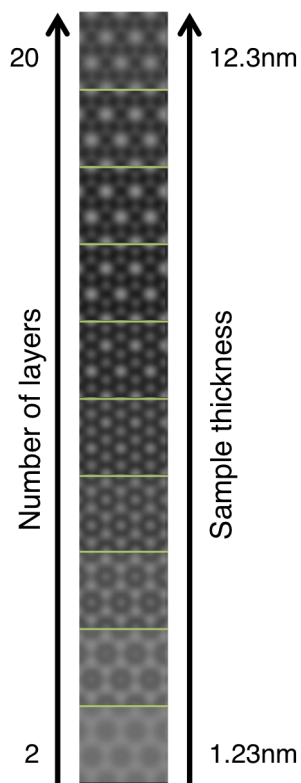


Figure 3-4: Example series of TEM images simulated with JEMS. In this series, the number of layers/sample thickness is varied.

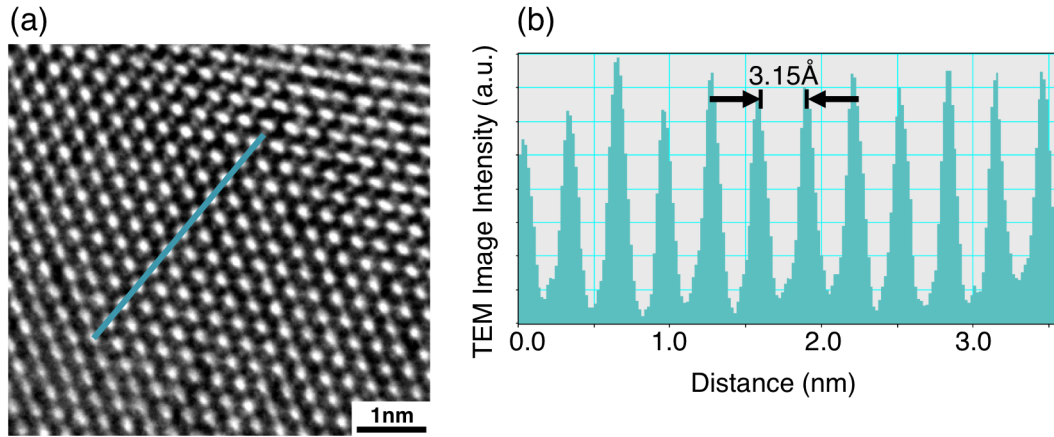


Figure 3-5: (a) High-resolution TEM micrograph of bulk MoS₂. (b) Intensity profile of the micrograph in part (a), taken along the teal line. The distance between adjacent intensity peaks is taken as a measure of the in-plane lattice parameter (here, that distance is ~ 3.15 Å).

In addition to thickness identification, the simulated image can be used to definitively locate the atomic columns in the experimental micrographs. These locations can then be used to extract the lattice parameter from the experimental images. The simulated bulk MoS₂ image is shown on top of the experimental micrograph in Figure 3-3(b). A good match between the simulated and experimental images is evident. This simulated image includes a 0.08 nm vibration of the atoms along the $[2\bar{1}\bar{1}0]$ direction; the vibration is attributed to thermal agitations. The dots in the upper left corner of the simulated image indicate the locations of the atomic columns along the $[0001]$ axis. We can translate these locations in the simulation to the experimental image as shown in Figure 3-3(c). The in-plane lattice parameter (for 2H-TMDs, this is the distance between adjacent like atomic positions) can now be extracted. This is done using the line profile tool in the DigitalMicrograph software program, which provides a bar graph of the TEM image intensity as a function of distance. The lattice parameter is the distance between

adjacent intensity peaks in such a bar graph. The line used to obtain the line profile is drawn based on the location of the atomic columns. An example line profile for a micrograph of bulk MoS₂ is shown in Figure 3-5. Several line profiles are taken from the micrograph; the extracted lattice parameters are averaged. This average results in the experimental value of the in-plane lattice parameter of bulk MoS₂ as $3.15 \pm 0.18 \text{ \AA}$. This is in good agreement with the previously reported value of $3.16 \text{ \AA}$ ⁵².

This method can be extended to determine the lattice parameters of few-layer MoS₂⁶⁷⁻⁶⁹. The experimental micrograph of few-layer MoS₂ and the simulated image overlay are shown in Figure 3-6. Comparison with the simulated image reveals that the MoS₂ sample is a bilayer film. As with the bulk MoS₂, the DigitalMicrograph line profile tool is used to extract the in-plane lattice parameter of bilayer MoS₂. Averaging several measurements produces the experimental in-plane lattice parameter of $3.12 \pm 0.18 \text{ \AA}$. This value is close to the in-plane lattice parameter extracted for bulk MoS₂.

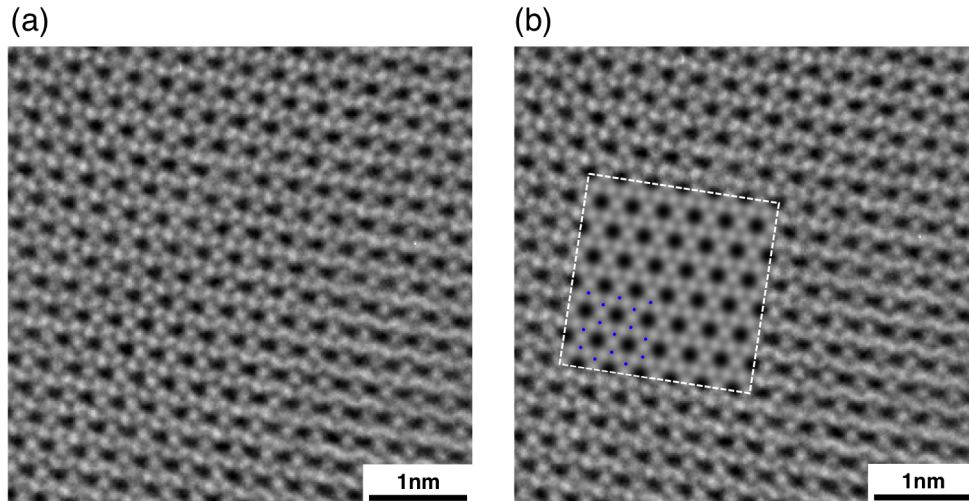


Figure 3-6: (a) High-resolution TEM micrograph of bilayer MoS₂. (b) High-resolution TEM micrograph of bilayer MoS₂ with simulation overlay. Simulation is outlined in white. The blue dots in the bottom left corner of the simulation indicate atomic column locations.

Similar results are found for the in-plane lattice parameters of bulk and few-layer MoSe₂, WSe₂, and WS₂^{67–69}. The experimental high-resolution TEM micrographs and simulated images of few-layer MoSe₂, WSe₂, and WS₂ are shown in Figure 3-7, Figure 3-8, and Figure 3-9. As with the simulation of the bulk MoS₂ image, a minor atomic vibration of 0.075 nm (0.05 nm) along the $[2\bar{1}\bar{1}0]$ direction was included in the simulation of the few-layer MoSe₂ (WS₂) image. The simulation for the few-layer WSe₂ image also includes a 0.075 nm vibration along the $[2\bar{1}\bar{1}0]$ direction, as well as a 0.125 nm/s drift of the atoms during image acquisition. Based on the film thickness used in the simulation, the few-layer MoSe₂ and WS₂ samples used in this micrograph are two monolayers thick and the few-layer WSe₂ is four monolayers thick.

The in-plane lattice parameters for few-layer and bulk MoSe₂, WS₂, and WSe₂ are extracted using the same method previously outlined for MoS₂. These results are presented in Table 3-1 along with the accepted values of the lattice parameter for the bulk crystals⁵², and in-plane lattice parameters for MoS₂ extracted earlier in this Chapter. The lattice parameters extracted from the high-resolution TEM micrographs of bulk MoS₂, MoSe₂, WS₂, and WSe₂ are in good agreement with the accepted values.

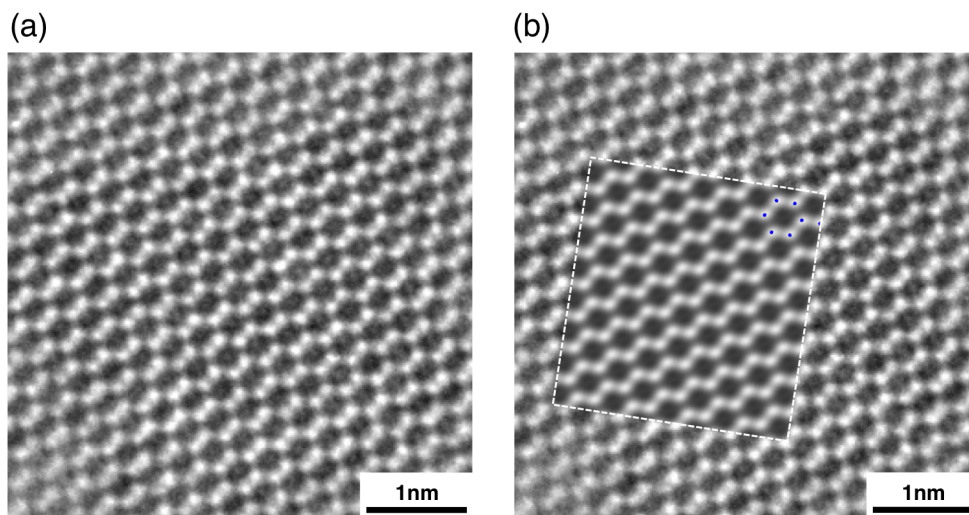


Figure 3-7: (a) High-resolution TEM micrograph of bilayer MoSe₂. (b) High-resolution TEM micrograph of bilayer MoSe₂ with simulation overlay. Simulation is outlined in white. The blue dots in the upper right corner of the simulation indicate atomic column locations.

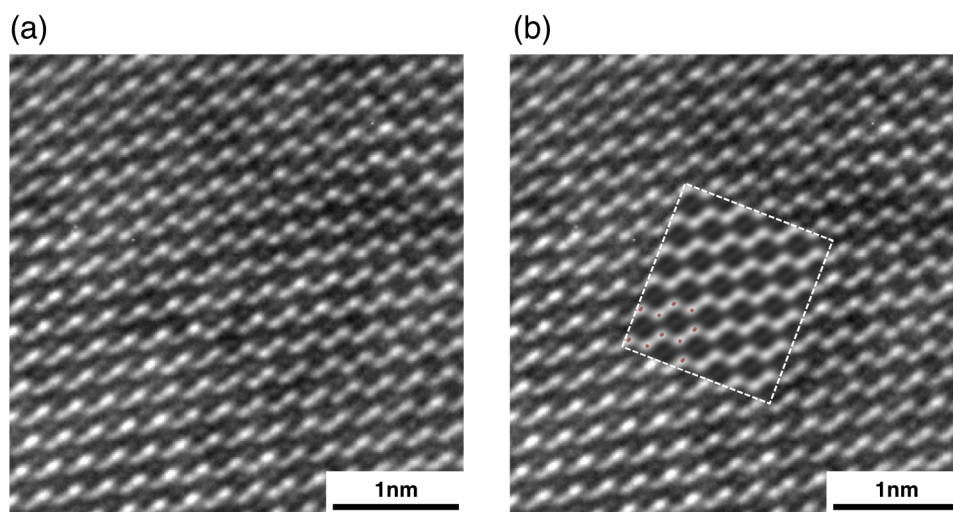


Figure 3-8: (a) High-resolution TEM micrograph of 4-layer WSe₂. (b) High-resolution TEM micrograph of 4-layer WSe₂ with simulation overlay. Simulation is outlined in white. The dark red dots in the bottom left corner of the simulation indicate atomic column locations.

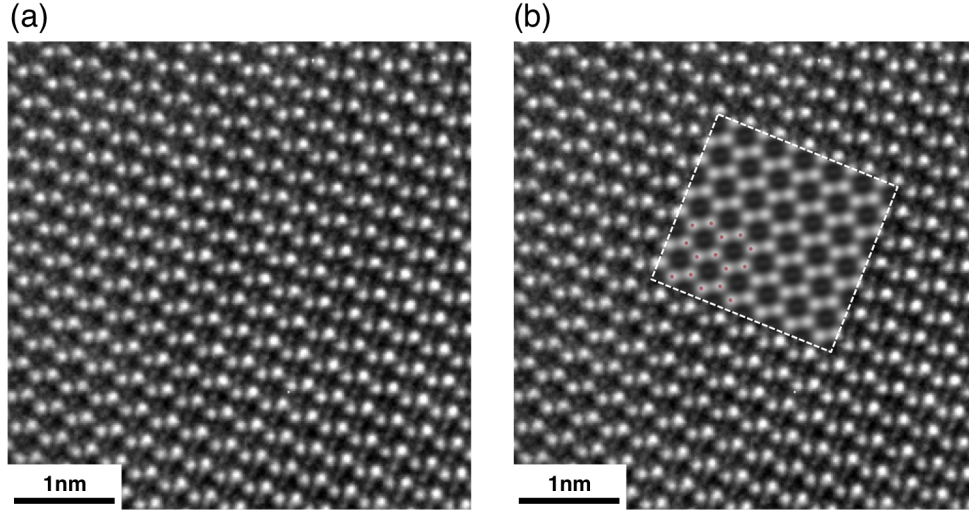


Figure 3-9: (a) High-resolution TEM micrograph of bilayer WS₂. (b) High-resolution TEM micrograph of bilayer WS₂ with simulation overlay. Simulation is outlined in white. The dark red dots in the left corner of the simulation indicate atomic column locations.

Material	Thickness	Powder x-ray diffraction	High-resolution TEM
MoS ₂	bulk	3.160 Å	3.15±0.18 Å
	bilayer	n/a	3.12±0.18 Å
MoSe ₂	bulk	3.288 Å	3.26±0.18 Å
	bilayer	n/a	3.22±0.18 Å
WSe ₂	bulk	3.286 Å	3.23±0.18 Å
	few-layer	n/a	3.29±0.18 Å
WS ₂	bulk	3.154 Å	3.12±0.18 Å
	bilayer	n/a	3.16±0.18 Å

Table 3-1: The in-plane lattice parameters of bulk and few-layer MoS₂, MoSe₂, WS₂, and WSe₂. This table includes values extracted from high-resolution TEM micrographs and previously measured bulk values obtained from powder x-ray diffraction⁵².

For all four materials there is negligible difference between the extracted experimental bulk and few-layer lattice parameter values. Theoretical studies have

estimated that in-plane lattice constants of TMD films are thickness-independent⁷², but those were not experimentally confirmed until now. The different bond strength of the in-plane versus out-of-plane bonding helps to explain the thickness-independent in-plane lattice parameters. The out-of-plane van der Waals bonds are significantly weaker than the in-plane covalent bonds. These weaker out-of-plane bonds are affected by removal or addition of layers, but the stronger in-plane bonds are less affected, keeping the in-plane structure intact.

The constant in-plane lattice structure of the 2D TMDs as a function of thickness suggests that thickness-dependent optical properties of the materials, such as electronic band structure and Raman vibrational modes, are not caused by in-plane structural changes. The lowest energy band gap in MoS₂, MoSe₂, WS₂, and WSe₂ is an indirect gap for thick films but becomes a direct gap at the K/K' point in the Brillouin Zone when the films are pared down to a single layer. By showing that the in-plane lattice structure is independent of TMD film thickness, we eliminate in-plane structural changes as a cause of the indirect to direct band gap transition. This is important because changes to in-plane lattice structure via strain have been known to alter the band structure and optical features of nanomaterials like 2D TMDs^{22,73}. Instead, the measured in-plane lattice parameters provided here support other studies that demonstrate that the indirect to direct band gap transition in the materials is a result of interlayer interactions^{4,48,74–76} or quantum confinement^{3,76,77}. *Ab initio* band structure calculations and photoluminescence spectroscopy-based evidence of the indirect to direct band gap transition for few-layer to monolayer TMD films is provided in Chapter 4.

The negligible variation of in-plane lattice structure of the TMDs as they are pared down from bulk to monolayer also elucidates the thickness-dependent Raman vibrational properties of these materials. Raman spectroscopy is an established and reliable method for determining the thickness of 2D MoS₂ ⁵⁹. The frequency of the active Raman vibration modes in few-layer MoS₂ is dependent on the number of layers present in the MoS₂ sample. This will be experimentally verified in Chapter 4 of this thesis. For now, we note that there are two main Raman active modes in 2D MoS₂: one that represents in-plane lattice vibrations (E_{2g}^1 mode) and one that represents out-of-plane lattice vibrations (A_{1g} mode). As shown in Chapter 4, the out-of-plane vibrational mode frequency changes over a slightly wider frequency range ($\sim 3.5 \text{ cm}^{-1}$) than the in-plane vibrational mode ($\sim 2 \text{ cm}^{-1}$) as the thickness of few-layer MoS₂ is reduced from bulk to monolayer. Raman modes are the allowed vibrational motions of atoms in a crystal lattice. These vibrational frequencies are mainly determined by the masses of the atoms in the crystal and the bonds (forces) between the atoms and their nearest neighbors, similar to objects connected by springs. The vibrational frequencies are therefore dependent on the crystal structure. Since the in-plane lattice structure is constant from bulk to monolayer transition-metal dichalcogenides, it reasonably follows that the *in-plane* E_{2g}^1 Raman mode frequency varies less than the *out-of-plane* A_{1g} mode with TMD thickness.

3.3 Observation of Crystal Symmetry

The experimental high-resolution TEM micrographs of transition-metal dichalcogenides exhibit the symmetry of the materials. The symmetry of the direct images as well as the

fast Fourier transforms (FFTs) of the images show hexagonal symmetry for this family of materials. The high-resolution TEM micrographs are taken along the $[0001]$ zone axis. One can readily observe mirror symmetries in the plane perpendicular to this axis, as highlighted in Figure 3-10⁶⁷⁻⁶⁹. The FFTs of the micrographs included in Figure 3-10 further highlight the mirror symmetry. There is also a 6_3 screw axis along the $[0001]$ direction, which manifests itself as 6-fold rotational symmetry in the TEM micrographs, as shown in Figure 3-11. Again, the FFTs of the micrographs are included to emphasize the 6-fold hexagonal symmetry.

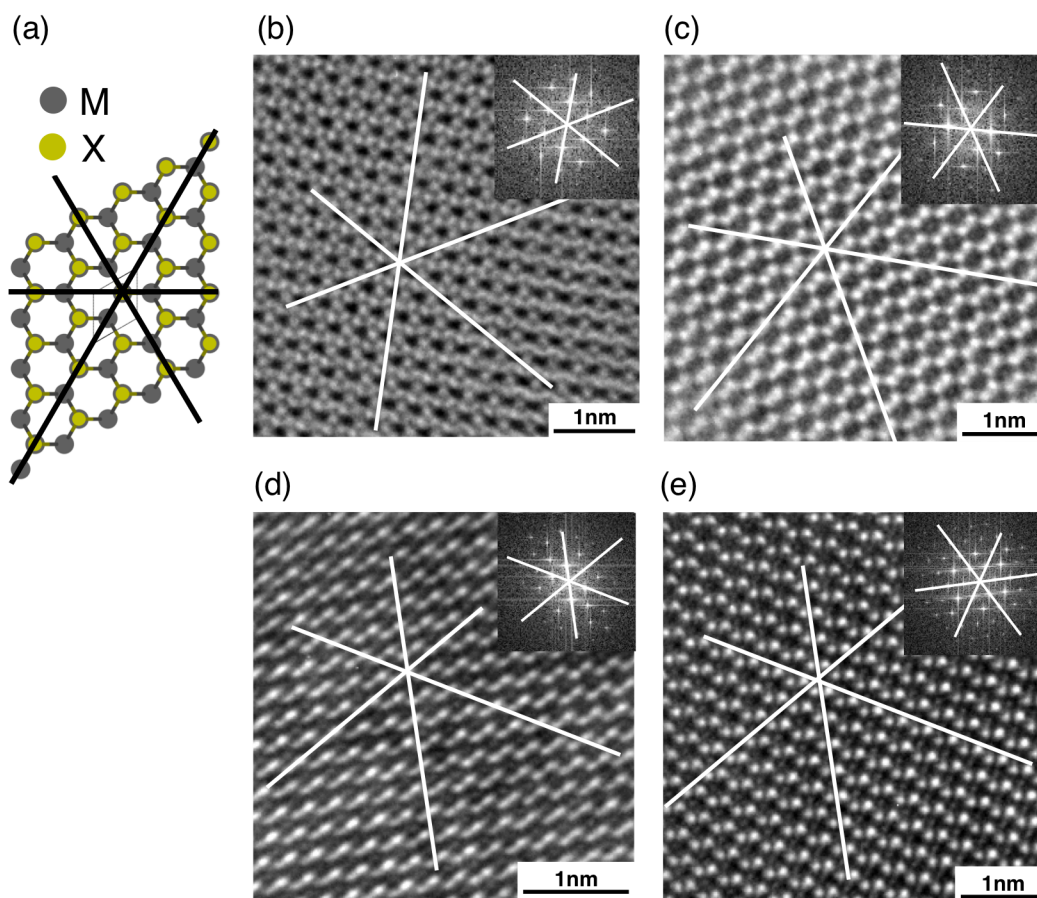


Figure 3-10: (a) View of transition-metal dichalcogenide atomic structure along the $[0001]$ direction. Mirror planes are indicated by the black lines. Metal (M: Mo or W) and chalcogen (X: S or Se) are represented by the grey and yellow atoms, respectively. High-resolution TEM micrographs and fast Fourier transforms (inset) of (b) bilayer MoS_2 , (c) bilayer MoSe_2 , (d) 4-layer WSe_2 , and (e) bilayer WS_2 with mirror symmetry indicated by the white lines.

