Synthesis and device applications of atom-thin semiconducting chalcogenides

Fu, Qundong

2018

Fu, Q. (2018). Synthesis and device applications of atom-thin semiconducting chalcogenides. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/87458>

<https://doi.org/10.32657/10220/46749>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**SYNTHESIS AND DEVICE APPLICATIONS OF ATOM-THIN
SEMICONDUCTING CHALCOGENIDES**

FU QUNDONG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

SYNTHESIS AND DEVICE APPLICATIONS OF ATOM-THIN SEMICONDUCTING CHALCOGENIDES

FU QUNDONG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

13/08/2018

.....

Date

Fu Qundong

.....

FU QUNDONG

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

13/08/2018

.....
Date

.....
Asst. Prof. Zheng Liu

Authorship Attribution Statement

This thesis contains material from 1 paper published in and 1 paper submitted to the following peer-reviewed journals where I was the first author.

Chapter 4 is published as Qundong Fu, Xiaowei Wang, Jiadong Zhou, Juan Xia, Qingsheng Zeng, Danhui Lv, Chao Zhu, Xiaolei Wang, Yue Shen, Xiaomin Li, Younan Hua, Fucui Liu*, Zexiang Shen, Chuanhong Jin*, and Zheng Liu*. One-Step Synthesis of Metal/Semiconductor Heterostructure NbS₂/MoS₂, *Chem. Mater.*, **2018**, 30 (12), 4001–4007. DOI: 10.1021/acs.chemmater.7b05117.

The contributions of the co-authors are as follows:

- Dr. Jiadong Zhou and I proposed the idea.
- I prepared all the materials.
- Xiaowei Wang and I analyzed the data and composed the manuscript drafts under the instruction of Professor Chuanhong Jin and Asst. Prof. Zheng Liu.
- The manuscript was revised by Dr. Fucui Liu, Chao Zhu, Professor Chuanhong Jin and Asst. Prof. Zheng Liu.
- Dr. Juan Xia performed the Raman spectra and mapping experiments.
- Dr. Qingsheng Zeng helped to obtain the SEM images.
- Xiaowei Wang and Dr. Danhui Lv conducted the STEM characterization. Xiaowei Wang analyzed the STEM data.
- Yue Shen, Xiaomin Li and Dr. Younan Hua conducted the XPS characterization.
- Dr. Qingsheng Zeng and Chao Zhu conducted the device fabrication and measurement.
- I conducted the PL single spectrum and mapping, OM and AFM characterization.
- Asst. Prof. Zheng Liu draw the schematic figures.

Chapter 5 is published as Qundong Fu, Chao Zhu, Xiaoxu Zhao, Xingli Wang, Apoorva Chaturvedi, Chao Zhu, Xiaowei Wang, Qingsheng Zeng, Jiadong Zhou, Fucui Liu*, Tay

Beng Kang, Hua Zhang, Stephen. Pennycook*, and Zheng Liu*. Ultrasensitive Phototransistor Based on 2D Bi₂O₂Se on Silicon Substrates, *Adv. Mater.*, **2018**.

The contributions of the co-authors are as follows:

- I proposed the idea and prepared all the materials.
- I analyzed the data and composed the manuscript drafts under the instruction of Dr. Fucai Liu and Asst. Prof. Zheng Liu. The manuscript was revised by Dr. Fucai Liu, Chao Zhu and Asst. Prof. Zheng Liu.
- Chao Zhu, Dr. Xiaowei Wang and Dr. Qingsheng Zeng conducted the device fabrication and measurement.
- Xiaoxu Zhao and Dr. Chao Zhu conducted the STEM characterization.
- Dr. Xingli Wang propose the idea of PS-assisted transfer and I conducted the experiments.
- Dr. Qingsheng Zeng helped to obtain the SEM image and EDS data.
- Miss Xingbin Jiang, Asst. Prof. Zheng Liu and I draw the schematic figures.

13/08/2018

.....
Date

.....
FU QUNDONG

Abstract

The ongoing scaling of silicon-based metal-oxide-semiconductor field-effect transistor is hindered by the serious short channel effect in sub-10 nm channel length. The discovery of graphene raised the booming development of 2D materials which have the merits of high mobility, efficient current regulation and high level of integration. However, the performance of 2D materials in electronic and optoelectronic applications still need to be improved, which is the aim, such as high mobility, high sensitivity and high gain, of this thesis.

Firstly, the aim of the first work is to improve the FET performance of MoS₂ via contact engineering of metal/semiconductor (M/S) vdW heterostructure with an atomically sharp interface prepared by CVD method. M/S vdW contact has shown great advantages, such as good stability, larger size and clean interface, in the improvement of M/S contact. In the CVD synthesis, M/S TMDC vdW heterostructures were less explored due to the high melting points and low chemical reactivity of metal oxide feedstocks and the crystal lattice mismatch. In this work, for the first time, the M/S TMDC vdW heterostructure NbS₂/MoS₂ was synthesized via a one-step halide-assisted CVD method. OM, SEM and XPS were used to identify the M/S vdW heterostructure. This method provides high crystal quality and clean interface of the heterostructure, confirmed by STEM characterization. A growth mechanism was proposed that MoS₂ finished the growth first and subsequently served as a superior substrate for the growth of NbS₂, verified by Raman mapping. The PL and device measurement provided physical supports of the M/S vdW heterostructure.

Secondly, the aim of the second work is to achieve high photodetector performance of Bi₂O₂Se via transferring high-quality Bi₂O₂Se onto 280 nm SiO₂/Si substrate (Si substrate) by a non-corrosive method. In the chasing of high-mobility 2D semiconductors, competitive candidate CVD-grown Bi₂O₂Se has superior stability and high mobility, which surpass that of MoS₂. However, the photodetector performance of Bi₂O₂Se regarding on/off ratio and specific detectivity was limited by the large dark current. Compared with f-mica substrate, Si substrate possesses inherent back gating, which could be used to reduce the

dark current. However, the hazardous and corrosive HF will etch Bi₂O₂Se during the transfer, which has been verified by OM, Raman and STEM characterizations. Therefore, a non-corrosive PS-assisted method was developed. The as-transferred Bi₂O₂Se retained a high quality and showed ultrasensitive phototransistors performance, including high responsivity of $3.5 \times 10^4 \text{ AW}^{-1}$, high photoconductive gain of 8×10^4 , and fast response rate of sub-millisecond. On Si substrate, the dark current could be reduced to several pA via back gating, which yields an ultrahigh specific detectivity of 9.0×10^{13} Jones. This is one of the highest values among 2D material photodetectors and two orders of magnitude higher than that of other CVD-grown 2D materials.

Thirdly, the aim of this work is to improve the performance and stability of the CMOS inverters based on 2D semiconductors. Although many 2D semiconductors have shown high CMOS inverter performance, such as MoS₂, WSe₂, MoTe₂, their stability is not satisfactory. In this work, CMOS inverters based on high-mobility and stable n-type Bi₂O₂Se were demonstrated with clear signal inversion on both f-mica and silicon substrate. On f-mica substrate, under the gating of ion liquid, a gain of 3.5 can be obtained at the supply voltage of only 1.0 V. Dynamic voltage response at the frequency of 100 Hz shows good response with almost no voltage lose. On silicon substrate, the CMOS inverter showed a high gain of 2.2 at the supply voltage of 5.0 V, a high noise margin of 5.2 V_{DD} and a low power consumption at the order of 10^{-9} W.

Lay Summary

The miniaturization of the microchip is encountering the problem of high power consumption. The chasing of new candidates has been a hot research topic in recent few decades. The discovery of graphene raised the boom development of atomically thin materials (2D materials) because these materials have high switch rate, efficient current control and high level of integration. Nevertheless, their performance in electronic and optoelectronic applications still need to be improved, which is the aim of this thesis.

The contact between the metal electrode and the semiconducting 2D materials is key to the performance of the transistors based on 2D materials. It has been found that the contact between metallic 2D materials and semiconducting 2D materials are much better than the metal and 2D material contact. The difficulty of this 2D metallic and semiconducting contact is the synthesis of the metallic 2D materials. In this work, a one-step method has been developed to synthesize the material with 2D metallic and semiconducting contact. Many characterization techniques have proved the high quality of the obtained materials. Moreover, this material with 2D metallic and semiconducting contact could be prepared with large size. Therefore, it is an essential step for the improvement in the contacts of 2D materials.

A new 2D semiconductor has shown very good response in the light detection. However, this material has high power consumption even when it is not working. By transferring this material to a new substrate, the power consumption could be effectively reduced. Unfortunately, this material will be etched during the conventional transfer. In this work, a non-corrosive method has been developed to transfer this material onto the new substrate. It is found that the as-transferred material maintained a high quality. In addition, the performance of this material in the detection of light has been significantly improved. Therefore, a high-performance photodetector with low power consumption has been demonstrated.

Currently, 2D materials used for some specific electronic application were limited by their poor stability. As this material has superior stability and at the same time high-speed switch, it was applied in an electronic application. It has been proved that this material has shown high potential, but the performance is the level it should be. The reason may be the dielectric layer which plays a significant role in this application. In the future, by encapsulating better dielectric layer, the performance in this application should be much improved.

Acknowledgements

Time of PhD student flies, like what is written in Mayday's lyric - 'Just an eye blink, it comes to the final chapter.' At the end of this period, I would like to thank the people I encountered in my life.

First of all, I would like to express my sincere gratitude to my supervisor, Asst. Prof. Zheng Liu and School of Materials Science and Engineering of Nanyang Technological University for giving me this opportunity to begin my research life here. I thank Asst. Prof. Zheng Liu for his guidance, encouragement and clear logical analysis in research. I thank him for providing all the resources and cooperative peers for the characterization and measurement. I also thank him for his patience and for sharing his experience and attitude in life.

Special thanks are conveyed to my thesis advisory committee members Prof. Xiaodong Chen, Assoc. Prof. Yizhong Huang, Assoc. Prof. Shuzhou Li for their guidance and patience, and to Prof. Zexiang Shen, Prof. Ting Yu, Prof. Hua Zhang for their help in research, and to Prof. Christian Kloc, Assoc. Prof. Jianyi Lin, Assoc. Prof. Can Xue, Assoc. Prof. Zhili Dong for the course teaching, and to Prof. Stephen John Pennycook, Prof. Chuanhong Jin and Prof. Guangtong Liu for their cooperation work.

I am grateful to my group members Dr. Fucai Liu, Dr. Jiadong Zhou, Mr. Chao Zhu, Dr. Hong Wang, Dr. Xiaowei Wang, Dr. Qingsheng Zeng, Dr. Haiyong He, Dr. Peng Yu, Dr. Yongmin He, Dr. Chao Zhu, Dr. Ya Deng, Dr. Xuewen Wang, Dr. Lu Zheng and cooperation partners Dr. Xingli Wang, Dr. Juan Xia, Dr. Yu Chen, Dr. Danhui Lv, Miss Xiaowei Wang, Mr. Xiaoxu Zhao, Dr. Apoorva Chaturvedi, Mr. Rohit Abraham John, Miss Jian Cui, Miss Yue Shen, Mr. Hongwei Hu, Dr. Bingbing Chen. I am also grateful to Mr. Bowei Zhang, Mr. Patrick Lai Chee Hoong and Mr. Nelson Ng Soon Ping, Ms Christina Lu Bee Lay and Miss Serika Cara Navarro. I appreciate your help in experiment and life and I enjoy the time with you.

I thank to the Funding Agency of the work in this thesis Singapore National Research Foundation, State Key Laboratory of Silicon Materials in Zhejiang University, National Basic Research Program in China.

Finally, I would like to thank my families and friends. I thank my parents for raising me up, educating me and supporting me for higher education because they think education is important even though they do not know how important it could be. I thank my friend Yijing Fu for her encouragement before my PhD tour. She brought me into the world of Mayday and I hope in the future she and I can be as 'tough' and 'stubborn' as Mayday.

