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Exploring the Novel Optical and Electrical Properties of Layered Transition Metal Chalcogenides

By Jian Zhou

A dissertation submitted in partial satisfaction of

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In Engineering - Material Science and Engineering

In the

Graduate Division

Of the

University of California, Berkeley

Committee in charge:

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Exploring the Novel Optical and Electrical Properties of Layered Transition Metal Chalcogenides

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By

Jian Zhou
Abstract

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By Jian Zhou

Doctor of Philosophy in Engineering - Material Science and Engineering

University of California, Berkeley

Professor Junqiao Wu, Chair

Layered Transition Metal Chalcogenides (LTMCs) exhibit a wealth of physical properties. Structurally, they are characterized by strong intra-layer bonding and weak inter-layer interactions. This strong structural anisotropy enables exfoliation into thin layers, sometimes even down to single unit cell thickness.

LTMCs have been studied for decades, but recent advances in nanoscale materials characterization and device fabrication have opened up new research opportunities. As the thickness of these materials go thinner and thinner, their properties may change significantly, which calls for re-exploring of their unique optical and electronic properties. During my PhD study, I have explored two categories of LTMCs: LTMC semiconductors and LTMC metals.

LTMC semiconductors such as MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$ have sizable bandgaps that change from indirect to direct in single layers, allowing applications such as transistors, photodetectors and electroluminescent devices. I have studied the optical properties of few layer WSe$_2$, and found a thermally induced direct-indirect band gap transition. The ultrathin body of these LTMC monolayer semiconductors also makes them sensitive to both the ambient and external electric field. By combining these two unique properties, I discovered a strategy for dynamically modulating the photoluminescence intensity of MoS$_2$ by orders of magnitude. The defect free, nanometer-thick LTMC layers are ideal tunneling media. Based on this, I proposed to use LTMC as the elastic tunneling medium to construct a non-impact nano-electro-mechanical switch, which shows 4 orders of magnitude modulation in the electrical resistance by applying a mechanical force.

LTMC materials span a wide range of categories. Some LTMC show semiconducting properties, while others are metallic, or even superconducting. Bi$_2$Te$_3$, a metallic LTMC, commonly known as a high performance thermoelectric material, also attracts renewed attention because it is found to be topological insulator. The conduction on its surface is
provided by topologically protected surface states, which has a massless Dirac like dispersion, with spin and momentum degree of freedom interlocked. It would be interesting to explore the possibility of engineering the geometry of these exotic conductive surfaces at nanoscale. During my PhD study, I introduced dense, nanosized antidot arrays into Bi$_2$Te$_3$ microflakes, and studied its magneto-transport properties. This modification completely altered the electrical properties of this material. I observed signature of Ahoronov-Bohm type oscillations in our device, indicating that charge carriers in topological insulators are indeed interacting with our antidot arrays, thus proved the possibility of creating new functionalities in this material via nano-structuring.
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List of Abbreviations

2D: Two-dimensional
AFM: Atomic force microscopy
CB: Conduction Band
CVD: Chemical Vapor Deposition
DFT: Density functional theory
DVT: Direct vapor transport
FET: Field effect transistor
LTMC: Layered transition metal chalcogenide
MR: Magneto-resistance
MIT: Metal-Insulator-Transition
MBE: Molecular beam epitaxy
NEM: Nano-Electro-Mechanical
PL: Photoluminescence
PMMA: polymethyl methacrylate
SEM: Scanning electron microscopy
TMC: Transition metal chalcogenide
TI: Topological insulator
VB: Valence band
Acknowledgements

In August 2009, I came to the University of California, Berkeley and joined Prof. Wu’s group at Material Science and Engineering department. During the last five years, I have had the pleasure to work in Wu group. This work leads to my PhD dissertation, which is presented here.

PhD study is challenging, sometimes stressful, and sometimes fun. Now, when I am graduating, I am proud that I am well trained in material science, and got three first author papers published. These would not happen without the support and help from my supervisor Prof. Wu. I am especially grateful to him for his guidance, never-ending enthusiasm, and inspiring discussions. I still clearly remember that when I started to work on the project alone, he came to my lab very often to discuss with me the problems and give me suggestions and help. I feel lucky and honored to be a student of his.

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Chapter 1. Introduction

1.1 Introduction to Layered Transition Metal Chalcoginide (LTMC)

At the broadest definition, a chalcogenide is a chemical compound consisting of at least one chalcogen anion and at least one more electropositive element. In practice, the term “chalcogenide” is commonly used for sulfides, selenides, and tellurides. Transition metal chalcogenides occur with many stoichiometries and many structures, and exhibit a wealth of physical and chemical properties, such as charge density waves [1] and superconductivities[2]. During recent years, there is renewed interest in the study of transition metal chalcogenides, especially those with layered structures, such as MoS\(_2\), WS\(_2\), MoSe\(_2\), WSe\(_2\), ReS\(_2\), Bi\(_2\)Te\(_3\), FeTe and etc.[3]-[11], largely inspired by the pioneering research in graphene, topological insulators and iron-based superconductors. These advances encourage researchers to re-examine the previously neglected exotic properties in these decades-old materials.
Fig.1.1 The periodic table of elements. “Chalcogenide” is commonly used for sulfides, selenides, and tellurides. The great variety of transition metal cations give the TMC materials wide range of physical properties.

One structural similarity among these transition metal chalcogenides is that they are often characterized by strong intra-layer bonding and weak inter-layer interactions. This strong structure anisotropy enables exfoliation of thin layers, sometimes even down to single unit cell thickness. Such a property enables new research opportunity for re-studying these materials in two-dimensional or quasi two-dimensional limit, in which new physical properties may emerge as the result of reduced dimensionality. One great example for this re-studying is the famous MoS2, which is a traditional lubricant material, now catches significant research attention across multi-disciplines.

Fig.1.2 The photograph of bulk MoS2 crystal. It is silver shining crystal, with layered structures.

Molybdite, with the chemical formula of MoS2, is a great example of this re-study. Due to its weak interlayer coupling, MoS2 has been used as a popular lubricant for decades. There are also few studies using bulk MoS2 as the electrode materials in the low-cost batteries [12]. However, in 2005, Novoselov et.al shows that, like graphane, MoS2 could be exfoliated into nano-sheet with single unit cell thickness[13]. Graphene received immediate attention due to its exotic electronic properties and promising application in next generation electronics. Later, people soon realized that graphene lacks a bandgap, making the graphene based filed effect transistors could be been effectively turned off. Much effort was devoted to open up a bandgap in graphene[14]-[16], but no sizeable bandgap has been reported so far. Due to this reason, MoS2 gradually catches researchers’ attention due to its sizeable bandgap and semiconducting properties. In 2011, A.Kis et.al reported Field Effect Transistor (FET) devices based on monolayer thick n-type MoS2, and achieved mobility as high as 200 cm²V⁻¹s⁻¹, with an on/off ratio of 10⁶ [17]. Soon
after that, Fang.et.al reported p-type FET with hole mobility \(~250 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}\), and an on/off ratio\(>10^6\). [18]

These pioneering work inspired the researchers to systematically study the synthesis and other exotic properties of LTMC semiconductors, as MoS\(_2\), MoSe\(_2\), WS\(_2\) and WSe\(_2\).

![Fig. 1.3 Structure of MoS\(_2\)](image)

The yellow spheres represent sulfur atoms, and the purple ones are Mo atoms. The interactions between three-atom layers are weak Van der Waals type.

![Fig 1.4 MoS\(_2\) crystals exfoliated onto 285nm thick SiO\(_2\) substrate](image)

The monolayers are visible because of the careful choice of the thickness of SiO\(_2\).

### 1.2 Layered Transition Metal Chalcogenide Semiconductors

Traditional semiconductors, like Si and GaAs can be grown as thin as few monolayer thick with advanced deposition technique such as Molecular Beam Epitaxy (MBE). However, due to the large number of dangling bonds, these ultrathin semiconductors are inherently vulnerable to oxidization. The mobility drops significantly after their thicknesses are thinner than 5nm. In sharp contrast, the surface of TMCs are typically inert and free of dangling bonds, making them stable even in monolayer thickness. High charge carrier mobility up to \(250 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}\) even in monolayer limit has be reported. [17][18]. Such properties are beneficial for fabricating transistors with ultimate body thickness (i.e. one molecule thickness), or ultrathin sensors, which could work in ambient condition. [19].

With the continuous scaling down the transistor size driven by Moore’s Law, fundamental limits of the field effect transistor have resulted in a power density crisis for integrated circuit chips.
Researchers are actively developing new materials, structures and device architectures for future ultra-short channel length field-effect transistors (FETs). However, at extreme down-scaling, the short channel effects come into play, and deteriorate the on/off ratio of transistors. One strategy for solving such a problem is to use ultrathin body channel to ensure effective electrostatic control from the gate. In this regard, graphene was proposed as the excellent channel material for ultrathin body transistors. It has room temperature mobility as high as 20,000 cm²V⁻¹S⁻¹,[20] combining a channel thickness of only 0.3 nm. Unfortunately, since graphene does not have a banggap, graphene-based FET cannot be effectively turned off, meaning large leakage current in the off state, which is unacceptable for digital circuits. A small bandgap (~150 meV) can be open in graphene nanoribbons [15], but it is still way to small for practical application.

On the other hand, some of the layered Transition Metal Chalcogenides (TMCs) semiconductors possess a sizeable bandgap of 1-2 eV, which is ideal for FET application. Like graphene, the weak interlayer coupling of these layered TMC semiconductors hints the possibility of using them as near-atomic thin channel materials. A.Kis et.al reported FET devices based on monolayer thick n-type MoS₂, and achieved mobility as high as 200 cm²V⁻¹S⁻¹, with an on/off ratio of 10⁶[17]. Soon after that, Fang.et.al reported p-type FET with hole mobility ~250 cm²V⁻¹S⁻¹, and an on/off ratio> 10⁶[18]. These pioneering work inspired the researcher to systematically study the synthesis and other exotic properties of ultrathin semiconductors.

For next generation electronics, flexibility and transparency are desirable characteristics. The sub-nanometer thickness of monolayer thick TMC semiconductors offers them superior mechanical flexibility over bulk counterparts. Researchers has demonstrated that single-layer MoS₂ show that it is 30 times stronger than steel and can sustain 11% of tensile strain [21], making it one of the strongest semiconducting materials. Thin TMC semiconductors can also be readily transferred onto flexible substrate, making them even more resilient against mechanical deformation. The sizable bandgap and extreme thinness also make monolayer TMC semiconductor almost transparent. Such properties may be useful for fabricating transparent electronic circuits for future consumer electronic products.

1.2.1 Synthesis of ultrathin LTMC semiconductors

Ultrathin LTMC semiconductors can be prepared thorough various ways, including chemical exfoliation, mechanical exfoliation and chemical vapor deposition (CVD). Here, I would like to briefly introduce these three methods.

(a) Synthesis of ultrathin semiconductors through chemical exfoliation

Layered semiconductors such as MoS₂ are stacked with weak Van der Waals force. Small ions such as Lithium can diffuse into the layers, expanding the interlayer distance, and resulting exfoliation of bulk crystals into few/monolayers[22]-[27]. The reaction products are typically a suspension of thin flakes. Chemical exfoliation has the advantage of low-cost and high yield. However, it has several drawbacks. First, the exfoliation involves flammable chemicals such as
butyl-lithium, which imposes serious safety requirement during the handling. Second, the Lithium ions react with LTMCs, and often significantly change the chemical/physical properties of LTMC. For example, the MoS$_2$ change from 2H structure into 1T structure after the chemical exfoliation method. [28]

**Fig 1.5 Schematics of chemical exfoliation of LTMC.**

**(b) Synthesis of ultrathin semiconductors through mechanical exfoliation**

Largely inspired by the pioneering work of Geim et.al on graphene [13], mechanical exfoliation method turns out to be a popular way for preparing high quality ultra-thin LTMCs, especially for research purposes.

In Wu group, we started exfoliating TMC semiconductors around May 2011. In the first month, the exfoliation was not very successful. Often, we got flakes with thickness of 20-100nm, with shining metallic color. Mechanical exfoliation is conceptually simple, but practically tricky. Here I want to summarize some to the tricks to improve the yield for preparing large area, clean monolayer TMCs.

1. **Use fresh crystals.** We noticed that, after a few repetitive peeling off, the average size of the TMC flake left on the Si substrate significantly reduced. In order to get large area monolayer TMC, we recommend use the freshly cleaved crystal and press it against the SiO$_2$ substrate.

2. **Apply moderate pressure to the tape/flakes.** If the crystal is gently laid onto the Si O$_2$ surface, the monolayers/ few layers do not stick. However, applying excessive pressure usually leaves large amount of glue residuals on the SiO$_2$ substrates, as well as around the
TMC thin layers. This contamination from glue is undesirable if the TMC thin layers need to go through subsequent device fabrication process.

(3) Surface treatment of SiO$_2$ substrate is critical for enhancing the yield of preparing TMC mono/ few layers. The successful preparation of TMC monolayers relies on the difference between TMC- SiO$_2$ adhesive energy and their interlayer coupling energy. Typically, the as-purchased SiO$_2$ substrate’s surface is partially passivated by ambient moisture and organic species, resulting in lower adhesive energy. I recommend performing an O$_2$ plasma cleaning of SiO$_2$ surface prior to the exfoliation. I also noticed that, F$_2$ plasma etched SiO$_2$ surface is rather inert, and non-sticky to TMC.