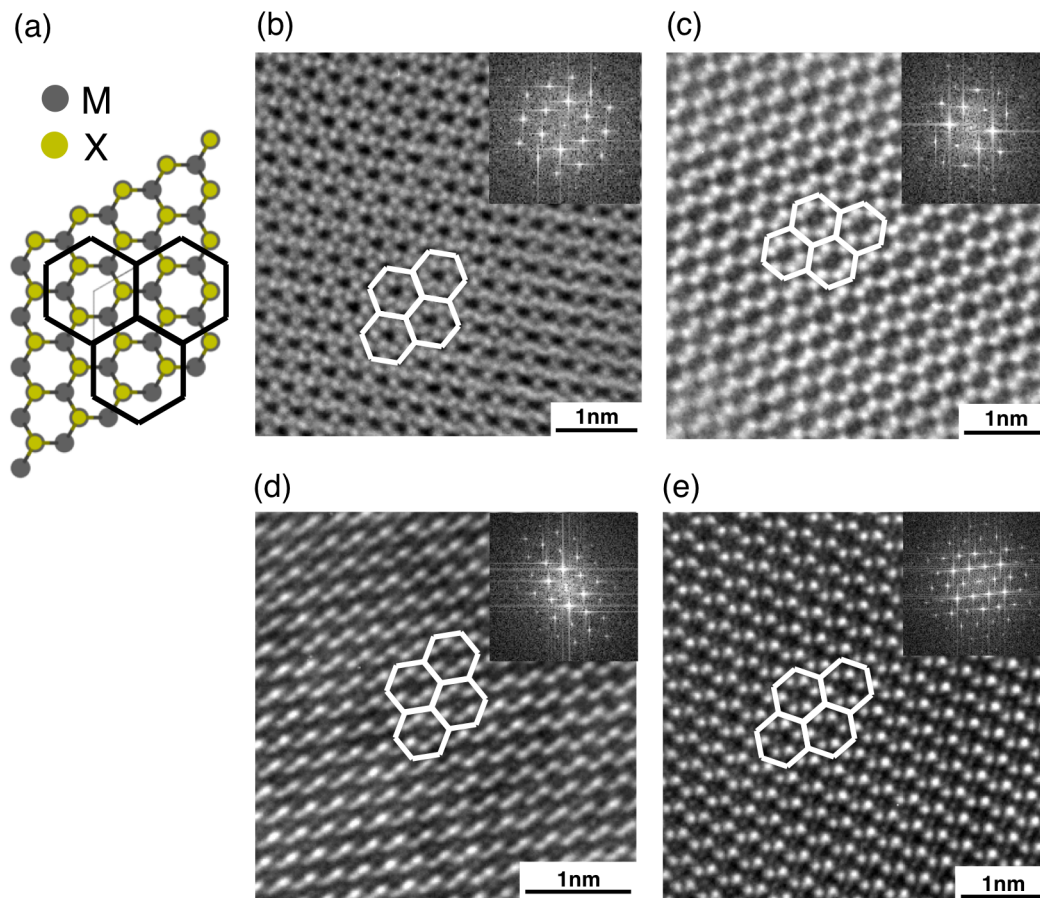


Figure 3-11: (a) View of transition-metal dichalcogenide atomic structure along the $[0001]$ direction. The 6_3 screw axis along this direction represents itself as six-fold rotational symmetry, emphasized by the black hexagons. Metal (M: Mo or W) and chalcogen (X: S or Se) are represented by the grey and yellow atoms, respectively. High-resolution TEM micrographs of (b) bilayer MoS_2 , (c) bilayer MoSe_2 , (d) 4-layer WSe_2 , and (e) bilayer WS_2 with six-fold hexagonal symmetry indicated by the white hexagons.

3.4 Summary

This Chapter has presented the experimental measurements of in-plane lattice parameters for few-layer MoS_2 , MoSe_2 , WS_2 , and WSe_2 as extracted from high-resolution TEM micrographs. These measurements and analyses of high-resolution TEM micrographs of high-quality, few-layer TMD samples provide a systematic study of the

experimental structural properties of these materials. Within a given material, the in-plane lattice parameter is constant, and is independent of film thickness. The experimental observation of thickness-independent in-plane lattice structures confirms that the thickness-dependent optical properties of the materials (such as the indirect to direct band gap transition as the materials are pared down from bulk to a single layer; and Raman vibrational frequencies) are not caused by in-plane structural changes. Finally, high-resolution TEM micrographs have provided direct observation of hexagonal symmetry and mirror plane symmetry in 2D TMDs.

Chapter 4. Intrinsic Optical Properties of Two-Dimensional Transition-Metal Dichalcogenides

This Chapter presents an investigation of the intrinsic optical properties of two-dimensional transition-metal dichalcogenides. The goal of this thesis is to investigate the properties of two-dimensional transition-metal dichalcogenides for use in optical devices, and elucidate approaches to controllably tune those properties. Prior to addressing methods to tune the optical properties in the following Chapters, this Chapter presents a necessary overview of the intrinsic optical properties of the materials. By systematically studying the optical features of these materials, we are able to directly observe how the features change as a function of material and as a function of thickness. In particular, this Chapter uses the experimental techniques of Raman and photoluminescence spectroscopies to study the optical properties of two-dimensional MoS₂, MoSe₂, WS₂, and WSe₂.

Previous studies have experimentally measured the Raman and photoluminescence spectra of the 2D transition-metal dichalcogenides^{3,4,59,78–83}, including demonstrations of how their optical properties vary with thickness, temperature⁸⁴, and strain^{20–22}. These studies provide an excellent base from which to continue studying 2D TMDs. By presenting a systematic study, as is done in this Chapter, the thickness-dependent properties of the four materials of interest (MoS₂, MoSe₂, WS₂, and WSe₂) can be compared. These results have been presented at several conferences^{67–69}.

Samples for these measurements are prepared via the scotch tape method^{1,2} to isolate atomically thin areas of MoS₂, MoSe₂, WS₂, and WSe₂ on SiO₂/Si substrates with ~265 nm thermal oxide. Details of this method are provided in the Appendix at the end

of this document. The ~ 265 nm SiO_2 thermal oxide thickness is chosen to optimize the optical contrast between few-layer transition-metal dichalcogenides and the substrate^{85,86}. In this way, even monolayers can be observed using an optical microscope. Example optical micrographs of monolayer and few-layer samples are shown in Figure 4-1. This mechanical exfoliation method provides high-quality two-dimensional films. The optical characterization is done using a Renishaw inVia combined Raman and photoluminescence system. The Renishaw instrument has resolutions of ~ 1 cm^{-1} for Raman scattering measurements and ~ 0.3 meV for photoluminescence measurements. The excitation source was a 532 nm laser. The silicon phonon frequency at ~ 520 cm^{-1} is used as a Raman calibration reference. Some of the Raman spectral data presented here were obtained with a homemade combined Raman and photoluminescence setup at the Center for Integrated Nanotechnologies at Sandia National Laboratories. This homemade setup uses a 532 nm excitation light source, with resolutions of ~ 0.3 cm^{-1} and ~ 0.7 nm for Raman and photoluminescence measurements. More details of the two Raman and photoluminescence measurement tools are provided in the Appendix.

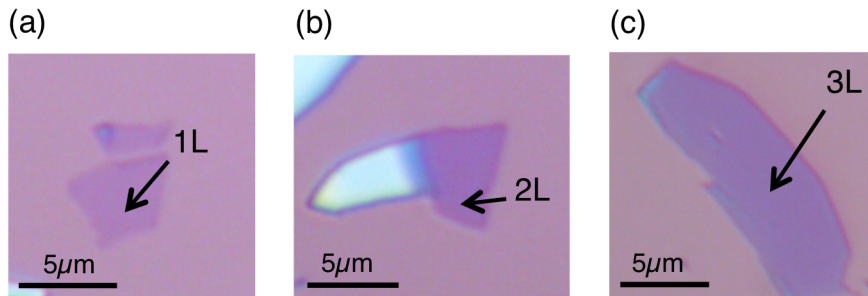


Figure 4-1: Optical microscope images of (a) monolayer, (b) bilayer, and (c) trilayer MoS_2 on SiO_2/Si .

This Chapter provides theoretical support for the experimental photoluminescence results. *Ab initio* band structure calculations obtained via density functional theory as implemented in the open-source software ABINIT^{87,88} are used to explain several photoluminescence results. These calculations were done using the projector augmented wave method^{89,90} (PAW), which provides results comparable to all-electron calculations while minimizing computational costs. More details about these calculations are provided in the Appendix.

4.1 Raman Spectroscopy

Raman spectroscopy measures the frequencies of allowed vibrational phonon modes in a material. The allowed Raman vibrational modes are related to the crystal symmetry in that the allowed modes must have vibrational symmetry that matches the symmetry of the crystal lattice. There are four theoretically predicted active Raman modes for transition-metal dichalcogenides. These include the out-of-plane A_{1g} mode and the in-plane E_{2g}^1 , E_{1g} , and E_{2g}^2 modes, as indicated in Figure 4-2. We are unable to measure the E_{1g} mode in our Raman experimental setup because this mode is inactive in basal plane backscatter geometry^{59,91}.

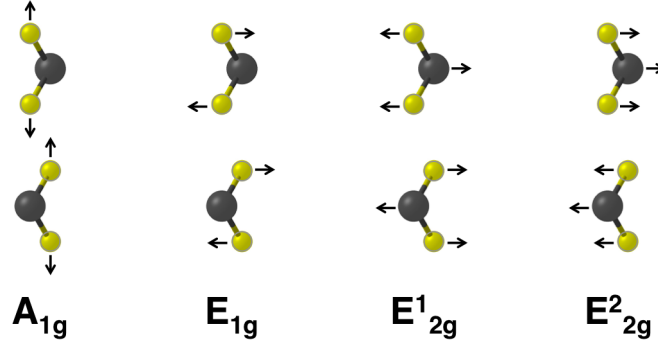


Figure 4-2: The Raman active modes allowed in transition-metal dichalcogenide films, based on the lattice structure and symmetry.

The nomenclature of the vibrational modes follows the Mulliken notation convention. The Mulliken notation depends on the point group symmetry classification, and thus the notation is different for bulk (point group D_{6h}) and monolayer (point group D_{3h}) transition-metal dichalcogenides. Few-layer crystals can be categorized into the D_{6h} or D_{3h} point group depending on whether or not the number of layers in the few-layer crystal is even or odd. Films with an even number of layers retain inversion symmetry and belong to the D_{6h} point group of bulk crystals, whereas an odd number of layers breaks the inversion symmetry and places the films in the D_{3h} point group with single layer films. Due to broken inversion symmetry in monolayer crystals, the E^2_{2g} vibrational mode is not allowed because it requires inversion symmetry. Out of the four active Raman modes listed in Figure 4-2, we focus on the A_{1g} and E^1_{2g} vibrational modes.

4.1.1 Observation of the A_{1g} and E^1_{2g} Vibrational Modes

We observe the A_{1g} and E^1_{2g} vibrational modes in the Raman spectrum of bulk, few-layer, and monolayer MoS_2 , $MoSe_2$, and WS_2 , as shown in Figure 4-3a, b, and d. These

modes are indistinguishable in the Raman spectrum of WSe₂ (Figure 4-3c) because the frequencies of the A_{1g} and E¹_{2g} modes are nearly degenerate around 250 cm⁻¹ in this material⁹². Due to this degeneracy, we focus on MoS₂, MoSe₂, and WS₂.

Interlayer interactions affect the vibrational frequencies of the A_{1g} and E¹_{2g} modes such that the frequencies shift as the crystals are pared down from bulk to single layer. It is expected that both modes will stiffen as the crystal thickness increases⁵⁹. Stiffening is observed in the A_{1g} mode in MoS₂, MoSe₂, and WS₂ while the opposite shift is seen in the E¹_{2g} mode of these materials.

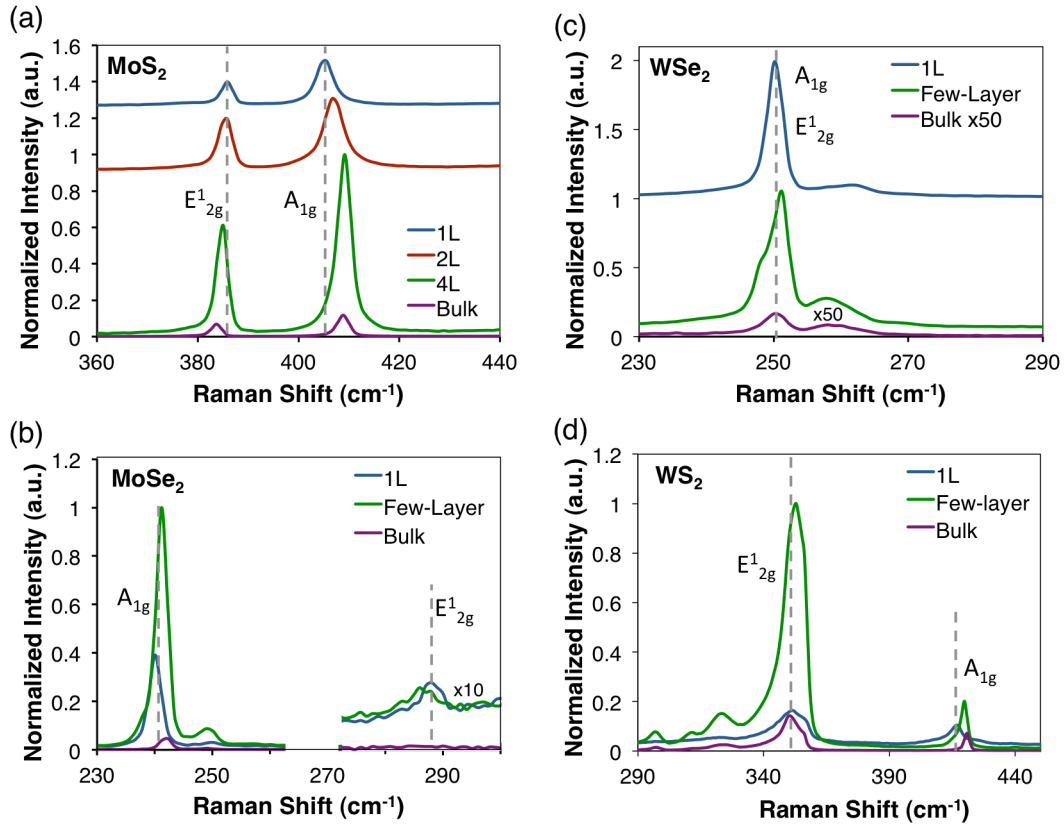


Figure 4-3: Raman spectra of monolayer, few-layer, and bulk (a) MoS₂, (b) MoSe₂, (c) WSe₂, and (d) WS₂. The expected A_{1g} and E¹_{2g} phonon modes are observed. Dashed lines indicate the approximate locations of the monolayer film spectral peaks. Some spectra are plotted vertically offset for clarity.

The A_{1g} vibrational mode has a slightly larger frequency shift between bulk and monolayer thicknesses than the E_{2g}^1 mode in MoS_2 , MoSe_2 , and WS_2 . For example, there is a 2 cm^{-1} difference between the vibrational frequency of the E_{2g}^1 mode of bulk and monolayer MoS_2 . However, the frequency difference between the A_{1g} mode of bulk and monolayer MoS_2 is 3.5 cm^{-1} . We attribute this to the different nature of these vibrations as well as the different strengths of the in-plane and out-of-plane bonding in these materials. As an out-of-plane mode, the A_{1g} vibrations are more sensitive to the addition or removal of layers than the in-plane E_{2g}^1 vibration. As discussed in Chapter 3, the in-plane crystal structure is invariant as films are pared down from bulk to monolayer. It therefore follows that the in-plane phonon vibrations would be less affected by film thickness than the out-of-plane vibrations.

4.1.2 Determination of Crystal Thickness

The simultaneous stiffening of the A_{1g} mode and the softening of the E_{2g}^1 mode as the few-layer samples are thinned to a single layer allows the frequency difference between these modes to be used as a measure of the number of layers present in a film⁵⁹. The Raman spectral peak properties can predict the thickness of a few-layer MoS_2 or WS_2 film^{59,80}. The Raman spectra of single-layer, few-layer, and bulk MoS_2 (WS_2), shown in Figure 4-3 a(d) have two distinct spectral peaks: one at $\sim 385 \text{ cm}^{-1}$ ($\sim 350 \text{ cm}^{-1}$) due to the E_{2g}^1 vibrational mode, and one at $\sim 410 \text{ cm}^{-1}$ ($\sim 418 \text{ cm}^{-1}$) due to the A_{1g} vibrational mode. As the number of layers in a given sample is decreased from bulk to a single layer, the E_{2g}^1 peak red-shifts and the A_{1g} peak blue-shifts for both MoS_2 and WS_2 . Measuring the spectral separation between the two peaks for different layer thicknesses provides a

reliable method of determining the number of layers present in a sample^{59,80}. For example, the frequency difference between the E_{2g}^1 and A_{1g} vibrational modes of WS_2 is $\sim 59\text{ cm}^{-1}$ for a monolayer but $\sim 65\text{ cm}^{-1}$ for a bulk sample. We find that the frequency difference between these modes for monolayer (bulk) MoS_2 is $\sim 19\text{ cm}^{-1}$ ($\sim 25\text{ cm}^{-1}$). A plot of the average difference between the MoS_2 A_{1g} and E_{2g}^1 Raman mode frequencies as a function of film thickness is shown in Figure 4-4, along with a range of similar values extracted from other studies^{13,59,60,75,93,94}. We can correlate the Raman spectral peak separation of our measurements with established distributions of separation vs thickness^{13,59,60,75,93,94} as a method to determine the thickness of MoS_2 samples. Initial thickness approximations are obtained from optical microscopy based on the optical contrast between MoS_2 films and SiO_2/Si substrates. These thickness approximations are verified with Raman spectroscopy. Additionally, the thickness-dependent photoluminescence properties of these materials can be used as a third confirmation of thickness. Photoluminescence spectra are discussed later in this Chapter.

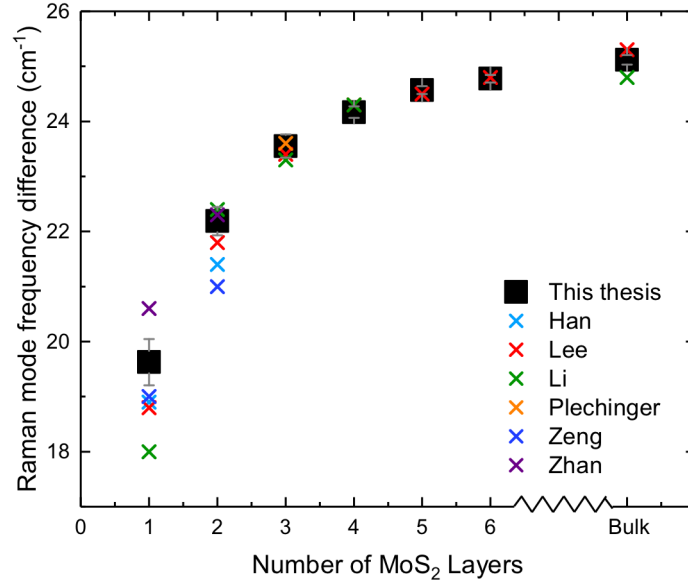


Figure 4-4: The difference between the frequency for the MoS₂ A_{1g} and E_{2g}¹ Raman modes as a function of MoS₂ film thickness. Data from samples measured in this thesis as well as values from previously published studies (Li⁶⁰, Lee⁵⁹, Han⁷⁵, Zhan⁹³, Plechinger⁹⁴, and Zeng¹³) are shown.

One can further examine the trend of Raman frequencies as a function of film thickness. The frequency difference between the MoS₂ vibrational modes is a monotonic function with respect to film thickness. Figure 4-5 shows a plot of the spectral separation between the peak locations of the E_{2g}¹ and A_{1g} modes as a function of 1/N, where N is the number of layers of MoS₂. The peak spectral separation $\Delta\omega_R$ as a function of 1/N can be fit to a linear function shown in equation 4-1. This quantitative empirical fit can provide a simple rule-of-thumb for estimating the number of layers in a MoS₂ sample once its Raman spectrum is measured and the spectral location of the two fundamental active phonon modes are determined.

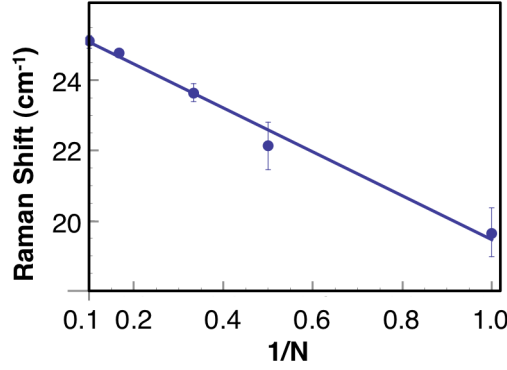


Figure 4-5: The vibrational frequency difference between the A_{1g} and E_{2g}^1 Raman modes of MoS_2 as a function of number of layers in the MoS_2 crystal. This frequency difference can be used to determine the number of layers present.

$$\Delta\omega_R = 25.712 - 6.251(1/N) \quad (4-1)$$

4.2 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy measures the emission spectrum due to electron-hole recombination processes, providing an indication of the quality of a material as well as the spectral location of the band gap. The relative peak intensities of our PL spectra confirm that transition-metal dichalcogenides such as MoS_2 , MoSe_2 , WS_2 , and WSe_2 change from indirect band gap to direct band gap semiconductors as the materials are pared down to single layer films, as suggested in previous studies^{3,4}. Further confirmation of this indirect to direct band gap transition is provided by *ab initio* band structure calculations. As discussed in Chapter 3, the in-plane lattice structure of the 2D TMDs is unaffected by the number of TMD layers in a film, and thus the indirect to direct band gap transition is not caused by changes to the crystal structure but may be caused by interlayer interactions or quantum confinement. By monitoring the spectral peak location

for each material as a function of thickness, one can examine the trend of band gap energy. The band gaps of MoS₂, MoSe₂, WS₂, and WSe₂ are in the visible to infrared range of the electromagnetic spectrum. The intensity of the photoluminescence emission suggests highly efficient radiative recombination processes in these materials, making them advantageous for optical applications. These results have been presented at several conferences^{67–69}.

4.2.1 Band Gaps of MoS₂, MoSe₂, WS₂, and WSe₂

The peak energy of photoluminescence emission from a material is related to its approximate band gap. When excited electrons (such as those produced via stimulation from a laser excitation source during photoluminescence spectroscopy) relax from the bottom of the conduction band to the top of the valence band, they recombine with holes, releasing photons with energy approximately equal to the difference between the conduction band minimum and the valence band maximum. The highest probability for electron-hole recombination that leads to emission of a photon occurs when the initial and final wavevectors for the electron are the same. This is the case for direct band gap semiconductors such as monolayer transition-metal dichalcogenides. In transition-metal dichalcogenides, the amount of energy released by recombination of the electron-hole pair (called an exciton) is a good measure of the band gap. This recombination at the direct band gap is termed the A exciton transition. In monolayer MoS₂, MoSe₂, WS₂, and WSe₂, the A exciton transition occurs at the K point in the Brillouin zone, as shown in the *ab initio* calculated band structures in Figure 4-6.