Table of Contents

Abstract	i
Lay Summary	iii
Acknowledgements	v
Table of Contents	vii
Table Captions	xi
Figure Captions	xiii
Abbreviations	xix
 Chapter 1 Introduction.....	 1
1.1 Problem Statement and Hypothesis.....	2
1.2 Objectives and Scope	4
1.3 Dissertation Overview	5
1.4 Findings and Outcomes/Originality	7
References.....	8
 Chapter 2 Literature Review	 11
2.1 The Rise of 2D High-mobility Semiconductors.....	12
2.2 Contact Engineering of 2D TMDCs.....	15
2.2.1 The Compositions, Structures and Properties of 2D TMDCs.....	15
2.2.2 The Contact Engineering in MoS ₂ FETs.	18

2.2.3	Problems in the Preparation of 2D vdW Contact.....	28
2.3	Synthesis and Applications of High-mobility Bi ₂ O ₂ Se	35
2.3.1	Exploration of High-mobility 2D Semiconductors	35
2.3.2	Discovery and Synthesis of High-mobility 2D Bi ₂ O ₂ Se	40
2.2.3	Problems and Opportunities in Applications of 2D Bi ₂ O ₂ Se	43
2.4	Questions to be Answered Based on Literature Review	46
	References	47
Chapter 3 Experimental Methodology		55
3.1	The Rational for the CVD Synthesis of 2D Materials	56
3.2	Characterization Techniques	57
3.2.1	Optical Microscopy.....	58
3.2.2	Atomic Force Microscopy	59
3.2.3	Raman and Photoluminescence Spectroscopy	61
3.2.4	X-ray Photoelectron Spectroscopy	66
3.2.5	Scanning Electron Microscopy	68
3.2.6	Scanning Transmission Electron Microscopy	71
3.3	Device Fabrication and Measurement.....	77
	References	79
Chapter 4 Synthesis and Contact Engineering of MoS₂		81
4.1	Introduction	82
4.2	Experimental Methods	84
4.2.1	CVD Synthesis of NbS ₂	84
4.2.2	CVD Synthesis of NbS ₂ /MoS ₂	84

4.2.3	XPS, SEM and Raman Characterizations	85
4.2.4	Transfer and STEM Characterization and Image Simulation	85
4.2.5	Devices Fabrication and Measurement	86
4.3	Results and Discussions	86
4.3.1	Halide-assisted CVD Synthesis and Characterization of NbS ₂	86
4.3.2	CVD Synthesis and Characterization of NbS ₂ /MoS ₂	88
4.3.3	Possible Mechanism for the Growth of NbS ₂ /MoS ₂	94
4.3.4	Physical Properties Characterizations of NbS ₂ /MoS ₂	98
4.4	Conclusions	100
	References	101
Chapter 5 Synthesis and Phototransistor Application of Bi₂O₂Se.....		105
5.1	Introduction	106
5.2	Experimental Methods	107
5.2.1	CVD Synthesis of Bi ₂ O ₂ Se on f-mica	107
5.2.2	AFM, SEM EDS and Raman Characterizations	108
5.2.3	Transfer of Bi ₂ O ₂ Se Onto Cu Grid and STEM Characterization	108
5.2.4	PS-assisted Transfer of Bi ₂ O ₂ Se Onto Si Substrate	108
5.2.5	Devices Fabrication and Measurement	109
5.3	Results and Discussions	109
5.3.1	Synthesis and Characterization of Bi ₂ O ₂ Se on f-mica	109
5.3.2	PS-assisted Transfer of Bi ₂ O ₂ Se onto Si substrate	112
5.3.3	The Phototransistor Application of Bi ₂ O ₂ Se on Si Substrate	116
5.3.4	Direct CVD Synthesis of Bi ₂ O ₂ Se on Si Substrate and its Application	122

5.4	Conclusions	125
	References	126
 Chapter 6 High-performance CMOS Inverters Based on n-type Bi₂O₂Se and p-type WSe₂129		
6.1	Introduction	130
6.2	Experimental Methods	131
6.2.1	CVD Synthesis of Bi ₂ O ₂ Se on f-mica.....	131
6.2.2	AFM and Raman Characterizations.....	131
6.2.3	Transfer of Bi ₂ O ₂ Se Onto Cu Grid and STEM Characterization	132
6.2.4	PS-assisted Transfer of Bi ₂ O ₂ Se Onto Si Substrate.....	132
6.2.5	Devices Fabrication and Measurement.....	133
6.3	Results and Discussions	133
6.3.1	Synthesis and Characterization of Bi ₂ O ₂ Se on f-mica	133
6.3.2	The CMOS Inverter Application of Bi ₂ O ₂ Se on f-mica Substrate	136
6.3.3	The CMOS Inverter Application of Bi ₂ O ₂ Se on Si Substrate	140
6.4	Conclusions	143
	References	143
 Chapter 7 Conclusions and Recommendations for Future Work145		
7.1	Conclusions	146
7.2	Discussions on the Hypotheses	149
7.3	Future Work and Recommendations.....	151
	References	152

Table Captions

Table 2.1 The summary of melting points (MP) of the metal oxides (IV-VI B) and elementary substance (X B).

Table 2.2 DFT calculation prediction of high-mobility 2D semiconductors at RT.

Figure Captions

Figure 2.1 2010 ITRS summary of microprocessing unit half pitch and gate length trends.

Figure 2.2 The crystal structure and property of graphene.

Figure 2.3 Element summary of TMDCs (MX_2).

Figure 2.4 Summary of general crystal structures of TMDCs.

Figure 2.5 The orbital splitting of degenerated d orbitals and electron filling in CFT.

Figure 2.6 The FET performances of MoS_2 .

Figure 2.7 The contact and band structure between the metal electrode and the semiconductor channel.

Figure 2.8 The reason for the FLP in layered TMDCs.

Figure 2.9 The contact improvement by phase engineering.

Figure 2.10 The contact improvement by chemical doping.

Figure 2.11 The contact improvement by vdW contact.

Figure 2.12 The contact improvement by vdW contact (metal/semiconductor heterostructure).

Figure 2.13 The $\text{NbS}_2/\text{MoS}_2$ vdW heterostructure.

Figure 2.14 The process of ME to prepare 2D TMDC vdW heterostructure.

Figure 2.15 The selenization of the pre-deposited metal precursors.

Figure 2.16 The WSe₂/MoSe₂ heterostructure prepared by the step-by-step sequential growth method.

Figure 2.17 The WS₂/MoS₂ vdW heterostructure prepared by the one-step method.

Figure 2.18 The samples produced by metal chlorides precursors.

Figure 2.19 The band structure and mobility of 2H-MoTe₂ and 1T-HfSe₂.

Figure 2.20 The band structure and mobility of 1T-PtSe₂ and PdSe₂.

Figure 2.21 Black phosphorus.

Figure 2.22 γ -indium selenide.

Figure 2.23 Bi₂O₂Se.

Figure 2.24 The CVD synthesis and characterization of Bi₂O₂Se.

Figure 2.25 The photodetector application of Bi₂O₂Se.

Figure 2.26 The CMOS inverter application of TMDCs.

Figure 3.1 CVD processes of the TMDC growth.

Figure 3.2 The working principles of OM.

Figure 3.3 The working principle of AFM.

Figure 3.4 The working principle of Raman spectroscopy.

Figure 3.5 The DFT simulation of band formation of MoS₂.

Figure 3.6 Verification of the band structure by PL spectrum.

Figure 3.7 The working principle of XPS.

Figure 3.8 The XPS characterization of TMDCs.

Figure 3.9 The electron-specimen interaction volume.

Figure 3.10 The schematic setup of SEM.

Figure 3.11 The schematic setup of TEM.

Figure 3.12 Three major types of electrons in TEM and the Fraunhofer diffraction effect.

Figure 3.13 The aberration correction of STEM.

Figure 3.14 The applications of STEM in the characterization of TMDC.

Figure 3.15 The device fabrication (EBL) processes.

Figure 4.1 Schematic of the CVD setup for the synthesis of NbS₂.

Figure 4.2 Synthesis of large-area layered NbS₂ single crystal.

Figure 4.3 Schematic of the CVD setup for the synthesis of NbS₂/MoS₂.

Figure 4.4 NbS₂/MoS₂ vdW heterostructure.

Figure 4.5 Intensity line profiles of few-layer NbS₂/MoS₂ sample.

Figure 4.6 Atomic structure of the NbS₂/MoS₂ vdW heterostructure.

Figure 4.7 Atomic structure of the NbS₂ and MoS₂ heterostructure.

Figure 4.8 Comparison of the experimental image with simulation images of H-type and R-type stacking structures.

Figure 4.9 Quantitative analysis of intensity profiles (along lines in region 1, 2 and 3) and comparison of experimental images (center) with simulation images of H-type (left) and R-type (right) stacking structure.

Figure 4.10 Optical images of NbS₂/MoS₂ vdW heterostructure with different morphologies.

Figure 4.11 Proposed mechanism for the vertical heterostructure growth.

Figure 4.12 Raman spectra and mapping analysis of NbS₂/MoS₂ vdW heterostructure.

Figure 4.13 Multipeak fitting analysis of the Raman peak of NbS₂/MoS₂ at 379.2 cm⁻¹.

Figure 4.14 Photoluminescence (PL) characterization of the NbS₂/MoS₂ heterostructure.

Figure 4.15 Device performance of NbS₂/MoS₂.

Figure 5.1 Schematic of the CVD setup for the synthesis of Bi₂O₂Se on f-mica.

Figure 5.2 Synthesis and characterization of Bi₂O₂Se.

Figure 5.3 STEM characterization of $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.4 Demonstration of the etching effect of HF acid.

Figure 5.5 STEM of the etched $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.6 PS-assisted transfer of $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.7 Characterization of the transferred $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.8 AFM, SEM and EDS characterization of the transferred $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.9 Photoresponse performances of the transferred $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.10 Dynamic time response of $\text{Bi}_2\text{O}_2\text{Se}$ phototransistor.

Figure 5.11 Schematic of the $\text{Bi}_2\text{O}_2\text{Se}$ phototransistor on Si substrate.

Figure 5.12 Gate-tunable photoresponse of the transferred $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.13 Characterizations of direct-method $\text{Bi}_2\text{O}_2\text{Se}$ on Si substrate.

Figure 5.14 The FET and photoresponse performances of the direct-method $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.15 The power dependence of the photoresponse properties of the direct-method $\text{Bi}_2\text{O}_2\text{Se}$ under various gate voltages.

Figure 6.1 Schematic of the CVD setup for the synthesis of $\text{Bi}_2\text{O}_2\text{Se}$ on f-mica.

Figure 6.2 Schematic of the transfer process of $\text{Bi}_2\text{O}_2\text{Se}$ using HF acid for TEM characterization.

Figure 6.3 Synthesis and characterization of $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 6.4 STEM characterization of $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 6.5 FET performance of $\text{Bi}_2\text{O}_2\text{Se}$ on f-mica.

Figure 6.6 FET performances of WSe_2 and $\text{Bi}_2\text{O}_2\text{Se}$ in a CMOS inverter.

Figure 6.7 CMOS transfer curves and gains under different V_{DD} .

Figure 6.8 The power consumption of the CMOS inverter under different V_{DD} .

Figure 6.9 Dynamic switch behavior of the CMOS inverter under different frequencies.

Figure 6.10 Schematic of the non-corrosive PS-assisted transfer process.

Figure 6.11 FET performances of WSe_2 and $\text{Bi}_2\text{O}_2\text{Se}$ in a CMOS inverter on Si substrate.

Figure 6.12 CMOS transfer curves and gains under different V_{DD} .

Figure 6.13 The power consumption of the CMOS inverter under different V_{DD} .