![Fig 1.6 MoS$_2$ crystals exfoliated onto 90nm thick SiO$_2$ substrate.](image)

The monolayers are typically found along with thicker layers.
Fig 1.7 Optical image of WS₂ crystals exfoliated onto 90nm thick SiO₂ substrate. The monolayers are visible because of the careful choice of the thickness of SiO₂.

Fig 1.8 Optical image of a piece of extremely large monolayer MoS₂ exfoliated onto 90nm SiO₂/ Si substrate.

Fig 1.9 Electrical characteristics of a field effect transistor (FET) based on monolayer thick MoS₂. The device shows n-tye FET behavior, and turns on at
certain threshold gate voltage. The source drain voltage is set at 100mV. Inset: the optical image of monolayer MoS$_2$ FET.

Fig1.10 Atomic Force Microscopy (AFM) image of few/mono layer thick WSe$_2$. The number of layers can be calculated by dividing the flake thickness by 0.7nm, which is the thickness of monolayer.

Fig1.11 Scanning electron Microscope (SEM) image of monolayer thick MoSe$_2$ exfoliated onto SiO$_2$ substrate. The monolayers still show a contrast; largely because of it is less conductive than the bulk. Reprinted with permission from Ref [30], Copyright 2013, American Chemical Society

(3) Synthesis of LTMC semiconductors through chemical vapor deposition

Synthesizing large area and uniform layers of ultrathin semiconductors are critical step towards their wide applications as electronic devices and flexible, transparent optoelectronics. It has been shown, in the case of graphene, wafer scale monolayer samples can be grown on Cu foil via
Chemical Vapor Deposition (CVD) method [31]. Due to its complex chemical composition, CVD growth of monolayer TMCs is still in its nascent stage.

Few CVD methods for growing atomically thin TMCs are reported[32]-[35]. MoS₂ is the most explored TMC material so far. Several strategies have been developed for growing Monolayer MoS₂. These methods use different solid precursors heated to high temperature, and the reaction products were deposited onto oxides surfaces (SiO₂, or sapphire, cleaved mica, etc.). These CVD growth method results in film thickness dependent on the concentration of precursors and growth temperature. Reliable growth of chip scale, single layer thickness MoS₂ has not been demonstrated so far.

In Wu group, we started CVD growth of MoS₂ and WS₂ in 2012. The synthesis methodology is adapted from the pioneering work by Liu et.al [32]. We use Ar as the carrier gas, passing the heated sulfur powder source. A small quartz boat, with 1-2mg of MoO₃ power was placed in the center of the furnace, where is temperature is around 600-700 °C. The MoO₃ partially loses its oxygen, and become volatile MoOₓ. The MoOₓ reacts with sulfur vapor, get sulfurized and deposited on the down-facing SiO₂ substrate.

**Fig1.12  Schematic showing the CVD growing monolayer thick MoS₂/ WS₂ on SiO₂ substrate.**
Fig 1.13 The experimental setup for growing monolayer thick MoS$_2$/ WS$_2$ with CVD method.

Fig 1.14 The AFM image of an unsuccessful growth. The MoS$_2$ forms droplet-like plates, with the average size of 200nm in diameter.

At the early stage of our expletory experiments, we always grow granular MoS$_2$ thin films rather than desired MoS$_2$ single crystal monolayers (as shown in Fig. 1.13). After many trial & error, we were able to grow high quality MoS$_2$/WS$_2$ single crystal monolayers, with grain size reaching 30 micro meters. Here are the key points for the growth conditions:
(1) The SiO2 substrate needs to be thoroughly cleaned with H₂SO₄ and Piranha before introduced into the growth tube. We also noticed coating the SiO₂ substrate with a thin layer of PITAS increases the monolayer size, presumably due to the organics act as catalytic size to facilitate the growth. [32]

(2) The TMC monolayers’ morphology strongly depends on the pressure of the pressure of the carrying gas. According to our experience, the higher the pressure, the larger the grain size.

![Image of a successful CVD growth of monolayer MoS₂](image)

**Fig 1.15 The optical image of a successful CVD growth of monolayer MoS₂.** The MoS₂ shows six-fold symmetry, consistent with its honeycomb in-plane lattice.
1.3 Introduction to metallic layered transition metal chalcogenide

LTMC semiconductors are promising candidates for next generation electronics. However, the LMTC materials show great abundance of variety in their physical properties. Some other LTMC, which might be metallic, also merits our re-exploring, with similar reason as what we have in LTMC semiconductors. Up to now, we didn’t see as much literature report on studying the metallic LTMC as on semiconducting LTMC, presumably due to the expensive measurements required for exploring the metallic LTMC materials. Exotic transport properties may exist in metallic LTMC, ranging from charge density waves [2], superconductivity[3], and topological surface states conduction[36]. Unfortunately, all these phenomena typically require low temperature, high magnetic field measurement tools, such as Physical Property Measurement System (PPMS), which is a liquid helium cooled, precision system. The prohibitive initial cost (~300K USD), and maintenance cost (15K USD/ month) limited the research effort to a handful well-funded laboratories.

Besides my main research effort in studying the physical properties of ultrathin LTMC semiconductors, I also devoted some of my time into the study of metallic LTMC materials. I am particularly interested in materials that could be exfoliated into extreme thin layers—ideally, monolayer if possible. I have explored a few LTMC metals, including topological insulator Bi$_2$Te$_3$ and iron-based superconductor FeTe$_{0.5}$Se$_{0.5}$. 

Fig 1.16 The AFM image of CVD grown of monolayer MoS$_2$. Nanoparticles are typically observed on these flakes. And the grain boundary is broken in this image.
Bi$_2$Te$_3$, another LTMC, commonly known as a high performance bulk thermoelectric material, also attracted renewed attention in recent years. Bi$_2$Te$_3$ is theoretically predicted and experimentally confirmed as topological insulator. Topological insulators (TIs), which has a semiconducting bulk and gapless surface, are of great importance for their promising application in next generation nanoelectronics[37]. The layered structure of Bi$_2$Te$_3$ enables this material to be exfoliated into extreme thin flakes, in which the conduction on the topological surface states might dominate the transport process. This opens up new research opportunities for studying its exotic transport properties.

Fig. 1.18 shows a Bi$_2$Te$_3$ crystal that is exfoliated onto SiO$_2$ substrate. Unlike MoS$_2$ and similar semiconducting LTMC, Bi$_2$Te$_3$ is hard to be exfoliated into layers less than 10nm. The brittleness of the crystal makes them easily fragment into small pieces when they are thin (as shown in Fig 1.17).

However, occasionally, we do observe thin Bi$_2$Te$_3$ flakes ~20-50nm thick, as shown in Fig 1.20 and Fig. 1.21. This thickness is not ideal if we want to observe two-dimensional transport properties, which may require <3nm thick crystals. But these 20~50nm quasi-two dimensional crystals do provide us a unique opportunity for novel device fabrication. For example, as I would show later in Chapter 6, we are able to drill dense array of nano-sized holes on these flakes, and study the novel quantum interference phenomenon in it. All these device geometry will not be possible with bulk crystals.

![Fig. 1.17 Optical image for Bi$_2$Te$_3$ crystal exfoliated onto SiO$_2$ substrate. The blue parts are thin flakes< 30nm.](image)
Fig. 1.18 The SEM image of a Bi$_2$Te$_3$ crystal exfoliated onto SiO$_2$ substrate. We clearly see the brittle crystal breaks along their high-symmetry directions.

Fig. 1.19 AFM image of Bi$_2$Te$_3$ thin flakes exfoliated onto SiO$_2$ substrate. The surface of the crystal is atomically smooth, with roughness< 0.5nm. We see a small part of this sample is ~20nm thick.
Fig. 1.20 The SEM image of a thin Bi$_2$Te$_3$ ribbon exfoliated onto SiO$_2$ substrate. Occasionally, we got ribbon like Bi$_2$Te$_3$ flakes, with the thickness around 50nm.

FeTe$_{0.5}$Se$_{0.5}$ is another metallic LTMC I have studied. This material is the archetypical material of the important iron-based superconductors. Up to now, most study is on its bulk form. Fabricating this material into two-dimensional thin layers or one dimensional nanowires are challenging, because of the volatility of the Te and Se content. Interestingly, I found that this material could be exfoliated into two-dimensional thin layers (~10nm thick). It would be interesting to investigate how the superconductivity change at such reduced dimensions.

Fig. 1.22 shows optical image of a thin FeTe$_{0.5}$Se$_{0.5}$ exfoliated onto SiO$_2$ substrate. The blue-purple color indicates extreme thinness. The thinnest part of this sample is only 5nm thick. Interestingly, we sometimes found FeTe$_{0.5}$Se$_{0.5}$ nanowire with the scotch-tape method. These wires can be as long as 50 microns, with cross section as small as 10nmX200nm. I fabricated four probe devices on these thin crystals, and tried to explore the possible new transport behavior of superconductivity at such samples.

As shown in Fig. 1.23, for a micro-sized flake, we still observe bulk-like behavior. The Tc does not change compared with bulk crystal, around 13.5K. However, for thinner nanowires, its R Vs T shows completely different trend. This drastic change is unlikely be caused by reduced dimension, since the coherence length in this material is ~2nm, which is too short to perceive the dimensional reduce in our 10nmX200nm cross-section wire. I suspect the wire has been oxidized, and its chemical composition has been completely changed. Future study in which the whole process being carried out in inert gas environment may elucidate the real origin of such a change, but it is out of the scope of this thesis.
Fig. 1.21 The optical image of a thin FeTe$_{0.5}$Se$_{0.5}$ exfoliated onto SiO$_2$ substrate. The blue-purple color indicates extreme thinness. The thinnest part of this sample is only 5nm thick.

Fig. 1.22 The optical image of a thin FeTe$_{0.5}$Se$_{0.5}$ nanowire exfoliated onto SiO$_2$ substrate. The length of nanowire is around 15 microns, while the cross section is 10nmX200nm. Inset: AFM image of the portion in white rectangle.
Fig 1.23 The four-probe resistance of a FeTe$_{0.5}$Se$_{0.5}$ microflake. The flake is 20nm in thickness, and 10 µmX20µm in area. Similar to bulk crystal, this 20nm thick flake still show a sharp superconducting transition around 15K.
Fig 1.24 The four-probe resistance of a FeTe$_{0.5}$Se$_{0.5}$ nanowire. The cross-section of this nanowire is 10nmX 200nm. The R vs T shows a completely semiconducting behavior, presumably due to the nanowire has been oxidized in air, and changed its chemical composition.

1.4 Organization of dissertation

This dissertation will focus on the study of novel optical and transport properties of LTMCs, especially those properties arising from reduced dimensionality. There are six chapters in total, which are organized in the following manner.

In the first chapter, I have introduced the general background of layered TMC materials, the method for material preparation and characterization. My study for layered TMC materials can be divided into two category, TMC semiconductors and TMC metals.

In Chapter 2, I will explore the direct-indirect bandgap transition in LTMC semiconductors. Often, the LTMC semiconductors show indirect-direct bandgap transition around their monolayer limit. Interestingly, in MoSe$_2$, its direct-indirect bandgap are almost degenerate in few-layer limit, and a thermally induced crossover is observed. In this chapter, I will present my study on this novel phenomenon. Also, I will describe the experimental methodology for preparing and characterizing ultrathin semiconductors, such as Raman spectroscopy and photoluminescence technique.
In Chapter 3, I will explore deeper into the photoluminescence of layered TMC semiconductors. The large surface area of 2D TMC semiconductors make them sensitive to the ambient and substrates. We will study the gas absorption and interaction with layered TMC semiconductors and the effect on their photoluminescence properties. By understanding these effects, we were able to modulate the photoluminescence of LTMC semiconductors by orders of magnitude, through either thermal annealing or electrical gating.

In Chapter 4, I will explore the idea of using monolayer TMC material as the elastic insulating barrier to realize the non-impact tunneling nano-electro-mechanical (t-NEM) switches. As I would present in this chapter, by applying a pressure to monolayer MoS$_2$, its vertical tunneling resistance could be modulated by 4 orders of magnitude. At the end of this chapter, I will also describe a device schematic that is more practical for real device application.

In Chapter 5, I will present my study on non-semiconducting layered TMC materials. Bi$_2$Te$_3$ is the material I choose, not only because of its layered structure, but also for its exotic electric transport properties. Bi$_2$Te$_3$ is a prototypical topological insulator, i.e. the conduction on the surface is provided by topologically protected surface states, which has a massless Dirac like dispersion, with spin and momentum degree of freedom interlocked. The layered nature of Bi$_2$Te$_3$ allows me to exfoliate them into high quality thin flakes. By creating a dense nanoscale antidote array, I can successfully modify the transport properties of Bi$_2$Te$_3$. Periodic magneto resistance oscillations are observed, and correlated with the structure we introduced.