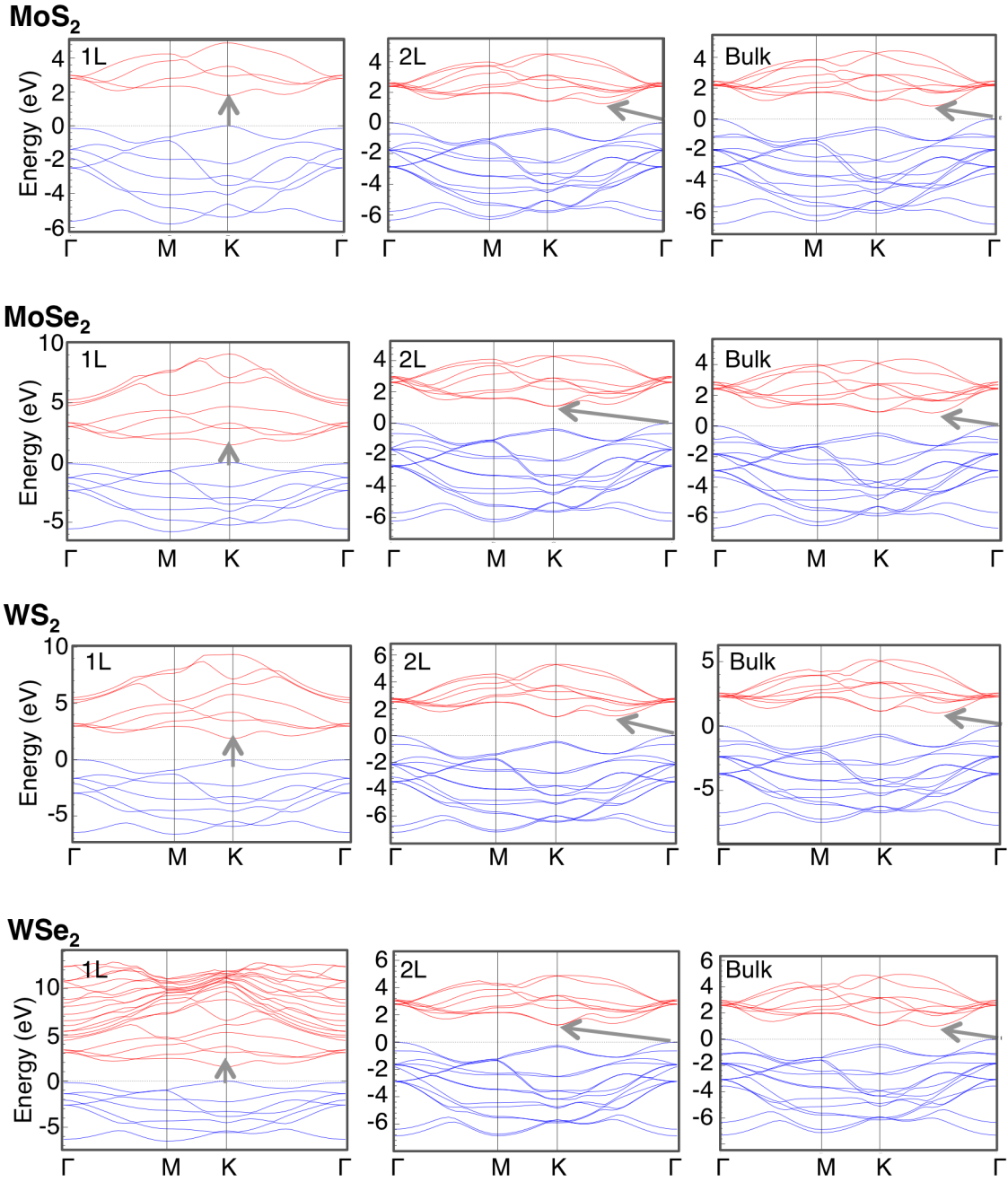


Figure 4-6: *Ab initio* electronic band structures of monolayer, bilayer, and bulk MoS₂, MoSe₂, WS₂, and WSe₂. These were calculated using the projector augmented wave method⁸⁹ as implemented in ABINIT^{87,88}. Zero eV energy represents the Fermi level of an undoped film. The grey arrows indicate the lowest energy transition between the valence band and conduction band. For monolayers, this is a direct transition at the K point. For bilayer and bulk materials, this is an indirect transition.

The photoluminescence spectra of monolayer MoS₂, MoSe₂, WS₂, and WSe₂ are shown in Figure 4-7. The average experimental band gaps of monolayer MoS₂, MoSe₂, WSe₂, and WS₂ are ~1.87 eV, ~1.57 eV, ~1.65 eV, and ~1.96 eV, respectively. The band gaps calculated by the *ab initio* method are compared with the experimental direct band gaps extracted from photoluminescence spectra of monolayer MoS₂, MoSe₂, WS₂, and WSe₂ in Figure 4-8. The trend of band gap as a function of material is the same for the experimental and *ab initio* direct band gap energies, with the lowest (highest) energy direct band gap for MoSe₂ (WS₂). It is known⁷⁷ that density functional theory underestimates the band gap of semiconductors, and this is seen by the ~0.1 eV discrepancy between the *ab initio* and experimental photoluminescence direct band gap values. With emission energies spanning a range of almost 0.5 eV, the choice of two-dimensional semiconductor for a given application can be driven by choice of band gap energy (similar to choosing a traditional 3D semiconductor for devices).

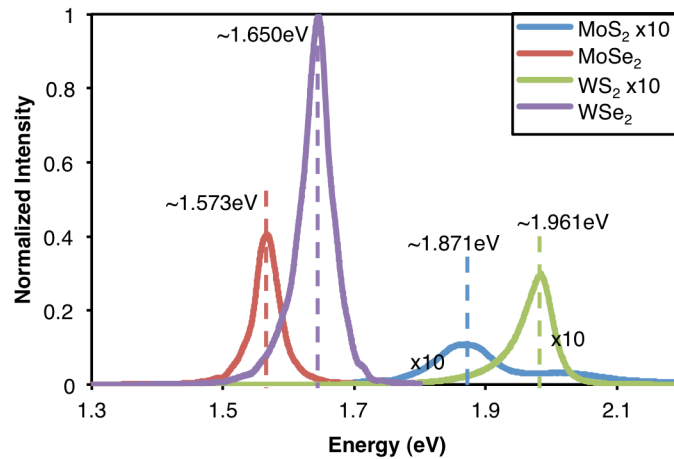


Figure 4-7: The photoluminescence spectrum of monolayer MoS₂, MoSe₂, WSe₂, and WS₂. The energy of the spectral peak location is indicated by the dashed lines, corresponding to the approximate direct band gap in the materials.

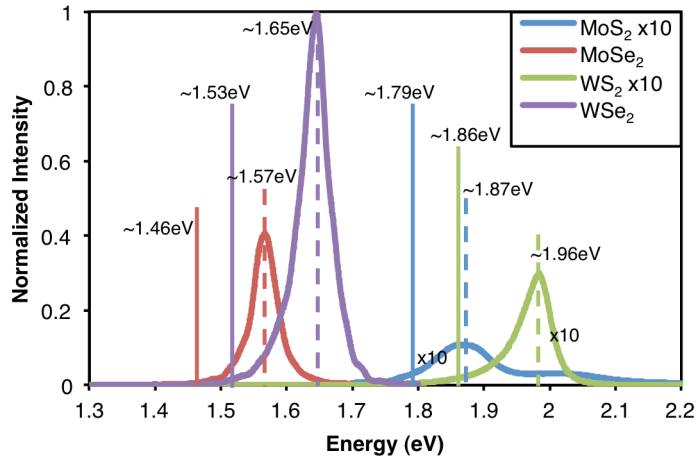


Figure 4-8: The photoluminescence spectrum of monolayer MoS₂, MoSe₂, WSe₂, and WS₂. The energy of the spectral peak location is indicated by the dashed lines. This energy corresponds to the approximate direct band gap in the materials. Direct band gap energies extracted from *ab initio* calculations are given by the solid vertical lines.

4.2.2 Indirect to Direct Band Gap Transition

The luminescence of monolayer transition-metal dichalcogenide films is significantly more intense than that of few-layer and bulk samples, as shown in Figure 4-9. This is explained by the fact that bulk and few-layer transition-metal dichalcogenides are indirect band gap semiconductors while monolayer films are direct band gap semiconductors. The electronic band structures of these crystals predict that as the crystals are pared down to a single layer, the band structure changes such that a monolayer is a direct band gap semiconductor^{3,4,72}, as shown in Figure 4-6. The smallest energy gap between the valence band and conduction band of bulk transition-metal dichalcogenide crystals occurs at different points in the Brillouin zone, rendering them indirect band gap semiconductors. In bulk and bilayer crystals, the valence band maximum is located at the Γ point in the Brillouin zone while the conduction band minimum is located at the K

point or between the K and Γ points. When pared down to a single layer, the conduction band minimum and valence band maximum align at the K and K' points. As a result, monolayer MoS_2 , MoSe_2 , WS_2 , and WSe_2 are direct band gap semiconductors. An indirect electronic relaxation from the conduction band to the valence band is less likely than a direct transition because an indirect transition requires a phonon interaction to conserve momentum. Thus, the indirect band gap bilayer and thicker materials produce weaker photoluminescence emission than the direct band gap monolayer materials.

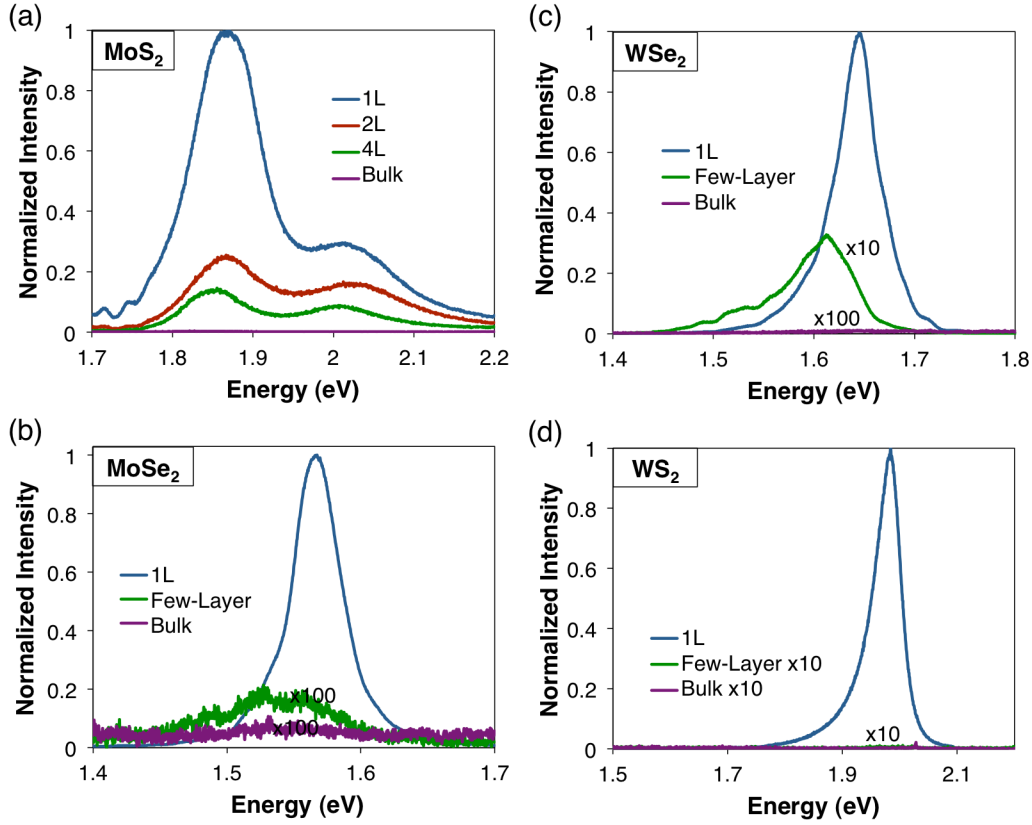


Figure 4-9: The photoluminescence spectra of monolayer, few-layer, and bulk (a) MoS_2 , (b) MoSe_2 , (c) WSe_2 , and (d) WS_2 .

As emission is related to absorption, the intense luminescence is an indication that these materials, particularly the monolayer films, could be useful in photodetection or light emitting devices. If a strong emission is required for a given device application, monolayer transition-metal dichalcogenides should be used instead of few-layer films. It is interesting to note that out of the materials studied in this thesis, the selenides exhibit relatively stronger emission than the sulfides, suggesting that the selenides may be best suited for optical device applications.

The indirect to direct band gap transition is one of the thickness-dependent optical properties of the transition-metal dichalcogenides that was discussed in Chapter 3. That chapter concluded that the in-plane crystal lattice structure of the transition-metal dichalcogenides is approximately constant as the materials are thinned down from bulk to monolayer films. This demonstrates that the indirect to direct band gap transition elucidated in this section is not caused by any in-plane structural changes. Instead, it is suggested that the indirect to direct band gap transition is a result of interlayer interactions^{4,48,74–76} or quantum confinement^{3,76,77}.

4.2.3 Dependence of Luminescence Emission on MoS₂ Film Thickness

The location of the peak luminescence energy for MoS₂ monotonically red-shifts as the thickness increases from the monolayer to the bulk. Experimental verification of this trend is shown in Figure 4-10 and the data is fit to the empirical relationship in equation 4-2. This empirical formula can be used to estimate the expected spectral location of the A exciton peak for a given number of layers of a MoS₂ sample without recourse to measurement. Alternatively, one can measure the spectral location (in energy units), E_{PL} ,

of the A exciton peak to determine the number of layers in the sample by using the expression in equation 4-2.

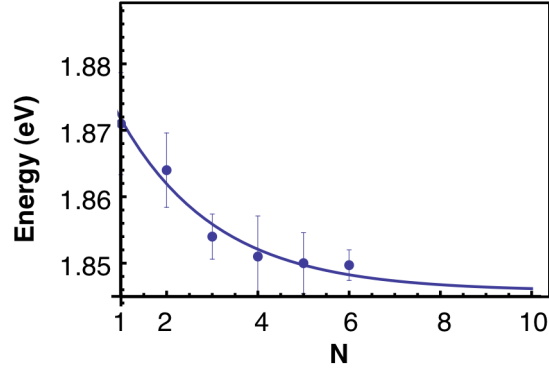


Figure 4-10: The spectral peak energy of MoS₂ as a function of N number of layers.

$$E_{PL} = 1.846 + 0.042\exp(-0.471N) \quad (4-2)$$

There is a weak, broad peak observed in the photoluminescence spectra of few-layer transition-metal dichalcogenides. The previous section examined the indirect to direct band gap transition that occurs when the transition-metal dichalcogenides are pared down to a single layer from bulk films. The photoluminescence emission from the direct band gap is stronger than emission due to an indirect transition, which is still observable. Emission from an indirect band gap material such as bilayer and trilayer MoS₂ has a broad photoluminescence peak with energy less than the direct A exciton energy. Photoluminescence spectra of MoS₂ taken over a wider energy range (in order to highlight the indirect band gap emission) are shown in Figure 4-11. As predicted by the *ab initio* band structure calculations shown in Figure 4-6, the indirect band gap decreases

in energy as the films get thicker. Also observable in Figure 4-11 is a luminescence peak due to the B exciton; this exciton will be discussed further in the next section.

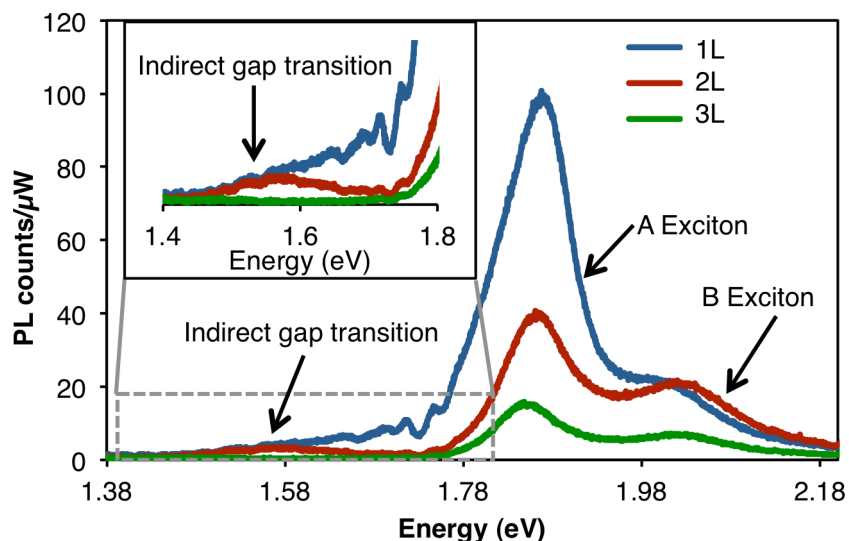


Figure 4-11: Photoluminescence spectra of monolayer, bilayer, and trilayer MoS₂ measured over a broad energy range to observe the indirect band gap transition peak (located ~1.58 eV). Inset is an enlarged portion of the spectrum focusing on the indirect band gap transition peak.

4.2.4 Evidence of Spin-Orbit Coupling

There are two distinct emission peaks in the photoluminescence spectrum of a MoS₂ sample; these arise from different direct gap transitions at the K/K' point in the Brillouin zone. The responsible transitions are a consequence of the split valence band at the K/K' point due to spin-orbit coupling³. This split valence band is shown in the inset of Figure 4-12⁹⁵. One of the peaks in the experimental spectrum arises from a transition from the minimum of the conduction band to the maximum of the upper valence band, the second is from the conduction band to the split-off valence band. These peaks are usually

labeled, respectively, as the A and B excitons and are shown in Figure 4-12. The A exciton transition here is the same as the one discussed previously. The origin of the two peaks can be understood as follows: when MoS₂ is pumped with light of appropriate wavelength, with energy well above the direct band gap, electrons from both the upper and split-off valence bands are promoted to the conduction band. These promotions leave behind holes in the valence bands. When the electrons relax from the conduction band back to the valence band, some relax to the upper valence band and others relax to the split-off band. This results in the two observed peaks.

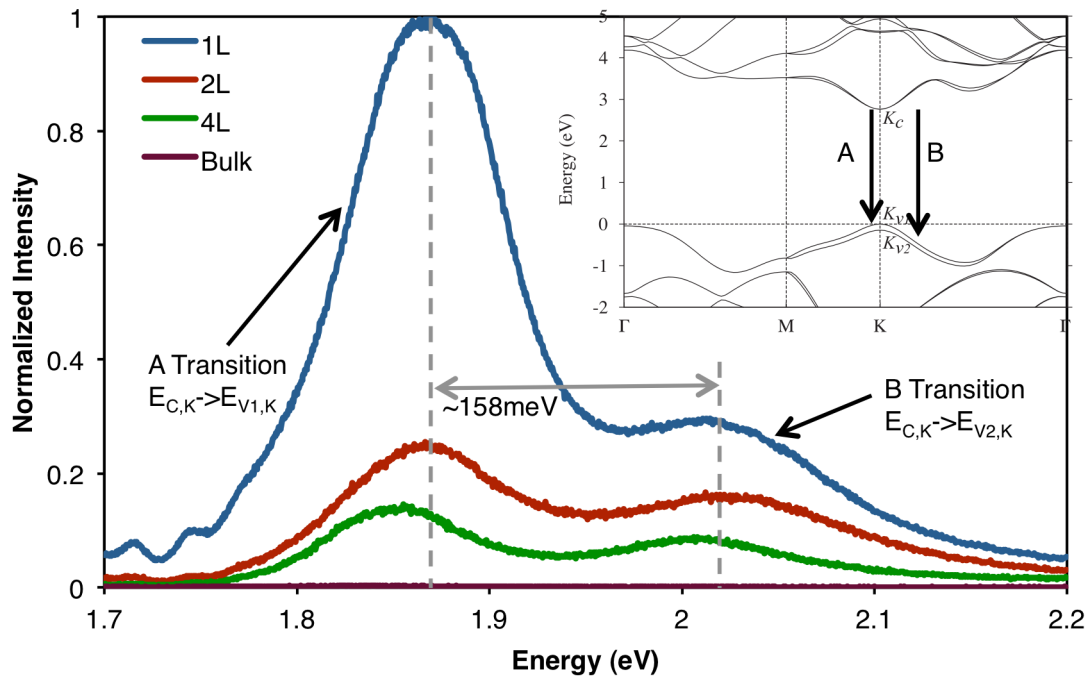


Figure 4-12: The photoluminescence spectrum of MoS₂, with the energy difference between the spectral peaks indicated. Inset is the electronic band structure of monolayer MoS₂ with spin-orbit coupling⁹⁵. A and B exciton transitions are labeled.

The spectral separation between the A and B exciton peaks can be used to determine the approximate value of the split-off valence band. Theoretical calculations^{95,96}

predict that the energy of the split-off band is different for different numbers of MoS₂ layers. However, we measure an average split of about 157.5 ± 12.4 meV for all samples (irrespective of the number of layers in them). The calculated estimate for the split for monolayer MoS₂ ranges from 112 to 148 meV^{95–97}. It is estimated to be between 160 and 174 meV^{95,96} for bilayer MoS₂. The measured average split of 157.5 meV is therefore in reasonable agreement with the theoretical estimates.

It is predicted that spin-orbit coupling splits the degenerate valence band of monolayer MoSe₂, WS₂, and WSe₂ at the K/K' point in the Brillouin zone by a value of 183 meV, 426 meV, and 456 meV, respectively⁹⁷. However, as can be seen in Figure 4-7, only one emission peak is observed in the spectra of these materials. The lifting of the valence band degeneracy by spin-orbit coupling is expected to split the band, thus leading to the observation of the A and B excitons as in monolayer MoS₂. For WS₂, the energy of the B exciton (~2.41 eV) is outside the range of our photoluminescence spectroscopy measurement capabilities. In WSe₂, the B exciton photoluminescence peak intensity is several orders of magnitude lower than the A exciton peak⁷⁹; this may explain why the B exciton peak is not observed in our photoluminescence measurements of WSe₂. The B exciton photoluminescence peak has not been previously observed in MoSe₂ spectra⁸¹, possibly due to a relatively low intensity similar to WSe₂.

The energy of the spin-split valence band in monolayer transition-metal dichalcogenides^{95,97–102} is exceptionally large. For comparison, the split valence band in monolayer TMDs ranges from 100-500 meV⁹⁷ but a similar split in graphene is only ~10⁻³ meV¹⁰³. Unique spin and conduction band valley physics have been discovered in the 2D transition-metal dichalcogenides^{13–16}. Due to the remarkable spin interactions in

these materials, the monolayer TMDs are promising for spintronic applications. Spintronics is the study of controlling spin for the manipulation of information using electron spin instead of electron charge. The possibility of using electron spin to encode information may provide an extra degree of freedom for information manipulation.

4.3 Summary

In this chapter, the optical properties of few-layer MoS₂, MoSe₂, WS₂, and WSe₂ have been investigated through Raman and photoluminescence spectroscopy. The photoluminescence results have been correlated to *ab initio* band structure predictions of the band gap obtained through density functional theory calculations. It is shown that Raman spectroscopy can be used to determine the number of layers of few-layer MoS₂ and WS₂ films. The photoluminescence emission is also dependent on the thickness of the films. Indirect gap bulk and few-layer materials become direct gap semiconductors when pared down to a single layer. This evolution can be observed in the photoluminescence spectra by monitoring the intensity of the A exciton and through observation of the indirect gap transition. This evolution is also evident in the electronic band structures of these materials as calculated by the *ab initio* method of density functional theory. The photoluminescence emission peak energy of the A exciton varies monotonically as a function of thickness. Finally, spin-orbit coupling causes a split in the valence band of these materials at the K/K' point in the Brillouin Zone. This valence band split manifests itself as the A and B exciton peaks in the photoluminescence spectrum of the MoS₂ film.

Chapter 5. Optical Interference Effects

In this Chapter, we investigate the effect of optical interference on the luminescence emission of few-layer MoS_2 . Optical interference of multiple reflections of light within a two-dimensional material and its substrate affects the emission spectrum of the two-dimensional material. Future optical devices will require two-dimensional materials to be incorporated with other materials adjacent to the two-dimensional film. It is critical to know how device performance will be affected by optical interference effects due to these other materials. Optical devices require transparent electrical contacts and gates; the effect of transparent conducting oxides (which are often used as contact or gate layers) is therefore of particular importance.

We focus on optical interference effects from substrates with transparent conducting oxide layers. Two transparent conducting oxides are used: indium tin oxide (ITO) and aluminum zinc oxide (AZO). Theoretical predictions show the contribution to few-layer MoS_2 luminescence emission due to optical interference effects. We demonstrate the ability to tune the luminescence emission intensity and wavelength of few-layer molybdenum disulfide (MoS_2) using substrate-based optical interference effects. Several of the theoretical predictions are experimentally confirmed with photoluminescence spectroscopy.

A revised version of this chapter that focuses on the cavity model presented in Section 5.3 will be submitted as a journal manuscript in the immediate future.

5.1 Introduction

To achieve successful integration of 2D materials in device applications, external parameters must be considered. Due to the atomic thinness of the materials, they have a large surface to bulk ratio and are highly influenced by their surrounding environment. Optical devices made with 2D materials may require that the 2D films be placed above/below layers of other materials. It is critical to predict how the surrounding materials may affect the properties of the 2D films and therefore the performance parameters of the device. For transparent devices requiring electrical contacts and gates, the effects of transparent conducting oxides are vitally important.