Abbreviations

0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
vdW	van der Waals
TMDC	Transitional Metal Dichalcogenide
CDW	Charge Density Wave
SHG	Second Harmonic Generation
CVD	Chemical Vapor Deposition
ME	Mechanical Exfoliation
CVT	Chemical Vapor Transport
M/S	Metal/Semiconductor
S/S	Semiconductor/Semiconductor
SBH	Schottky Barrier Height
FLP	Fermi Level Pinning
MIGS	Metal Induced Gap State
MOSFET	Metal Oxide Semiconductor Field-Effect Transistor
FET	Field-Effect Transistor
CMOS	Complementary Metal Oxide Semiconductor
MESFET	Metal Semiconductor Field-Effect Transistor
EELS	Electron Energy Lose Spectroscopy
SKPM	Scanning Kelvin Probe Microscopy
OM	Optical Microscopy
SEM	Scanning Electron Microscopy
AFM	Atomic Force Microscopy
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
EDS	Energy Dispersive X-ray Spectroscopy
PL	Photoluminescence

XPS	X-Ray photoelectron spectroscopy
ARPES	Angle-Resolved Photoemission Spectroscopy
N.A.	Numerical Aperture
IR	Infrared Spectroscopy
BZ	Brillouin Zone
BSE	Back Scattered Electrons
SE	Secondary Electrons
AE	Auger Electrons
TE	Transmitted Electrons
CL	Cathodoluminescence
ADF	Annular Dark-Field
HAADF	High Angle Annular Dark-Field
Z	Atomic Number
FFT	Fast Fourier Transformation
SAED	Selected Area Electron Diffraction
EBL	Electron Beam Lithography
PS	Polystyrene
PDMS	Polydimethylsiloxane
BOE	Buffered Oxide Etchant
BP	Black Phosphorus
LTPS	Low Temperature Polycrystalline Silicon
RT	Room Temperature
h-BN	Hexagonal Boron Nitride
DC	Direct Current
AC	Alternating Current
ITRS	International Technology Roadmap for Semiconductors
HCP	Hexagonal Close Packing
FCC	Face-Centered Cubic Close Packing
CFT	Crystal Field Theory
HOMO	Highest Occupied Molecular Orbital
DOS	Density of State

DFT	Density Functional Theory
S.S	Subthreshold Slope
CBM	Conduction Band Minimum
VBM	Valence Band Maximum
STO	Strontium Titanate (SrTiO ₃)

Chapter 1

Introduction

This chapter will provide a brief introduction to the framework of this thesis: First of all, the hypotheses of this thesis, such as the chemical vapor synthesis of 2D transitional metal dichalcogenides metal/semiconductor vdW heterostructure and ternary compound, the non-corrosive transfer of $\text{Bi}_2\text{O}_2\text{Se}$, the back gate contribution to the photoresponse performance of $\text{Bi}_2\text{O}_2\text{Se}$ and the CMOS inverter performance of $\text{Bi}_2\text{O}_2\text{Se}$ will be discussed; Based on these, the objectives and scope of this thesis will be described; Then the overview of this dissertation will be provided; And finally, the findings and outcomes are summarized.

1.1 Problem Statement and Hypothesis

As the miniaturization of silicon devices is hindered by the increasing leaking current,^[1] two-dimensional (2D) materials have drawn tremendous interests in the next-generation electronic and optoelectronic application^[2-5] owing to their diverse electronic properties,^[6,7] dangling free surface and atomic thickness, which brings the virtues of high mobility, efficient vertical gate regulation, high integration level. For instance, transitional metal dichalcogenides (TMDCs), ranging from superconducting NbSe₂,^[8,9] semimetallic MoTe₂,^[10] semiconducting MoS₂^[3] and charge density wave (CDW) TaS₂,^[11] provide wide choices for researchers to explore. Bi₂O₂Se, a new member of 2D materials, which possesses a high mobility while has superior stability in ambient condition,^[12-14] shows high potential in lots of applications. In the preparation of 2D materials, compared with the mechanical and liquid exfoliation methods, chemical vapor deposition (CVD) has proven surpassing advantages in the synthesis of TMDC van der Waals (vdW) heterostructure (larger scale, interlayer orientation control and clean interface)^[15-19] and also the synthesis of ternary compounds (good chemical stoichiometric ratio).^[20] Here the hypothesis is that CVD could be applied in the synthesis of novel metal/semiconductor TMDC vdW heterostructure and new 2D ternary compounds. Then the applications of these new 2D vdW heterostructures and ternary compounds will be explored.

TMDC vdW heterostructure, vertically stacked by diverse TMDC, have shown great potentials on novel physical applications and next generation optoelectronic devices such as atomically thin P-N junction.^[21-23] However, to date, almost all the TMDC vdW heterostructures prepared via CVD method are focused on semiconductor/semiconductor vdW heterostructure^[16-19] while metal/semiconductor (M/S) counterparts are less explored. The reason might be the high melting point and low chemical reactivity of metal oxide precursors and the crystal lattice parameters mismatch in the preparation of M/S vdW heterostructures. Hence, the hypothesis here is that by utilizing fluxing reagent,^[27-30] the drawbacks of the metal precursors will be overcome and the sequent growth of MoS₂ and NbS₂ could be achieved via regulating the growth time and temperature. As M/S vdW contact owns an atomically sharp interface, which is expected to eliminate the Fermi level

pinning effect.^[24] Therefore, the hypothesis here is by choosing suitable metallic TMDC with suitable work function, this M/S vdW contact will lead to a good contact between the metal and the semiconductor, which will definitely improve the field-effect transistor (FET) performance of the TMDC semiconductor.^[25,26]

Although graphene has a very high mobility,^[31] the lack of an energy band gap leads to a high off current and small on/off ratio, which is not suitable for the application of photodetector.^[32] Thus, the seeking of high mobility 2D material with a finite band gap has become a hot research topic.^[33,34] While MoS₂ has limited performance even after the device optimization. the new competitive candidate Bi₂O₂Se has suitable band gap and high mobility. Bi₂O₂Se has been prepared with a large scale on the fluorine mica (f-mica) substrate and also proved to have good photoresponsivity.^[35] However, the large dark current limits its performance regarding on/off ratio and specific detectivity. Although a gate configuration can be used to regulate the dark current, it is difficult to realize on f-mica substrate in the photoresponse application. As the 280 nm SiO₂/Si substrate (Si substrate) possesses inherent back gating, if Bi₂O₂Se can be transferred onto Si substrate, not only the optoelectronic performance could be much improved, but also the applications of Bi₂O₂Se will be broadened since almost all integrated circuits are rooted in the silicon substrate. In the wet transfer of Bi₂O₂Se, hydrofluoric acid (HF) becomes the only f-mica etchant, due to the inertness of f-mica and strong electrostatic interaction between the sample and the substrate. Nevertheless, the highly corrosive HF which has the ability to penetrate issues is hazardous to handle.^[36] More importantly, since HF is well known as one component of typical buffered oxide etchant (BOE), Bi₂O₂Se will be inevitably etched by HF during the transfer process.^[37] Hence, the hypothesis here is CVD-grown Bi₂O₂Se could be transferred onto silicon substrate via a save and non-corrosive method. And the hypothesis here is the back gating provided by silicon substrate will lead to better performance of the phototransistor, especially the dark current and specific detectivity.

Bi₂O₂Se has shown high FET performance (high mobility and high on/off ratio), which is of high potential in amounts of electronic applications, such as complementary metal oxide semiconductor (CMOS) inverters. As Bi₂O₂Se shows n-type behavior, a p-type TMDC

WSe₂ was chosen to fabricate the CMOS inverter. The hypothesis here is that the high-performance n-type and p-type channel will match well (good symmetry of the FET curve) and show high CMOS inverter performance with a high gain. Also, different dielectric layer is expected to bring different performance when keeping the same channel material. Moving further, Bi₂O₂Se on the silicon substrate was also used to fabricate CMOS inverter and to examine the possibility of integration with the state-of-the-art silicon technologies.

1.2 Objectives and Scope

Based on the hypotheses mentioned above, the objectives and scope will be discussed below:

First, with the addition of NaCl, the drawbacks of the metal oxide (Nb₂O₅) precursor (high melting point and low chemical reactivity) will be overcome, as metal oxychloride (NbOCl₃) has much lower melting point and higher chemical reactivity than metal oxide. After the growth condition (time and temperature) is figured out, MoS₂ is chosen as the epitaxy growth substrate since MoS₂ shares close crystal lattice parameters and same anion with NbS₂. Moreover, the growth temperature of MoS₂ is much lower than that of NbS₂, which allows the sequential growth to form a vdW heterostructure instead of in-plane alloy. Besides, this sequential growth which reduces the possibility of interlayer alloying will produce a high-quality interface. This high-quality interface in the vdW heterostructure will facilitate the contact between the metal and the semiconductor.

Second, after the successful synthesis of Bi₂O₂Se using Bi₂Se₃ and Bi₂O₃, material characterization, such as optical microscopy (OM), atomic force microscopy (AFM), Raman spectrum and scanning transmission electron microscopy (STEM) will be conducted to verify the quality of the obtained sample. Also, the etching effect of HF acid in the wet transfer process will be verified by the corresponding characterization techniques. Thus, a non-corrosive method utilizing polystyrene (PS) will be developed to transfer the CVD-grown Bi₂O₂Se onto silicon substrate. The as-transferred Bi₂O₂Se is expected to retain a high quality as the one on mica. In the photoresponse application, without gating,

the photoresponse will be tested concerning the I_d - V_d curves and on/off response under different illumination powers and the response time test will be also performed by using the mechanic chopper. Both high photoresponsivity and fast response rate are expected. Then, with the back gate of silicon substrate, the phototransistor performance will be evaluated regarding the I_d - V_g curves under different illumination powers. Both low dark current and high specific detectivity are expected.

Third, two types of samples will be used to fabricate the CMOS inverters, the Bi₂O₂Se on f-mica and the as-transferred Bi₂O₂Se on Si substrate, to examine the dielectric layer effect. For the sample on f-mica, WSe₂ will be transferred onto f-mica to form the p-FET. Under the gating of ionic liquid, both high mobility and good CMOS performance (high gain) are expected in the static behavior with a DC input. Also, the dynamic behavior with an AC input will be tested based on same device. For the as-transferred sample on Si substrate, using the back gate of Si substrate, the static behavior and power consumption will be also tested and is expected to have good performance. The dielectric layer effect will be examined by comparing the performances of these two types of devices.

1.3 Dissertation Overview

This thesis is aimed to improve the performance of 2D materials in electronic and optoelectronic applications, such as high mobility, high sensitivity and high gain. The first work is focused on the contact engineering via the preparation of metal/semiconductor TMDC vdW contact by one-step CVD method. To achieve this, how to overcome the drawbacks of the metal oxide precursors by adding NaCl to the metal precursors is addressed. The second work in this thesis addresses the substrate engineering to improve the photodetector performance of Bi₂O₂Se. This was completed by developing a safe and non-corrosive method to transfer high-mobility CVD-grown Bi₂O₂Se onto Si substrate. The third work in this thesis is to improve the performance and stability of the CMOS inverters based on 2D semiconductors.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literatures concerning the rise of 2D materials as promising building blocks of next-generation electronic and optoelectronic application, and the contact engineering of MoS₂ field-effect transistors, and the advantages of TMDC vdW contact, and the problems need to be solved in the preparation of TMDC vdW heterostructures, and the exploration of high-mobility 2D semiconductors, and the structure, properties and synthesis of Bi₂O₂Se, and the advantages of Bi₂O₂Se, and the problems and opportunities in the applications of Bi₂O₂Se.

Chapter 3 provides detailed discussion on: (i) the CVD setup used in the synthesis part, and the model and the growth determinants, and (ii) the principles of the characterization methods including OM, SEM and EDS, AFM, Raman (single spectrum and mapping), Photoluminescence (PL single spectrum and mapping), XPS, STEM imaging and EDS mapping, and (iii) the device fabrication process (electron beam lithography (EBL)) and the measurement details.

Chapter 4 elaborates the synthesis of 2D metal/semiconductor TMDC vdW heterostructure NbS₂/MoS₂ with a high-quality interface via a one-step CVD method. The high-quality interface provides a platform for the suppressing of the Fermi level pinning effect and the improvement of the metal/semiconductor contact. Detailly, this includes the breakthrough in the synthesis of metallic NbS₂, and for the first time, the synthesis of 2D M/S TMDC vdW heterostructure NbS₂/MoS₂, and the characterization of this heterostructure, and the proposed mechanism for the epitaxy growth.