Finally in Chapter 6, I will summarize all the contents of the dissertation and present my outlook for the research field of layered transition metal chalcogenide materials.
Chapter 2 Thermally driven direct-indirect bandgap transition in ultrathin LTMC semiconductors

2.1 Direct-indirect bandgap transition in ultrathin LTMC semiconductors

Layered semiconductors based on transition metal chalcogenides usually cross form indirect bandgap in the bulk limit over to direct bandgap in the quantum limit [37]. Such a crossover can be achieved by peeling off a multi-layer sample to a single layer. Upon the crossover, the photoluminescence of ultrathin semiconductors is much enhanced, due to the activation of the radiative recombination channels[37].

Let us first take a look at the electronic band structure of layered TMC semiconductors. Many LTMC have band structures that a similar in their general features. In general, MoX₂ and WX₂ (X=S, Se, Te) compounds are semiconducting and share similar crystal structures. These materials form layered structures of the form X-M-X, which the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms. A schematic in Fig 5.1 shows the their band structure in the bulk form. At the Γ-point, the bandgap transition in indirect for the bulk material, but gradually shifts to the direct for the monolayer. The direct excitonic transitions at the K-point remain relative unchanged with layer number.

![Fig. 2.1 Simplified band structure of MX₂ in bulk form. The Eg is the indirect gap.](image)

- Fig. 2.1 Simplified band structure of MX₂ in bulk form. The Eg is the indirect gap.
Fig. 2.2 Simplified band structure of MX$_2$ in monolayer form. Due to the quantum confinement, the band-states near the Γ-point raised, increasing the value for the indirect gap. At monolayer limit, the indirect gap becomes larger than the direct one, so now this material becomes direct band gap.

The change in the band structures with layer numbers of MX$_2$ is largely due to quantum confinement in Z direction. For MX$_2$, density functional theory (DFT) calculations show that the conduction band-states at the K-point are mainly due to d orbitals on the transition metal atoms. Since structurally, these transition metal atoms are located in the middle, their localized d orbitals are relatively insensitive to the interlayer coupling. On the other hand, the states near the Γ-point are due to hybridization of the antibonding Pz–orbitals on the chalcogen atoms and the d orbitals on the transition metal atoms, and has a strong interlayer coupling effect. As we thinning down these MX$_2$ semiconductors to few layers, such effect become pronounced, i.e. the excitonic transition at the Γ-point shift from an indirect one to a direct one. All MX$_2$ compounds are expected to undergo a similar indirect to direct bandgap transition with decreasing layer numbers. This trend can be summarized as “the thinner, the brighter”. There are occasions where this rule of thumb breaks. For example, in the case of ReS$_2$, in which the interlayer coupling is already very weak in the bulk limit, is always a direct bandgap materials.
2.2 Thermally driven direct-indirect bandgap transition in MoSe₂

For direct bandgap semiconductors, the lower the temperature, the higher the photoluminescence efficiency. This rule is opposite for indirect bandgap semiconductors. The recombination of exited charge carriers in indirect bandgap semiconductor needs the assistance of phonons, thus the higher the temperature, the stronger the photoluminescence. Typically, a semiconductor is either direct bandgap or indirect bandgap, and their electronic band structure is hard to be changed with mild external stimuli. Layered semiconductors, such as MoS₂ and MoSe₂, as shown above, can change the type of their bandgap by varying their thickness. They change from indirect bandgap in bulk to direct bandgap in the single layer limit. However, this thinning down process is not reversible, i.e. we cannot convert MoS₂ or MoSe₂ back to indirect bandgap once they are already thinned down. For future device applications, it is much desired to reversibly modulate such direct-indirect bandgap transition in a reversible way.

We noticed that, by increasing the temperature, the interlayer distance of layered materials are expected to expand. The interlayer coupling would decrease accordingly. As we discussed in the previous chapter, as the interlayer coupling decreased, we expect the few layer TMC semiconductors be pushed towards their monolayer limit. i.e. a thermally driven in-direct to direct bandgap transition might be possible in few layer TMC semiconductors. In this chapter, we explore this idea with two commonly seen layered TMC semiconductors, MoS₂ and MoSe₂.
2.3 Basic properties of MoSe$_2$: from bulk to monolayers.

MoSe$_2$ is an indirect bandgap semiconductor with a 1.1eV band gap value, and therefore the bandgap PL is expected to be rather weak [38]. However, the few-layer MoSe2 flakes show gradual enhancement in PL intensity around 1.5-1.6 eV and the PL intensity reaches its maximum value for a single-layer MoSe2 as shown in Fig. 2.3. Similar to this observation, enhancement in PL for single-layer MoS$_2$ have been also observed, and attributed to an indirect to direct bandgap crossover associated with the quantum confinement in the perpendicular direction[37]. The weak PL in few layer MoSe$_2$ is somewhat intriguing, and merits further discussion.

The DFT calculation shows that two and three layer MoSe$_2$ have an indirect bandgap but with almost degenerate direct and indirect bandgap values. In such case, hot carriers are expected to transiently occupy the available states around the K symmetry point and result in hot PL although with weaker intensity compared to the single layer case. This hot PL model was invoked and justified by Mak et.al. [39] to explain the weak PL in few-layer MoS$_2$. The hot PL effect is expected to be stronger in MoSe$_2$ due to the closer values of direct and indirect bandgaps.

2.4 Raman spectroscopy for MoSe$_2$ and MoS$_2$: thickness dependence

Raman spectroscopy is a powerful tool for materials characterization. The basic working principle for Raman spectroscopy involves an incident photon, which interacts with the lattice vibration (phonon). This interaction would induce a small frequency change in the outgoing photon. By recording the difference in wave number between the incident and outgoing photon, the so-called Raman Shift, we can get information about the bonding and constituents in the solid. Typically, each solid has their distinct Raman spectrum. In our case, we are particularly interested in the Raman modes in layered TMC materials.

In Fig 2.4, I show the schematic the characteristic Raman modes for MX$_2$ materials—the so called E$_{2g}$ and A$_{1g}$ modes. E$_{2g}$ modes are closely related to the in-plane vibration, while A$_{1g}$ is the fingerprint for out of plane vibration. Interestingly, most layered TMC materials show thickness dependent Raman spectrum, which is readily explained by the thickness dependent interlayer coupling in these materials.
Fig. 2.4 The characteristic Raman modes in layered TMC materials, $E_{2g}$ and $A_{1g}$. $E_{2g}$ modes are closely related to the in-plane vibration, while $A_{1g}$ is the fingerprint for out of plane vibration.

Fig. 2.5 Raman spectroscopy of MoS$_2$ and MoSe$_2$: from bulk to monolayer. Reprinted with permission from Ref [30], Copyright 2012, American Chemical Society
Fig. 2.5 show the Raman spectrum for few/ single layer MoS2 and MoSe2. As a general rule, when the thickness of layered TMC decreases, the interlayer coupling also reduces. As a result, we always observe the softening of the A1g mode in few to monolayer TMCs. Interestingly, accompanying this softening of A1g, E2g modes always get stiffened. Since interlayer coupling is absent in the single layer limit, the out-of-plane A1g mode is expected to soften as a result of reduction of the restoring forces arising from the absence of interlayer coupling. However this model does not account for the stiffening of the in-plane E2g mode.

More interestingly, the intensity ratio between the A1g and E2g modes changes from 4.9 for few-layer (~10 layers) to 23.1 for the single-layer MoSe2, while the ratio remains nearly a constant (~1.2) in the MoS2 case. This thickness dependence of Raman spectrum turns out to be a powerful tool for identifying the number of layers of thin TMC materials, analogous to graphene Raman spectroscopy.

2.5 Temperature dependence of photoluminescence for semiconductors

The temperature dependence of the photoluminescence of semiconducting materials reveals important information regarding their band structure. For bulk semiconductors, their temperature dependent PL behaviors have been systematically investigated, and a wealth of literature can be found. However, since the layered TMC semiconductors have not been exfoliated into high quality mono/few layers prior to 2005, research in their photoluminescence is still in nascent stage. The photoluminescence of few/momolayer MoS2 was first studied by T. Heinz group in Columbia University [37]. The observed that the single layer MoS2 is much more luminescent than its bulk form, mainly due to the direct-in direct bandgap transition we discussed in the previous chapter. This one monolayer thick (0.7 nm), luminescent MoS2 is the thinnest light emitting material reported so far. Their results open up the possibility for utilizing layered TMC semiconductors as the ultrathin light emitting components in future optoelectronic devices. Since then, a huge international research effort was devoted into searching efficient light emitting monolayer TMC materials. WS2, with similar direct-indirect bandgap transition was soon reported [41]. Our group is the first one who successfully prepared monolayer thick, high quality MoSe2 materials, and systematically studied its photoluminescence properties. Interestingly, I found that in the few layer MoSe2, a thermally induced indirect-direct bandgap transition exists, and gives this material very interesting temperature PL dependence. Unlike MoS2, the few layer MoSe2 shows increase in PL at higher temperature. In the following parts of this chapter, I will discuss our investigation on this material in detail.

2.6 Sample preparation for high quality MoSe2 few layer/ monolayer.

Even though mechanical exfoliation technique is widely used to transfer single layer graphene from graphite onto Si/SiO2, exfoliating other layered materials is not trivial. The difficulty to
obtain single layers of other layered materials comes from the fact that (i) while the interlayer coupling is at most 100meV in graphene, this value is around 150-220 meV depending on the choice of material, making the exfoliation more difficult comparing to graphene, (ii) currently laboratory grown highly oriented pyrolitic graphite (HOPG) is widely studied, available, and possesses large grain sizes. On the contrary, other layered materials are rather rare in nature, and are typically disordered, preventing us to exfoliate large area single-layers. During my study, I noticed that it is much harder to get large size, monolayer MoSe\textsubscript{2} than MoS\textsubscript{2}, presumably due to even higher interlayer coupling strength in MoSe\textsubscript{2}. Despite such difficulties, various techniques can be used to improve the single-layer yield after exfoliation.

In this study, I use the following techniques to improve the yield:

(1) Freshly cleaved surfaces increase the single-layer yield: I believe that this is related to the larger number of (slightly) decoupled layers soon after fresh exfoliation. Once the surface is pressed onto Si/SiO\textsubscript{2} surface and cleaved, the single-layers couple back to the MoX\textsubscript{2} bulk crystals. Once the cleaved surface is pressed onto the substrate, we cleave the surface again before the next exfoliation.

(2) Choice of tape: We observe that using 3193MS (single-sided), 120°C release temperature, 7.2N/mm from Nitto Denko Inc. yields larger area and glue-free single-layer materials. However, the yield rate is typically low (1 out of 3 samples). Use of 3M magic tape brand single sided tape give higher yields but the flakes are typically 1-3 microns and mostly contain glue (either at the edge, under the flake, or near the flake).

(3) Cleavage speed: After pressing the tape softly on the substrate, we try to cleave the tape slowly. We notice that this typically improves the flake size. On the contrary, fast cleavage yields smaller flakes.

(4) Applied pressure during the transfer: Applying high pressure to the tape on the substrate typically leaves glue-residues around the flake. However, if no pressure is applied, slightly decoupled single-layers (on the freshly cleaved surface) do not adhere to the substrate which reduces the transfer rate.

(5) Quality of the starting material: We believe that the above techniques can be applied to MoSe\textsubscript{2} (or any other layered material) powder with big grain sizes. However, in this study the MoSe\textsubscript{2} (or any MX\textsubscript{2}) crystals were grown by the well established direct vapor transport technique (DVT) using Br\textsubscript{2} as a transport agent.

(6) Substrate surface quality: We find that any residue on the Si/SiO\textsubscript{2} surface reduces the yield rate mainly due to the lack of enough coupling between the substrate and the flake. Cleaning the SiO\textsubscript{2} surfaces using piranha solution for a minute improves the yield rate.
2.7 Experimental Setup.

Since the typical size of MoSe\(_2\) few/mono layers are less than 10 microns, conventional methods for probing the photoluminescence/ Raman spectrum are not suitable due to the lack of enough spatial resolution. We modified our Renishaw Micro Raman/PL system. This system operates in confocal mode, and the exciting/probing laser spot can be tuned to be as small as 1 micron\(^2\). We also mounted our sample on a heat/cooling stage, which could cover the temperature range from 77K to 500K. The sample is sealed in a vacuum chamber, which is pumped continuously with a small turbo-molecule pump. The base pressure in the chamber is below 10\(^{-6}\) Torr.

![Schematics of the experimental setup for measuring the PL/Raman temperature dependence of MoS\(_2\) and MoSe\(_2\).]