Previous studies have shown that the surrounding environment can alter the properties of 2D films through doping/charge transfer^{27–31}, dielectric screening¹⁹, strain^{20–22}, and optical interference^{23–26}. This Chapter focuses on optical interference effects. For 2D films placed on substrates, light incident on or emitted from the 2D films will undergo multiple reflections at the interfaces between layers in the substrate and between the substrate and the 2D film. The constructive and destructive interference of these multiple reflections will alter the emission spectrum of the 2D film. An understanding of these optical interference effects is necessary to efficiently integrate the two-dimensional semiconductors into devices.

Knowledge of optical interference effects from substrates or superstrates with transparent conducting layers is critical for future transparent devices. Optical devices have been made with few-layer MoS₂ films; such devices include photodetectors⁵ and phototransistors/transparent transistors^{18,35–40}. Transparent gates are required for these devices. Until now the impact of optical interference effects from those gates on device

performance has not been addressed. We contribute new analysis by demonstrating the effects of optical interference from a substrate with transparent conducting oxide layers on the luminescence emission of few-layer MoS₂ films. We also investigate the ability to control and tune the optical emission of 2D semiconducting transition-metal dichalcogenides (TMDs) via optical interference effects.

Previous studies have explored the effect of optical interference from substrates on the optical emission *intensity* of 2D materials. The 2D materials in those studies include graphene^{25,32} and TMD films^{23,24,26,33,34}. Those studies focused on how substrate-based optical interference affects the intensity of Raman and photoluminescence emission, and they concentrate on the standard SiO₂/Si substrates. Lien, *et al.*²⁶ experimentally demonstrate that by changing the SiO₂ thickness in a SiO₂/Si substrate or by suspending monolayer WSe₂, the photoluminescence (Raman) emission intensity from the WSe₂ can be increased up to 11x (30x). Zhang, *et al.*²⁴ observe similar results from monolayer MoS₂. Wang, *et al.*²⁵ and Zhang, *et al.*²⁴ have shown how the Raman spectral intensity from graphene and MoS₂ on SiO₂/Si varies with 2D film thickness as a result of optical interference effects. Other studies have shown that the contribution to an emission spectrum from interference effects can be removed with a normalization process using a calculated interference enhancement factor. The normalization process allows one to focus on other substrate-related effects^{23,34}, and has been applied to substrates including hexagonal boron nitride²³, mica²³, LaAlO₃³⁴ and SrTiO₃³⁴.

In this Chapter, we investigate the optical interference effects from a set of multilayered substrates underneath few-layer MoS₂ films, specifically substrates with transparent conducting oxide layers. The few-layer MoS₂ material is placed on top of a

dielectric/transparent conducting oxide stack to emulate a transparent gate and gate dielectric. Two common transparent conducting oxides are used: indium tin oxide (ITO) and aluminum zinc oxide (AZO). We demonstrate how the optical interference effects can be predicted without recourse to fabrication and measurement. The effect of the complex refractive index and thickness of substrate layers is systematically addressed. We use optical interference effects to engineer a substrate underneath MoS₂ films that will not only tune the MoS₂ photoluminescence emission *intensity*, but also the emission *wavelength*.

5.2 Derivation of Interference Factor $I(\lambda)$

To quantify the effects of optical interference, an interference factor $I(\lambda)$ can be derived. This factor represents the contribution of optical interference effects to the emission spectrum of 2D films such as MoS₂. Such a factor has been developed for monolayer MoS₂ on substrates that include SiO₂/Si^{24,33}, Au/SiO₂/Si²³, and SrTiO₃³⁴. We extend this factor to include the effects of up to four substrate layers, each with variable thickness and variable complex refractive index ($\tilde{n} = n - ik$). The interference factors can be used to predict the effect of a broad range of substrates extending beyond the traditional SiO₂/Si substrate.

For the interference factor derived here, a substrate stack consisting of four layers is considered, as shown in Figure 5-1(a). Each substrate layer and the 2D material is treated as a homogeneous medium with a given thickness and complex refractive index. Due to the geometry of photoluminescence and Raman spectroscopy measurement systems, normal incidence is assumed. Interfaces are taken to be smooth. Light incident

on interfaces between the layers in Figure 5-1(a) will be transmitted or reflected according to Fresnel's equations (shown in equations 5-1(b) and 5-1(c) for normal incidence). The light may be reflected multiple times within a given layer as shown in Figure 5-1(b), resulting in interference between these multiple reflections. The effects of these multiple reflections are incorporated into the interference factor $I(\lambda)$.

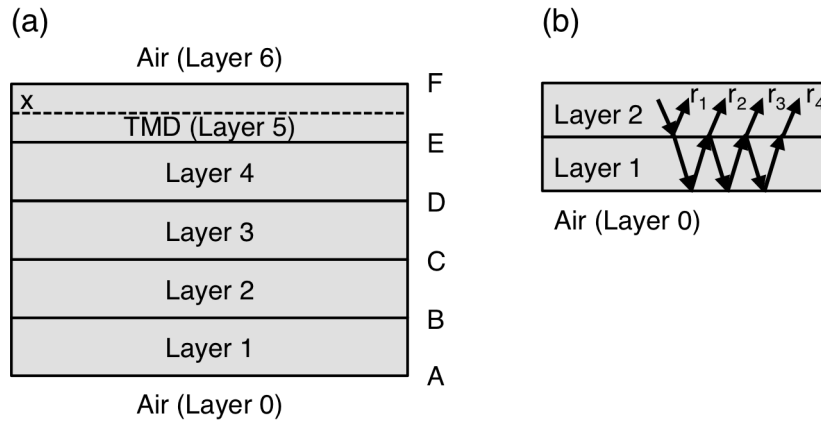


Figure 5-1: (a) Schematic of a four-layer substrate stack with few-layer TMD film on top. Layers are not to scale. (b) Example of multiple reflections within substrate Layer 1. Out of the light incident upon Layer 1 from Layer 2 at interface B, the total reflected light will include the sum of all multiply reflected beams $r_1, r_2, r_3, r_4, \dots, r_i$.

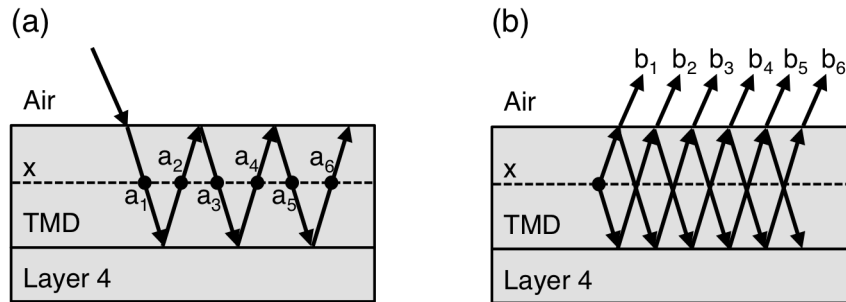


Figure 5-2: (a) Schematic of multiple reflections of the laser excitation that can be absorbed at plane x in the TMD layer. (b) Schematic of the multiple beams emitted from the structure due to multiple reflections of emission from plane x within the TMD layer. Layer thicknesses are not to scale.

Equations 5-1(a-e) define several expressions to be used in $I(\lambda)$. The refractive indices of the substrate layers and the TMD film are taken to be complex (equation 5-1a). The reflection and transmission coefficients are extracted from Fresnel's equations by considering normal incidence and are defined in equations 1b and 1c. When traveling through part or all of a substrate layer/2D material, light will undergo a phase change given by equation 5-1d (when traveling through a full layer) or 5-1e (when traveling through part of the 2D layer).

$$\tilde{n}_j = n_j - ik_j \quad (5-1a)$$

$$r_{ij} = \frac{\tilde{n}_i - \tilde{n}_j}{\tilde{n}_i + \tilde{n}_j} \quad (5-1b)$$

$$t_{ij} = \frac{2\tilde{n}_i}{\tilde{n}_i + \tilde{n}_j} \quad (5-1c)$$

$$\varphi_i = \frac{2\pi\tilde{n}_i d_i}{\lambda} \quad (5-1d)$$

$$\varphi_x = \frac{2\pi\tilde{n}_{2D}x}{\lambda} \quad (5-1e)$$

We derive an effective reflection coefficient for the substrate stack. This is done sequentially by first determining an effective reflection coefficient for the Layer1/Layer0 stack, $r_{\text{eff}} = r_B$. This effective reflection coefficient is obtained by considering multiple reflections of light within substrate Layer1. The effective reflection coefficient for the Layer2/Layer1 interface is built off of the first effective reflection coefficient. This process is repeated until all interfaces are accounted for.

A schematic of the multiple reflections within substrate Layer1 is shown in Figure 5-1(b). The effective reflection coefficient is determined by summing over all of the beams reflected from the Layer1/Layer2 interface, $r_0' + r_1' + r_2' + r_3' + r_4' + \dots = r_{eff}$. Expressions for the partial coefficients r_0' , r_1' , r_2' , r_3' , and r_4' are shown in equation 5-2. Reflection coefficients are given by r_{ij} (equation 5-1b), transmission coefficients are given by t_{ij} (equation 5-1c), and the phase is given by φ_i (equations 5-1d and 5-1e), where i and j subscripts correspond to a given substrate layer.

$$r_0' = r_{21} \quad (5-2a)$$

$$r_1' = t_{21}t_{12}r_{10}e^{-2i\varphi_1} \quad (5-2b)$$

$$r_2' = t_{21}r_{10}r_{12}r_{10}t_{12}e^{-4i\varphi_1} = r_1'r_{10}r_{12}e^{-2i\varphi_1} \quad (5-2c)$$

$$r_3' = t_{21}r_{10}r_{12}r_{10}r_{12}r_{10}t_{12}e^{-6i\varphi_1} = r_1'r_{10}^2r_{12}^2e^{-4i\varphi_1} \quad (5-2d)$$

$$r_4' = t_{21}r_{10}r_{12}r_{10}r_{12}r_{10}r_{12}r_{10}t_{12}e^{-8i\varphi_1} = r_1'r_{10}^3r_{12}^3e^{-6i\varphi_1} \quad (5-2e)$$

The effective reflective coefficient $r_{eff} = r_B$ is obtained by summing over the r_i' , and identifying the sum of a geometric series:

$$\begin{aligned} r_{eff} &= r_0' + \sum_{k=0}^{\infty} r_1'(r_{12}r_{10}e^{-2i\varphi_1})^k = r_0' + \frac{r_1'}{1 - r_{12}r_{10}e^{-2i\varphi_1}} \\ &= r_{12} + \frac{t_{12}t_{21}r_{10}e^{-2i\varphi_1}}{1 - r_{12}r_{10}e^{-2i\varphi_1}} \end{aligned} \quad (5-3)$$

This expression can be simplified to the expression in equation 5-4 by employing the relations $r_{ij} = -r_{ji}$ and $t_{ij}t_{ji} - r_{ij}r_{ji} = 1$.

$$r_{eff} = \frac{r_{21} + r_{10}e^{-2i\varphi_1}}{1 + r_{21}r_{10}e^{-2i\varphi_1}} \quad (5-4)$$

This effective reflection coefficient is only for the interface between the substrate Layer1 and Layer2, labeled as interface B in Figure 5-1(a). The reflection coefficient at interface A is r_{10} . The effective reflection coefficients at interfaces C, D, and E can all be derived similarly to r_B :

$$r_B = \frac{r_{21} + r_{10}e^{-2i\varphi_1}}{1 + r_{21}r_{10}e^{-2i\varphi_1}} \quad (5-5a)$$

$$r_C = \frac{r_{32} + r_B e^{-2i\varphi_2}}{1 + r_{32}r_B e^{-2i\varphi_2}} \quad (5-5b)$$

$$r_D = \frac{r_{43} + r_C e^{-2i\varphi_3}}{1 + r_{43}r_C e^{-2i\varphi_3}} \quad (5-5c)$$

$$r_E = \frac{r_{54} + r_D e^{-2i\varphi_4}}{1 + r_{54}r_D e^{-2i\varphi_4}} \quad (5-5d)$$

We now derive the amplitude of the laser excitation at a given plane x in the 2D material layer due to multiple reflections. A schematic of the multiple reflections of the laser excitation within the 2D layer is given in Figure 5-2(a). The total laser excitation amplitude at plane x in the TMD layer is given by: $A_{laser} = \sum a_i$.

$$a_1 = t_{65}e^{-i\varphi_x} \quad (5-6a)$$

$$a_2 = t_{65}r_E e^{-i\varphi_5} e^{-i(\varphi_5 - \varphi_x)} = t_{65}r_E e^{-2i\varphi_5} e^{+i\varphi_x} \quad (5-6b)$$

$$a_3 = t_{65}r_E r_{56} e^{-2i\varphi_5} e^{-i\varphi_x} \quad (5-6c)$$

$$a_4 = t_{65}r_E^2 r_{56} e^{-3i\varphi_5} e^{-i(\varphi_5 - \varphi_x)} = t_{65}r_E^2 r_{56} e^{-4i\varphi_5} e^{+i\varphi_x} \quad (5-6d)$$

$$a_5 = t_{65}r_E^2 r_{56}^2 e^{-4i\varphi_5} e^{-i\varphi_x} \quad (5-6e)$$

$$a_6 = t_{65}r_E^3 r_{56}^2 e^{-5i\varphi_5} e^{-i(\varphi_5 - \varphi_x)} = t_{65}r_E^3 r_{56}^2 e^{-6i\varphi_5} e^{+i\varphi_x} \quad (5-6f)$$

$$a_{2n+1} = t_{65}r_E^n r_{56}^n (e^{-2i\varphi_5})^n e^{-i\varphi_x} = a_1 (r_E r_{56} e^{-2i\varphi_5})^n \quad (5-6g)$$

$$a_{2n+2} = t_{65}r_E r_E^n r_{56}^n (e^{-2i\varphi_5})^n e^{+i\varphi_x} e^{-2i\varphi_5} = a_2 (r_E r_{56} e^{-2i\varphi_5})^n \quad (5-6h)$$

$$A_{laser} = \sum_{n=0}^{\infty} (a_{2n+1} + a_{2n+2}) = \sum_{n=0}^{\infty} [(a_1 + a_2)(r_E r_{56} e^{-2i\varphi_5})^n] \quad (5-6i)$$

Employing the relation for the sum of a geometric series, the final expression for A_{laser} becomes:

$$A_{laser} = \frac{(a_1 + a_2)}{1 - r_E r_{56} e^{-2i\varphi_5}} \quad (5-7a)$$

With $a_1 = t_{65}e^{-i\varphi_x} \quad (5-7b)$

$$a_2 = t_{65}r_E e^{-2i\varphi_5} e^{+i\varphi_x} \quad (5-7c)$$

Similarly, the total amplitude of the emission of the 2D layer is given by $A_{emit} = \sum b_i$.

The coefficients b_i are a result of multiple reflections in the 2D layer, as shown in Figure 5-2(b).

$$b_1 = t_{65}e^{-i\varphi_x} \quad (5-8a)$$

$$b_2 = r_E t_{56} e^{-i\varphi_5} e^{-i(\varphi_5 - \varphi_x)} = r_E t_{56} e^{-2i\varphi_5} e^{+i\varphi_x} \quad (5-8b)$$

$$b_3 = r_{56} r_E t_{56} e^{-2i\varphi_5} e^{-i\varphi_x} \quad (5-8c)$$

$$b_4 = t_{56} r_E^2 r_{56} e^{-3i\varphi_5} e^{-i(\varphi_5 - \varphi_x)} = t_{56} r_E^2 r_{56} e^{-4i\varphi_5} e^{+i\varphi_x} \quad (5-8d)$$

$$b_5 = t_{56} r_E^2 r_{56}^2 e^{-4i\varphi_5} e^{-i\varphi_x} \quad (5-8e)$$

$$b_6 = t_{56} r_E^3 r_{56}^2 e^{-5i\varphi_5} e^{-i(\varphi_5 - \varphi_x)} = t_{56} r_E^3 r_{56}^2 e^{-6i\varphi_5} e^{+i\varphi_x} \quad (5-8f)$$

$$b_{2n+1} = t_{56} r_E^n r_{56}^n (e^{-2i\varphi_5})^n e^{-i\varphi_x} = b_1 (r_E r_{56} e^{-2i\varphi_5})^n \quad (5-8g)$$

$$b_{2n+2} = t_{56} r_E r_E^n r_{56}^n (e^{-2i\varphi_5})^n e^{+i\varphi_x} e^{-2i\varphi_5} = b_2 (r_E r_{56} e^{-2i\varphi_5})^n \quad (5-8h)$$

$$A_{emit} = \sum_{n=0}^{\infty} (b_{2n+1} + b_{2n+2}) = \sum_{n=0}^{\infty} [(b_1 + b_2) (r_E r_{56} e^{-2i\varphi_5})^n] \quad (5-8i)$$

The final expression for A_{emit} is:

$$A_{emit} = \frac{(b_1 + b_2)}{1 - r_E r_{56} e^{-2i\varphi_5}} \quad (5-9a)$$

$$b_1 = t_{65} e^{-i\varphi_x} \quad (5-9b)$$

$$b_2 = r_E t_{56} e^{-2i\varphi_5} e^{+i\varphi_x} \quad (5-9c)$$

The total luminescence emission intensity as a result of optical interference is given in equation 5-10. The final expression for $I(\lambda)$ is found by integrating over the combined amplitudes of light absorbed (A_{laser}) and emitted (A_{emit}) from a given plane x in the 2D material (with thickness d_{2D}) as a result of optical interference of multiple reflections²³⁻

26,32,33

$$I_{substrate}(\lambda) = \int_0^{d_{2D}} |A_{laser} * A_{emit}|^2 dx \quad (5-10)$$

5.3 Cavity Model

We improve upon the model outlined in the previous section(s) by presenting a model that highlights the physics of the system. One can consider that the auxiliary materials around a 2D film act as mirrors and form a Fabry-Perot etalon cavity. This cavity functions as an optical filter. As the resonance of such a filter is tuned, the wavelength of light outside the cavity that was emitted from inside the cavity will be shifted. The cavity resonance can be tuned by adjusting the thickness or index of refraction of the mirror or cavity media.

For a 2D film on a substrate, the substrate acts as the bottom cavity mirror and the thickness of the 2D film is the thickness of the cavity. To fully illustrate the cavity, we place a thin oxide layer on top of the 2D film in the model to act as the top mirror of the cavity. For a system with uncovered 2D film on a substrate, the thickness of this top oxide layer can simply be taken to zero. This model is illustrated in Figure 5-3. As in the previous section, we consider a substrate with four layers and smooth interfaces between layers. For the rest of the discussion in this section, MoS₂ will be used as the 2D film; the model should be valid for other two-dimensional transition-metal dichalcogenide films as well.

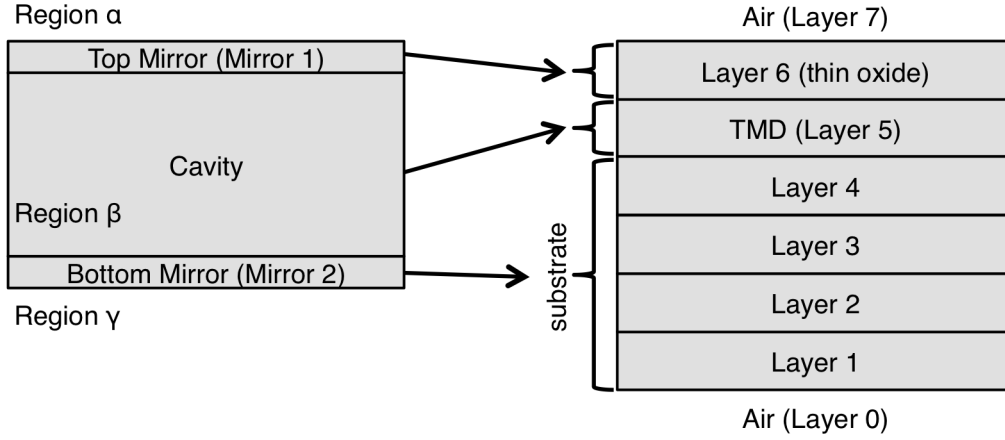


Figure 5-3: Schematic of the cavity model (left) with its corresponding parts in the thin oxide/TMD/substrate structure (right). Layer thicknesses are not to scale.

When the MoS_2 emitter is placed within a cavity (or half-cavity), the cavity alters the emission spectrum compared to that of a freestanding MoS_2 film. The alteration is due to optical interference between multiple reflections of light in the cavity/substrate structure. Light emitted isotropically from MoS_2 within the cavity will be reflected and transmitted according to the reflection and transmission coefficients of the mirrors and the cavity. The portion of emitted light exiting through the top mirror can be collected during a photoluminescence measurement. By changing the material properties (layer thickness and index of refraction) that govern the reflection and transmission coefficients (and thus the cavity filter resonance), we expect to tune the photoluminescence emission of the 2D MoS_2 film in the cavity.

Consider the photoluminescence spectrum of freestanding MoS_2 as an input function that will be acted upon by the system response function of the cavity, resulting in the output of the photoluminescence spectrum of MoS_2 in the cavity. In this case, the cavity system response function is the ratio of emitted light that has exited the cavity (above the top mirror) to the emitted light in the cavity. In other words, it is the

transmission of light from inside the cavity (region β in Figure 5-3) through the top mirror to the region outside the cavity (region α). By viewing this arrangement as an input and system response, it follows that the output spectrum is given by the convolution of the input spectrum with the system response function. This is shown in equation 5-11, where the input is the photoluminescence spectrum of freestanding MoS₂ ($PL_{\text{freestanding}}$), the system response function is the transmission $T_{\beta\alpha}$, and the output is the photoluminescence spectrum of MoS₂ within the cavity/on the substrate ($PL_{\text{substrate}}$).

$$\begin{aligned}
 PL_{\text{substrate}}(\lambda) &= T_{\beta\alpha}(\lambda) * PL_{\text{freestanding}}(\lambda) \\
 &= \int_{-\infty}^{\infty} T_{\beta\alpha}(\tau) PL_{\text{freestanding}}(\lambda - \tau) d\tau
 \end{aligned} \tag{5-11}$$

The photoluminescence spectrum of freestanding MoS₂ is proportional to equation 5-12¹⁰⁴, where E_g is the band gap energy, k_B is the Boltzmann constant, and the temperature T is taken to be room temperature. To transform this proportionality into an equality, the probability of a transition from one state (in the conduction band) to another state (in the valence band) would need to be included. For a given optical transition this probability can be taken as a constant. Initially, we will apply this cavity model to a freestanding photoluminescence spectrum with a single emission peak. However, it was established in Chapter 4 that there are multiple possible electronic transitions in few-layer MoS₂ films that produce separate (or overlapping) photoluminescence peaks. By summing the photoluminescence spectra of individual emission peaks (each given by equation 5-12 with E_g as the band gap energy of the given transition), the full multi-peak photoluminescence spectrum can be obtained. For the multi-peak case, the transition

probability for each transition should be included because said probability will affect the relative intensities of the photoluminescence spectral peaks.

$$PL_{freestanding}(\lambda) \propto \left(\frac{hc}{\lambda} - E_g\right)^{\frac{1}{2}} \exp\left[-\frac{\left(\frac{hc}{\lambda} - E_g\right)}{k_B T}\right], \frac{hc}{\lambda} > E_g \quad (5-12)$$

To obtain the cavity response function $T_{\beta\alpha}$, we consider the 2D film as a point emitter in the center of the cavity. The emission from this point will be isotropic. However, because photoluminescence spectra are typically collected at an angle normal to the 2D film/substrate, we only need to consider light that is emitted from the point emitter normal to the cavity mirrors, as shown in Figure 5-4.