Chapter 5 elaborates the CVD synthesis of high-quality Bi₂O₂Se on f-mica, the etching effect of HF acid during the wet transfer process and the new developed method for the transfer of Bi₂O₂Se onto Si substrate, and the ultrasensitive phototransistor performance of the as-transferred Bi₂O₂Se achieved with the assistance of the back gating of Si substrate.

Chapter 6 elaborates CMOS inverter performance based on n-type Bi₂O₂Se and p-type WSe₂ on both f-mica and silicon substrate, and the difference brought by the dielectric

layers (ion liquid on f-mica and SiO₂ on Si substrate).

Chapter 7 brings a conclusion to the whole thesis, addressing the outcomes again and analysing how these outcomes, to what extent, prove the hypotheses and what should be done next, and finally what are the opportunities in the future work.

1.4 Findings and Outcomes/Originality

Several novel outcomes in this thesis are summarized:

1. The role of NaCl in reducing melting point and improving chemical reactivity of Nb₂O₅ via forming NbOCl₃ has been proved in the synthesis of large area metallic NbS₂. And for the first time, 2D M/S TMDC vdW heterostructure NbS₂/MoS₂ has been prepared via a one-step CVD method and identified by OM, SEM, XPS. This one-step method provided high crystal quality and clean interface of the heterostructure, which was confirmed by STEM. The possible growth mechanism that owing to the difference of the growth temperature, MoS₂ finished the growth first and served as a superior epitaxy substrate for the growth of NbS₂ is proposed and examined by Raman spectrum and mapping. PL characterization and device measurement provide physical proofs of the M/S vdW junction. This method provides a high-quality metal/semiconductor interface for the improvement of the contact.

2. The etching effect of HF acid to Bi₂O₂Se during the transfer process has been verified by OM, Raman and STEM characterizations. Based on this, a new non-corrosive method with the assistance of PS has been developed to transfer Bi₂O₂Se onto Si substrate. High-performance phototransistors of the transferred Bi₂O₂Se have been demonstrated: (i) High responsivity of $3.5 \times 10^4 \text{ AW}^{-1}$; (ii) High photoconductive gain of 8×10^4 ; (iii) Fast response timescale of 0.308 ms for the rise and 0.448 ms for the decay times and (iv) With the back gating of silicon substrate, the dark current could be reduced to several pA, yielding an ultrahigh sensitivity with specific detectivity of 9.0×10^{13} Jones. Hence, the improvement of the photodetector performances by the back gating on Si substrate has been proved.

3. The CMOS inverters based on n-type Bi₂O₂Se and p-type WSe₂ have been demonstrated on both f-mica and silicon substrates. On f-mica, the gain of the inverter in the static measurement (DC) could be as high as 3.5 under the supply voltage of only 1.0 V. The dynamic measurement (AC) also showed very almost no voltage lose at the frequency of 100 Hz. On Silicon substrate, the CMOS inverter showed a high gain of 2.2 at the supply voltage of 5.0 V, a high noise margin of 5.2 V_{DD} and a low power consumption at the order of 10⁻⁹ W. Further optimizations such as the usage of high-mobility p-type material (2D tellurene), encapsulation of high- κ dielectric layer and improvement of the WSe₂ contact are properly to improve the performance of the Bi₂O₂Se based CMOS inverter.^[38-41]

References

- [1] P. S. Peercy, *Nature* **2000**, 406, 1023.
- [2] M. Liu, X. Yin, E. Ulin-Avila, B. Geng, T. Zentgraf, L. Ju, F. Wang, X. Zhang, *Nature* **2011**, 474, 64.
- [3] B. Radisavljevic, A. Radenovic, J. Brivio, i. V. Giacometti, A. Kis, *Nat. Nanotech.* **2011**, 6, 147.
- [4] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, H. Zhang, *ACS Nano* **2011**, 6, 74.
- [5] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, *Nat. Nanotech.* **2013**, 8, 497.
- [6] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotech.* **2012**, 7, 699.
- [7] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, *Nat. Chem.* **2013**, 5, 263.
- [8] X. Xi, Z. Wang, W. Zhao, J.-H. Park, K. T. Law, H. Berger, L. Forró, J. Shan, K. F. Mak, *Nat. Phys.* **2016**, 12, 139.
- [9] H. Wang, X. Huang, J. Lin, J. Cui, Y. Chen, C. Zhu, F. Liu, Q. Zeng, J. Zhou, P. Yu, *Nat. Commun.* **2017**, 8, 394.
- [10] K. Deng, G. Wan, P. Deng, K. Zhang, S. Ding, E. Wang, M. Yan, H. Huang, H. Zhang, Z. Xu, *Nat. Phys.* **2016**, 12, 1105.

- [11] Y. Yu, F. Yang, X. F. Lu, Y. J. Yan, Y.-H. Cho, L. Ma, X. Niu, S. Kim, Y.-W. Son, D. Feng, *Nat. Nanotech.* **2015**, 10, 270.
- [12] J. Wu, Y. Liu, Z. Tan, C. Tan, J. Yin, T. Li, T. Tu, H. Peng, *Adv. Mater.* **2017**, 29.
- [13] J. Wu, C. Tan, Z. Tan, Y. Liu, J. Yin, W. Dang, M. Wang, H. Peng, *Nano Lett.* **2017**, 17, 3021.
- [14] J. Wu, H. Yuan, M. Meng, C. Chen, Y. Sun, Z. Chen, W. Dang, C. Tan, Y. Liu, J. Yin, *Nat. Nanotech.* **2017**, 12, 530.
- [15] Y. H. Lee, X. Q. Zhang, W. Zhang, M. T. Chang, C. T. Lin, K. D. Chang, Y. C. Yu, J. T. W. Wang, C. S. Chang, L. J. Li, *Adv. Mater.* **2012**, 24, 2320.
- [16] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, *Nat. Mater.* **2014**, 13, 1135.
- [17] Y. Gong, S. Lei, G. Ye, B. Li, Y. He, K. Keyshar, X. Zhang, Q. Wang, J. Lou, Z. Liu, *Nano Lett.* **2015**, 15, 6135-6141.
- [18] X. Li, M.-W. Lin, J. Lin, B. Huang, A. A. Puretzky, C. Ma, K. Wang, W. Zhou, S. T. Pantelides, M. Chi, *Sci. Adv.* **2016**, 2, e1501882.
- [19] T. Zhang, B. Jiang, Z. Xu, R. G. Mendes, Y. Xiao, L. F. Chen, L. W. Fang, T. Gemming, S. L. Chen, M. H. Rummeli, L. Fu, *Nat. Commun.* **2016**, 7, 13911.
- [20] X. Duan, C. Wang, Z. Fan, G. Hao, L. Kou, U. Halim, H. Li, X. Wu, Y. Wang, J. Jiang, *Nano Lett.* 2015, 16, 264.
- [21] X. Hong, J. Kim, S.-F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, F. Wang, *Nat. Nanotech.* **2014**, 9, 682.
- [22] C. H. Lee, G. H. Lee, A. M. van der Zande, W. C. Chen, Y. L. Li, M. Y. Han, X. Cui, G. Arefe, C. Nuckolls, T. F. Heinz, J. Guo, J. Hone, P. Kim, *Nat. Nanotech.* **2014**, 9, 676.
- [23] P. Rivera, J. R. Schaibley, A. M. Jones, J. S. Ross, S. Wu, G. Aivazian, P. Klement, K. Seyler, G. Clark, N. J. Ghimire, *Nat. Commun.* **2015**, 6, 6242.
- [24] A. R. Kim, Y. Kim, J. Nam, H. S. Chung, D. J. Kim, J. D. Kwon, S. W. Park, J. Park, S. Y. Choi, B. H. Lee, J. H. Park, K. H. Lee, D. H. Kim, S. M. Choi, P. M. Ajayan, M. G. Hahm, B. Cho, *Nano Lett.* **2016**, 16, 1890.
- [25] S.-L. Li, K. Komatsu, S. Nakaharai, Y.-F. Lin, M. Yamamoto, X. Duan, K. Tsukagoshi, *ACS Nano* **2014**, 8, 12836.

- [26] H. G. Shin, H. S. Yoon, J. S. Kim, M. Kim, J. Y. Lim, S. Yu, J. H. Park, Y. Yi, T. Kim, S. C. Jun, *Nano Lett.* **2018**, 18, 1937.
- [27] W. Y. Ge, K. Kawahara, M. Tsuji, H. Ago, *Nanoscale* **2013**, 5, 5773.
- [28] S. Li, S. Wang, D.-M. Tang, W. Zhao, H. Xu, L. Chu, Y. Bando, D. Golberg, G. Eda, *Appl. Mater. Today* **2015**, 1, 60.
- [29] T. Yanase, S. Watanabe, M. Weng, M. Wakeshima, Y. Hinatsu, T. Nagahama, T. Shimada, *Cryst. Growth Des.* **2016**, 16, 4467.
- [30] S. H. Zhao, T. Hotta, T. Koretsune, K. Watanabe, T. Taniguchi, K. Sugawara, T. Takahashi, H. Shinohara, R. Kitaura, *2d Mater.* **2016**, 3, 025027.
- [31] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666.
- [32] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. De Arquer, F. Gatti, F. H. Koppens, *Nat. Nanotech.* **2012**, 7, 363.
- [33] S. Cho, S. Kim, J. H. Kim, J. Zhao, J. Seok, D. H. Keum, J. Baik, D.-H. Choe, K. Chang, K. Suenaga, *Science* **2015**, 349, 625.
- [34] D. A. Bandurin, A. V. Tyurnina, L. Y. Gelang, A. Mishchenko, V. Zólyomi, S. V. Morozov, R. K. Kumar, R. V. Gorbachev, Z. R. Kudrynskyi, S. Pezzini, *Nat. Nanotech.* **2017**, 12, 223.
- [35] J. Li, Z. Wang, Y. Wen, J. Chu, L. Yin, R. Cheng, L. Lei, P. He, C. Jiang, L. Feng, *Adv. Funct. Mater.* **2018**, 28, 1706437.
- [36] T. G. Mayer, P. L. Gross, *Annals of Emergency Medicine* **1985**, 14, 149.
- [37] R. Chow, W. Lanford, W. Ke - Ming, R. S. Rosler, *J. Appl. Phys.* **1982**, 53, 5630.
- [38] Y. F. Lin, Y. Xu, S. T. Wang, S. L. Li, M. Yamamoto, A. Aparecido-Ferreira, W. Li, H. Sun, S. Nakaharai, W. B. Jian, *Adv. Mater.* **2014**, 26, 3263.
- [39] M. Tosun, S. Chuang, H. Fang, A. B. Sachid, M. Hettick, Y. Lin, Y. Zeng, A. Javey, *ACS Nano* **2014**, 8, 4948.
- [40] A. Pezeshki, S. H. Hosseini Shokouh, P. J. Jeon, I. Shackery, J. S. Kim, I.-K. Oh, S. C. Jun, H. Kim, S. Im, *ACS Nano* **2015**, 10, 1118.
- [41] J. Y. Lim, A. Pezeshki, S. Oh, J. S. Kim, Y. T. Lee, S. Yu, D. K. Hwang, G. H. Lee, H. J. Choi, S. Im, *Adv. Mater.* **2017**, 29, 1701798.

Chapter 2

Literature Review

This chapter reviews the literatures on the rise of 2D materials as promising building blocks of next-generation electronic applications, and the structures and properties of 2D TMDCs, and the contact engineering of MoS₂ field-effect transistors, and the advantages of TMDC vdW contact, and the problems need to be solved in the preparation of TMDC vdW heterostructures, and the exploration of high-mobility 2D semiconductors, and the structure, properties and synthesis of Bi₂O₂Se, and the advantages of Bi₂O₂Se, and the problems and opportunities in the applications of Bi₂O₂Se.