2.8 Different temperature dependence of photoluminescence, MoSe\(_2\) Vs MoS\(_2\)

Now, let us turn our attention to the temperature dependence of PL measured on single- and few-layer samples of MoSe\(_2\) and MoS\(_2\) (As shown below). Such measurements not only yield the bandgap dependence on temperature but also allow us to understand the physical mechanism that governs the light emission process. Before discussing the effect of temperature on the bandgap
(Eg), we focus on the change in PL intensity as a function of temperature. As seen in Figure 2.7, the temperature dependence of PL intensity of the single-layer and few-layer MoSe₂ show striking differences. While the PL intensity is much reduced at high temperatures for single-layer MoSe₂, it is surprisingly enhanced for few-layer MoSe₂. Generally the PL of semiconductors decreases in intensity as the PL peak broadens with increasing temperature. The suppression in PL intensity and peak broadening are typically attributed to the exponential enhancement in nonradiative electron–hole recombination processes, reducing the probability of radiative transition. Even though this model applies well to single-layer MoSe₂, it fails for the few-layer MoSe₂ samples where the PL intensity is enhanced at high temperatures. We also employed similar measurements on a single-layer and few-layer MoS₂ flakes in the same temperature window, and we have found that the PL intensity of MoS₂ decreases at high temperatures regardless of the layer thickness just like in the case of single-layer MoSe₂ and other conventional semiconductors. The distinct difference in the temperature behavior of these two materials points out to intrinsic differences in their band structure.

**Fig 2.7.** The temperature dependence of the PL spectrum of Single layer (a) MoSe₂, (b) MoS₂. Since both of them are direct bandgap semiconductors, the PL intensity decreases as the temperature increases. *Reprinted with permission from Ref [30], Copyright 2012, American Chemical Society*
To gain further insight, we compare the band structures of MoSe₂ and MoS₂ from bulk to few-layer and to the single-layer limit. According to DFT calculations as well as previously reported studies on MoSe₂ and MoS₂ [37], these two materials possess indirect bandgap in bulk and become direct bandgap in the 2D limit. Therefore in those limits, one would expect MoSe₂ and MoS₂ to behave similarly. However, we find that the rate of the indirect-to-direct bandgap crossover differs significantly between MoS₂ and MoSe₂. Even though single-layer MoSe₂ is a direct bandgap semiconductor (1.34 eV), the indirect bandgap value (1.50 eV) lies close to the direct bandgap. This difference of 0.16 eV is much smaller than the difference of 0.35 eV between the direct (1.54 eV) and indirect (1.89 eV) bandgap of single-layer MoS₂. As the number of layers increases, the quantum confinement in the perpendicular direction is relaxed, and therefore the indirect bandgap value becomes smaller, while the direct bandgap value remains largely unchanged, due mostly to the heavier effective mass associated with the K symmetry point. During this crossover the direct and indirect gaps in the case of bilayer and few-layer MoSe₂ becomes nearly degenerate. An increase in temperature slightly expands the interlayer distance as evidenced by the temperature-dependent Raman and tends to decouple neighboring MoSe₂ layers, pushing the system further toward the bandgap degeneracy. In this case, the contribution from the hot PL across the direct bandgap to the PL intensity becomes much stronger at high temperatures without any need for a phonon-assisted process. The abnormal increase in PL intensity at high temperatures, on the other hand, cannot be attributed to Boltzmann tailing of equilibrium electrons populating the conduction and valence bands at the K.
point where the direct bandgap occurs. This is because this K point bandgap is still 0.18 eV above the indirect bandgap which is much larger than $k_B T$. In a 3D semiconductor with similar band configuration, Ge, the direct bandgap is 0.14 eV above the indirect bandgap, but such an unusual PL behavior as in MoSe$_2$ has never been observed in Ge[42]. This contrast highlights the uniqueness of 2D semiconductors that they support a high efficiency hot PL process.

To further support our argument, our collaborator Ataca et.al from MIT performed temperature dependent DFT calculation for the variation of the bandgap values between different symmetry points as a function of layer spacing.
Fig 2.9 Variation of the bandgap values between different symmetry points as a function of layer spacing on (a) bilayer MoSe$_2$, (b) trilayer MoSe$_2$, and (c) bilayer MoS$_2$. A fully relaxed (equilibrium) position is fixed to zero, and additional layer spacing imitates the effect of temperature on the interlayer coupling. Reprinted with permission from Ref [30], Copyright 2012, American Chemical Society

As seen from the figure, at the equilibrium, the indirect bandgap (Γ to Γ−K) defines the fundamental bandgap but is close in value to the direct band (K to K). Increasing the interlayer spacing reduces the coupling between the layers and leads to an increase in Γ to Γ−K gap, while the direct gap K−K remains unchanged. During this transition, the indirect and direct bandgaps in bilayer and trilayer MoSe$_2$ would become degenerate as discussed above. For larger interlayer spacing, the coupling would be weakened to a point that individual layers in the few layer system start to behave as single layers with a 1.34 eV direct bandgap. On the contrary, since the indirect and direct gaps are well-separated in the bilayer MoS$_2$, band degeneracy cannot be thermally approached unless the layers are physically decoupled from each other. This distinct difference between these two similar materials leads to a drastic difference in the temperature dependence of their PL intensity.

2.9 Temperature dependence of Raman spectrum: evidence of decoupling

In the previous sections, we argue that an increase in temperature slightly expands the interlayer distance and tends to decouple neighboring MoSe$_2$ layers, pushing the system further toward the bandgap degeneracy. As a result of this, the PL intensity becomes much stronger. To elucidate this point, we performed temperature dependent Raman measurements on few-layer MoSe$_2$. We first note that the out-of-plane A$_{1g}$ mode is expected to soften as a result of reduction of the restoring forces. This is similar to softening of the A$_{1g}$ mode from bulk to single-layer limit where the interlayer coupling becomes absent. As shown in Fig 2.10, we show temperature dependence of the A$_{1g}$ mode from 423K down to 83K. As the temperature increases, A$_{1g}$ mode softens (shifts to the lower wavenumber). The softening in the Raman peak position is consistent with the interlayer decoupling mentioned in this work and provides a direct evidence for the increase in interlayer distance and reduction in the interlayer coupling.
Fig 2.10  Temperature dependence Raman peak  (a) Temperature dependence of the out-of-plane (A\textsubscript{1g}) Raman peak in few-layer MoSe\textsubscript{2}. (b) The change in the A\textsubscript{1g} peak position as a function of temperature. Reprinted with permission from Ref [30], Copyright 2012, American Chemical Society

2.10 Temperature dependence of the bandgap for monolayer MoSe\textsubscript{2}

Since this is the first experimental observation of single-layer MoSe\textsubscript{2}, for completeness, we discuss the effect of temperature on the bandgap (PL peak position) of the single-layer MoSe\textsubscript{2}.

In Figure 2.11, I show the temperature dependence of the bandgap extracted out from Figure 2.7. The observed decrease in the bandgap as a function of temperature is very similar to that observed in conventional semiconductors where such a decrease at higher temperatures due to increased electron–phonon interactions as well as slight changes in the bonding length.[43] Even though the origin of the temperature dependence in Eg is known, a physically meaningful and accurate formula of Eg(T) is lacking. Often times, the temperature dependence is fitted by the empirical Varshni relation[44], where the parameters lack clear physical meaning. Here, we employ a semiempirical fitting function[45]:

$$E_{g}(T) = E_{g0} - S \langle \hbar \omega \rangle \left[ \cosh(\langle \hbar \omega \rangle / 2k_{B}T) - 1 \right]$$

where $E_{g0}$ is the zero-temperature bandgap value, $S$ is a parameter describing the strength of the electron–phonon coupling, $\langle \hbar \omega \rangle$ is the average acoustic phonon energy involving in the electron–phonon interaction, and last the cosh term is related to the density of phonons at the specific temperature. We find that this model fits the temperature dependence of the bandgap
well as shown in Figure with $E_g^0 = 1.64$ eV, $S = 1.93$, and $\langle \hbar \omega \rangle = 11.6$ meV ($93$ cm$^{-1}$). In comparison, similar fitting to single-layer MoS2 yields $E_g^0 = 1.86$ eV, $S = 1.82$, and $\langle \hbar \omega \rangle = 22.5$ meV ($182$ cm$^{-1}$).

**Fig 2.11** Variation of the single-layer MoSe$_2$ bandgap values (PL peak energy) in the 87–450 K range. Reprinted with permission from Ref [30], Copyright 2012, American Chemical Society

### 2.11 Conclusions

To summarize, we have experimentally shown the first optical emission studies of single-layer and few-layer MoSe$_2$ semiconductors. While single-layer MoSe$_2$ possesses a direct bandgap, in the few-layer limit the indirect and direct bandgap are nearly degenerate. As a result, we find that this system can be effectively driven toward the 2D limit by thermally decoupling neighboring layers via interlayer thermal expansion. This finding leads to an enhancement in photoluminescence of few-layer MoSe$_2$ at high temperatures, similar to the enhancement of photoluminescence due to the bandgap crossover going from the bulk to the quantum limit. However, observed temperature dependence of the PL in few-layer MoSe$_2$ is strikingly different from the well-explored MoS$_2$ where the indirect and direct bandgaps are far from degenerate.
This effect points to potential applications involving external modulation of optical properties in 2D semiconductors.
Chapter 3. Modulation of light emission in two-dimensional LTMC semiconductors

3.1 Introductions

As I have shown in previous chapters, layered TMC semiconductors become direct-bandgap, light emitting materials. The quantum yield of light emission is low and extremely sensitive to the substrate used, while the underlying physics remains unclear.

PL quantum yield of monolayer TMC semiconductors has been found to be still low even in monolayers. For example, the PL yield for MoS$_2$ monolayers is on the order of $10^{-3}$ [37]. We noticed that monolayer TMC materials have extremely high surface-to-volume ratio, making them sensitive to the ambient and substrate. However, up to now, very few literature reports have systematically studied this ambient effect, and exploring their effect on the TMC photoluminescence properties.

In this chapter, I will explore the wide range of modulation of PL intensity in monolayer TMCs by exposing the sample to different gas environment. The modulation is completely, quantitatively reversible at room temperature by simply pumping and purging the gas, indicating that physi-sorption of the gas molecules is responsible for the modulation. Density functional theory (DFT) calculations suggest that the O$_2$ and H$_2$O molecules bond weakly to the LTMC monolayers, and withdraw electrons from the latter. The charge transfer depletes n-type LTMCs (MoS$_2$ and MoSe$_2$) and stabilises excitons that would be otherwise screened; consequently a new radiative recombination channel is activated, resulting in a remarkable enhancement in the PL intensity.

In addition to the PL intensity modulation, the PL peak position also slightly shifts, which is explained by a transition from neutral exciton recombination to charged exciton recombination. Such results and understanding not only shed new light on many-body physics in 2D semiconductors, but also provides a foundation for new optoelectronic devices where strong PL modulation by external means is desired.

3.2 Annealing induced photoluminescence enhancement

MoS$_2$ is the first monolayer TMC semiconductors which has been shown to have photoluminescence properties [37]. The as-exfoliated MoS$_2$ monolayers has a direct bandgap and show a prominent PL peak $\sim 1.84$ eV. The quantum yield for monolayer MoS$_2$ is low, presumably due to its large surface area and the nonradiative recombination channels on its surface. During our study of this material, we noticed that the PL intensity of MoS$_2$ can be
drastically enhanced after proper thermal annealing in vacuum. The PL spectrum of monolayer MoS$_2$ exfoliated onto SiO$_2$ substrate after different annealing time is shown in Fig. 3.1. The PL intensity in air is much enhanced after 45 min of annealing. However, prolonged annealing would decrease PL intensity eventually.

![PL spectrum of monolayer MoS$_2$](image)

**Fig. 3.1** The PL spectrum of monolayer MoS$_2$ exfoliated onto SiO$_2$ substrate after different annealing time at 450℃ in vacuum. The PL intensity in air is much enhanced after 45 min of annealing. However, prolonged annealing would decrease PL intensity eventually. *Reprinted with permission from Ref [46]. Copyright 2013, American Chemical Society*

Similar effect is observed in other layered TMC semiconductors. As shown below, monolayer MoSe$_2$ and WSe$_2$ show similar enhancement after thermal annealing.
3.2.2 The effects of thermal annealing

Such a general trend of PL enhancement after thermal annealing merits further investigation. To gain more insight into this effect, we performed micro PL/Raman spectroscopy study on the annealed monolayer MoS$_2$.

Fig. 3.3 Normalized PL spectrum for pristine and optimally annealed monolayer MoS$_2$. The PL peak position of MoS$_2$ blued shifted by 40meV after thermal annealing. Inset, Raman spectrum of pristine and annealed monolayer MoS$_2$. Reprinted with permission from Ref [46], Copyright 2013, American Chemical Society.
A comparison between the Raman spectrum of pristine (i.e., as-exfoliated) and optimally annealed monolayer MoS$_2$ (Fig. 3.3 inset) shows that the FWHM and peak intensity of the $A_{1g}$ and $E_{2g}$ peaks remain largely unchanged, therefore the thermal anneal does not degrade the crystalline quality of the material. However, the in-plane Raman mode ($E_{2g}$) softens from 384.5 to 383 cm$^{-1}$, possibly attributed to desorption of contamination molecules.

### 3.2.3 The ambient effects on PL enhancement of MoS$_2$ monolayer after thermal annealing

We accidentally noticed that, although the annealed MoS$_2$ monolayers show drastically enhanced PL intensity in ambient air, this effect immediately disappear if the PL measurements is carried out in vacuum. So certain gas in the ambient air may also participate to enhance the PL intensity.