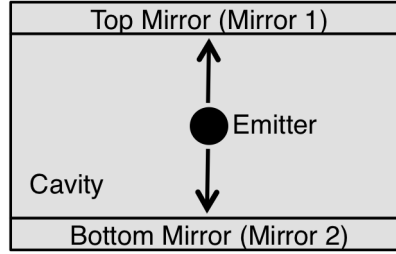


Figure 5-4: Schematic of the 2D MoS₂ film modeled as a point emitter at the center of the cavity, with emission normal to the mirrors.

The interference factor model presented in Section 5.2 is used in the remainder of this chapter. The cavity model presented in this section will be the focus of a paper manuscript to be submitted in the immediate future.

5.4 Photoluminescence Prediction Process Using Interference Factor $I(\lambda)$

When calculated with specific substrate and 2D material properties, the interference factor derived in Section 5.2 can be used to predict how optical interference from said substrate will affect the 2D material emission spectrum. The prediction process begins with an experimental photoluminescence spectrum of the 2D TMD film on a known substrate. To predict the luminescence emission from the film on a different substrate by accounting for optical interference, the experimental emission spectrum is multiplied by the ratio of the interference factor calculated for the new substrate to the interference factor calculated for the known substrate ($I_{\text{new-substrate}}/I_{\text{known}}$), as shown in equation 5-13.

$$PL_{\text{new-substrate}} = PL_{\text{known-substrate}} \left(\frac{I_{\text{new-substrate}}(\lambda)}{I_{\text{known-substrate}}(\lambda)} \right) \quad (5-13)$$

This method eliminates the contribution to the experimental spectrum from optical interference with the known substrate, and replaces it with optical interference effect contributions from the new substrate. An example of this is shown in Figure 5-5, where the photoluminescence emission spectrum of monolayer MoS₂ on an Al₂O₃/SiO₂/Si substrate is predicted, starting with an experimental luminescence spectrum of monolayer MoS₂ on SiO₂/Si.

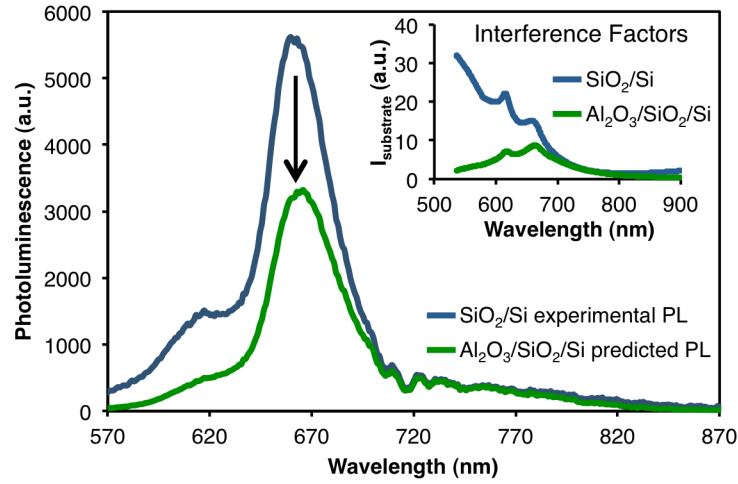


Figure 5-5: Experimental photoluminescence spectrum of monolayer MoS₂ on SiO₂/Si and the predicted spectrum of monolayer MoS₂ on Al₂O₃/SiO₂/Si. The prediction is obtained from substrate-based optical interference included in an interference factor $I_{\text{substrate}}$ by multiplying the experimental spectrum by $I_{\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}}/I_{\text{SiO}_2/\text{Si}}$. Inset: Interference factors $I_{\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}}$ and $I_{\text{SiO}_2/\text{Si}}$.

5.5 Predicted Photoluminescence of Mono- and Bilayer MoS₂ on SiO₂/Si, Al₂O₃/ITO/SiO₂/Si, Al₂O₃/AZO/SiO₂/Si, and Al₂O₃/SiO₂/Si Substrates

Using the process described in the previous section, we can predict the effect of optical interference on the luminescence spectrum of few-layer MoS₂ on substrates with transparent conducting oxide layers. The particular substrates investigated in this section are SiO₂/Si, Al₂O₃/ITO/SiO₂/Si, Al₂O₃/AZO/SiO₂/Si, and Al₂O₃/SiO₂/Si. In these substrates, Al₂O₃ and SiO₂ are the dielectrics aluminum oxide and silicon dioxide, and ITO and AZO are the transparent conducting oxides indium tin oxide and aluminum zinc oxide. Schematics of these substrates are shown in Figure 5-6. The MoS₂/Al₂O₃/ITO/SiO₂/Si and MoS₂/Al₂O₃/AZO/SiO₂/Si substrates are chosen to investigate the effects of a transparent conducting oxide substrate layer. The ITO/AZO and Al₂O₃ layers could be used as a transparent gate/gate dielectric stack in a device. The

$\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate helps determine the effect of a substrate without a transparent conductor, but with the MoS_2 film still in direct contact with Al_2O_3 . The substrate layer thicknesses are 270 nm for SiO_2 , 50 nm for Al_2O_3 , and 65 nm for ITO and AZO.

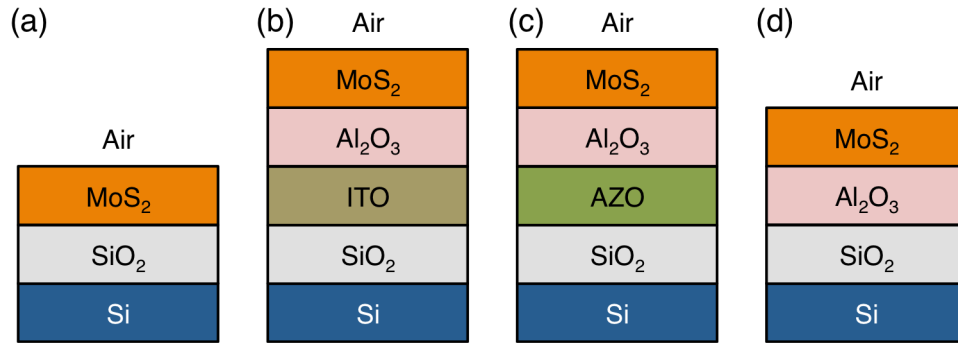


Figure 5-6: Schematic of MoS_2 on (a) SiO_2/Si , (b) $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$, (c) $\text{Al}_2\text{O}_3/\text{AZO}/\text{SiO}_2/\text{Si}$, and (d) $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrates. Layer thicknesses are not to scale.

Beginning with experimental photoluminescence spectra of monolayer and bilayer MoS_2 on SiO_2/Si , we use $I(\lambda)$ to predict the photoluminescence spectrum of MoS_2 on $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$, $\text{Al}_2\text{O}_3/\text{AZO}/\text{SiO}_2/\text{Si}$, and $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrates. The interference factors for monolayer and bilayer MoS_2 on those substrates are shown in Figure 5-7. The predicted luminescence spectra of monolayer and bilayer MoS_2 on $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$, $\text{Al}_2\text{O}_3/\text{AZO}/\text{SiO}_2/\text{Si}$, and $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ and the experimental luminescence spectrum of MoS_2 on SiO_2/Si are shown in Figures 5-8 (a) and (c). Several peaks observed in the spectra are identified according to their corresponding electronic band structure transition: the A exciton, the A- exciton (trion), the B exciton, and the indirect band gap transition. The A and B excitons were defined in Chapter 4. The A- exciton (also called a negatively charged trion) is a quasiparticle similar to an exciton. However, the A- exciton has one more electron than the A exciton, such that it is a bound

complex made of two electrons and one hole. The bilayer MoS₂ photoluminescence spectra does not have an A- exciton peak because A- excitons (trions) have not been observed in bilayer MoS₂ at room temperature²⁸. Optical interference effects are predicted to affect both the intensity and peak wavelength of the A/A- exciton, B exciton, and indirect gap transition in the photoluminescence spectrum of MoS₂.

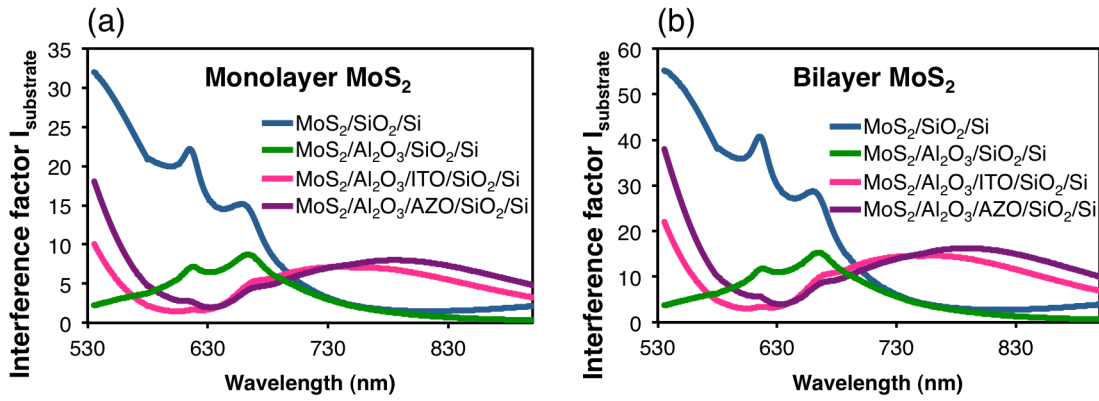


Figure 5-7: Interference factors $I_{\text{substrate}}(\lambda)$ for (a) monolayer and (b) bilayer MoS₂ on SiO₂/Si, Al₂O₃/ITO/SiO₂/Si, Al₂O₃/AZO/SiO₂/Si, and Al₂O₃/SiO₂/Si substrates.

In particular, when compared to SiO₂/Si substrates, the Al₂O₃/ITO/SiO₂/Si and Al₂O₃/AZO/SiO₂/Si substrates are predicted to red-shift the A exciton emission wavelength (as shown in Figures 5-8 (b) and (d)) while simultaneously reducing the intensity of the A exciton photoluminescence spectral peak. The Al₂O₃/ITO/SiO₂/Si and Al₂O₃/AZO/SiO₂/Si substrates are also predicted to increase the intensity of the indirect gap spectral peak of monolayers and bilayers, and reduce the intensity of the B exciton spectral peak. The Al₂O₃/SiO₂/Si substrates are not predicted to strongly affect the MoS₂ photoluminescence spectral peak wavelengths compared to SiO₂/Si substrates.

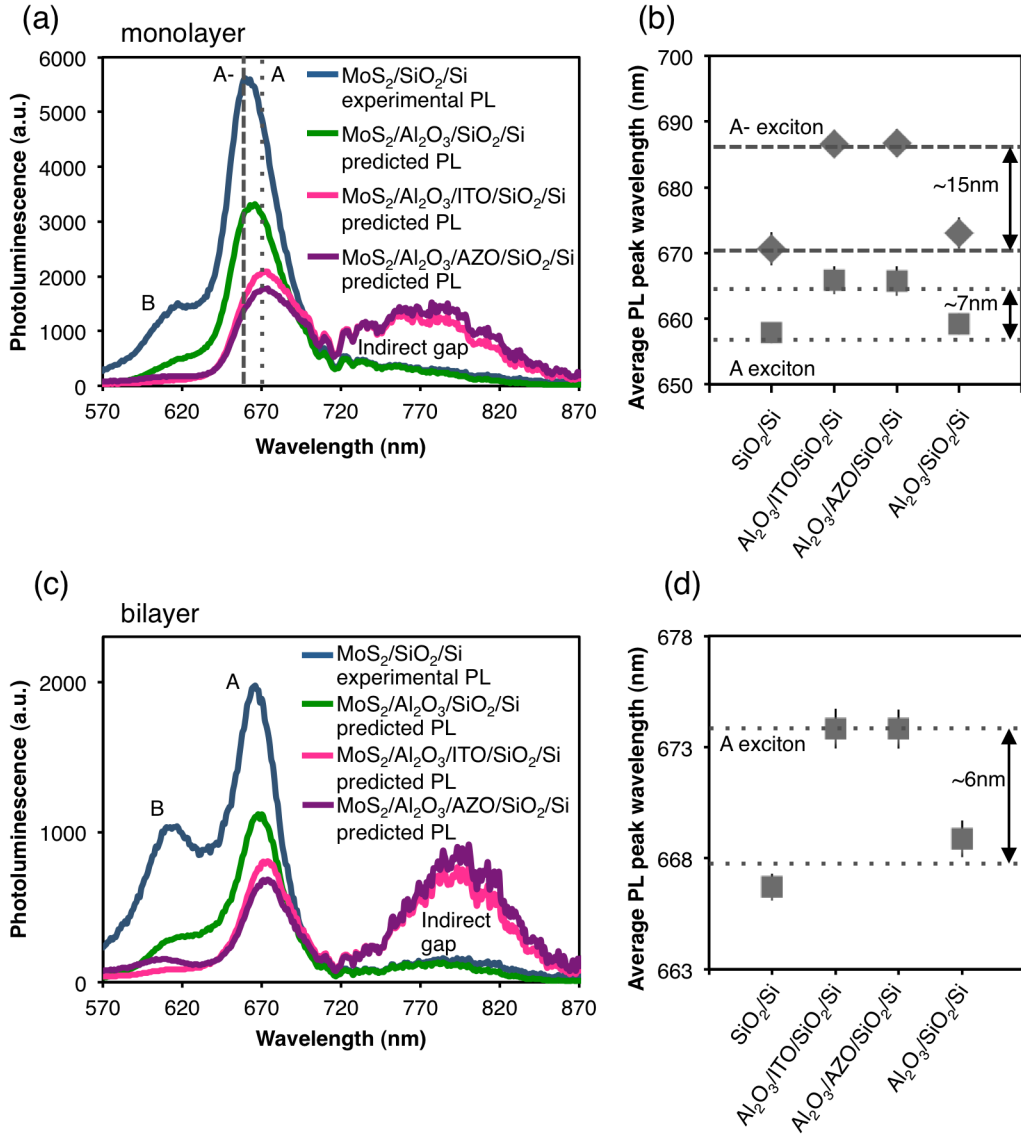


Figure 5-8: Predicted photoluminescence spectra of (a) monolayer and (c) bilayer MoS₂ on Al₂O₃/SiO₂/Si, Al₂O₃/ITO/SiO₂/Si, and Al₂O₃/AZO/SiO₂/Si substrates and experimental spectrum of MoS₂ on SiO₂/Si substrate. Spectral peak wavelengths of the A/A- exciton as a function of substrate for (b) monolayer and (d) bilayer MoS₂. Average values with error bars are shown.

5.6 Experimental Photoluminescence of Mono- and Bilayer MoS₂ on SiO₂/Si, Al₂O₃/ITO/SiO₂/Si, Al₂O₃/AZO/SiO₂/Si, and Al₂O₃/SiO₂/Si Substrates

In this section, we experimentally verify the predictions from the previous section and demonstrate controllable tuning of the luminescence spectrum of monolayer and bilayer

MoS₂ through optical interference effects. For these measurements, mono- and bilayer MoS₂ films are mechanically exfoliated onto four different substrates: SiO₂/Si, Al₂O₃/ITO/SiO₂/Si, Al₂O₃/AZO/SiO₂/Si, and Al₂O₃/SiO₂/Si (see Appendix for fabrication details).

Experimental photoluminescence spectra of monolayer and bilayer MoS₂ films on the substrates are shown in Figures 5-9 (a) and (c). In Figure 5-10, the average A/A- exciton peak intensity and wavelength are compared with the predicted peak intensity and wavelength as a function of substrate. The experimental spectral peak wavelengths match the predictions based on optical interference effects. As shown in Figure 5-9(b), the Al₂O₃/ITO/SiO₂/Si and Al₂O₃/AZO/SiO₂/Si substrates red-shift the A (A-) exciton peak by 8.5 nm (13.5 nm) compared to the monolayer MoS₂ on Al₂O₃/SiO₂/Si and SiO₂/Si substrates. For bilayer MoS₂, the red-shift is quantified in Figure 5-9(d) and is taken to be ~6 nm. These red-shifts are within 2 nm of the predicted red-shifts, as shown in Figures 5-10(a) and 10(b). The luminescence peak intensities of the experimental spectra match the predictions for the B exciton peak and for most of the A/A- exciton peaks. Some discrepancies are observed between measured and predicted luminescence intensity of the A/A- exciton peaks (for monolayer MoS₂ on Al₂O₃/SiO₂/Si and bilayer MoS₂ on Al₂O₃/ITO/SiO₂/Si and Al₂O₃/AZO/SiO₂/Si), as seen in Figures 5-10(c) and 10(d).

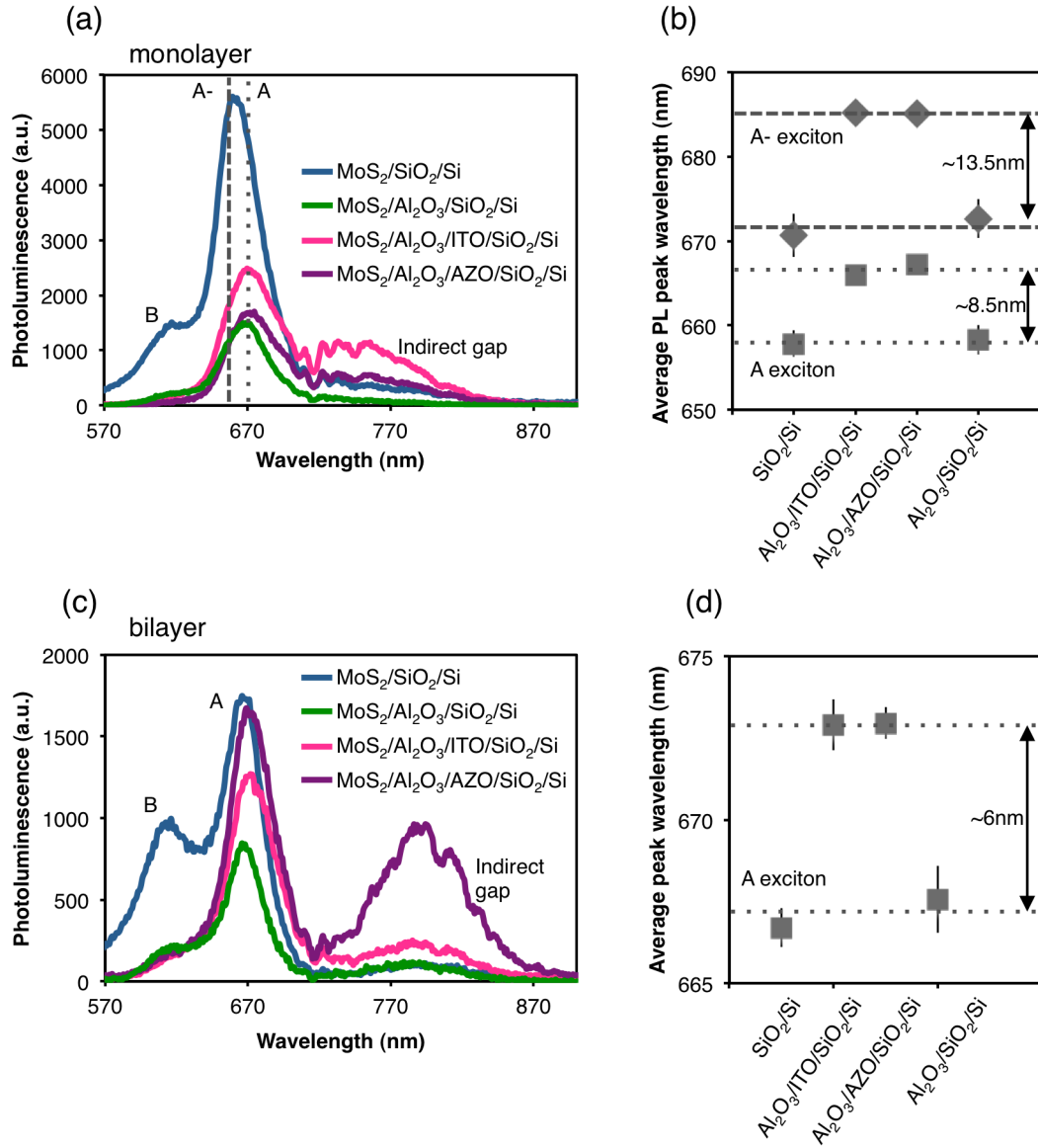


Figure 5-9: Experimental photoluminescence spectra of (a) monolayer and (c) bilayer MoS₂ on SiO₂/Si, Al₂O₃/SiO₂/Si, Al₂O₃/ITO/SiO₂/Si, and Al₂O₃/AZO/SiO₂/Si substrates. Spectral peak wavelengths of the A/A- exciton as a function of substrate for (b) monolayer and (d) bilayer MoS₂. Average values with error bars are shown.

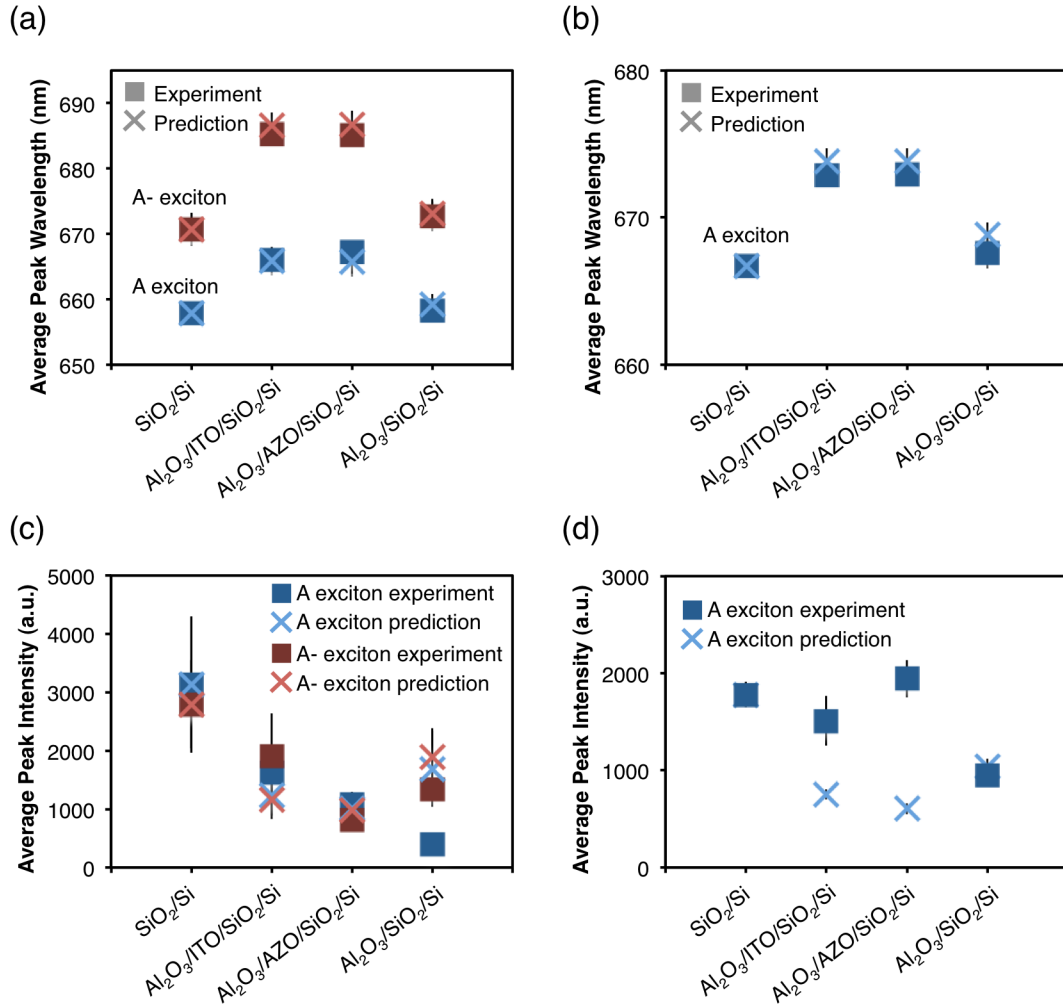


Figure 5-10: Luminescence peak (a-b) wavelength and (c-d) intensity for the A/A- exciton spectral peaks of (a, c) monolayer and (b, d) bilayer MoS₂. Values obtained from fitting the A/A- exciton peaks with Lorentzian curves. Average values with error bars are shown.