2.1 The Rise of 2D High-mobility Semiconductors

As the silicon-based field-effect transistors (FETs) have been miniaturized to 14/10 nm nodes in industry (Figure 2.1), the supply voltage is lowered to 0.7 V to reduce the power consumption.^[1,2] However, the thermal excitation mechanism results in the lower limit of subthreshold slope of 60 mV/dec at room temperature, which requires that the supply voltage should be larger than 0.64 V in order to meet the operating current requirement of International Technology Roadmap for Semiconductors (ITRS).^[3,4] Therefore, to find suitable candidates to carry on the miniaturization has been a hot research topic in recent two decades. Low dimensional materials, such as zero-dimensional (0D), one-dimensional (1D) and two-dimensional (2D) materials, have come into being the research focus owing to the atomic thickness and novel properties brought by quantum confinement effect.^[5]

Figure 2.1 2010 ITRS summary of micro-processing unit half pitch and gate length trends.^[6]

Since graphene was discovered by Andre Geim's group in 2004, the booming development of 2D materials was raised since then and the researches of 2D materials remain highly attractive in the last decades.^[7-11] Graphene is single-layer form of graphite (one allotrope of carbon), in which carbon atoms are stacked in a honeycomb structure (Figure 2.2a).^[12]

In momentum space, this structure symmetry gives rise to the formation of Dirac cones (Figure 2.2b)^[10] at the edge of Brillouin zone (Figure 2.2a). Hence, the effective mass of the electron at the Dirac points are zero, producing a very high mobility ($2.0 \times 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, Figure 2.2c).^[13] The merit of high mobility together with atomic thickness, flexibility and stability draw huge attentions in amounts of research fields, such physics, chemistry, materials and microelectronics.^[14-22] It did deliver the goods, showing outstanding performance in almost all these areas, especially in the electronics and optoelectronics.^[23-27] This is because the nature of atomic thickness and non-dangling surface in graphene, which bring the advantages of high mobility, efficient gate regulation and higher level of vertical integration.

Figure 2.2 The crystal structure and property of graphene. (a) The crystal structure and reciprocal space of graphene.^[12] (b) The Dirac cones in the momentum space. Inset: the conduction and valence band meet at the Dirac point K .^[21] (c-d) Comparison of mobility, bandgap and on/off ratio between graphene, black phosphorus, organics and TMDs. Graphene has high mobility (up to $10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) but low on/off ratio ($10^1 \sim 10^3$).^[13]

However, as mentioned above, the conduction and valence bands meet at the Dirac points, which leads to a zero bandgap of graphene (inset of Figure 2.2b). In FETs based on graphene, the lack of the band gap leads to a high off current and thus low on/off ratio (Figure 2.2c and 2.2d), which definitely limits the application of graphene.^[7,28] Moving forward, layered transitional metal dichalcogenides (TMDCs) become new promising candidates since they possess diverse electronic properties, such as superconducting NbSe₂,^[29] semimetallic MoTe₂,^[30] semiconducting MoS₂^[31] and charge density wave (CDW) TaS₂,^[32] which provides a wide choice for the researchers. This is because of the versatile crystal structures and chemical compositions in TMDCs. Comparing with the semimetallic graphene, the semiconducting MoS₂ became fascinating because of a direct bandgap of 1.9 eV and the on/off ratio could be as high as 10⁶.^[31] Therefore, many potential applications including FETs, phototransistors and CMOS inverters have been explored.^[33,34] However, the Fermi level pinning (FLP) effect which is originated from the bad contact between the channel MoS₂ and the metal electrode has become a major limiting factor. This significantly brought down the FET performance of MoS₂. Many solutions, such as chemical doping,^[35,36] phase engineering,^[37,38] tunneling layer insertion^[39] and vdW contact,^[40] have been developed to improve the metal/semiconductor (M/S) contact. Among these methods, M/S vdW contact has shown surpassing advantages because of the good stability, larger size and clean interface. Moreover, it is highly possible to produce these M/S vdW heterostructures with CVD method.^[39,41-44] Nevertheless, the synthesis of M/S vdW heterostructure is hindered by the high melting points and low chemical reactivity of the corresponding metal oxides and the crystal lattice. Therefore, it has become challenging but crucial to develop CVD method to synthesize high-quality TMDC M/S vdW heterostructures.

Although MoS₂ prepared by mechanical exfoliation has shown high potentials in the mobility and on/off ratio, it is not suitable for scale-up production. In contrast, CVD-grown MoS₂ has been prepared with large area, their performances and stability are yet satisfactory. Hence, the chasing of large-area stable high-mobility 2D semiconductors has been continuously undergoing in the past few years.^[37,45-51] Although 1T-PtSe₂, PdSe₂, black phosphorous (BP) and indium selenide (InSe)^[45,49-51] have shown competitive

properties (high mobility and on/off ratio), they are either too expensive or not stable in the air condition. Moreover, these samples are all prepared by mechanical exfoliation, which is not proper for large-area production. Bi₂O₂Se, which is a new reported high-mobility 2D semiconductor prepared by CVD and has shown good stability, becomes coveted to the researchers.^[52-55] The high mobility and good stability made it promising in the photodetector application. However, the high dark current which results in the low on/off ratio is a pressing problem need to overcome.^[52,55] Besides, how to explore more promising applications of Bi₂O₂Se, such as CMOS inverters, become challenging but attracting.

2.2 Contact Engineering of 2D TMDCs

2.2.1 The Compositions, Structures and Properties of 2D TMDCs

Figure 2.3 Element summary of TMDCs (MX_2). M stands for 4B-7B and 10B transitional metal elements (marked with dark green color in the table) while X stands for 6A elements, namely, S, Se and Te (marked with orange color in the table).^[56] Inset: the layered structure of TMDCs.^[31]

In fact, known as layered materials stacked like graphene, which means the interlayer interaction is the vdW force, TMDCs have been studied for several decades. The structure of TMDCs is shown in the inset of Figure 2.3.^[31] TMDCs have a general formula of MX_2 , in which M stands for the transitional metal elements in the range of 4B-7B, and 10B while X stands for the chalcogen (6A) elements, namely, S, Se and Te (summarized in Figure

2.3).^[56] Different combinations of metal elements and chalcogen atoms provide different properties. At the same time, the property of each combination also depends on the crystal structure that these two types of atoms adopt.

Figure 2.4 Summary of general crystal structures of TMDCs. (a) Close packing of atoms in a single layer. There are two types of voids formed inter the atoms, marked with yellow and red color triangles (B and C voids). (b) Upper: three types of unit cells of monolayer with different stacking orders, in which AbA is noted as 1H, and AbC is noted as 1T. The distorted 1T is called 1T'. Lower: the side view of monolayer with three types of units, 1H, 1T and 1T'.^[57] (c) Top view of crystal structures with three kinds of stacking orders, 1T, 2H and 3R.^[58] (d) Sectional side view of 2H (AbA BaB) and 3R (AbA CaC BcB) structures.^[59]

In general, all the TDMCs crystallize in three types of structures, specifically, 1T, 2H and 3R (Figure 2.4),^[58] in which the front digits indicate the number of layers in the unit cell, while the capital letters (T, H and R) are short for trigonal, hexagonal and rhombohedral, respectively. According to the calculation and experiment data, the thickness of a monolayer sample is about 6.5~6.8 Å.^[34] Intra each layer, the stacking orders of X-M-X could be AbA and AbC, in which A, B, C refer to the position or voids (Figure 2.4a) used in atom close packing (hexagonal close packing, HCP and facial-center cubic close packing, FCC), and chalcogen atom is noted as capital letter while metal is lowercase. Therefore, for the unit cell of each layer, the packing order of AbA (HCP) is a trigonal prism while

the packing order of AbC (FCC) is an octahedron (Figure 2.4b).^[57] If the unit cell of the crystal is only one layer with intra-layer octahedral unit, it is noted as 1T (D_{3d} , Figure 2.4b lower), while the one with intra-layer trigonal prism unit is noted as 1H (D_{3h}). 2H and 3R are different inter-layer stacking orders of 1H that the layer stacking order of 2H is AbA BaB whereas that of 3R is AbA CaC BcB (Figure 2.4c and 2.4d).^[58-60] Note that in some case, the size of the chalcogen atom is large, such as Te atom, the 1T structure will be distorted to release the repulsion, forming the more stable 1T' structure (Figure 2.4b).

From the stacking orders in Figure 2.4b and 2.4d, it could be deduced that 1T and 2H are centrosymmetric while 1H and 3R are non-centrosymmetric, in which the broken inversion symmetry brings some charming properties of TMDCs, such as piezoelectricity, second harmonic generation (SHG) and spin polarization.^[61-66]

Figure 2.5 The orbital splitting of degenerated d orbitals and electron filling in CFT. In CFT, for 1T (D_{3d}) structure, d orbitals are split into two sets: d_{xy} , d_{yz} , d_{xz} , and $d_{x^2-y^2}$, d_{z^2} , while for 1H (D_{3h}) structure, d orbitals are split into three groups: d_{z^2} , d_{xy} and $d_{x^2-y^2}$, d_{yz} and d_{xz} . After the electrons are filled in (blue section), it could be summarized that group 5B in H and group 7B in T structure are metallic as their d orbitals are half filled, while group 4B in T, group 6B in H and group 10B in T are semiconducting.^[34]

Physical properties of materials are determined by their crystal structures. For instance, the electronic properties of TMDCs could be partially explained by using the crystal field theory (CFT).^[34] In CFT, two important factors are considered: (i) the coordination

environment and (ii) the nonbonding d electrons involving the formation of chemical bonding. For the octahedral coordination (1T or D_{3d}), because of the interaction which is originated from the orientations of the orbitals, d orbitals from the metal ion will be split into two sets of degenerated orbitals, d_{xy} , d_{yz} , d_{xz} , and $d_{x^2-y^2}$, d_{z^2} , while in 1H or D_{3h} , they will be split into three groups of degenerated orbitals: d_{z^2} , d_{xy} and $d_{x^2-y^2}$, d_{yz} and d_{xz} (Figure 2.5). The valence state of metal ions in MX_2 is + 4. Therefore, the nonbonding d electrons are 0, 1, 2, 3 and 6 for group 4B, 5B, 6B, 7B and 10B elements, respectively. After the effective electrons are filled from low to high energy level, the energy of the orbital that the last electron is filled in is called the highest occupied molecular orbital (HOMO). According to CFT, the lower value HOMO is, the more stable this case will be. Hence, after comparing the HOMO of D_{3d} and D_{3h} for each metal, the conductive properties for elements in each group can be predicted: Group 5B in D_{3h} and group 7B in D_{3d} are metallic, i.e., 2H-NbSe₂; Group 6B in D_{3h} and group 4B, 10B in D_{3d} are semi-conductive, such 2H-MoS₂. However, this prediction is exclusive of the effect of the coordinating chalcogen atoms. Taking the latter into consideration, a bandgap of decreasing trend from S to Te can be observed (2H-MoS₂ with 1.3 eV to 2H-MoTe₂ with 1.0 eV).^[67] Note that although this simple model help to understand the electronic properties, it might be not accurate. For instance, as it is known now, 1T-TiSe₂ (4B) is a metallic conductor which has CDW.^[68] 1T-ReS₂ (7B) is semiconducting^[69] while 1T-PtTe₂ (10B) is metallic^[70] according to the reports.

In summary, the broad range of physics and electronic properties (metallic, semi-metallic, semiconducting, SHG,^[71] CDW,^[32,72-74] piezoelectricity, and spin polarization) has made 2D TMDCs attractive and competitive. As discussed before, featured with a 1.9 eV direct energy bandgap and high on/off ratio, the FET performance and contact engineering of MoS₂ will be discussed in the next section.

2.2.2 The Contact Engineering in MoS₂ FETs.

Figure 2.6 The FET performances of MoS₂. (a) First layered MoS₂ FET device.^[75] (b) Schematic of the MoS₂ FET device encapsulated by HfO₂. (c) The device configuration of the encapsulated MoS₂ device. (d) The FET I_d - V_g transfer curve (back gating). The mobility of this encapsulated MoS₂ is about 217 cm²V⁻¹s⁻¹ (top gating). (e) The FET I_d - V_g transfer curve (top gating). The subthreshold slope with a value of 74 mV dec⁻¹ could be obtained.