So we repeated this experiment in different gas ambient, including Ar, N$_2$, O$_2$, wet Ar (Ar gas going through a water bottle, carrier H$_2$O gas). The results are in shown in Fig. 3.4. It turns out that H$_2$O and O$_2$ are enhancing the PL, while N$_2$ and Ar has no effects.
Here we have traced down the gas molecules that are responsible for enhancing the PL, it is natural to ask the reason for it.

### 3.2.4 Density functional theory calculations

To provide a physical picture for the effect of O\textsubscript{2} and H\textsubscript{2}O, our collaborators in MIT have simulated the interaction between monolayer MoS\textsubscript{2} and O\textsubscript{2} or H\textsubscript{2}O molecules using density functional theory (DFT) calculations. Calculating the van der Waals energy between the molecule and the MoS\textsubscript{2} as a function of angle and distance reveals that O\textsubscript{2} and H\textsubscript{2}O molecules can be physi-sorbed on the MoS\textsubscript{2} surface with 79 and 110 meV binding energies, respectively. Once physi-sorbed, the O\textsubscript{2} or H\textsubscript{2}O molecule is blocked from chemi-sorption by a high energy barrier (~ 2eV). Moreover, when the molecules are physi-sorbed onto the MoS\textsubscript{2}, approximately 0.04 electrons per O\textsubscript{2} and 0.01 electrons per H\textsubscript{2}O are transferred to the molecules, depleting the monolayer MoS\textsubscript{2}, as shown in Fig.3a and b. Due to the monolayer thickness of the MoS\textsubscript{2}, the total number of charge transferred from the MoS\textsubscript{2} to the gas molecules adds up to remarkably high sheet densities. Assuming that only one O\textsubscript{2} molecule is physi-sorbed on an area of 10 unit cells of MoS\textsubscript{2}, the charge transfer would reduce the original sheet carrier density as much as 5×10\textsuperscript{12}/cm\textsuperscript{2}. This number can reach even higher values if the physi-sorption occurs at defect sites where the charge transfer is higher. For example, we find that the O\textsubscript{2} and H\textsubscript{2}O molecules bind more strongly at sulphur-vacancy sites (110 meV for O\textsubscript{2} and 150 meV for H\textsubscript{2}O), and for H\textsubscript{2}O the charge transfer per molecules increases by a factor of 5.

![Figure 3.5](image-url) *Calculated charge transfer under physi-sorbed O\textsubscript{2} or H\textsubscript{2}O.* (a) Charge density distribution of an O\textsubscript{2} molecule physi-sorbed on the MoS\textsubscript{2} surface. The colour scale is in the units of e/Å\textsuperscript{3}. (b) Charge density difference between pristine MoS\textsubscript{2} and O\textsubscript{2}-adsorbed MoS\textsubscript{2}. The isosurface is for electron density of 2×10\textsuperscript{-4} e/Å\textsuperscript{3}. Red is charge accumulation and blue is charge depletion. *Reprinted with permission from Ref [46], Copyright 2013, American Chemical Society*
3.4.5 Competing Recombination channels: charged vs neutral exitons

It is intriguing to note not only the change in the PL intensity, but also the peak position and line profile when the PL is modulated by exposure to O2 / H2O (Fig.3.3). According to literature[47]-[49], the high-energy peak at ~1.88 eV is associated with recombination of neutral excitons (X0), while the low-energy peak at 1.84 eV with negatively charged excitons (trion, X-), that is, an electron bound to a neutral exciton. The energy difference of ~40 meV is attributed to the binding energy (Eb1) of the second electron in X-. It has been predicted that due to a higher Eb1, it is much easier to observe radiative recombination of trions in quantum confined systems [50]. Values of Eb1 ranging from 2 to 6 meV were reported for semiconductor quantum dots and quantum wells at temperatures typically below 10K. It was recently reported to be 40 meV for un-gated monolayer MoS2 at 14K, and 30 meV for monolayer MoSe2 at 20K[51]. In those experiments, the relative PL intensities and peak positions of X- and X0 could be tuned by electrostatically controlling the charge state of the material.

Figure 3.6 Schematics of neutral and charged excitons. (a) Neutral exciton, the electron-hole pair are exited and recombined freely. (b) Negatively charged excitons. After he electron-hole pair are ecited, they were bond to anther electron, and forming an e-e-h complex (trions). Trions have energy levels below the conduction band (the dashed green line). In case of MoS2, this level is 50 meV lower than conduction band.

The as-exfoliated MoS2 is known to be unintentionally n-type doped, with a high sheet density of equilibrium electrons (neq) up to 10^13/cm^2. The rate equation of non-equilibrium free electrons (n) under photo-excitation and recombination is,

\[
dn/dt = G - (n \cdot \eta_{nr}) / \tau_{nr} - n \cdot \eta_{X0} / \tau_{X0} - n \cdot \eta_{X-} / \tau_{X-},
\]

where G is the photo-excitation rate, and the subscription “nr”, “X0” and “X-” stands for non-radiative (including defects-mediated and Auger process), neutral exciton radiative, and trion radiative recombination process, respectively. \( \tau \) is recombination lifetime; \( \eta \) is the probability of an electron falling into one of these three pathways (Fig.3.7), which satisfies \( \eta_{nr} + \eta_{X0} + \eta_{X-} = 1 \). In the presence of high neq, the probability of forming X0 and X- (i.e., \( \eta_{X0} \) and \( \eta_{X-} \)) is expected to rapidly decrease due to electrostatic screening between free electrons and holes; on
the other hand, high $n_{eq}$ favours formation of X (but not $X^0$) by providing the second electron for trions. As a result, $\eta_{X^-}$ and $\eta_{X^0}$ have very different functional dependence on $n$ and $n_{eq}$. In steady state, the $n_{eq}$-dependence of the rate of non-radiative recombination, exciton radiative, and trion radiative recombination is schematically shown in Fig. 3.7. It can be seen that for as-exfoliated monolayer MoS$_2$ where $n_{eq}$ is high, $X^0$ is destabilized due to charge screening while $X^-$ recombination is relatively high due to the abundance of free electrons. The total radiation intensity is low, because most photo-excited electrons and holes are forced to recombine non-radiatively; The non-radiative recombination may be dominated by the Auger process at such high $n_{eq}$. As the monolayer MoS$_2$ physi-sorbs electronegative molecules such as O$_2$ and H$_2$O, $n_{eq}$ is much depleted by the charge transfer. Consequently, $X^0$ is stabilized while $X^-$ is depleted, resulting in a high intensity of $X^0$ and a diminishing $X^-$ peak in the PL spectrum. Therefore, the modulation of PL between the $X^0$ peak at 1.88 eV and $X^-$ peak at 1.84 eV is a direct result of competition between charge screening that destabilizes both excitons and trions, and charge accumulation that is needed for trions but not for excitons.

![Figure 3.7 Schematics for competing recombination channels in monolayer MoS$_2$. Reprinted with permission from Ref [46], Copyright 2013, American Chemical Society](image)

### 3.3 Electric field modulated photoluminescence in monolayer MoS$_2$

#### 3.3.1 Experimental design and device fabrication

As we have shown in previous section, the H$_2$O and O$_2$ gas molecules can effectively deplete the charge carriers in thermally annealed MoS$_2$, supressing its trion emission, and enhancing the PL intensity by orders of magnitude. However, this thermal annealing process is not reversible. It is
much more desired to find out a strategy that can modulate the light emitting of layered TMC in a reversible way.

Inspired by the concept of field effect transistor, in which the carrier density in the channel can be readily controlled by the application of a gate electric field, we propose to achieve similar PL modulation effect as in the thermal annealed sample by electrically deplete the electrons in monolayer MoS$_2$.

In Fig.3.8, I show the experimental set up. A monolayer MoS$_2$ flake is exfoliated onto the 90nm thick SiO$_2$/ Si substrate. The Si wafer is heavily doped, in order to apply the back gating. Fig. 3.9 shows the optical image of the device, along with the gold contact. The whole device was sealed in vacuum chamber, in case we need to study the gas ambient effect. Except for otherwise noted, all the data are take at room temperature, in ambient.

![Fig. 3.8. The experimental set up for modulating the PL emission with electrical gating.](image)
3.3.2 Electrically modulated PL of Monolayer MoS$_2$ in air

As shown in previous sections, our DFT calculations suggest that the observed PL modulation is associated with the charge depletion of the monolayer TMD by the O$_2$ or H$_2$O molecules. To test this hypothesis, we deplete a monolayer MoS$_2$ by electrical field gating (Fig.3.10) and simultaneously monitor the PL spectrum. Similar to the O$_2$ / H$_2$O exposure measurements, once the monolayer MoS$_2$ is electrostatically depleted, the PL intensity increases significantly and the peak position shifts from 1.84 to 1.88 eV. This is consistent with previously reported electrical modulation of PL in monolayer MoS$_2$. [47]
3.3.3 Gas ambient effect on electrically modulated PL of Monolayer MoS$_2$

Different from the experiments on thermally annealed MoS$_2$, here we rely on the gating electric field to deplete the electrons in MoS$_2$, thus do not expect gas ambient effect. We repeated our experiment in vacuum, in order to prove this idea.

Surprisingly, however, such a PL modulation by gating is observed when the sample is in air, but mostly disappears when the sample is measured in vacuum, as shown in Fig. 3.11. This implies that the main gating effect still originates from the interaction between the molecules in air (more specifically, H$_2$O) and the MoS$_2$. The electrical gating catalyses the interaction between the
molecules and MoS$_2$, possibly by deepening the physi-sorption potential and enhancing the amount of charge transfer per molecule.

Figure 3.11 Gate modulation of light emission in monolayer MoS$_2$ in air and vacuum. We observed PL intensity is much enhanced by applying a depletion voltage in air. However, this modulation completely disappear if the experiment is carried in vacuum. *Reprinted with permission from Ref [46], Copyright 2013, American Chemical Society*

3.3.4 Electric field assisted physio-sorption in Monolayer MoS$_2$

The observed absence of PL modulation in vacuum is unexpected for a purely electrostatic gating picture, and merits further discussion.

Before proceeding, let me summarize our observations for both thermal annealing and electric gating experiments here:
Before thermal annealing, the as-exfoliated MoS2 show no PL enhancement in air. So thermal annealing presumably create some structural defects, which prone to interact with gas molecule such as H2O and O2. These physio-sorbed molecules deplete the electrons in MoS2, surpressing the trion excitation, and enhancing the PL.

For electrical gating experiments, we do not need to anneal the MoS2. By applying a positive voltage to the MoS2, it becomes sensitive to the H2O molecules in air. With the help of H2O molecule, we observe similar PL modulation effect as in the thermal annealing experiments. However, different from thermal annealing experiment, O2 is not affecting the PL intensity when a depleting electric filed is applied.

It is clear that, in both experiments, the physiosorption of gas molecule is necessary to enhance the PL. Consistent with the DFT calculation results, only the gas molecule DEPLETE electrons form MoS2 could enhance the PL. So our gating experiments can be understood as electric field assisted physio-sorption in monolayer MoS2. As shown in Fig. 3.12. The physics picture can be described as follows:

In pristine MoS2, the naturally exist sulphur vacancies (red circled crosses) donated free electrons, doping this material into n type. Gas molecule, such as H2O in air, can not bind to these sulphur vacancies because there were screened by free electrons.

When a positive gate voltage is applied to MoS2 monolayer, part of its free electrons are depleted by the gating electric field. Now the positively charged sulphur vacancies get exposed. Locally, the electric field around these positively charged sulphur vacancies are highly NON-UNIFORM.

This NON-UNIFORM electric filed attract polar molecule like H2O in the air. These H2O molecules, once physically absorbed on to the vacancy sites, strongly deplete the MoS2, draining out the remaining free electrons. Since only polar molecule can be attract, this explains why O2 has no effect in our gating experiment, even though it can also deplete electrons from MoS2 once it was absorbed on MoS2. In the thermal annealing experiment, the heating process likely generates different type of defects, which can readily attract both O2 and H2O.
Fig. 3.12 Electric field assisted physio-sorption in monolayer MoS$_2$. (a) In pristine MoS$_2$, the naturally exist sulphur vacancies (red circled crosses) donated free electrons, doping this material into n type. H$_2$O in air, can not bind to these sulphur vacancies because there were screened by free electrons. (b) When a positive gate voltage is applied to MoS$_2$ monolayer, part of its free electrons are depleted by the gating electric field. The NON-UNIFORM electric filed near sulphur vacancies attract polar molecule like H$_2$O in the air. These H$_2$O molecules, once physically absorbed on to the vacancy sites, strongly deplete the MoS$_2$, draining out the remaining free electrons.