5.7 Discussion of Other Substrate-Based Effects

In this section, substrate effects other than optical interference are addressed, including strain^{20–22}, dielectric screening¹⁹ and doping/charge transfer^{27–31}. We eliminate these effects as the cause of any substrate-based luminescence tuning observed in the luminescence spectra presented in the previous section. This discussion, along with the match of optical interference-based photoluminescence predictions to experimental

spectra, confirms that any substrate-based luminescence tuning observed in this Chapter is a result of optical interference effects.

Effects of dielectric screening and strain are primarily determined by the substrate layer in direct contact with the 2D material (SiO_2 or Al_2O_3 in this study). There are differences between the luminescence spectrum of MoS_2 films on two different substrates ($\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ and $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$) where MoS_2 is adjacent to the same material (Al_2O_3). This suggests that dielectric screening and strain are not responsible for the luminescence tuning observed in the previous section. Previous studies have shown that charge transfer from a substrate material can be observed through the relative luminescence intensities of the neutral A exciton and charged A- trion^{30,31}. We do not observe a shift in relative intensity between the A and A- exciton spectral peaks as a function of substrate in the emission of monolayer MoS_2 , as shown in Figure 5-10(c). In addition, the use of an Al_2O_3 buffer layer between ITO/AZO and MoS_2 should prevent charge transfer between the conductive ITO/AZO layers and the MoS_2 film.

5.8 Predicted Photoluminescence of Monolayer MoS_2 on SiO_2/Si and $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$ Substrates with Varied Substrate Material Parameters

In this section, we further explore possibilities of tuning the luminescence emission of monolayer MoS_2 using optical interference effects by predicting the effect of varying the substrate material parameters. In particular, luminescence emission of monolayer MoS_2 on SiO_2/Si and $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$ is systematically predicted for a series of SiO_2 , Al_2O_3 , and ITO layer thicknesses and refractive indices.

The initial layer thicknesses are 273 nm, 50 nm, and 65 nm for SiO₂, Al₂O₃, and ITO. All substrate layer thicknesses are tuned from 50 nm to 400 nm in steps of 50 nm. The real refractive index (n) of each layer is varied while the imaginary index (k) is kept constant; then k is varied while n remains constant. The photoluminescence emission of monolayer MoS₂ on the substrates is predicted for each variation. The predicted spectra are interpolated and plotted as a function of the varied material parameter, as shown in Figures 5-11 to 5-14. From these results, it is clear that varying the thickness and refractive index of the substrate layers tunes the luminescence emission of monolayer MoS₂ films on said substrates.

The A exciton photoluminescence intensity of monolayer MoS₂ on the SiO₂/Si substrate is tuned by about an order of magnitude as a result of varying the SiO₂ thickness (as shown in Figure 5-11(a)). This is similar to the results obtained by Zhang, *et al.*²⁴. We observe a shift of ~8 nm of the A exciton wavelength as the SiO₂ thickness is varied; this had not been previously reported. The shift is highlighted in Figure 5-11(b), where the photoluminescence intensity is normalized to 1 and plotted as a function of SiO₂ thickness and emission wavelength.

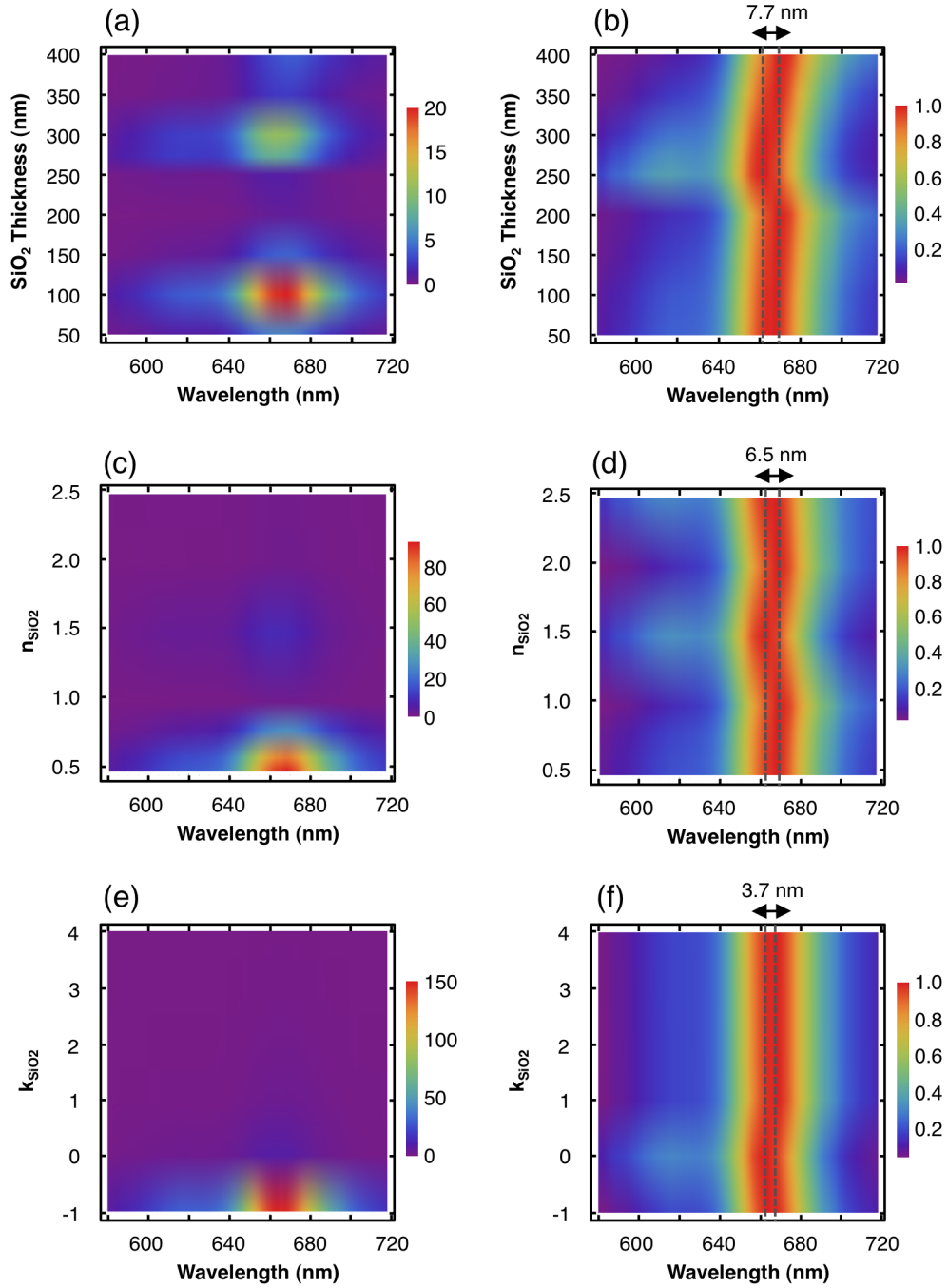


Figure 5-11: Predicted photoluminescence spectra of monolayer MoS₂ on SiO₂/Si when (a-b) the SiO₂ thickness, (c-d) the real part of the SiO₂ refractive index (n_{SiO_2}) and (e-f) the imaginary part of the SiO₂ refractive index (k_{SiO_2}) are varied. The luminescence is predicted for SiO₂ thicknesses of 50 nm, 100 nm, 150 nm, 200 nm, 250 nm, 273 nm, 300 nm, 350 nm, 400 nm; n_{SiO_2} values of 0.46, 0.56, 0.76, 0.96, 1.46, 1.96, 2.46 (at 532 nm); and k_{SiO_2} values of -1, 0, 1, 2, 3, 4, 5. The photoluminescence intensity (a, c, e) and the intensity normalized to 1 (b, d, f) are plotted as a function of varied property (thickness, n_{SiO_2} , or k_{SiO_2}) and emission wavelength.

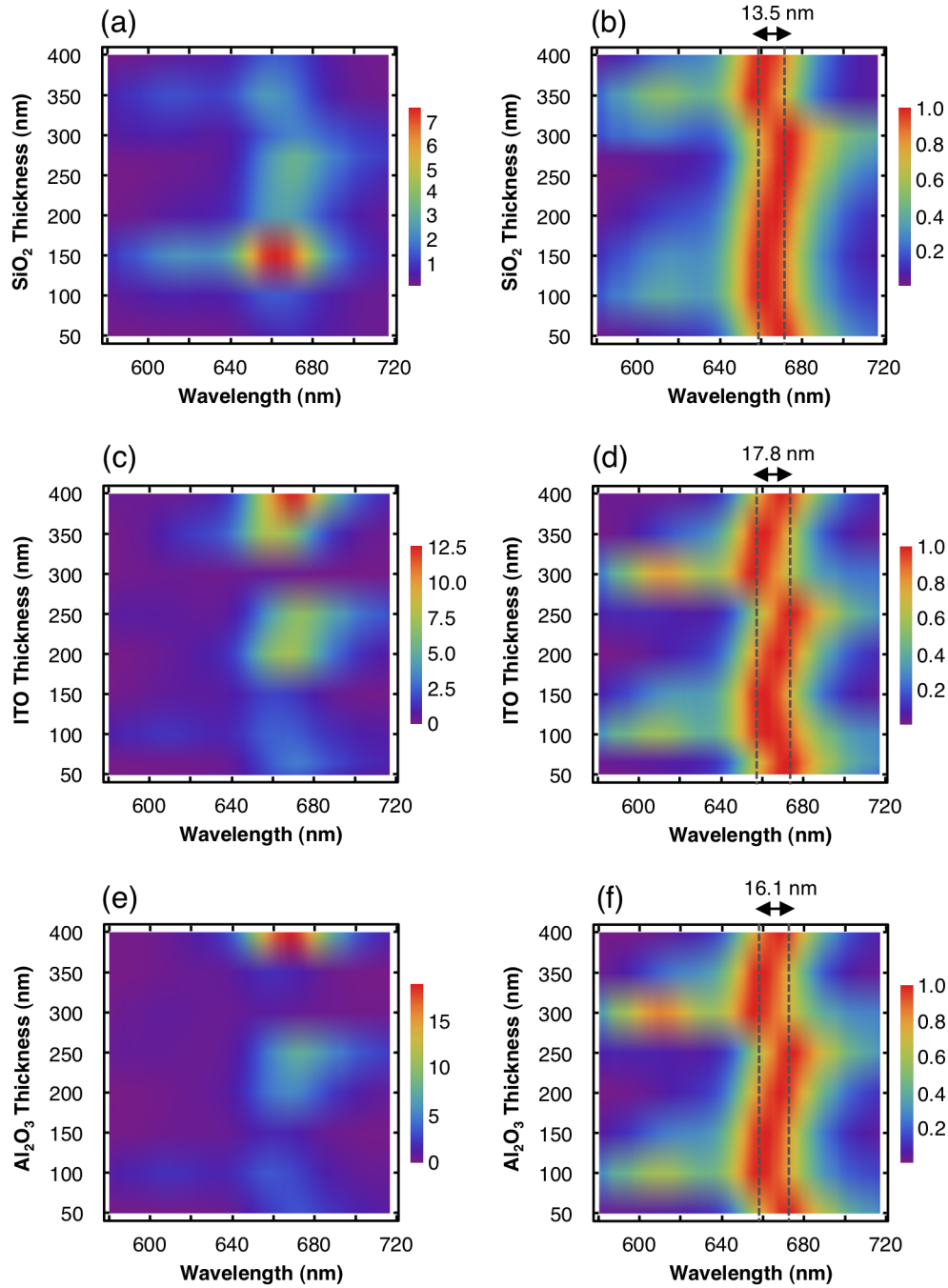


Figure 5-12: Predicted photoluminescence spectra of monolayer MoS₂ on Al₂O₃/ITO/SiO₂/Si when the thickness of (a-b) the SiO₂ layer, (c-d) the ITO layer, and (e-f) the Al₂O₃ layer are varied. The luminescence is predicted for SiO₂ thicknesses of 50 nm, 100 nm, 150 nm, 200 nm, 250 nm, 273 nm, 300 nm, 350 nm, 400 nm; ITO thicknesses of 50 nm, 65 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm; and Al₂O₃ thicknesses of 50 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm. The photoluminescence intensity (a, c, e) and the intensity normalized to 1 (b, d, f) are plotted as a function of layer thickness and emission wavelength.

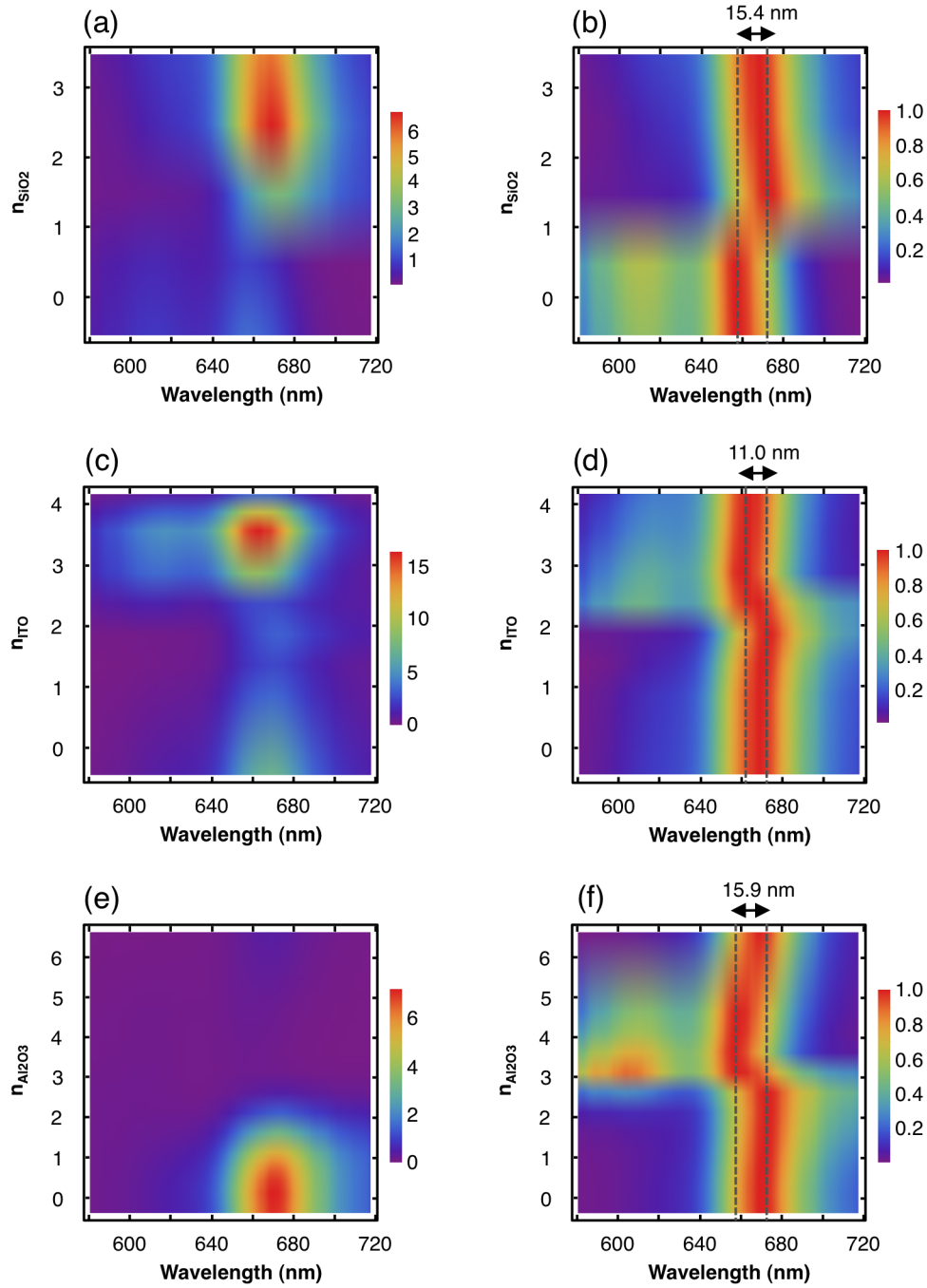


Figure 5-13: Predicted photoluminescence spectra of monolayer MoS₂ on Al₂O₃/ITO/SiO₂/Si when the real refractive index n of (a-b) the SiO₂ layer, (c-d) the ITO layer, and (e-f) the Al₂O₃ layer are varied. The luminescence is predicted for n_{SiO_2} values of -0.54, 0.46, 1.46, 2.46, 3.46 (at 532 nm); n_{ITO} values of -0.44, 0.86, 1.36, 1.86, 2.36, 2.86, 3.56, 3.86, 4.16 (at 532 nm); and $n_{\text{Al}_2\text{O}_3}$ values of -0.37, 0.13, 0.43, 0.63, 0.73, 0.93, 1.13, 1.63, 2.13, 2.63, 3.13, 3.63, 4.13, 4.63, 6.63 (at 532 nm). The photoluminescence intensity (a, c, e) and the intensity normalized to 1 (b, d, f) are plotted as a function of n and emission wavelength.

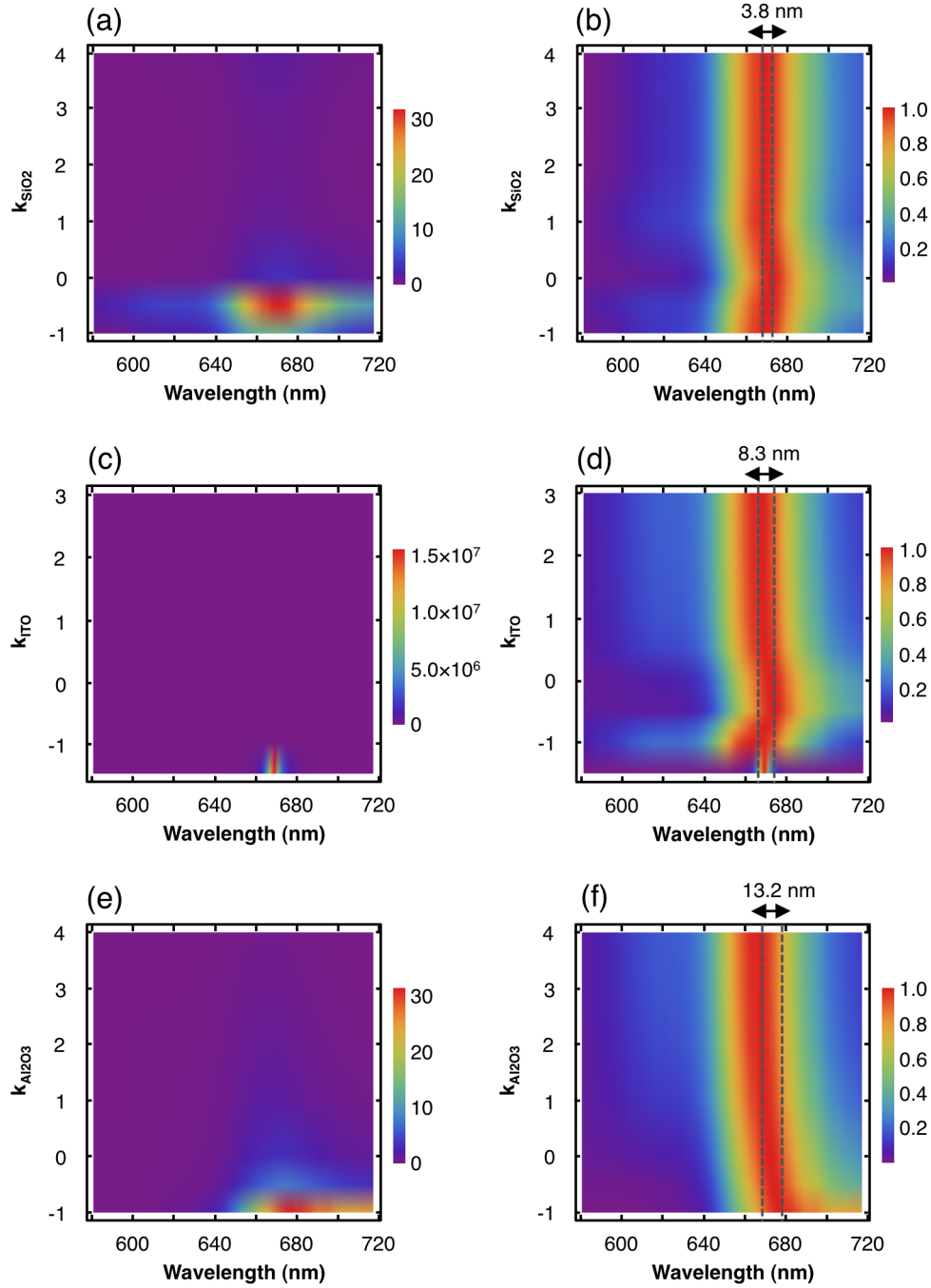


Figure 5-14: Predicted photoluminescence spectra of monolayer MoS₂ on Al₂O₃/ITO/SiO₂/Si when the imaginary refractive index k of (a-b) the SiO₂ layer, (c-d) the ITO layer, and (e-f) the Al₂O₃ layer are varied. The luminescence is predicted for k_{SiO_2} values of -1, -0.5, 0, 1, 2, 3, 4; k_{ITO} values of -1.485, -0.985, -0.735, -0.485, 0.015, 0.515, 1.015, 2.015, 3.015 (at 532 nm); and $k_{\text{Al}_2\text{O}_3}$ values of -1, -0.5, 0, 1, 2, 3, 4. The photoluminescence intensity (a, c, e) and the intensity normalized to 1 (b, d, f) are plotted as a function of k and emission wavelength.

As with the SiO₂/Si substrate, altering the substrate layer thicknesses in the Al₂O₃/ITO/SiO₂/Si substrate tunes both the emission intensity and spectral peak wavelength of the MoS₂ luminescence spectrum, as shown in Figure 5-12. The four-layer substrate may provide the opportunity for luminescence tuning over a wider wavelength range than the two-layer substrate. When the thickness of SiO₂ is varied in the Al₂O₃/ITO/SiO₂/Si substrate, the A exciton emission wavelength can be tuned over a range ~6 nm larger than when the thickness of SiO₂ is varied in the SiO₂/Si substrate. This is seen by comparing Figures 5-11(b) and 5-12(b). The tunable wavelength range when the thickness of a layer in the Al₂O₃/ITO/SiO₂/Si substrate is varied is about the same irrespective of the adjusted layer (Al₂O₃, ITO, or SiO₂), as shown in Figure 5-11(b, d, f). When the thickness of any of the three layers is varied, the emission wavelength is tuned by ~15 nm. This suggests that, when varying the thickness of a substrate layer, the refractive index of the chosen layer may not strongly affect the tuning wavelength range. The ability to tune the emission wavelength by altering the thickness of any substrate layer improves the versatility of this emission tuning method.