MoS₂ FET was first reported by K. S. Novoselov in 2005,^[75] which showed a n-type semiconductor behavior and a gate regulation of the drain current. However, the mobility of the devices here is just about 0.5 to 3 cm²V⁻¹s⁻¹ (Figure 2.6a). Although this value was of consistency with the corresponding 3D crystal at room temperature, several factors may affect the FET performances, such as the Coulomb scattering, channel length and contact resistance. As the thickness decreases, the dimension of crystal is lowered and at the same time the Coulomb scattering increases, which reduced the mobility significantly. Therefore,

to improve the mobility, high- κ layer (Figure 2.6b)^[31] was deposited on the surface of the MoS₂ channel to suppress the Coulomb scattering. For example, by encapsulating a high- κ HfO₂ layer (Figure 2.6c), the mobility of MoS₂ could be elevated to 200 cm²V⁻¹s⁻¹ and the on/off ratio could be as high as 10⁸ (Figure 2.6d), as reported by Andras Kis's group in 2011. In addition, the subthreshold slope with a value of 74 mV dec⁻¹, which is close the room temperature limit, was achieved (Figure 2.6e). Moreover, this method is also applicable to other high- κ dielectric materials, such Al₂O₃ and ZrO₂. It is this work that showed the real potential of MoS₂ FETs and inspired quantities of device optimization works later.

The difficulty of this method is the absence of dangling bonds or other active sites for the deposition of high- κ dielectrics on the surface.^[76] In addition to the encapsulation of the high- κ dielectric layer, many methods such as shortening of the channel length^[77] and chemical doping^[78] of the channel were also developed to improve the FET performance of MoS₂. However, the most critical section should be the contact resistance between the metal electrode and the semiconductor channel, as it determines whether the charges could be easily conducted in the devices.

In ideal situation, a contact barrier (Schottky barrier) will be formed when the metal and the semiconductor come into contact, which is expressed by the Schottky-Mott rule: $\phi_B = \phi_M - \chi$, in which ϕ_B is the Schottky barrier height (SBH), ϕ_M is the work function of the metal and χ is the electron affinity. In practical condition, there will be inevitable interaction of the two materials in the interface. For example, in traditional bulk semiconductor, the surface dangling bonds will form covalent bonds with the metal (Figure 2.7a).^[79] As the finite surface is different with the infinite bulk state, when contacted with the metal, to match the work function, the wave function of the surface states is altered and the forbidden gap states in the bulk become allowed at the surface, which is called the metal induced gap state (MIGS). The calculation revealed that the energy difference between the surface state and the valence band is always around 1/3 of the energy bandgap. As a result, despite of the metal used, the ϕ_B will not change according to the Schottky-Mott rule, which is called Fermi Level Pinning (FLP) effect. This leads to an obvious barrier in the interface (Figure

2.7d). The FLP effect can be quantified as the dependence of the ϕ_B on the ϕ_M by $S = d\phi_B/d\phi_M$, in which $S = 1$ corresponds to the Schottky limit, and normally if S is close to 0, it is related to the FLP.

Figure 2.7 The contact and band structure between the metal electrode and the semiconductor channel. (a) and (d) Metal and traditional bulk semiconductor. (b) and (e) Metal and layered TMDC (weak hybridization). A tunneling barrier and a flat band region could be observed due to the vdW gap between the metal and semiconductor. (c) and (f) Metal and layered TMDC (strong hybridization). The tunneling barrier and flat band region are eliminated owing to the strong hybridization of atom orbitals in the interface.^[79]

As the layered TMDC semiconductor is quite different with the bulk semiconductor, such as the atomic thickness and the vdW surface, the contacts between the metal and the layered semiconductor are expected to be different. From Figure 2.7b and 2.7c, different with the traditional bulk semiconductor, the contact between the metal and the layered TMDC semiconductor could be divided into two types: weak hybridization and strong hybridization, instead of forming chemical bonds. For weak hybridization, there is a vdW

gap existing between the metal and the channel, which is reflected as a tunneling barrier and a flat band region in the band diagram (Figure 2.7e). This will increase the contact resistance of the device. For strong hybridization, through the overlap of the orbitals of the metal and sulfur, the vdW gap is eliminated in this case and at the same time, the property of the TMDC under the metal is changed and become a new metallized state. Hence, the tunneling barrier is suppressed and there is not flat band after the tunneling barrier any more (Figure 2.7f). This greatly improve the contact between the metal and the channel. As a result, Ti or Cr as a strong hybridization layer is widely adopted to improve the n-type contact while MoO_x is used for the p-type contact in the device fabrication. However, DFT calculation reveals the hybridization also lead to the charge redistribution at the surface (Figure 2.8a) and the gapped states of Mo d orbitals character (Figure 2.8b) due to the weakened interlayer Mo-S bonding. This results in a small deviation from the Schottky-Mott limit ($S=0.71$).^[80]

Figure 2.8 The reason for the FLP in layered TMDCs. (a) The charge redistribution at the metal/semiconductor interface.^[80] (b) The gap states of Mo d orbitals character (black dots) resulted from the weakened Mo-S bonding. (c) The damage to the semiconductor in the metal deposition process, which is proved in the cross-sectional TEM (e). (d) The S values of two different electrode

fabrication methods.^[81] (f) The cross-sectional TEM of the interface between the transferred electrode and semiconductor.^[82]

Meanwhile, this strong hybridization relies heavily on the clean interface and high-quality surface of the semiconductor. In practice, it has been reported that the weak dependence of the ϕ_B on the ϕ_M ($S=0.09$) indicates the serious FLP in multilayer MoS₂ (Figure 2.8d).^[81] The reason might be the bad-quality interface caused by the contamination of organic residuals and the damage of the semiconductor surface during the ‘high-energy’ metal deposition process (Figure 2.8c), which has been identified by the cross-sectional TEM (Figure 2.8e). Alternatively, when the metal electrode was fabricated via a transfer method which prevented the surface from being damaged (Figure 2.8f), the device can achieve an almost Schottky-Mott limit with a S value of 0.96 (Figure 2.8d).^[82]

Figure 2.9 The contact improvement by phase engineering. (a) The optical image of 1T-2H MoS₂ heterostructure prepared by the intercalation of Li ions. (b) The contact resistance of 1T-2H contact, which is reduced to 200 Ω μm. (c) The FET I_d - V_g curve of Au-2H and 1T-2H contact.^[38] (d-e) The optical image and schematic of 1T'-2H heterostructure. (f) The temperature dependence of the conductance. The extracted Schottky barriers were 200 and 10 meV for 2H and 1T' contact, respectively. (g) The temperature dependence of mobility of 2H and 1T' contact.^[37]

Apart from the electrode transfer method, several methods have been designed to improve

the metal/semiconductor contact, including phase engineering, chemical doping, tunneling layer and vdW contact. As discussed before, different structures offer different properties. 2H-MoS₂ is a semiconductor while 1T-MoS₂ is metallic. By intercalating lithium ions, 2H-MoS₂ can be converted into 1T-MoS₂, forming an in-plane 1T-2H MoS₂ heterostructure (Figure 2.9a).^[38] As the metal electrode is deposited on the 1T region, the contact resistance is shifted to the 1T-2H heterostructure, which is reduced from 1.1 kΩ μm to 0.2 kΩ μm (Figure 2.9b). In the FET I_d - V_g curve, under the gate of 30 V, the drain current is increased from 40 μA to 100 μA and the mobility is increased from 15 to 50 cm²V⁻¹s⁻¹.

The same strategy was also applied in the 1T'-2H MoTe₂ heterostructure, where 2H-MoTe₂ was converted by shining a laser light (Figure 2.9d and 2.9e).^[37] In this case, the Schottky barrier was lowered from 200 meV to 10 meV, which is smaller than the thermal excitation barrier. Since an Ohmic contact was achieved, the mobility was increased from 1 to 50 cm²V⁻¹s⁻¹. Hence, phase engineering is an effective method to reduce the contact resistance.

Figure 2.10 The contact improvement by chemical doping. (a) The Cl-doped MoS₂ device. (b-c) FET I_d - V_d curves of the Cl-doped and undoped MoS₂ devices.^[35] (d) The K-doped MoS₂ device. (e-

f) FET I_d - V_d curves of the MoS₂ device before and after K doping.^[36]

Chemical doping is widely used in the silicon-based metal oxide semiconductor FET (MOSFET) to improve the metal semiconductor contact. However, in layered material, it is hard to do the treatment due to the atomic thickness. Therefore, several surface doping methods were developed. As shown in Figure 2.10a, a few-layer MoS₂ was first immersed in 1, 2-dichloroethane for 12 h.^[35] The doping is originated from the filling of Cl atoms in the sulfur vacancies and since Cl atom has one more electron than S atom, it is a n-type doping. As compared in Figure 2.10b and 2.10c, the Cl-doped device showed much higher drain current (400 $\mu\text{A}/\mu\text{m}$) than the undoped device (60 $\mu\text{A}/\mu\text{m}$). Also, the reduced Schottky barrier could be seen from the linearity of the I_d - V_d curve (Figure 2.10b). Another method using Potassium as the electron donor dopant was also developed, the drain current was elevated about 4 times thanks to the reduced barrier.^[36] However, these two methods are limited by the poor stability of conductive phase (1T and 1T') or the doped MoS₂.

Figure 2.11 The contact improvement by vdW contact. (a) The MoS₂ device configuration using graphene as electrodes. (b-c) FET I_d - V_g curves of the MoS₂-graphene and MoS₂-Ti devices.^[40] (d) The MoS₂ device configuration using h-BN as tunneling layer. (e) Cross-sectional HRTEM image of the interface between electrode and MoS₂. (f) FET I_d - V_d curves of the Ni/ h-BN/ MoS₂ and Ni/ MoS₂ devices. (g) The gate dependence of the tunneling energy (TE).^[39]

In addition to the phase engineering and chemical doping, vdW contact which introduced 2D metallic materials as electrodes was also developed. As shown in Figure 2.11a, graphene was applied as electrodes to contact the semiconductor channel instead of the direct contact of metal and channel. In this way, an atomic flat and high-quality interface was achieved, which eliminated the MIGS. Therefore, a much lower barrier together with a better FET performance was demonstrated in Figure 2.11b and 2.11c.^[40] Interestingly, a high-quality interface could also be obtained via inserting a single or two layered h-BN between the metal electrode and the MoS₂ channel (Figure 2.11d and 2.11e).^[39] Taking advantages of the atomic thickness, the electron can tunnel through the h-BN layers and thus the Schottky barrier is reduced. As shown in Figure 2.11f, the FET performances of the tunneling device is much better than the Ni/Au direct contact. The tunneling barrier of 31 meV (Figure 2.11g), which is close to the thermal excitation energy, accounted for the better performances.

Figure 2.12 The contact improvement by vdW TMDC. (a) DFT DOS of NbS₂ (metallic) and MoS₂ (semiconducting).^[83] (b) NbS₂/MoS₂ vdW heterostructure. (c) 2D metals approach the Schottky-Mott limit in the contact with 2D semiconductor.^[84] (d) The Au/Nb_{0.005}W_{0.995}Se₂/WSe₂ structure with a p-doped contact layer Nb_{0.005}W_{0.995}Se₂. (e) The working principle of the p-doped contact layer in reducing the contact barrier. (f) The FET I_d - V_d curve of the device with a p-doped contact layer.^[85]

Therefore, it turned out that a flat and high-quality interface plays a significant role in the contact improvement. As discussed above, TMDCs have wide range of electronic properties (Figure 2.12a), such as metallic TMDC (i.e. NbS₂) and semiconducting TMDC (i.e. MoS₂).^[83] This provides a platform for the combination of various TMDCs to produce metal/semiconductor vdW heterostructures, in which a sharp atomic interface is expected.