3.4 Conclusions

In summary, we have shown a universal effect that the light emission efficiency in 2D semiconductors is dominated by charge transfer to physically adsorbed electronegative gas molecules such as O$_2$ and H$_2$O. The process is unique in such 2D system not only because of its high surface area that is prone to interactions with gaseous molecules, but also its 2D nature that
stabilizes many-body exciton effects. The effect enables reversible, quantitative control of light emission intensity with gas pressure and gate voltage, a much-desired function for new applications such as sensors, phosphors and optical switch.
Chapter 4  Mechanically Modulated Tunneling Resistance in Monolayer MoS₂

4.1 Introductions

With continuous down scaling of transistor size driven by the Moore’s law, fundamental limits of the field effect transistor have resulted in a power density crisis for integrated circuit chips. This is because the transistor operating voltage has not been proportionally reduced in recent technology generations, due to the non-scalability of the threshold voltage. The minimum threshold voltage for a given off-state leakage current specification is set by the sub-threshold swing, which is constrained by Boltzmann statistics to be no less than 60 mV/decade at room temperature, and which ultimately limits the energy efficiency of CMOS technology[53]. To circumvent this limit in order to continue to advance information technology, nano-electro-mechanical (NEM) switches have been proposed as an alternative technology for future ultralow-power digital integrated circuits on the basis of two apparent advantages: zero OFF-state current and abrupt ON/OFF switching, which give rise to zero standby power consumption and extremely steep switching (< 0.1 mV/decade), respectively[54]. However, conventional NEM switch designs operate by making and breaking physical contact between the conducting electrodes to turn the device ON and OFF, and therefore are inherently susceptible to reliability issues such as contact material degradation, surface adhesion, etc[55]-[56]. In order to lessen or eliminate these issues, a NEM switch without impacting parts, based on piezoelectric transduction, recently has been proposed by IBM researchers[57]. The channel of the switch is composed of a piezoresistive material which undergoes pressure-induced metal-insulator transition (MIT) upon compression by an expanding piezoelectric in response to an applied gate voltage. It is noted that piezoresistive behavior exists in different materials and structures, and can be triggered not only by stress-induced MIT, but also by other mechanisms such as mechanically controlled quantum tunneling[58]-[59], as in a tunneling NEM (tNEM) switch. For tNEM switch applications, the piezoresistive material needs to be (1) sufficiently thin (on the order of a few nanometers or less) in order for significant tunneling to occur, (2) non-metallic and (3) free of point defects, dislocations or grain boundaries so as to minimize the OFF-state leakage current. These requirements impose serious constrains on the choice of tunneling materials. For example, SiO₂ can be deposited with ultra-thin thickness, but then current leakage through grain boundaries and defects becomes significant[60]; Graphene can be made down to atomic thick and almost defect-free by simple exfoliation, but the metallic property limits its switching behavior.
Fig 4.1 The schematics of a contact NEM switch. It operates by making and breaking physical contact between the conducting electrodes to turn the device ON and OFF, and therefore are inherently susceptible to reliability issues such as contact material degradation. Also, due to the adhesion of the electrodes, the device turns “ON” and “OFF” at different voltage, as shown in (b).

Fig 4.2 The schematics of a phase transition NEM switch. It operates by pressure induced metal-to-insulator (MTI) transition of the active material. Materials such as VO$_2$, which have MTI temperature around room temperature are good candidates.
4.2 The Concept of t-NEM switch based on layered TMC semiconductors

In order to solve the challenging technical/ material problems haunting the development of tNEM switches, I came up with the idea of using transition-metal dichalcogenide semiconductor MoS$_2$ as the tunneling barrier. Before I start, I would like to express my gratitude for professor Eli Yablonovitch. His lecture on “Advanced Topics in Solid State Devices” inspired me to come up this idea during class.

As we discussed in the introduction part, in order to build an tNEM switch, we need a tunneling barrier which is extremely thin and free of defect. Layered semiconductors like MoS$_2$ seems to be ideal material for this tunneling barrier. A bulk crystal of MoS$_2$ comprises S-Mo-S layers held together by van der Waals forces; each S-Mo-S layer (referred to as a monolayer) consists of two planes of S atoms and an intermediate plane of Mo atoms covalently bonded to each other. Because of the relatively weak inter-layer interaction and the strong intra-layer bonding, ultrathin, defect-free crystals of MoS$_2$ down to a single monolayer (~ 0.65 nm) can be formed by mechanical exfoliation, as I have shown in previous chapters. The fact that thusly-obtained MoS$_2$ monolayers are semiconducting, ultra-thin, and nearly defect-free makes them an ideal material for implementing tNEM switches. In this chapter, I will demonstrate mechanical modulation of tunneling resistance through monolayer MoS$_2$, and discuss the possibility of using it as the active tunneling material in non-impacting tNEM switches.

![Fig 4.3. The schematics of a tNEM switch. It operates by controlled tunneling through the layered TMC semiconductors. In this design, the electrode is always in touch with the TMC](image)
semiconductor layers, eliminating the electrode breaking/ adhesion problem, thus longer device life is expected.

4.3 Fabricating t-NEM switch based on layered TMC semiconductor MoS2

4.3.1 Exfoliating Monolayer MoS2 flakes onto Pt coated SiO2 substrate.

To fabricate t-NEM switch based on layered TMC semiconductor MoS2, we need to lay the MoS2 monolayer on a conductive substrate. However, due to the extreme thinness of MoS2 monolayer, the monolayers are typically invisible on normal substrates. Even for SiO2 substrate, we need to carefully choose the thickness of SiO2, so that the optical interference would enhance the contrast for monolayer TMC semiconductors. There are two optimal SiO2 thickness for enhancing the optical contrast ultrathin semiconductors, one is 90nm, while another is 270nm. [61]. We have experimentally confirmed this. Monolayer TMC show blue-purple color on 90nm thick thermal SiO2 substrate, while red-purple on 270nm SiO2 substrate.

We might deposit a thin layer of ITO (off course, with certain thickness to enhance the contrast) on Si wafer to serve as this conductive substrate. However, our top electrode, which would be a conductive AFM tip, is Pt coated. The work function difference between ITO and Pt, would introduce asymmetry to the tunneling barrier, complicating the experiment. Considering all of these restrictions, I decided to use an extremely thin layer of Pt coated on 90nm thick thermal SiO2 as the bottom conductive substrate. The coating of Pt must be thick enough to form a continuous layer, while thin enough to be optically transparent.

Due to the poor adhesion between SiO2 and Pt, I also pre-deposit 1nm thick Cr as adhesion layer. The following mechanical exfoliation process is similar to what I have done on SiO2 substrate. Since Pt surface lacks sticky dangling bonds as on SiO2 surface, the yield for monolayer is much less. Nevertheless, I managed to find monolayer/ few layers of MoS2 on the Pt surface. The optical image is shown in Fig.4.4 (below). Contact mode AFM images were also recorded, as shown in Fig.

![Image](image.png)

Fig. 4.4 The MoS2 exfoliated onto Pt/Cr coated 90nm thick thermal SiO2 substrate. (a) optical image. (b) Contact mode AFM image. Flake A are monolayer, confirmed by AFM
measured thickness ~0.7nm. Flake B and C are few-layers, ~3-4 layers. Reprinted with permission from Ref [52], Copyright 2013, AIP Publishing LLC

At my best knowledge, this is the first time people have exfoliated MoS$_2$ onto metallic surface, for completeness of this study, I and my collaborator Dr. Fu did Raman and PL study of these mono/few layers, the results are summarized in Fig 4.5 (a) and (b)

![Fig. 4.5 The Raman/PL spectrum of MoS$_2$ flakes exfoliated onto Pt surface. The “A”, “B”, “C” referring to the same flake labeling in Fig.3. In the Raman spectrum (a), we observe similar layer dependence of E$_{2g}$ stiffening and A$_{1g}$ softening as on the SiO$_2$ substrate. In the PL spectrum (b), the monolayer A shows strong PL at 1.9eV, while this emission is much suppressed in few-layer B and C. Reprinted with permission from Ref [52], Copyright 2013, AIP Publishing LLC](image)

In Fig. 4.5., the multilayer flakes (B and C) show characteristic A$_{1g}$ (out-of-plane) and E$_{2g}$ (in-plane) Raman modes located at around 408.4 cm$^{-1}$ and 384.3 cm$^{-1}$ respectively. For monolayer flake (A), the A$_{1g}$ mode softens to 406.7 cm$^{-1}$ while the E$_{2g}$ mode stiffens to 385.9 cm$^{-1}$, which is consistent with the observation for MoS$_2$ exfoliated on SiO$_2$ substrate, as shown in previous chapter. Also, since MoS$_2$ undergoes a progressive crossover from indirect bandgap of ~ 1.29 eV in bulk crystal to direct bandgap of ~ 1.88 eV in a monolayer. As shown in Fig. 4.5(b), the monolayer MoS$_2$ indeed shows strong band-edge photoluminescence (PL) at 1.88 eV, while for multilayer MoS$_2$, the direct-bandgap PL is drastically suppressed and a new PL peak emerges around 1.43 eV.
4.3.2 Experimental Setup for t-NEM based on monolayer MoS$_2$.

Next we measure the vertical tunneling resistance of the monolayer MoS$_2$ using conductive-AFM as shown schematically in Fig. 4.6. A Pt-coated conductive AFM probe is used as the top electrode and indents the MoS$_2$ flake in the contact mode. This configuration allows us to apply compressive force directly onto the MoS$_2$ flake while simultaneously recording the current-voltage (I-V) relationship. By calibrating the spring constant of the AFM probe, I can accurately control the applied force. At each force point, the probe is stabilized for 1 min, and then an I-V curve is swept three times to check stability. The maximum bias voltage we applied is small (~50 mV) that the I-V curve is in the linear regime, therefore the resistance can be defined from the linear slope of the I-V curve near the origin. It is argued that capillary condensation effect at ambient condition may play an important role in the measurement of local conductance [60]. In our case, however, the measured adhesion force (which is composed of capillary force, van der Waals force, etc.) between the AFM tip and sample is much smaller than the applied mechanical force, therefore its influence can be neglected.
In order to quantify the mechanical pressure exerted onto the MoS₂ flakes, we employed the Hertzian contact model as depicted in Fig 4.7. The model shows that an elastic sphere of radius \( r \) indents an elastic half-space to depth \( d \), and creates a contact area of \( A = 2\pi rd \). Here \( d \) is related to the applied force by 

\[
F = \frac{4}{3} E^* r^{1/2} d^{1/2},
\]

where \( E^* \) is the reduced Young’s modulus defined as 

\[
\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2},
\]

\( E_1, E_2 \) are the Young’s moduli, and \( \nu_1, \nu_2 \) the Poisson's ratios associated with each contact material (Pt and MoS₂).

### 4.4 Results and Discussion

In our setup, the MoS₂ monolayer act as both the tunneling barrier and the elastic spacer. Defining the thickness of MoS₂ monolayer in our system is tricky in our case. As shown in Fig 4.8, the typical definition of the atomic-scale thickness of monolayer MoS₂ actually takes into account the three atomic planes (S-Mo-S) plus the van-der-Waals gap, therefore its effective thickness could be modulated under pressure by shrinking the van der Waals gap as well as deforming the S-Mo-S bonding angles. Initially the monolayer MoS₂ deforms conformably with the bottom Pt substrate when the AFM tip indents it. Afterwards, the pressure exerted on the MoS₂ increases with the applied tip force, resulting in a decrease of the effective thickness of the monolayer MoS₂ separating the AFM tip and the bottom electrode.
Fig. 4.8 The definition of “effective thickness” of the MoS$_2$ monolayer.

Without applying force to the AFM tip, the contact between the AFM tip and the MoS$_2$ monolayers is poor and un-reliable. So we apply a small pressure around 0.5 GPa to insure the reproducibility of the recorded resistance. In Fig 4.9, we show the measured resistance of the monolayer MoS$_2$ flake as a function of the calculated pressure.
In order to confirm reproducibility of the measurements, we ramped the force up and down for multiple cycles. The resistance changes by ~ 4 orders of magnitude, and is highly reversible within the experimental sensitivity limited by instability factors such as thermal drift of the stage. It should be pointed out that this large ON/OFF ratio cannot be explained solely by contact resistance change between the tip and MoS₂ flake, because the estimated contact area varies only by a factor of 10 in the applied pressure range.

We also noticed that the stress-induced resistance change is exponential, which is indicative of quantum tunneling process as the thickness of the monolayer MoS₂ (~ 0.65 nm) is modulated by the tip force. The resultant enhancement in quantum tunneling lowers the system’s resistance to a point that is limited by the intrinsic contact resistance in the system. When the applied force is gradually removed, the system relaxes back and the resistance increases due to reduced tunneling.