There is evidence that a non-zero imaginary refractive index impacts the spectral peak intensity. In general, the largest emission intensities occur when one of the substrate layers has $k < 0$, which corresponds to an emitting material. The largest emission intensity occurs when $k_{ITO} = -1.5$, as shown in Figure 5-14(c). This can be explained by considering the relationship between the imaginary refractive index k and the absorption coefficient $\alpha = \frac{4\pi k}{\lambda}$. It follows that varying the imaginary refractive index of a substrate layer provides the largest emission intensity tuning range out of the substrates investigated here.

The widest predicted photoluminescence emission wavelength tuning range is ~18 nm and occurs when the thickness of the ITO layer in the $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$ is varied, as shown in Figure 5-12(d). This is greater than the wavelength tuning range when tuning the MoS_2 A exciton luminescence emission by other methods such as dielectric screening (~5 nm)¹⁹ or by doping MoS_2 to adjust the relative luminescence intensity of the A excitons and A- trions (~14 nm)²⁷. Optical interference effects are therefore an advantageous method to engineer substrates that produce specific emission wavelengths of few-layer MoS_2 films.

5.9 Summary

This Chapter presented the optical interference effects from a substrate with transparent conducting oxides on the emission spectrum of monolayer and bilayer MoS_2 . In particular, $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$ and $\text{Al}_2\text{O}_3/\text{AZO}/\text{SiO}_2/\text{Si}$ substrates. This knowledge is important for future transparent optical devices which require transparent conducting gates and contacts. This work has also demonstrated the use of optical interference effects to tune the luminescence emission of few-layer MoS_2 films. An interference factor is derived that takes into account optical interference effects in the luminescence spectrum of a 2D material on a substrate with up to four layers. Using this factor, the photoluminescence spectra from monolayer MoS_2 on SiO_2/Si and $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$ substrates with variable substrate layer thicknesses and complex refractive indices are predicted. It is predicted that the emission wavelength of monolayer MoS_2 can be tuned over a range of 18 nm, and the intensity tuned over several orders of magnitude. Predicted luminescence tuning is confirmed via experimental photoluminescence

measurements of monolayer and bilayer MoS_2 on four substrates: SiO_2/Si , $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$, $\text{Al}_2\text{O}_3/\text{AZO}/\text{SiO}_2/\text{Si}$, and $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$. The ability to tune the luminescence emission of 2D materials using substrate-based optical interference effects can be used in future optical applications to design devices with specific emission or absorption characteristics. Understanding substrate-based optical interference effects (especially from substrates with transparent conducting oxide layers) and the ability to engineer substrates for a desired application will be useful when integrating few-layer MoS_2 into future optical devices.

Chapter 6. Effect of External Electric Field on the Band Gap of Few-Layer MoS₂

After successfully demonstrating the influence of optical interference effects from transparent conducting oxide-based substrates on the luminescence properties of MoS₂ in the previous Chapter, this Chapter explores the incorporation of transparent conducting oxides into a device and the effects of an electric field on the optical properties of few-layer MoS₂. This Chapter demonstrates the ability to tune emission from few-layer MoS₂ at room temperature when an out-of-plane external electric field is applied using a semi-transparent parallel plate capacitor structure. This Chapter outlines challenges of integrating the electrically tunable band gap property into efficient future optical device applications. This Chapter presents the second method used in this thesis to tune emission from few-layer MoS₂.

Performance parameters of semiconductor based optical devices are determined by the emission spectrum of said semiconductors. Manipulation of emission from 2D semiconductors potentially expands the functionality of optical devices made with these materials. The ability to continuously and nondestructively tune the transition-metal dichalcogenide band gap can be a promising route to wavelength-tunable optical devices, such as detectors and light emitters. One auspicious way this can be achieved is through application of an external electric field. Ramasubramaniam, *et al.*⁴⁴ were the first to theoretically predict that external electric field applied perpendicular to the layers of bilayer TMDs could reduce the band gap of 2D materials. With large enough electric fields ($\sim 1.5\text{-}3$ V/nm), the band gaps of the bilayer films are predicted to close, rendering the materials metallic. Further theoretical studies have confirmed these predictions in

MoS₂ and other TMDs^{45–49}. External electric field is also predicted to tune the band structures of heterostructures of 2D materials^{105–110}.

Initial experimental confirmation of band gap reduction in bilayer^{42,43} and few-layer⁴³ MoS₂ via external electric field has been demonstrated, but crucial steps remain before realizing integration of the property into efficient, wavelength-tunable optical devices. Certain steps in particular, such as integration of transparent conductive oxide contact layers, examination of the effect of optical interference on electrically tunable band gaps, and achieving the above at room temperature are investigated here. Experiments by Chu, *et al.*⁴² use a field effect transistor to apply perpendicular electric field and reduce the band gap of bilayer MoS₂ by ~300 meV when 1.2 V/nm is applied at room temperature. Klein, *et al.*⁴³ use a parallel plate capacitor to apply electric field perpendicular to the layers of few-layer MoS₂ and measure the emission spectra from the 2D films at low temperature (10 K). They find that, due to the Stark Effect, the A exciton energy of few-layer MoS₂ can be tuned by up to ~16 meV with external electric fields up to 0.4 V/nm.

The motivation for this work is to advance the electrically tunable band gap property of few-layer MoS₂ for potential integration with optical devices. This Chapter provides room temperature results for electrically tuning the band gap of few-layer MoS₂ in a device-like parallel plate capacitor structure, where the external electric field is applied through a semi-transparent contact. When up to ~0.3 V/nm is applied, the luminescence emission peak energy is shifted by an average of 6 meV for bilayer MoS₂. Tuning is also observed for monolayer and trilayer MoS₂. We attribute the spectral shift to band gap tuning caused by the Stark Effect. We discuss limitations to the effective

applied electric field due to inherent doping levels in natural MoS₂ crystal. This Chapter also demonstrates that optical interference effects do not prevent observation of the electric field tuning effects; this has not been shown before. A more detailed discussion of the motivation for this study is provided in the next section.

Capacitor fabrication and MoS₂ exfoliation methods are provided in the Appendix, along with details of the simultaneous photoluminescence-electric field measurement setup.

6.1 Motivation

Optical devices that emit or absorb light often require transparent layers to allow for transmission of the emitted or absorbed light. Realization of emission from tunable band gap MoS₂ therefore requires transparent conductive proximate films above and below the MoS₂ for contacts through which the tuning electric field can be applied. Previous experimental studies have used an opaque silicon back gate with a transparent top gate^{42,43} to tune the band gap of bilayer MoS₂ via out-of-plane external electric field. Experimental demonstration of the tuning of the band gap of few-layer MoS₂ via an electric field applied through a pair of transparent contacts has not yet been reported. The use of two transparent contacts could allow for fully transparent variable wavelength detectors and light emitters; this may be useful for applications such as transparent displays. In this work, an electric field is applied through transparent indium tin oxide (ITO) and semi-transparent thin metal (Ti/Pt, <15nm thick) contacts; silicon is only used as a structural support substrate. In future work, we envision replacing the Si support

with a transparent substrate (such as glass) to achieve a fully transparent device to which an external electric field can be applied perpendicular to MoS₂.

To facilitate integration of the electric field-induced band gap tuning property, a simple structure for application of the electric field should be used. This simplifies the device fabrication process and expands the utility range of the tuning property. To this end, we use a parallel plate capacitor structure to apply the perpendicular electric field to MoS₂. We choose this structure in order to demonstrate the tunable band gap in few-layer MoS₂ without the need for directly contacting the MoS₂. At this time, the lateral area of 2D MoS₂ films is so small that electron beam lithography (EBL) techniques are required when patterning the contacts onto the MoS₂. If this step can be removed and the band gap can still be tuned via external electric fields, the opportunities for using this property in optical devices will grow.

In this work, MoS₂ films must be embedded in other layers to apply an electric field. As already discussed in Chapter 5, optical interference effects from the surrounding layers will affect the emission from 2D MoS₂. In order to integrate an electrically tunable band gap into devices, it is critical to determine that optical interference effects do not prevent electric field-based tuning. Previous studies⁴² have chosen dielectric and electrical contact materials so as not to alter the emission from 2D MoS₂; here we demonstrate that emission due to optical interference effects does not prevent observation of electric field-based tuning effects. In addition, we demonstrate the seamless combination of the two MoS₂ emission tuning methods: optical interference effects and the electric field effect. Until now, the composite method of tuning the band gap of MoS₂ has not been realized.

Finally, for most applications, room temperature functionality is critical. The measurements reported in the Chapter were all performed at room temperature.

6.2 Effect of External Electric Field on Few-Layer MoS₂

Electric field is applied perpendicular to layers of 2D MoS₂ by embedding the films in a parallel plate capacitor structure. The fabrication details are given in the Appendix. For the parallel plate capacitor, we use Al₂O₃ as the dielectric layer and ITO and thin Ti/Pt as the bottom and top contact films, respectively. We also use a SiO₂/Si substrate as structural support, such that the complete capacitor structure is: Pt/Ti/Al₂O₃/MoS₂/Al₂O₃/ITO/SiO₂/Si. This structure is schematically shown in Figure 6-1. The semi-transparent Ti/Pt and the transparent ITO contacts allow us to measure the optical response of the MoS₂ film while applying voltage/electric field across the structure. The voltage is applied with a Keithley 2400 sourcemeter connected via wirebonds to the Ti/Au contact pads on the Ti/Pt and ITO contacts. Photoluminescence spectroscopy is used to probe the optical properties of the few-layer MoS₂ while an electric field is being applied; details of the photoluminescence/electric field measurement setup are given in the Appendix.

The electric field across the MoS₂ films is directly proportional to the applied voltage and is calculated using the finite element approximation method as implemented in the QuickField software¹¹¹. For electric field calculations, the thickness and dielectric function of Al₂O₃ were extracted from variable angle spectroscopic ellipsometry measurements: $d_{\text{Al}_2\text{O}_3}$ =40-48 nm and $\epsilon_{\text{Al}_2\text{O}_3}$ =2.67-2.75. The thickness of MoS₂ was taken to be 1.2 nm, which is the thickness of a bilayer film. Small variations (± 1 layer, or ± 0.6

nm) in the thickness change the electric field by only $1\text{-}3 \times 10^{-3}$ V/nm and can be neglected. The out of plane dielectric constant of MoS₂ was taken to be the average of theoretically calculated values^{95,112}: $\epsilon_{\text{MoS}_2}=2.8$. The dielectric constant of 1-8 layer MoS₂ has been shown to vary as a function of applied electric field¹¹³. However, for MoS₂ with 1-3 layers the dielectric constant is invariant with applied fields up to 2 V/nm, which is four times the amount of field applied in these experiments. An electrically tunable dielectric constant can therefore be disregarded in this study.

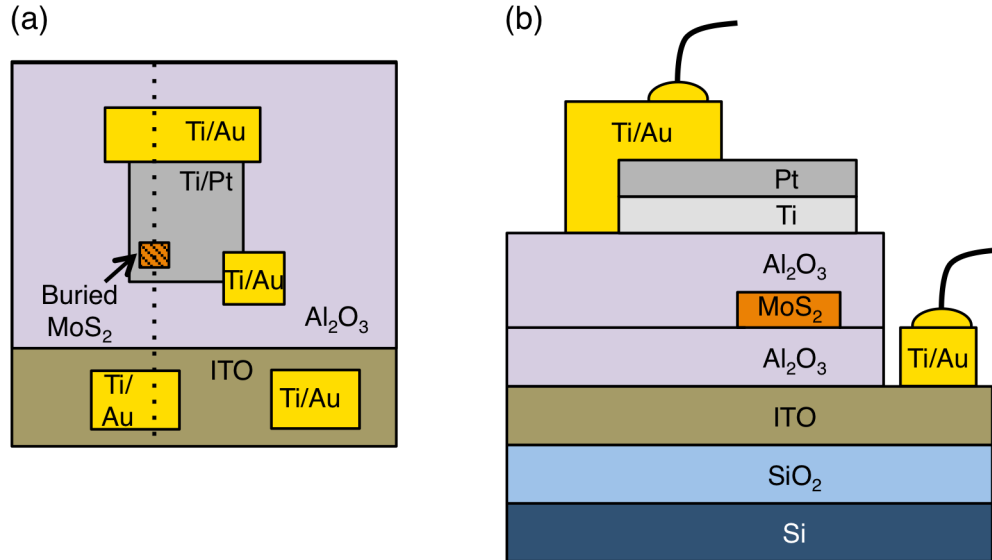


Figure 6-1: The parallel plate capacitor structure used to apply electric fields across the layers of few-layer MoS₂ films. (a) Plan view of the structure and (b) side view of the structure when cut along the dotted line shown in (a). Wire bonds are connected to the Ti/Au contact pads. Layer thicknesses are not to scale.

Electric fields up to ~ 0.4 V/nm are applied to monolayer, bilayer, and trilayer MoS₂. Representative photoluminescence spectra of monolayer, bilayer, and trilayer MoS₂ measured with 0 V/nm and 0.2-0.4 V/nm applied electric fields are shown in Figure 6-2. These spectra have been smoothed using the Savitzky-Golay method to make

the spectral peak features clearer. Unbiased measurements are taken with 0 V/nm applied before and after the biased measurements to demonstrate reversibility of the band gap tuning. The average peak energies for monolayer, bilayer, and trilayer MoS₂ as a function of applied electric field are shown in Figure 6-3. Applying ~0.2 V/nm, 0.4 V/nm, and 0.4 V/nm red-shifts (reduces) the band gap energy by 3 meV, 6 meV, and 7 meV for monolayer, bilayer, and trilayer MoS₂.

The observed electric field induced emission tuning can be explained by the Stark Effect. As electric field is applied, band structure degeneracy is lifted and the conduction band minimum and valence band maximum shift toward one another, reducing the band gap. For large enough electric fields (>1 V/nm), the band gap of bilayer MoS₂ is predicted to close⁴⁴. For smaller electric fields (such as the <0.5 V/nm fields applied in this Chapter), the band gap will monotonically decrease as electric field increases, as shown in Figure 6-3. Given the magnitude of electric fields applied here, the observed band gap tuning range is comparable to a previous Stark Effect study⁴³, but is smaller than another experimental study⁴² and less than the ~60 meV theoretically predicted tuning⁴⁴. These discrepancies and possible reasons for the minimal observed band gap tuning are discussed later in this Chapter.

Band gaps of monolayer MoS₂ are not predicted to have the same strong dependency on electric field as bilayer MoS₂^{42,44}. However, the Stark Effect has been shown to slightly perturb the band gap of monolayer MoS₂ on the order of 0.1-10 meV^{43,114,115}; this is similar to the tuning we observe from monolayer MoS₂. We suggest that if we were able to apply larger electric fields, we would observe a larger contrast between the effects of the electric field on monolayer and bilayer MoS₂.

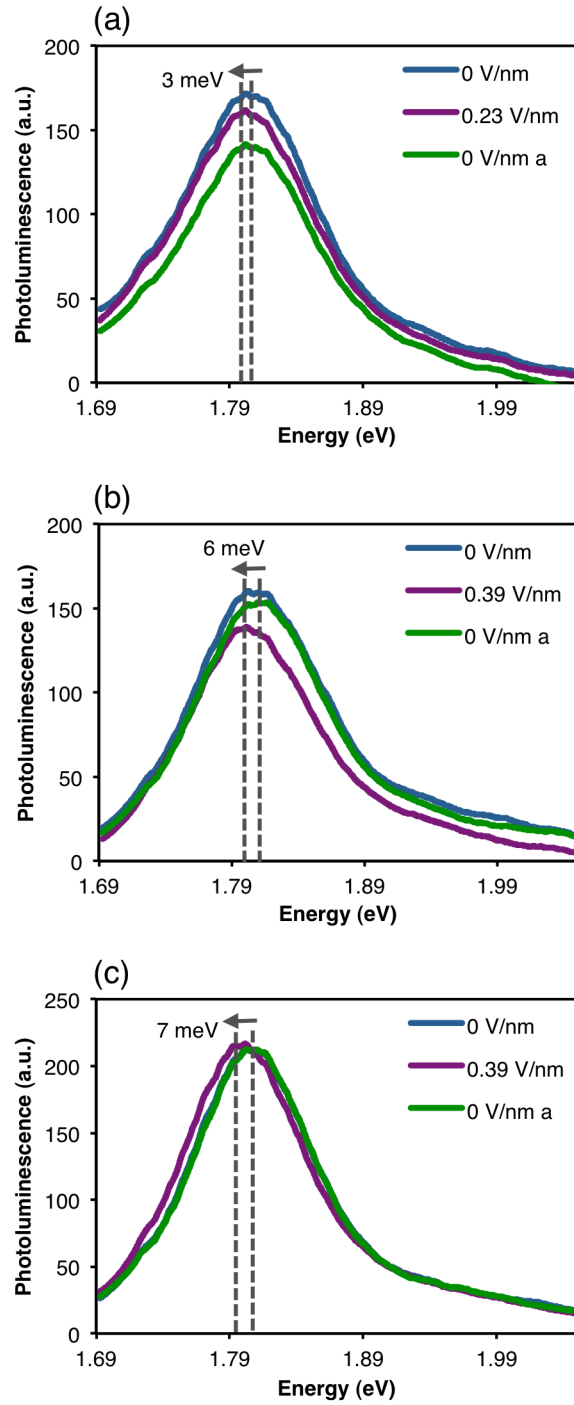


Figure 6-2: Photoluminescence spectra of (a) monolayer, (b) bilayer, and (c) trilayer MoS₂ with applied electric fields of 0 V/nm, 0.2-0.4 V/nm, and 0 V/nm (the second 0 V/nm is labeled as 0 V/nm a). Magnitude of photoluminescence peak energy shift is indicated.

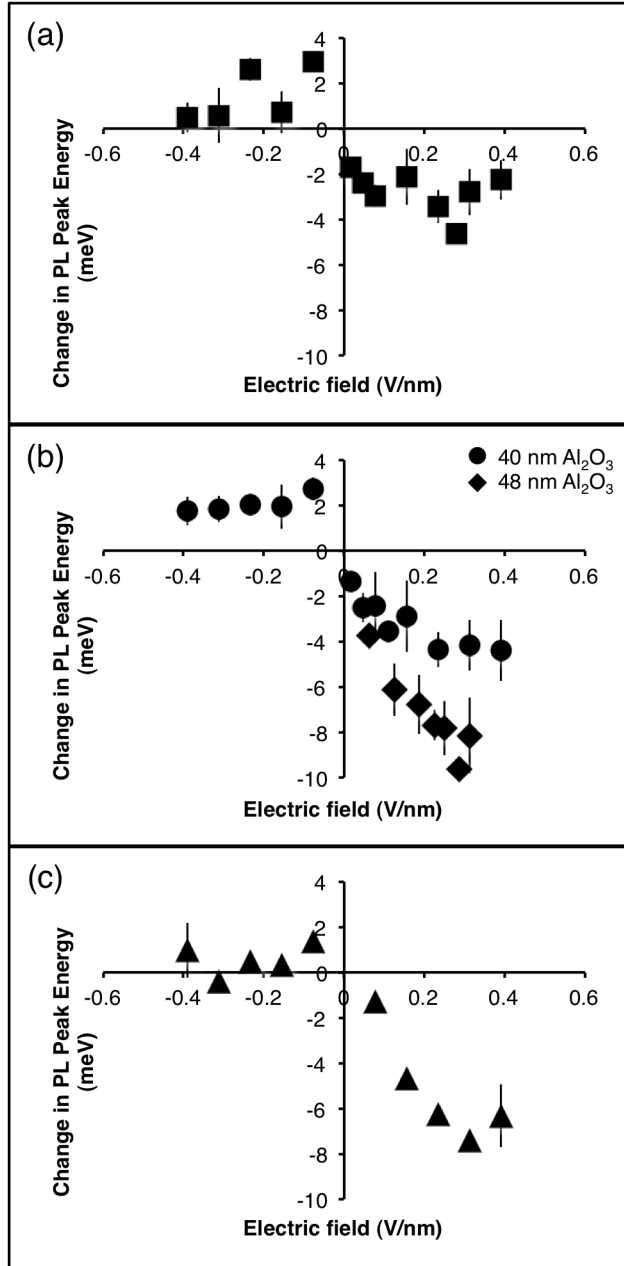


Figure 6-3: Average difference between unbiased (0 V/nm) and biased photoluminescence peak energy from (a) monolayer, (b) bilayer, and (c) trilayer MoS₂ as a function of electric field. The two sets of data for bilayer MoS₂ correspond to two different groups of samples, one with Al₂O₃ layer thicknesses of 40 nm and the other with 48 nm. The different Al₂O₃ thicknesses result in different applied electric fields for the same applied voltage, such that the two datasets cannot be directly averaged and must be presented separately.

The minimal band gap tuning from few-layer MoS₂ may be attributed to free carriers (unintentional doping) present in the MoS₂ films. Natural MoS₂, which was used

in this thesis, has been shown to be n-type^{116–118}. When subjected to an external electric field, free carriers will move to oppose the applied field, forming a built-in electric field that effectively reduces the external field acting on the MoS₂ film. The MoS₂ film will only feel the effects of the effective external field^{43,119} (the applied field minus the built-in field), minimizing the band gap tuning in the material.

A second consequence of the inherent doping in natural MoS₂ is that there is a region in the plot of change in band gap vs. applied field where the band gap is static. As seen in Figure 6-3, this region occurs when electric field <0 V/nm. The unchanging band gap can be understood by considering the built-in electric field. The band gap energy will remain constant until enough voltage is applied to form an electric field that overcomes the built-in electric field, similar to a threshold voltage. This phenomenon has been demonstrated in bilayer WSe₂ with various doping levels¹¹⁹. At charge neutrality, any non-zero applied bias will tune the band gap. As doping levels rise, no Stark Effect is observed until enough voltage is applied to overcome the threshold voltage. This results in a region of static band gap as a function of applied voltage, similar to what we observe. However, the observed static band gap region is not centered around the unbiased (V=0 V) condition. This suggests that for a given magnitude of applied voltage, the magnitude of the effective electric field acting on the MoS₂ may differ depending on whether the voltage is positive or negative. This may be caused by disparate conductivities in the top and bottom contact layers or non-uniform conductivity in either contact layer.