In DFT calculation, it has been reported that the MIGS is suppressed in the 2D vdW metal/semiconductor heterojunction, such as NbS₂/MoS₂ (Figure 2.12b).^[84] This is because the interface in these heterojunctions are atomically sharp and the surface is almost defect-free. Therefore, these 2D metal/semiconductor vdW heterostructures comply very well to the Schottky-Mott rule (Figure 2.12c). In addition, as the density of state (DOS) of the 2D metals is limited, which means the Fermi level of these metals as well as the contact barrier are gate tunable, it will be of great advantage in comparison with the traditional metal. In experiment, a p-doped WSe₂ (Nb_{0.005}W_{0.995}Se₂) layer was used as contact layer between the metal electrode and the semiconducting WSe₂ (Figure 2.12d).^[85] The working principle of this design is presented in Figure 2.12e, in which the Fermi level of p-doped contact layer is tuned by the gate voltage, leading to a smaller barrier between the electrode and the channel. Thus, the drain current as high as 320 $\mu\text{A}/\mu\text{m}$ could be obtained at room temperature (Figure 2.12f). And the linear I_d - V_d curve indicates a lower Schottky barrier. This p-doped contact layer proved the feasibility to achieve Ohmic contact via tuning the Fermi level of 2D TMDCs.

Recently, a metal/semiconductor vdW heterostructure based on metallic NbS₂ and semiconducting MoS₂ was reported (Figure 2.13a),^[44] in which the current rectification behavior reveals the existence of Schottky barrier (Figure 2.13b). And the height of the barrier was found out to be 0.5 eV via the measurement of I_d - V_d curves under various temperatures (Figure 2.13c). Besides, the surface potentials (4.81 eV for NbS₂ and 4.53 eV for MoS₂) were obtained by Scanning Kelvin Probe Microscopy (SKPM), the band structure of this heterostructure was depicted in Figure 2.13d. Finally, a metal semiconductor FET (MESFET) was demonstrated with a superior subthreshold slope (S.S) of about 67 mV/dec. The M/S junction as a gate in the MESFET also revealed the tunability

of the Schottky barrier height.

Figure 2.13 The NbS₂/MoS₂ vdW heterostructure. (a) Schematic of the NbS₂/MoS₂ vdW heterostructure device. (b) I_d - V_d curve of the device show the current rectification behavior. (c) The deduction of the Schottky barrier by linear dependence of the current on temperature. (d) The band alignment of this heterostructure. (e) The I_d - V_g curve of the MESFET. A superior S.S around 67 mV/dec is obtained.^[44]

In summary, many methods including phase engineering, chemical doping, tunneling layer and vdW contact have been proved effective to reduce the contact barrier. Among these, vdW contact showed surpassing advantages in terms of not only the stability, but also the preparation, which will be discussed below.

2.2.3 Problems in the Preparation of 2D vdW Contact

As discussed above, the quality of the interface in the heterostructure relies heavily on the preparation process, which determines the performances of the semiconductor. The same as the preparation of individual layered TMDCs, the vdW TMDC heterostructures mentioned above were mainly prepared by two methods: mechanical exfoliation (ME) and

CVD method.

ME is a method using the scotch tape to exfoliate the vdW layered single crystals to atomic thickness. As the interaction between the sample and the tape (or the targeted substrate) is larger than the weak vdW interlayer interaction, the layered single crystals will be delaminated as the exfoliation continues.^[86-90] The preparation of 2D TMDC vdW heterostructure by ME is the sequential stacking of various layered materials (Figure 2.14).^[83] In this process, the first material was exfoliated directly onto the targeted substrate while the second material was exfoliated onto a soft and transparent substrate (i.e. PDMS). Then these two materials were aligned under the microscopy and later PDMS was lift up while the second material is left on the top of the first material, forming the vdW heterostructure. Besides, a vacuum annealing treatment could be conducted to improve the quality of the interface.

Figure 2.14 The process of ME to prepare 2D TMDC vdW heterostructure. (a-c) The exfoliation of the first material. (d-e) The alignment of the second material. (f) The device fabrication.^[83]

This ME method can acquire heterostructures with high-quality crystal. Besides, the single crystals are much easier to grow using the chemical vapor transport (CVT) method.^[91-95] As a result, this ME method is widely adopted in the preparation of TMDC vdW heterostructure,^[96-100] such as most of the experimental samples aforementioned. Nevertheless, the drawbacks of this method are also obvious, the low yield and the possible

contamination of the interface. It is also hard to obtain heterostructure composed of two monolayer sample, which is a limitation of this method.

CVD methods provide a good trade-off between the scalability and the crystal quality. Different with the exfoliation from crystal down to few-layer or monolayer sample (top-down method), CVD method grows sample from single molecule up to the layered sample (bottom-up method). In the synthesis of the TMDC vdW heterostructures, CVD methods could be divided into three main types, chalcogenization method, step-by-step method and one-step method.

Figure 2.15 The selenization of the pre-deposited metal precursors. (a) Schematics of selenization of pre-deposited Nb₂O₅ and WO₃ vertical heterostructure to produce the NbSe₂/ Nb_xW_{1-x}Se₂/ WSe₂ vdW heterostructure.^[101] (b) The cross-sectional STEM image of the interface in the obtained heterostructure, which clearly shows the mixing behavior of the W and Nb atoms. (c) The line intensity profile of (b) and the simulation image, which match well with the STEM image. (d) The EELS spectrum demonstrates the coexistence of three elements W, Nb and Se.^[102]

The first method is the chalcogenization (sulfurization or selenization) of the pre-deposited metal precursors. As shown in Figure 2.15a, the metal oxides WO₃ and Nb₂O₅ were first deposited in sequence to form a vertical heterostructure on the substrate. This was followed by the selenization of the obtained metal oxide heterostructure to prepare the NbSe₂/ Nb_xW_{1-x}Se₂/ WSe₂ vdW heterostructure.^[101] It is much easier to synthesize the heterostructure by this chalcogenization method since the reaction is much easier to undergo. This method can be used to design the patterns, to control the thickness of the heterostructure and even for the mass production. More importantly, it is versatile to

prepare heterostructure composed of different metal elements and properties, such as p-n junction and M/S junction. However, it is hard to acquire high-quality crystal since the deposited metal layers are polycrystalline and nonuniform, the obtained heterostructure is also polycrystalline. Besides, it is also hard to obtain high-quality interface by this method because of the serious interlayer alloying at the interface. This has been exemplified by STEM image which provides firm evidence of the interlayer mixing behavior of W and Nb atoms at the interface (Figure 2.15b).^[102] It was also verified by the line intensity profile (Figure 2.15c) and the electron energy lose spectroscopy (EELS, Figure 2.15c). Furthermore, it is hard to get a thin sample, especially the monolayer sample.

Figure 2.16 The WSe₂/MoSe₂ heterostructure prepared by the step-by-step sequential growth method. (a) The schematic of the step-by-step sequential growth. (b-d) The optical images of pure MoSe₂, type I and type II WSe₂/MoSe₂ heterostructure.^[103]

The other two methods are all-vapor method, which are the sequential growth of the two materials. More detailly, the first material grows first and serves as the epitaxy substrate for the growth of the second material. Figure 2.16a depicts the step-by-step method,^[103] in which the first material is grown and taken out from the chamber (Figure 2.16b), and reloaded in the chamber again for the second experiment. The requirement of the isolation in the growth temperature of the two materials by this step-by-step method is not rigorous,

which provides more choices in the selection of materials. However, as shown in the Figure 2.16a, it is hard to control the mode of the growth (in-plane or vertical). Hence, both the type-I and type-II structures are the mixture of in-plane and vertical heterostructures (Figure 2.16c and 2.16d), which may be ascribed to the contamination of the sample surface and edge after the first material is taken out.

Different with the step-by-step method, Figure 2.17a shows the process of one-step growth method, in which precursors of MoS_2 and WS_2 are loaded at the same time and the MoS_2/WS_2 vdW heterostructure are prepared by the sequential growth of the two materials in one time due to the different growth temperatures. The clear difference in contrast between MoS_2 and WS_2 can be seen in the optical image (Figure 2.17b). STEM EDS mappings of elements Mo, W and S prove the vertical stacking of this heterostructure (Figure 2.17c-e).^[104] The key control of this one-step growth is the difference in the growth temperature. As a result, MoS_2 finished the growth first and served as the epitaxy substrate for WS_2 . In this case, a cleaner interface and a higher quality of the individual layers are expected in comparison with the sulfurization method. Compared with the step-by-step method, much purer phase of vertical heterostructure is expected in this one-step method.

Figure 2.17 The WS_2/MoS_2 vdW heterostructure prepared by the one-step method. (a) The schematic of the one-step sequential growth.^[105] (b) The optical image of the obtained WS_2/MoS_2 vdW heterostructure. (c-e) STEM EDS mappings of elements S, Mo and W.^[104]

In summary, these all vapor methods offer higher crystal and interface quality of the

heterostructure and larger (up to 40 μm) area than the ME methods. Therefore, it is promising to scale up for the electronic applications. However, the drawback of this method is hard to achieve a good control, which needs meticulous selection of the materials. Therefore, up to now, only a hand of TMDC vdW heterostructures have been prepared by CVD methods.^[103-105]

In addition, most of the reported heterostructures are semiconductor/semiconductor (S/S) junctions, such as MoS_2/WS_2 , ReS_2/WS_2 and $\text{MoSe}_2/\text{WSe}_2$, leaving metal/semiconductor (M/S) junctions less explored. This might be primarily ascribed to the difficulty in the synthesis of metallic TMDCs owing to the high melting points and low chemical reactivity of the metal oxide precursors (Table 2.1).^[106] As discussed above, the selenization of the pre-deposited vertical oxide heterostructure $\text{Nb}_2\text{O}_5/\text{WO}_3$ provided a way to produce the sandwiched $\text{NbSe}_2/\text{Nb}_x\text{W}_{1-x}\text{Se}_2/\text{WSe}_2$ heterostructure (Figure 2.15a).^[102] Nevertheless, such method will lead to interlayer alloying and relative high defects at the interface. Also, since the grain boundary concentration is high in this method, the quality of the crystal is limited.

Table 2.1 The summary of melting points (MP) of the metal oxides (IV-VI B) and elementary substance (X B).

Substance	MP(°C)	Substance	MP(°C)	Substance	MP(°C)	Substance	MP(°C)
IV B		V B		VI B		X B	
TiO_2	1843	V_2O_5	690				
ZrO_2	2715	Nb_2O_5	1512	MoO_3	790	Pd	1555
HfO_2	2758	Ta_2O_5	1872	WO_3	1473	Pt	1768

To overcome this, metal chlorides (i.e. NbCl_5 and TaCl_5) which are much easier to evaporate and undergo the reaction have been used. However, the higher chemical activity of the chlorides made the experiment more complicated and the growth hard to control. As shown in Figure 2.18, the samples produced by the chlorides are either too thick or too small and the morphology is out of control.^[107-112]

Another consideration might be the crystal structure mismatch. Although it has been proved that the mismatch could be up to 13% in the GaSe/WSe₂ heterostructure,^[113] it is prepared by the step-by-step method. For the one-step method, it is relatively easier for two components that have the same crystal structure, e.g. 2H-MoS₂ and 2H-WS₂. Since some of metallic TMDCs adopt 1T or 1T' structure, for different crystal structures (e.g. 2H and 1T), there are still not successful reports.

Figure 2.18 The samples produced by metal chlorides precursors. For the SEM or AFM images, it can be clearly seen that the samples are either too small or too thick. (a), (b) and (d) The vertical growth behavior indicates it is hard to control the process using metal chlorides.^[107-112]

Therefore, it becomes challenging but profound to synthesize Metal/semiconductor (M/S) TMDC vdW heterostructures with high-quality interface by the one-step CVD method.

2.3 Synthesis and Applications of High-mobility Bi₂O₂Se

The efforts to explore new high-mobility 2D materials with a suitable bandgap have never been suspended. The mobility is defined as how fast the charge carrier can move through the semiconductor, which is crucial for the semiconductor as it determines the ultimate

limit of the response rate. In 2D materials, graphene has high mobility of up to $2 \times 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at low temperature. However, the lack of band gap leads to the fact that transistors could not be switched off, which means low on/off ratio and high consumption of power. Although MoS₂ have shown high potential, it needs the device optimization including the high- κ layer encapsulation and the contact engineering. Unfortunately, even after the optimization, the mobility of MoS₂ is still not competitive with the low temperature polycrystalline silicon (LTPS). Therefore, moving further, to seek novel high-mobility 2D semiconductors with good stability becomes one of the focuses in 2D materials research.