![Fig4.10 The band diagram of Monolayer MoS2 sandwiched between two Pt surfaces under equilibrium condition.](image)

Now, let’s try to analyze the results in a more quantitative way. Since MoS₂ is in close contact with metal, charge transfer must occur. Due to the extreme thinness of monolayer MoS₂, we expect the metal depletes the MoS₂ of mobile charge carriers. For such a system, the proposed band diagram is illustrated in Fig 4.10, where the equilibrium Fermi level falls inside the bandgap of MoS₂, forming a typical symmetric metal-insulator-metal (MIM) tunneling diode.
structure. Depending on the metal quality and contact condition, the work function of Pt varies between 5.1 eV and 5.9 eV[62] Assuming that the monolayer MoS$_2$ has the same electron affinity as that of bulk MoS$_2$ (~ 4 eV)[63], the electrons on the two sides experience a tunneling barrier of 1.1 ~ 1.9 eV. Under the WKB approximation[64], the tunneling probability of charge carriers through a potential barrier height of $qV_b$ is: $T = e^{-2\sqrt{qV_b}}$, where $t$ is the barrier thickness and $m^*$ is the carrier effective mass. When applied bias voltage is smaller than the barrier height, i.e. $V < V_b$, the tunneling current density of the MIM structure can be derived as [64]:

$$J = J_0 \left[ (V_b - V/2) \exp \left( -C \sqrt{V_b - V/2} \right) - (V_b + V/2) \exp \left( -C \sqrt{V_b + V/2} \right) \right]$$  \hspace{1cm} (1)

where $J_0 \propto t^2$ and $C = 2t\sqrt{2m^*q/h^2}$. The first term describes the tunneling current from cathode to anode while the second term describes the tunneling current in the reverse direction. In our case, $V \ll V_b$, Eq. (1) can be further approximated as

$$J = -J_0 V e^{-C\sqrt{V_b}}$$  \hspace{1cm} (2)

which shows a linear relationship between current and voltage. For a given contact area of $A$, the tunneling resistance can then be defined as

$$R = V / JA = e^{-C\sqrt{V_b}} / J_0 A$$  \hspace{1cm} (3)

Since both contact area $A$ and barrier thickness $t$ change with applied force under the Hertzian contact model, it is more convenient to define an effective tunneling resistance as $R^* = R / t^2 = R_0 e^{\alpha t}$, where $R_0$ is a constant regardless of $A$ and $t$, and the coefficient $\alpha$ is defined as $\alpha = 2\sqrt{2m^*qV_b/h^2}$. For free electrons on the two sides of the barrier (monolayer MoS$_2$), they have the effective mass of $m_0$, therefore one can calculate the coefficient $\alpha$ to be in the range of 10 to 14 nm$^{-1}$. There is no report on the out-of-plane Young’s modulus of monolayer MoS$_2$ to date. If we follow the trend of graphene and assume the out-of-plane Young’s modulus $E$ of monolayer MoS$_2$ to be 3.5% of the in-plane $E$, [65][66] Fig. 4.9 can be re-plotted in Fig. 4.11, where the data points represent the average of the values shown in 4.9. Fitting the equation $R^* = R_0 e^{\alpha t}$ to the linear part of the experimental data yields $\alpha = 33$ nm$^{-1}$, which is larger than the estimated value, probably caused by uncertainties in the Young's modulus, tip radius, and electron affinity of monolayers.
4.5 Conclusions and Outlook.

In this chapter, I have explored a new concept of using monolayer MoS2 as the tunneling barrier to realize a non-impact t-NEM switch. The monolayer MoS2 act as both the insulating barrier and the elastic spacer. The sharp AFM tip allows us to apply large stress of a few GPa, under which the resistance of monolayer MoS2 is reversibly and exponentially modulated up to 4 orders of magnitude. The high ON/OFF ratio is attributed to quantum tunneling when the thickness of the monolayer MoS2 is modulated by the force exerted by the probe tip. Under the WKB approximation, the experimental data is explained in the framework of MIM tunneling diode model. Since mechanically exfoliated monolayer MoS2 is semiconducting, defect-free and nanometer thick, it can serve as a natural tunneling medium in a non-impacting NEM switch design. It should be noted that besides MoS2, any high-quality 2D semiconductors (such as monolayer WS2, MoSe2, Mg(OH)2, BN, etc.) can be used as the tunneling material in a tNEM switch, where the ON/OFF ratio and turn-on voltage are determined by their electrical conductivity and mechanical compressibility, respectively.

For future device application, however, using a AFM tip to modulate the tunneling process is not practical. I propose a device schematic as shown on Fig 4.12. Still a monolayer of MoS2 (or any other TMC semiconductors with large bandgap). The piezoelectric actuator is shaped in pyramid,
mimicking the AFM tip. The outside insulating capping provide both electrical insulation and mechanical support for the tNEM device. The ON and OFF of the device is controlled by $V_{SG}$.

Fig. 4.12 A conceptual design for non-impact tNEM switch based on monolayer TMC semiconductors. The piezoelectric actuator is shaped in pyramid, mimicking the AFM tip. The outside insulating capping provide both electrical insulation and mechanical support for the tNEM device. The ON and OFF of the device is controlled by $V_{SG}$.
Chapter 5 Exploring novel electrical transport properties of layered transition metal chalcogenide nanostructures

5.1 Introduction

In previous chapters, I have concentrated on the semiconducting layered transition metal chalcogenide materials. Since transition metal chalcogenides (TMC) have a wealth of physical properties, it is also interesting to explore other types of TMCs, such as metallic TMCs. Unlike normal metallic materials, in which the transport properties are largely isotropic, the TMC metals typically show strong anisotropy as the result of their layered nature.

Even in bulk form, the electrons in some layered TMC materials are largely confined in individual layers, thus showing strong two-dimensional (2D) nature[67]. It is known that, the electron-phonon interaction is much enhanced in 2D. As a result, some layered TMC materials become superconductors at low temperature. For example, the layered TMC Fe Te_{0.5} Se_{0.5} is a recently found iron-based superconductor, with an unexpected high Tc around 15K[68]-[77]. The iron-based superconductors possess very rich but intriguing physical properties, and are under intensive investigation.

Fig. 5.1 The optical image of a thin FeTe_{0.5}Se_{0.5} exfoliated onto SiO_{2} substrate. The blue-purple color indicates extreme thinness. The thickness of this flake is 12nm, as identified by contact mode AFM.
Bi$_2$Te$_3$, another metallic LTMC, commonly known as a high performance bulk thermoelectric material[78], also attracted renewed attention in recent years. Bi$_2$Te$_3$ is theoretically predicted and experimentally confirmed as topological insulator[79]. Topological insulators (TIs), which has a semiconducting bulk and gapless surface, are of great importance for their promising application in next generation nanoelectronics[80]-[90]. The layered structure of Bi$_2$Te$_3$ enables this material to be exfoliated into extreme thin flakes, in which the conduction on the topological surface states might dominate the transport process. This opens up new research opportunities for studying its exotic transport properties.

The surface states of topological insulators have been intensively studied by spectroscopic methods such as angle resolved photoemission[91]-[93] or scanning tunneling spectroscopy[94]-[97]. However for transport experiments, the measurement of surface states has often been obstructed by the contribution from bulk carriers, which is due to the inevitable formation of natural defects. One strategy to enhance the surface conduction is to increase the surface-to-volume ratio through nano-structuring. For example, thin films[98] and nano-ribbons[99] of topological insulators have been synthesized, and the surface state characters have been revealed through magnetotransport measurements.

In this chapter, I will present my work on the electrical transport properties of nanostructured Bi$_2$Te$_3$. I am particularly interested on the exfoliated single crystal microflakes, because its thinness allows various kinds of novel device fabrication. I will demonstrate that the transport of topological insulator Bi$_2$Te$_3$ could indeed be controlled by artificially created nanostructures, and paves the way for future technological applications of this class of materials. As a complement for my works in previous chapters, here I will also describe the process for fabrication and characterization of micro/nano devices.

### 5.2 Mechanical exfoliation of Bi$_2$Te$_3$

Bi$_2$Te$_3$ is a layered TMC material, with each quintuple layer as its building block. The structure of Bi$_2$Te$_3$ is shown in Fig 5.2. Unlike other layered TMC like MoS$_2$ and WSe$_2$, in which the interlayer coupling in Bi$_2$Te$_3$ is much stronger. Up to now there is no literature report which could reliably produce Bi$_2$Te$_3$ in monolayer form. I used the Scotch-tape method as described in previous chapters to exfoliate Bi$_2$Te$_3$ into flakes as thin as possible. However, the thinnest I could get is around 50 nm thick. In Fig. 5.3, I show the optical image of Bi$_2$Te$_3$ flakes exfoliated onto SiO$_2$ substrate.
Fig 5.2 The quintuple layer for Bi$_2$Te$_3$. A quintuple consists of five mono-atomic planes of Bi or Te atoms. Each quintuple layer is ~1nm thick.

Fig. 5.3 The optical image of a thin Bi$_2$Te$_3$ exfoliated onto 285nm thick SiO$_2$ substrate. The thickness of this flake is ~50nm, as identified by contact mode AFM.
5.2 Device fabrication

The Bi$_2$Te$_3$ microflakes were then mechanically exfoliated on a Si substrate coated with 300nm-thick thermal SiO$_2$. Micro-scale electrodes were defined with photolithography using g-line photoresist, followed by electron beam evaporation of 5 nm thick Ti and 95 nm Au. Typical contact resistance is around 0.1 Ω, well below the channel resistance, guaranteeing the accuracy of our 2-probe electrical measurements.

After initial measurements, the same device was coated with 400nm thick PMMA as etching mask. Then we use electron-beam lithography to define a dense array of nano-holes (170nm diameter with 30nm spacing) on the PMMA (polymethyl methacrylate) mask. The sample was then introduced into reactive ion etching chamber. We used 100 sccm CH$_4$ : Ar : H$_2$ = 1:1:1 as the etching gas ambient, the etching power setting was 100 W, and the etching time was 100s to ensure that the etching drilled holes completely through the thickness of the Bi$_2$Te$_3$ flake. After the patterning, the device was gently rinsed in isopropanol diluted developer solution (methyl isobutyl ketone) to remove the PMMA, and blown dry in N$_2$ gas. A schematic of the device is shown in Fig 5.4.

**Figure 5.4. Device schematics** (a) Schematic of the device. The sample consist of a 6×6 µm$^2$ exfoliated Bi$_2$Te$_3$ flake (100nm thick) and two-terminal metal contacts. (b) Schematic about the structure of the antidot array.
5.3 Electrical transport study

Transport measurements were carried out in a Quantum Design Physical Property Measurement System (PPMS) -14T. The process for low temperature device measurement is described in Fig. 5.6. I want to note that, for handling electrical devices with nano/micro conduction channels, special attention must be paid to during wire bonding and electrical measurements. Especially for metallic samples like Bi2Te3 and FeTe0.5 Se0.5, their low resistance exacerbates this damage. Most of my device was lost due to accumulated static charge in the system(as shown in Fig. 5.7).
Fig. 5.6 The procedure for low temperature measurement in PPMS. The sample typically needs to be cut to fit the sample stage. The special designed sample holder can rotate in three-axis inside the PPMS chamber.

After a lot of device failure, I summarized the procedure for reducing the risk of discharging. The basic idea is to reduce the charge imbalance between different portion of the sample as well as the system. Two critical procedures are (1) short circuit the suspending electrode legs during wire bonding process, as described in Fig. 5.8. (2) Dissipate the possible charge imbalance on the sample loading stick before insert the sample, as shown in Fig. 5.9.
Fig. 5.7 The optical image of a Bi$_2$Te$_3$ microflake sample damaged by discharge. Since metallic LTMC are very conductive, the joule heating caused by discharge can easily damage the device.

Fig 5.8. The procedure for reducing the risk of static charge accumulation during wire bonding. I use aluminum foil to short circuit all suspending legs of sample stage before the wire bonding process. This could significantly reduce the charge imbalance between different electrodes.
Fig 5.9. The procedure for reducing the risk of static charge accumulation during sample mounting. Right before sample loading, the aluminum foil needs to be removed. Again, the legs of the sample stage are suspending, causing the charge imbalance. I use a piece of conductive foam to neutralize the charges on the loading stick, to reduce the risk of discharging.

As-grown crystals are typically degenerate semiconductors, with a bulk carrier density around $5 \times 10^{18}$ cm$^{-3}$ and a bulk resistivity about 1.5 mΩ·cm. The microflakes we exfoliated are 100nm thick, in which the transport is still dominated by the bulk carriers. Fig. 5.10(a) shows the temperature dependence of the resistance (red) for a microflake before writing the antidot arrays. The 100nm-thick square flake has a resistance around 150Ω at room temperature.

After writing the antidot arrays, the resistance of the device increases by more than two orders of magnitude, reaching a value around 50KΩ, as shown in Fig. 5.10(b). Since the cross-sectional area for the current path is significantly reduced after etching, it is expected that the resistance should increase due to the reduction of geometric factor. However, assuming the antidot diameter 170nm and lattice constant of the hole array 200nm, the increase in resistance due to the reduction of geometric factor is only about ten times. Therefore, the 300-fold increase of resistance can only be explained by the simultaneous increase in bulk resistivity, which has gone up to 100 mΩ·cm after writing the antidots.
Fig. 5.10 Temperature dependence of the zero-field resistance of the device before (a) and (b) after writing the antidot array. We note the resistance of the device increases by 500 folds after writing the antidot array, yet still shows metallic behavior. The small up-turn at low temperature is likely a result of the disorder-enhanced electron-electron interaction effect, which is commonly observed in highly disordered system.

One possible cause for such a large increase of bulk resistivity is the energetic ions used in the ion etching process. It has been reported that these high energy ions could damage the bulk of nanoflake or thin films, and hence suppress the bulk conduction. (The kinetic energy of these plasma ions is round 200eV) [100]. On the other hand, the width of the wall separating the two adjacent antidote holes is only 30nm, which is comparable to the depletion length of Bi$_2$Te$_3$ near the surfaces. Therefore the band bending effect could also reduce the carrier density in these regions, which effectively increase the bulk resistivity.