We can estimate the threshold voltage and extract the free carrier concentration in the MoS₂ films. Experimental results obtained by Chu, *et al.*⁴² at charge neutrality show

that the band gap of bilayer MoS₂ is tuned by ~275 meV per 1 V/nm of applied field. Based on that tuning rate, 0.3 V/nm applied electric field should tune the band gap by ~82 meV. However, we observe band gap tuning ~6 meV for 0.3 V/nm applied field. If our samples were charge neutral, an electric field of only ~0.02 V/nm (or 1.6 V applied voltage) would be required to tune the band gap by 6 meV. Instead, 0.3 V/nm (25V) is required. This suggests a threshold voltage of 23.4 V. The threshold voltage is given by equation 6-1, where V is the threshold voltage, Q the charge from free carriers, C the capacitance of the device, n is the free carrier concentration, A is the Ti/Pt top contact area (4 cm²), e is the elementary charge (1.6*10⁻¹⁹ C), $\epsilon_{\text{Al}_2\text{O}_3}$ is the dielectric constant of Al₂O₃ (2.67), ϵ_0 is vacuum permittivity (8.85*10⁻¹² F/m), and d is the distance between the Ti/Pt and ITO top and bottom contacts (97 nm). Taking 23.4 V as the threshold voltage, we estimate the inherent free carrier concentration in MoS₂ to be ~3.5*10¹² cm⁻², which is comparable to values found in other studies^{118,120}.

$$V = \frac{Q}{C} = \frac{nAe}{\epsilon_{\text{Al}_2\text{O}_3}\epsilon_0 A/d} = \frac{ned}{\epsilon_{\text{Al}_2\text{O}_3}\epsilon_0} \quad (6-1)$$

The ability to apply as much field as possible is important to maximize the band gap tuning range. Therefore, the presence of unintentional doping and free carriers in MoS₂ is a challenge that should be addressed. To minimize threshold voltage and maximize the band gap tuning range, MoS₂ should be kept as close to charge-free conditions as possible.

We now discuss the possibility of luminescence tuning as a result of charge injection, and establish that charge injection does not occur in the measurements

presented here. It has been shown that transfer of charges into/out of MoS₂ will affect the relative neutral exciton and charged exciton (trion) populations in the film^{27,28}. Changes to the exciton/trion population ratio affect the photoluminescence intensity ratio of the exciton and trion recombination peaks, resulting in a tuning of the luminescence spectrum. We provide evidence that the luminescence tuning observed in this Chapter is caused by the Stark Effect, and not by charge injection. Note that injected charges are separate from the previously discussed inherent free carriers present in MoS₂ due to unintentional doping.

The initial evidence against charge injection is that voltages applied across the capacitor are kept below the breakdown voltage to minimize leakage current. To ensure breakdown has not occurred during the photoluminescence measurements, current between the Ti/Pt and ITO contact layers is monitored. During all the measurements the current remained ≤ 1 nA; a sudden rise in current up to 10 nA and beyond indicates breakdown has occurred. The expected leakage current for these capacitors is calculated from equation 6-2, where I is the leakage current, V is the maximum applied voltage (30 V), A is the capacitor plate area (average of 4 cm²), d is the Al₂O₃ thickness (95 nm), and ρ is the Al₂O₃ resistivity (10¹⁶ $\Omega \cdot \text{cm}$)^{121,122}. We calculate anticipated leakage currents of ~ 1.26 nA; the measured leakage currents in these experiments remain below this value. With minimal leakage current, there is no charge injected into the MoS₂ layer.

$$I = \frac{V * A}{\rho * d} \quad (6-2)$$

We use a second method to check that the observed luminescence tuning is explained by the Stark Effect and is not a result of charge injection. Consider the case when charge injection were to cause the observed luminescence tuning. Then the tuning magnitude should continue to increase after the dielectric breakdown has occurred, as long as voltage is still being applied (and therefore current is flowing and charges are being injected). However, this does not occur. As shown in Figure 6-4, once breakdown occurs ~ 0.47 V/nm, the luminescence emission peak returns to its unbiased (0 V/nm) state. This suggests that our results are due to the applied electric field (not charge injection), which drops to zero once breakdown occurs.

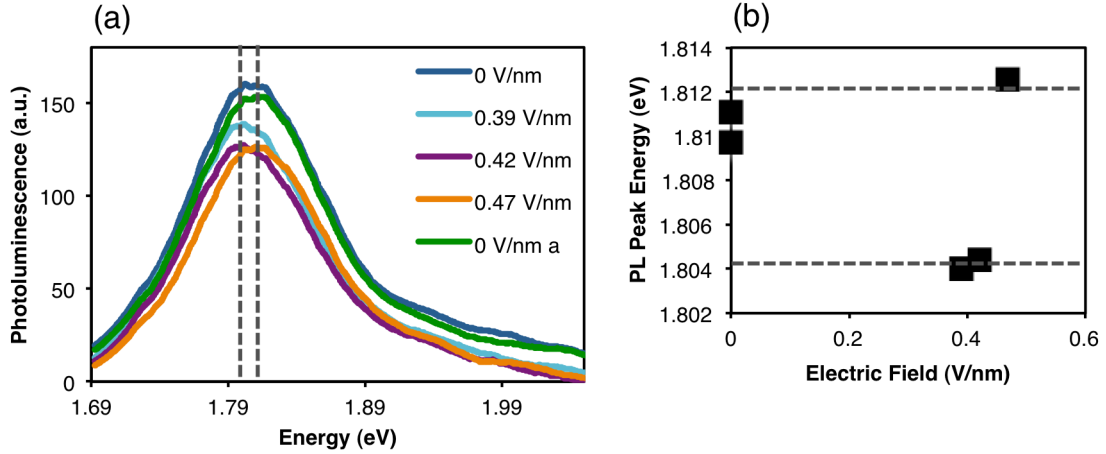


Figure 6-4: (a) Photoluminescence spectra of bilayer MoS₂ when unbiased (0 V/nm), biased before (0.39 and 0.42 V/nm) and after (0.47 V/nm) dielectric breakdown, and unbiased again after dielectric breakdown (0 V/nm a). (b) The photoluminescence peak energy as a function of applied electric fields. The peak energy returns to the unbiased value after dielectric breakdown.

6.3 Optical Interference Effects and Electric Field Induced Band Gap Tuning

As shown in Figure 6-1, the structure used in this Chapter to apply electric field is Pt/Ti/Al₂O₃/MoS₂/Al₂O₃/ITO/SiO₂/Si. To fabricate this structure, MoS₂ is exfoliated

onto an $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$ substrate. As demonstrated in Chapter 5, optical interference effects from this substrate red-shift the luminescence emission from MoS_2 when compared to emission from MoS_2 on SiO_2/Si substrates. One may be initially wary of changes to luminescence emission, because that can be a sign of 2D film damage or degradation. In particular, luminescence emission quenching can suggest damage to a 2D film¹²³. When fabricating a structure for applying electric fields to bilayer and few-layer MoS_2 , others have tailored the structure to avoid altering the luminescence emission⁴² or have observed changes to luminescence but did not specify the mechanism of the changes⁴³. To facilitate integration of an electrically tunable band gap into device structures, it is important to fully understand the effects of other foreign films surrounding the MoS_2 , and how those effects may enhance or inhibit the electrically tunable band gap property. The red-shift we observe from MoS_2 luminescence on $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$ vs SiO_2/Si substrates is caused by optical interference effects. These optical effects do not prevent observation of changes to the band gap of few-layer MoS_2 on $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$ due to electric field effects.

By demonstrating the simultaneous tuning of luminescence from optical interference effects and from applied electric fields, we realize the first experimental combination of MoS_2 luminescence tuning methods. Combined tuning methods could be useful in the improvement of future devices or in the design of their performance parameters. For example, foreign films adjacent to MoS_2 may be engineered such that optical interference effects from them enhance the luminescence intensity while applying an electric field. This could be particularly useful in increasing the emission intensity of bilayer MoS_2 , which is strongly affected by the Stark Effect^{42,44}, but whose naturally

indirect band gap produces a lower emission intensity than the direct band gap of monolayer MoS₂.

6.4 Summary

We have demonstrated that an electric field applied perpendicular to layers of few-layer MoS₂ tunes the band gap and luminescence emission of the films. The results of this work were measured at room temperature using device structures with semi-transparent and transparent conductive films, with no direct contact to the MoS₂ layer. The work in this Chapter clearly shows progress toward integration of the electrically tunable band gap property in optical devices. Because of unintentional doping in the MoS₂ films, we observe a limit to the band gap tuning. This suggests that the MoS₂ samples should be kept as pure as possible by limiting the unintentional dopants in the films in order to maximize the electric field effects. By using transparent ITO and semi-transparent Ti/Pt contact layers, we have addressed the challenge of integrating electric field tunability of the band gap into optical devices; we have used device structures that are optically transparent to the emitted light. Finally, we have combined two luminescence tuning methods: optical interference effects and an electric field effects. The optical interference effects do not appear to inhibit luminescence tuning with electric fields.

Chapter 7. Summary and Future Work

This Chapter summarizes the results and contributions of this thesis and suggests future work.

7.1 Summary

The results presented in this thesis successfully contribute to a key objective by investigating two-dimensional transition-metal dichalcogenides for optical device applications. We used a combination of high-resolution transmission electron microscopy, Raman and photoluminescence spectroscopies, and theoretical considerations to systematically analyze the intrinsic structural and optical properties of bulk and few-layer MoS₂, MoSe₂, WS₂, and WSe₂. In-plane lattice parameters of the materials were extracted from high-resolution transmission electron micrographs. Optical properties were extracted from Raman and photoluminescence spectroscopies; the dependence on 2D film thickness of these properties (such as band gap) was addressed. The in-plane lattice structure of the materials was shown to be independent of the thickness of the films; this verified that the thickness-dependent optical properties of the materials are not caused by changes to the crystal structure.

We investigated the effect of optical interference from substrates with transparent conducting oxide layers (specifically Al₂O₃/ITO/SiO₂/Si and Al₂O₃/AZO/SiO₂/Si) on the luminescence emission of monolayer and bilayer MoS₂. Effects from these substrates tuned the luminescence spectral emission peak wavelength and intensity. We used optical interference factors to predict the contribution from optical interference effects to

the luminescence emission of few-layer TMD films. Understanding these effects is important for the realization of transparent optical devices with 2D films. By varying the thickness and complex refractive indices of substrate layers, the luminescence emission of monolayer MoS₂ on said substrates is predicted to shift by up to 17 nm; the emission intensity is predicted to shift by orders of magnitude. Experimental results confirmed the ability to engineer substrates to shift the emission wavelength of mono- and bilayer MoS₂. The tunable emission of 2D MoS₂ films can expand the application space of the materials in devices.

We contributed to the study of tunable emission by demonstrating an electric field-induced continuously tunable emission from few-layer MoS₂ films. Continuously tunable emission is particularly important for variable wavelength light emitters and detectors. Although electric field-induced band gap tuning of bilayer MoS₂ had been previously reported, we demonstrated the effect with electric field applied from a parallel plate capacitor structure with a pair of transparent or semi-transparent contacts. We showed a tunable band gap due to electric field effects at room temperature and without the use of direct electrical contacts to MoS₂; this can facilitate integration of the band gap tuning property into devices. The small band gap tuning range observed in our results was attributed to unintentional doping in the MoS₂; we suggest that the tuning range can be maximized by keeping MoS₂ charge neutral.

We contributed the first experimental realization of a combination of multiple emission tuning methods (optical interference effects and electric field effects). We showed that optical interference effects do not prevent observation of electric field-induced band gap tuning. The contributions and results provided in this thesis advance

the study of two-dimensional transition-metal dichalcogenide films and inform their integration in future optical devices.

7.2 Future Work

The results and contributions from this thesis may inform several future investigations. The predictions of optical interference effects on the luminescence emission of few-layer MoS₂ may be applied to other TMD films. For transparent optical devices, predicting optical interference effects from substrates where silicon is replaced by glass may be useful. The glass or silicon support may also be replaced by a flexible polymer such as polydimethylsiloxane (PDMS) for flexible and transparent device applications.

Similarly, we suggest replacing the silicon support with glass in the parallel plate capacitor structure used to apply electric fields. This is the next step toward integration of electric field-induced band gap tuning in fully transparent devices.

Optical interference effects from transparent conducting oxides in contact with few-layer TMD films may be investigated. This may inform the use of transparent conducting oxides as possible Ohmic contacts to the 2D films. For these types of contacts, charge transfer and band alignment should be addressed.

Finally, the contributions and results of this thesis suggest the possible realization of a transparent and wavelength-tunable light emitter or detector with few-layer transition-metal dichalcogenide films.

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Appendix: Methods

This Appendix provides details for experimental fabrication processes, measurement techniques, and theoretical calculations.

Exfoliation Process

All two-dimensional films in this thesis were isolated using mechanical exfoliation. Mechanical exfoliation is colloquially known as the “scotch tape method” and was popularized by Geim and Novoselov when they used it to isolate few-layer graphene on SiO_2/Si substrates^{1,2}. To obtain few-layer samples via mechanical exfoliation, we begin with a bulk crystal (at least 100 layers thick). For this thesis, natural MoS_2 bulk crystals were purchased from SPI Supplies, Inc. Bulk crystals of the selenide materials (WSe_2 and MoSe_2) were grown crystals purchased from High Quality Graphene (<http://www.hqgraphene.com/>). The WS_2 bulk crystal was grown and purchased from the Tennessee Crystal Center (TennXC) (<https://utr.f.tennessee.edu/product-category/tenn-xc/>).

To obtain a 2D film from bulk, a small piece of bulk crystal is placed onto the adhesive side of a clean piece of scotch tape. To exfoliate the samples used in this thesis, Scotch brand was not always available, so other brands of clear adhesive tape were also used. No variations in the final samples were observed as a result of different tape brands. Once the bulk material is on the scotch tape, the tape is repeatedly folded over on itself to thin down the bulk material. Gel-film is used as an intermediate carrier between the scotch tape and the target substrate¹²⁴. This helps reduce the amount of adhesive residue left on the target substrate after exfoliation. A piece of Gel-Film

(<http://www.gelpak.com/--pf-film>) is placed on the sticky side of the tape such that the transition-metal dichalcogenide material is sandwiched between the Gel-Film and the tape. The Gel-Film is gently pressed down to ensure full contact with the transition-metal dichalcogenide material, and then quickly peeled away from the tape, leaving some material on the Gel-Film. The Gel-Film is placed onto the target substrate with the transition-metal dichalcogenide side in contact with the substrate. The substrate has been cleaned with acetone and isopropyl alcohol prior to exfoliation. The Gel-Film is gently pressed onto the substrate to ensure contact between the substrate and the transition-metal dichalcogenide material. The Gel-Film is slowly peeled off of the substrate. Due to van der Waals forces, some transition-metal dichalcogenide material remains on the target substrate. The transition-metal dichalcogenide films on the target substrates are soaked in acetone for at least a day to remove residual adhesive material. After soaking in acetone, the samples are rinsed with acetone and isopropyl alcohol.

The exfoliation method outlined above was used for all substrate-supported samples presented in this thesis, except for some samples which were made without the use of the Gel-Film. The few-layer samples used for high resolution TEM characterization were made using an exfoliation method that does not include any type of adhesive material. The TEM sample preparation process was described in Chapter 3.

Layered Substrate Fabrication Process

This section outlines the fabrication process to make the $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$, $\text{Al}_2\text{O}_3/\text{AZO}/\text{SiO}_2/\text{Si}$, and $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrates. Each of these substrates begins with a SiO_2/Si substrate with ~ 270 nm thermal oxide layer. The SiO_2/Si substrates were

purchased from WRS materials (now Pure wafer, <https://www.purewafer.com/>). The SiO_2/Si substrate is cleaned with acetone and isopropyl alcohol prior to the deposition of any other layers, and the substrate stacks are cleaned using the same process in between each layer deposition step. The $\text{Al}_2\text{O}_3/\text{ITO}/\text{SiO}_2/\text{Si}$, $\text{Al}_2\text{O}_3/\text{AZO}/\text{SiO}_2/\text{Si}$, and $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrates are fabricated by sequentially depositing ITO, AZO, and/or Al_2O_3 layers on top of SiO_2/Si . The deposition processes for ITO, AZO, and Al_2O_3 are described below. The thickness and dielectric constants of deposited films are characterized with variable angle spectroscopic ellipsometry.

The ITO and AZO films are deposited by radio frequency sputtering in a physical vapor deposition system. The ITO (AZO) is sputtered at room temperature from a single target with 90 % InO_2 / 10 % SnO_2 (98 % ZnO / 2 % Al_2O_3) composition. Post-deposition annealing is required to make the oxides electrically conductive. For ITO (AZO), annealing occurs in forming gas at 425 °C (450 °C) for 3 minutes (30 minutes) using a rapid thermal annealing process. The thickness of the ITO and AZO films ranges from 65-80 nm.

Aluminum oxide (Al_2O_3) is deposited with atomic layer deposition (ALD) from water and trimethylaluminum (TMA) precursors. The Al_2O_3 films are thermally deposited at 200 °C for 500 cycles with a deposition rate of $\sim 0.8\text{-}1.0$ Å/cycle, resulting in a final film thickness of $\sim 40\text{-}50$ nm.

Capacitor Fabrication Process

Chapter 6 of this thesis investigates the effect of electric fields on the band gap of two-dimensional MoS_2 films. In particular, the photoluminescence spectra of few-layer MoS_2

are measured over a range of applied electric fields. Parallel plate capacitor structures are used to apply the electric fields. These capacitors consist of few-layer MoS₂ sandwiched by dielectric layers, which are then sandwiched by transparent electrical contact layers with a final structure of Pt/Ti/Al₂O₃/MoS₂/Al₂O₃/ITO/SiO₂/Si. Gold contact pads are used to contact the Ti/Pt and ITO.

The capacitor fabrication begins with an Al₂O₃/ITO/SiO₂/Si substrate, whose fabrication process was described in the previous section. Few-layer MoS₂ films are exfoliated onto the substrate using the scotch tape method. The thickness of the MoS₂ films is initially characterized with optical microscopy, then verified with Raman and photoluminescence spectroscopies. After monolayer, bilayer, and trilayer MoS₂ areas are identified, the top capacitor layers are deposited. The top Al₂O₃ dielectric layer is deposited onto the MoS₂/Al₂O₃/ITO/SiO₂/Si stack using the same ALD process as the bottom Al₂O₃ layer.

Holes are etched into the Al₂O₃ layers to expose the bottom ITO layer for electrical contact. The holes are patterned using a photolithography process. Photoresist is patterned to expose some areas of Al₂O₃ while covering the rest of the sample. The areas of exposed Al₂O₃ are dry etched in a chlorine-based chemistry. The remaining photoresist is removed from the sample with acetone.

A second photolithography step is used to pattern the top contact layer. Photoresist is patterned with holes that will become the Ti/Pt top contact layer. The thin metal top contact layer is deposited onto the patterned sample with electron-beam evaporation. A titanium (Ti) adhesion layer 4-5 nm thick is deposited before 6-7 nm of

platinum (Pt). Liftoff (photoresist removal) is achieved by soaking the substrate in acetone, then rinsing with acetone and isopropyl alcohol.

A final photolithography process is used to pattern Ti/Au contact pads on the Ti/Pt and ITO layers. Photoresist is patterned with openings over the exposed Ti/Pt and ITO layers. The Ti/Au layer is deposited with electron-beam evaporation by depositing a Ti adhesion layer ~10 nm thick followed by ~100 nm of Au. The sample is soaked in acetone and rinsed with acetone and isopropyl alcohol to remove remaining photoresist.

Wirebonding is used to connect the Ti/Au pads to a chip carrier with gold wire. The chip carrier is placed into a breadboard circuit to apply an electric field across MoS₂ for electric field/photoluminescence measurements.

Photoluminescence Spectroscopy Measurement

Two different photoluminescence measurement setups were used to obtain the results in this thesis. One is a Renishaw inVia system at Carnegie Mellon University (CMU) and the other is a homemade setup at the Center for Integrated Nanotechnologies (CINT) at Sandia National Laboratory in Albuquerque, NM. Part of the experimental work in this thesis was performed at Carnegie Mellon University and part of it was performed at CINT.

The Renishaw inVia system at CMU uses a 532 nm laser excitation with maximum power of 50 mW. The laser power on the sample is kept low (<1 mW) in order to prevent damaging the transition-metal dichalcogenide films. The laser is focused on the sample using a 50x objective lens, which produces a spot of ~16.7 μm^2 . This same objective lens collects the photoluminescence emission from the sample in a normal

incidence, backscatter geometry. A filter removes the 532 nm reflected light. A 600 groove/mm grating diffracts the emission before it is collected by a charge coupled device (CCD). The photoluminescence spectrum is displayed in the Renishaw proprietary WiRE software. Photoluminescence resolution using the 600g/mm grating with the Renishaw system is ~ 0.3 meV.

The system at CINT involves similar specifications to the Renishaw system. A 532 nm continuous wave laser is incident on the sample through an objective lens. With this system, a 60x magnification objective lens is typically used. The laser power on the sample ranges from ~ 50 μ W-300 μ W; low enough to prevent damage to the transition-metal dichalcogenide films. Light emitted from the sample is collected through the same 60x objective lens and filtered to remove 532 nm reflections. The remaining emission is guided to an Acton 2400 spectrometer. For these measurements, a 600 groove/mm grating in the spectrometer is used. The resulting spectrum is displayed by Princeton Instruments WinSpec software. The spectral resolution of these measurements is ~ 0.2 meV, which is comparable to the resolution of measurements obtained with the Renishaw system. For photoluminescence measurements taken while applying an electric field across 2D MoS₂, a long working distance 50x objective lens was used instead of the 60x lens. More details of those measurements are provided in a later section in the Appendix.

Raman Spectroscopy Measurement

Raman spectroscopy measurements were collected using the same instruments at CMU and CINT as those used for photoluminescence spectroscopy, but with different data

acquisition parameters: a 2400 groove/mm grating is used instead of 600 groove/mm. The resolution of the Raman measurements at CMU (CINT) is $\sim 1 \text{ cm}^{-1}$ ($\sim 0.3 \text{ cm}^{-1}$).

Measurement Setup for Photoluminescence Spectroscopy with Applied Electric Field

Chapter 6 of this thesis explores the effect of an electric field applied perpendicular to the layers of monolayer, bilayer, and trilayer MoS₂ on the photoluminescence emission from the 2D material. The photoluminescence measurements presented in that Chapter were all taken using the photoluminescence spectroscopy setup at CINT. The photoluminescence specifications and acquisition parameters were the same as those outlined in the Photoluminescence Spectroscopy section of this Appendix except a long working distance 50x objective lens was used instead of the short working distance 60x objective lens. In order to fit the sample, chip carrier, and breadboard used to apply electric field underneath the objective lens, a long working distance lens is required. In addition, the laser power is kept below 200 μ W to prevent damaging the samples.

An electric field is applied to few-layer MoS₂ using a parallel plate capacitor structure. The fabrication of such a structure was discussed earlier in the Appendix. The capacitor structures are secured to a chip carrier using double-sided carbon tape or silver paint. Using gold wire, the Ti/Au contact pads on the device are wirebonded to the contact pads on the chip carrier. The chip carrier is then secured in a breadboard, which is attached to the photoluminescence spectroscopy setup microscope stage. The electric field is supplied by applying a voltage between the top and bottom contacts of the capacitor. This voltage is supplied through two leads (lo and hi) connected to a Keithley

2400 sourcemeter with a maximum voltage of 210 V. For these measurements, the lo lead was connected to the top Ti/Pt contact layer and the hi lead connected to the bottom ITO contact layers. The leads from the Keithley are connected to the Ti/Au contacts pads in the capacitor structure via the breadboard. Due to the transparent conducting layers, photoluminescence spectra of the few-layer MoS₂ can be measured while simultaneously applying electric fields.

Density Functional Theory Calculations

The *ab initio* band structure calculations presented in this thesis were obtained through density functional theory calculations as implemented in the open source software ABINIT^{87,88,125}. The projector augmented wave (PAW) method within ABINIT was used^{89,126}. For the band structure calculations, an energy cutoff of 30 Ha was used.