Fig. 5.10 (b) shows the resistance of the antidot array device as a function of temperature. Surprisingly, the temperature dependence shows an overall metallic behavior, with only a small upturn below T = 20 K. Since the sheet 2D resistance of the device is only half of a quantum resistance (e$^2$/h), one would expect the conduction is strongly localized, showing an insulating behavior. Even if we treat the device conduction as a three dimensional transport, it has also been shown that in the Bi$_x$Sb$_{1-x}$Pb$_{3-x}$Se$_x$ alloy the bulk channel turns into an Anderson insulating state for bulk resistivity above 30 m$\Omega$·cm [101]. The fact that we are still seeing a metallic temperature dependence might suggests that surface conduction plays a significant role, which is robust against localization. This could be a consequence of the large surface-to-volume ratio resulted from the writing of the antidot arrays.
5.4 Magneto-transport study of Bi$_2$Te$_3$ antidot arrays

Figure 5.11. Magnetoresistance of the Bi$_2$Te$_3$ antidot arrays. (a) Magnetoresistance of the Bi$_2$Te$_3$ antidot arrays measured at $T = 2$ to 20K. Thin solid curves shows the fit based on the three-dimensional weak antilocalization theory as described in the main text. (b) Same data as (a)
plotted against $B^{1/2}$. It clearly shows the magnetoresistance here scales linearly with $B^{1/2}$.

Coherence length $l_\phi$ as a function of temperature obtained from the weak antilocalization fitting.

Fig. 5.11 shows magnetoresistance (MR) of our antidot array as a function of magnetic field from 2 to 20K. The MR is positive with a cusp-like shape. Such behavior is indicative of a weak anti-localization effect. The weak anti-localization could arise from scattering off impurities with a high atomic number, or the strong spin orbit coupling of the conducting quasi-particles[102]. For the topological insulator surface state, since the spin and momentum quantum numbers are interlocked due to the protected topological ground state, it is expected that the MR shows a perfect two-dimensional weak anti-localization effect, which has a $\ln(B)$ field dependence in the strong field limit.[103]

However, the MR of the antidot arrays does not follow a $\ln(B)$ field dependence. Instead, the MR appears to have a functional form of square root of $B$, as shown in Fig 5.11(b). $B^{1/2}$ MR is in fact the signature of three-dimensional weak anti-localization effect instead of two dimensions. The three-dimensional weak anti-localization can be described by the following formula[104]:

$$\frac{R(B) - R(0)}{R(0)} = \frac{\rho_0 e^2}{2\pi^2\hbar} \sqrt{\frac{eB}{\hbar}} f_3\left(\frac{4el_\phi^2B}{\hbar}\right)$$

(1)

Where $\rho_0$ is the zero-field resistivity, $f_3$ is the Plank’s constant, $l_\phi$ is the coherent length, and $f_3(1/x) = 2(\sqrt{2+x} - \sqrt{x}) - [\sqrt{0.5+x} + \sqrt{1.5+x} + 2\sqrt{2.03+x}] / 48$

We fit our data by this equation, and the fitting is plotted as the thin solid curves in Fig.2(a). The extracted coherence length as a function of temperature is shown in Fig. 2(c). We note that the coherence length of electrons exceeds 100nm below 15K, which is comparable to the characteristic length scale of our antidot arrays structure.

As we discussed above, the transport of the antidot arrays is likely dominated by the surfaces. Intuitively, one would expect a two-dimensional weak anti-localization effect to be found in the MR, which is inconsistent with our measurements. An explanation for this contradiction might be drawn from a recent theoretical calculation, which proposed that quantum percolation could occur in a topological insulator antidot arrays if the antidots are dense enough[105]. In this case, the surface states on the inner walls of the antidots could hybridize with each other and restore the bulk-like conduction, thus the sample transport appears to be three-dimensional. We note that in this theoretical study only two-dimensional topological insulators have been considered, therefore a generalization to three dimension is highly desirable.

The introduction of antidot arrays does not simply change the resistance of the sample; it also completely modified the magnetotransport properties of Bi$_2$Te$_3$. After subtracting the smooth polynomial background [106], we extract out the oscillatory parts of MR for the sample before
and after writing the antidot array, and plot them in Fig 5.12. For the microflake before writing the antidot array (as shown in Fig5.12 (a)), it shows typical Shubnikov–de Haas (SdH) type oscillations, i.e. the oscillation amplitude increases at higher B field, and the oscillation is periodic in $B^{-1}$, all indicating typical bulk Bi$_2$Te$_3$ properties [107]. In sharp contrast, after introducing the antidot arrays, the MR oscillations show different behavior, as shown in Fig 5.12 (b). We find that its oscillatory MR consists of two features: a fast oscillating signal superimposed on a slowly varying background. Interestingly, the fast oscillating signal show very regular periodicity of $\Delta B=1.25T$, and the oscillation amplitude doesn’t increase at high B field. All of these feature suggesting they may originate from electrons circulating around certain small periodic features in the antidot arrays, resembling Ahoronov-Bohm (AB) oscillations which have been observed in similar systems [107][108].

In order to further investigate the origin of these MR oscillations, we extracted out the oscillatory MR of the Bi$_2$Te$_3$ antidot arrays from 2K to 20K (as shown in Fig 5.12 (c)). We find that the fast oscillating signal show very strong temperature dependence, whereas the slow varying feature persists up to T = 20K. To better visualize the data, we performed fast Fourier transforms (FFT) and obtained the frequency spectrum, as shown in Fig.5.12 (d). In the FFT spectrum, the peak centered at the $0.8T^{-1}$ (i.e. $\Delta B=1.25T$), as indicated by the arrow, quickly smears out when temperature approach 20K. On the other hand, the FFT peaks near zero periodicity (i.e. the slow varying background) are much less sensitive to temperature variations. As observed in previous studies on different antidot array systems, these slow varying features could be due to the pinning of classical cyclotron orbits with the antidot lattice[109]. Since it is a classical effect and depends only on elastic scattering rates, it is less sensitive to the decoherence process at higher temperatures.
Figure 5.12. Antidot arrays interacting with charge carriers and modifying the magneto-transport properties of topological insulator Bi$_2$Te$_3$. (a) Oscillatory part of the magnetoresistance of the device before and after (b) writing the antidot arrays, obtained by subtracting the smooth polynomial backgrounds for $T = 2K$. By carefully examining the oscillations, we see that by writing the antidot array, the oscillations of the device changed from Shubnikov–de Haas (SdH) type to Aharonov-Bohm (AB) type. The oscillation periodicity in microflake scales with $B^{-1}$, while stays constant ($\Delta B=1.25T$) in antidot arrays. (c) Temperature dependent study of the magneto-resistance oscillation of the antidot arrays from 2K to 20K (background subtracted). (d) Fast Fourier transform spectrum of the data shown in (c). The arrow indicates the prominent oscillation ($\Delta B=1.25 T$) that shows strong temperature dependence.

On the other hand, the very strong temperature dependence of the $\Delta B=1.25T$ oscillations indicates their origin form non-trivial quantum interference effect. The periodicity in these oscillations corresponds to one magnetic flux quantum penetrating through a closed conduction loop in the unit cell of a periodic lattice, which can be expressed by the following equation: $\Delta B = \frac{h}{e}/A$, where $A$ is the loop area. Substituting the periodicity $\Delta B$ by 1.25T, we obtain an effective area of $3.32\times10^{-15}$ m$^2$, roughly corresponds to a circular circumference of 100nm. We also notice that in figure 5.11 (c), the coherence length of the electrons, i.e. the length electrons can travel before loosing its phase information, drops blew 100nm when temperature is higher.
than 15K, exactly where we see the smearing out of these oscillations. Combining all these
information, we are able to pin down the origin of these oscillations: electrons coherently
interfere over small loops of 100nm in circumference. Since our antidot circumference is
~500nm, electrons are unlikely circulating them. If we carefully examine the structures of the
antidot arrays, we find that the thin bridges connecting two adjacent antidot have the
circumference around 100nm (which is also the part has the highest surface-to-volume ratio).
This might be the location the electrons circulating around and inducing the AB type oscillations
we have observed in the antidot array sample.

5.5 CONCLUSIONS

In summary, we introduced nanosized antidot arrays into single crystal Bi$_2$Te$_3$ microflake. The
antidot arrays increased the surface-to-volume ratio, and manifested the surface conduction
effect. Also, the smallest feature size in our antidot arrays is comparable to the coherence length
of electrons at low temperatures, as a result, non-trivial AB type quantum oscillations are
observed in our structure. Our study suggests that the electrons in topological insulators can
indeed interact with artificially designed nanostructures and significantly modify the transport
properties of topological insulators. Following this direction, we are expecting a wealth of
interesting quantum transport phenomena and novel topological insulator based functional
devices to be explored in the future.
Chapter 6. Summary and Outlook

6.1 Summary

The goal of this dissertation is to explore the novel optical and electronic properties of Layered Transition Metal Chalcogenide (LTMC) materials. I am especially interested in those could be exfoliated into extremely thin layers. As these material’s thickness reduces, new properties such as change in band structures may emerge. Also these two dimensional or quasi-two dimensional materials make novel device structures possible, thus opens up possibility for fundamental research as well as future technology applications. The materials I studied include LTMC semiconductors such as MoS$_2$, WS$_2$, MoSe$_2$, and metallic LTMC Bi$_2$Te$_3$.

Specifically, I have studied direct-indirect bandgap transition in LTMC semiconductors. Often, the LTMC semiconductors show indirect-direct bandgap transition around their monolayer limit. Interestingly, in MoSe$_2$, its direct-indirect bandgap are almost degenerate in few-layer limit, and a thermally induced crossover is observed. In chapter 1, I have presented my study on this novel phenomenon. I have employed characterization techniques such as Raman spectroscopy and photoluminescence technique to probe the change in structural interaction and optical properties of LTMC at various temperatures. Theoretical explanations involving DFT calculation is also discussed.

Then I continue to explore the gas ambient effect on the photoluminescence (PL) properties of LTMC materials. The large surface area of LTMC monolayer semiconductors makes them sensitive to the ambient. We noticed this and systematically studied the effect of thermal annealing and electrical gating on the PL spectrum of monolayer MoS$_2$. By understanding the physics, I found a strategy to reversibly modulate the PL intensity of MoS$_2$ by orders of magnitude. Interestingly, these modulations are directly induced by gas molecule physically absorbed on the defect site of MoS$_2$, which depletes the free electrons and enables efficient band edge photoluminescence.

In Chapter 4, I explored the idea of using monolayer TMC material as the elastic insulating barrier to realize the non-impact tunneling nano-electro-mechanical (t-NEM) switches. The ultrathin body thickness and defect free LTMC monolayers are ideal tunneling barrier medium with intrinsic elastic property. As I have presented in this chapter, by applying a pressure to monolayer MoS$_2$, its vertical tunneling resistance could be modulated by 4 orders of magnitude. At the end of this chapter, I also described a device schematic that is more practical for real device application.

For non-semiconducting layered TMC materials, I chose Bi$_2$Te$_3$ as the model material, not only because of its layered structure, but also for its exotic electric transport properties. Bi$_2$Te$_3$ is a prototypical topological insulator, i.e. the conduction on the surface is provided by topologically protected surface states, which has a massless Dirac like dispersion, with spin and momentum degree of freedom interlocked. The layered nature of Bi$_2$Te$_3$ allows me to exfoliate them into high quality thin flakes. By creating a dense nanoscale antidote array, I can successfully modify...
the transport properties of Bi$_2$Te$_3$. Periodic magneto resistance oscillations are observed, and correlated with the structure we introduced.

In summary, I have presented my PhD research of novel optical and electrical properties of layered LTMC in this dissertation. The first three subtopics focus on the LTMC semiconductors, including their novel optical and electrical properties originate from the reduced thickness. The last subtopic focused on the properties of metallic LTMC, Bi$_2$Te$_3$, a traditional material with newly discovered properties. I believe my results on the optical and electrical properties of LTMC would contribute to this rapidly developing research field.

8.2 Outlook

In my study, I focused on high quality thin flakes which are mechanically exfoliated from the bulk crystal. However, by no means, we should conclude the ultrathin LTMC materials cannot be fabricated by more scalable methods such as CVD, or chemical exfoliation. In the most recent two years, we see significant improvement about the material quality from these scalable synthesis routes. A wealth of new properties has been discovered in high quality exfoliated LTMC materials. However, can we reproduce these results with CVD grown monolayer LTMC materials? How can we reliably integrate these new, ultrathin materials into the electronic industry process? All these questions merits serious study before these materials can be proven useful for our future technology.

In my thesis, I have briefly mentioned our work on the exfoliated FeTe$_{0.5}$Se$_{0.5}$ nanowires. Limited by our time and recourses, I was unable to systematically finish this study. The questions are, how the superconductivity of this material would be affected by the reduced dimension? Also, the ultrathin body of exfoliated flakes implies that the carrier concentration in FeTe$_{0.5}$Se$_{0.5}$ can be effectively controlled by external electric field. This is unique compared with other bulk superconductors. How will the Tc change as a function of carrier concentration? Can we observe a “dome-like” curve as observed in chemically doped bulk samples? These questions are both interesting and important, since we may be able to build a superconductor switch which could be modulated by external electric field, much like in an FET. However, measures should be taken to prevent the oxidization of these ultrathin materials.
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