2.3.1 Exploration of High-mobility 2D Semiconductors

Generally, there is an empiric relationship between the mobility and bandgap that as the bandgap is increased, the mobility decreases.^[13] For MoS₂, as the thickness increases, the bandgap decreases (1.9 eV to 1.2 eV) while the mobility increases due to the suppression of the surface scattering. Hence, many small-bandgap materials have been predicted by DFT calculation, such as 2H-MoTe₂, 1T-HfSe₂, 1T-PtSe₂, PdSe₂, Black Phosphorus (BP) and γ -Indium Selenide (γ -InSe).^[37,45,47-50] In practice, some of these materials have been experimentally verified to be true while some are not.

Table 2.2 DFT calculation prediction of high-mobility 2D semiconductors at RT.^[114]

MX_2	a (a.u.)	c (a.u.)	V_s (km·s ⁻¹)	c_{11} ($\times 10^{11} \text{ N} \cdot \text{M}^{-2}$)	$m_{\Gamma-K(M)}$ (m_e)	m_{K-M} (m_e)	$E_{\text{el-ph}}$ (eV)	μ ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)
MoS ₂	5.927	2.926	7.93	6.25	0.45	0.45	3.90	340
MoSe ₂	6.168	3.156	6.01	4.94	0.52	0.52	3.65	240
MoTe ₂	6.618	3.411	5.04	4.45	0.53	0.57	0.92	2,526
WS ₂	6.047	2.992	6.67	6.52	0.24	0.26	3.92	1,103
WSe ₂	6.166	3.164	5.55	5.66	0.33	0.31	3.78	705
SnS ₂	6.879	2.797	6.18	3.42	2.11	0.21	3.55	306
SnSe ₂	7.165	2.999	4.83	2.71	2.91	0.17	2.91	447
HfS ₂	6.731	2.750	5.86	4.33	3.30	0.24	1.31	1,833
HfSe ₂	6.944	2.978	4.72	3.37	3.10	0.18	1.08	3,579
ZrS ₂	6.817	2.771	7.21	4.05	1.62	0.31	1.52	1,247
ZrSe ₂	7.007	3.008	5.42	3.18	2.03	0.22	1.25	2,316
PtS ₂	6.670	2.327	6.61	7.05	0.26	0.25	3.63	1,107
PtSe ₂	6.978	2.464	4.73	4.26	0.21	0.19	2.86	1,892
PtTe ₂	7.485	2.634	4.89	4.72	0.90	0.77	1.73	367

As shown in Table 2.2,^[114] the DFT calculation shows the bandgap of 2H-MoTe₂ is 1.16 eV (Figure 2.19a), which is smaller than that of monolayer 2H-MoS₂ (1.9 eV). 2H-MoTe₂ has been predicted to possess a high mobility up to 2500 cm²V⁻¹s⁻¹ at room temperature (RT). However, the FET transfer data show the value is only about 50 cm²V⁻¹s⁻¹ (Figure 2.19b), which may be due to the high effective electron mass (0.53 m_e).^[37] The same as this, the bandgap and mobility (RT) of 1T-HfSe₂ have been calculated to be about 0.45 eV and 3500 cm²V⁻¹s⁻¹ (Figure 2.19c and 2.19d),^[48] which was experimentally measured to be around 6.5 cm²V⁻¹s⁻¹. This difference was ascribed to the contact resistance and the surface scattering.

Figure 2.19 The band structure and mobility of 2H-MoTe₂ and 1T-HfSe₂. (a) The band structure of monolayer 2H-MoTe₂. A direct bandgap of 1.16 eV was predicted.^[37] (b) The temperature dependence of the mobility of 2H-MoTe₂ with 1T' contact and 2H contact. The mobility is much improved with 1T' contact. (c) The band structure of monolayer 1T-HfSe₂. An indirect bandgap of 0.45 eV was predicted.^[48] (d) The FET transfer I_d - V_g curve of 1T-HfSe₂. The mobility was extracted to be only 6.5 cm²V⁻¹s⁻¹.

In contrast to these, 1T-PtSe₂ has been predicted to have mobility of 1900 cm²V⁻¹s⁻¹ and

the bandgap is 0.66 eV for a 10 nm thick sample (Figure 2.20a). The FET mobility was measured to be around $210 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is quite good for non-optimized sample at RT (Figure 2.20b).^[47] The small bandgap and effective electron mass ($0.19 m_e$) contributed jointly to this high mobility. Besides, the same with Pt in the transitional metal of group X, 9 nm PdSe₂ has shown a high mobility of $216 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature (Figure 2.20d), with a band gap of 0.16 eV (Figure 2.20c).^[50] However, as it is well known that Pt and Pd (group X) are all noble metals, which is not suitable for mass production.

Figure 2.20 The band structure and mobility of 1T-PtSe₂ and PdSe₂. (a) The band structure of 10 nm 1T-PtSe₂. An indirect bandgap of 0.66 eV was predicted.^[37] (b) The FET transfer I_d - V_g curve of 11 nm 1T-PtSe₂. The mobility of this sample was calculated to be $210 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. (c) The band structure of PdSe₂. An indirect bandgap of 0.16 eV was predicted.^[48] (d) The FET transfer I_d - V_g curve of PdSe₂. The mobility was extracted to be $216 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Figure 2.21 Black phosphorus. (a) The crystal structure of BP. Every P atom bond with three near P atoms to form a zig-zag like layer structure. (b) The FET I_d - V_g transfer curves of BP with different thicknesses. Inset: the thickness dependence of mobility and on/off ratio. (c) The integer quantum hall effect of BP. (d) The quantum oscillations of BP.

Other than TMDCs, a lot of new 2D semiconductors have also been unearthed by calculation and experiments. Among these, the most representative materials are BP and γ -InSe.^[45,115-117] BP is one allotrope of phosphorus elementary substances, which include red, white, violet, black, and blue phosphorus. Figure 2.21a depicts the crystal structure of BP,^[45] in which every P atom bond with three near P atoms and a zig-zag like layer structure is formed. The sample with a thickness of 10 nm has been demonstrated to have a high FET mobility of up to $1000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at RT (Figure 2.21b). And The quantum oscillations have been observed in this few-layer BP flakes on the hexagonal boron nitride (h-BN) substrate due to the suppression of the surface scattering and the high capacitance provided by high- κ h-BN layer (Figure 2.21d).^[117] Moving forward further, when the multilayer BP was encapsulated between the h-BN, the integer quantum hall effect could be observed (Figure

2.21c).^[116] Need to mention that the mobility has a heavy reliance on the thickness of BP and when the thickness is less than 10 nm, it drops very quickly (inset of Figure 2.21b).^[115]

Figure 2.22 γ -indium selenide. (a) The crystal structure of γ -InSe. The stacking order is AbbA, where two layers of Indium atoms are sandwiched by the upper and lower layer of Selenium atoms. (b) The temperature dependence of the mobility of γ -InSe with different thicknesses. (c) The quantum hall effect of γ -InSe. (d) The quantum oscillations of γ -InSe.^[49]

In addition to BP, γ -InSe is another novel high-mobility 2D semiconductor reported recently.^[49] As shown in Figure 2.22a, a bit different with 2H structure in TMDC, the stacking order here is AbbA, in which two layers of Indium atoms are sandwiched by the upper and lower layer of Selenium atoms. Therefore, from the top view of monolayer, it is the same with 2H structure while from the side view, there is one more layer of metal atoms

(Figure 2.22a). The bandgap of a 6-layer γ -InSe is about 1.3 eV and the mobility of this 6-layer γ -InSe is around $1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at RT (Figure 2.22b). Based on this high mobility, the quantum hall effect and quantum oscillation have been demonstrated (Figure 2.22c and 2.22d).

Although these materials have very high mobility at RT, unlikely, they are not stable in air condition. In addition, it is a big challenge for the CVD synthesis as high vacuum condition is required. That's the reason why CVD-grown γ -InSe did not show a good performance^[118] and no BP produced by the CVD method has ever been reported. Hence, the further application of these materials will be definitely hindered by their synthesis until their stability could be improved. Hence, for high-mobility 2D semiconductors, the stability becomes a topic of major concern.

2.3.2 Discovery and Synthesis of High-mobility 2D Bi₂O₂Se

Recently, a new type of high-mobility 2D semiconductor Bi₂O₂Se has been prepared by CVD with a large area on the fluorine mica substrate. As shown in Figure 2.23a,^[54] layered Bi₂O₂Se belongs to I4/mmm space group, in which oxygen atoms form a tetragonal lattice and the upper and lower bismuth atoms are stacked at different sets of tetragonal interstitial sites, forming a [Bi₂O₂]²⁺ layer. Meanwhile, selenium atoms which are filled in the other set of sites bind the upper and lower [Bi₂O₂]²⁺ layers with weak electrostatic force, giving an interlayer spacing about 0.61 Å.

The mobility of the sample with the thickness of 6-10 nm was measured to be around $200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at RT, which is a quite high value for CVD-grown 2D semiconductor. This was explained by the small effective electron mass ($0.14 \pm 0.02 m_0$) at the CBM of the energy band. DFT calculation provides detailed band structures of the Bi₂O₂Se (Figure 2.23b), showing a sharp band structure at CBM and an indirect band gap of 0.85 eV. This was verified by the angle-resolved photoemission spectroscopy (ARPES), in which the sharp CBM structure could be clearly seen (Figure 2.23c). Also, a band gap of 0.80 eV was revealed, which showed good consistency with the DFT calculation. Like the high-mobility

materials mentioned above, the quantum oscillation was demonstrated (Figure 2.23e). Note that for the sample with a thickness less than 6 nm (Figure 2.23d), the mobility drops very quickly due to the surface scattering effect and the lower crystal quality.

Figure 2.23 Bi₂O₂Se. (a) The crystal structure of Bi₂O₂Se. (b) The band structure by DFT calculation. (c) The ARPES of Bi₂O₂Se. A sharp CBM band structure can be clearly observed and the bandgap was measured to be 0.80 eV. (d) The thickness dependence of Hall mobility at RT. (e) The quantum oscillations of Bi₂O₂Se.^[54]

As an oxide compound, Bi₂O₂Se has shown quite good stability over months in air condition. More significantly, the bilayer sample as large as 200 μm (Figure 2.24b) could be synthesized via CVD method (Figure 2.24a).^[53] For the monolayer sample (Figure 2.24c), it does not have a good square shape due to the electrostatic interaction between the sample and the substrate, which indicates a lower quality. The Raman spectra show the evolution from Bi₂Se₃ to Bi₂O₂Se (Figure 2.24d) and the product was further characterized by XPS and HRTEM (Figure 2.24e-2.24g). Besides, as the thickness decreases, the optical band gap will increase from 1.4 eV to 1.9 eV (Figure 2.24h), which may partially explain

the drop of the mobility in thinner samples. The virtues of large area and good stability make this material quite promising for many applications in the future.

Figure 2.24 The CVD synthesis and characterization of Bi₂O₂Se. (a) The schematic of the CVD setup. Bi₂O₃ and Bi₂Se₃ are used as precursors. (b) The bilayer sample as large as 200 μm could be prepared vis this method. (a) Non-square monolayer sample could be obtained. (d) The Raman spectra of few-layer and bulk Bi₂O₂Se and Bi₂Se₃. (e-f) The XPS characterization of Bi₂O₂Se in which the binding energies of Bi 4f and Se 3d are acquired. (g) HRTEM of Bi₂O₂Se. (h) The thickness dependence of the band gap.^[53]

2.3.2 Problems and Opportunities in Applications of 2D Bi₂O₂Se

The high mobility and good stability of Bi₂O₂Se (Figure 2.25a and 2.25d) shed light on the applications in many fields, especially the photoresponse. As shown in Figure 2.25b, the I_d - V_d curve was recorded under dark and different light power conditions (Figure 2.25b).^[55]

However, no obvious photocurrent could be observed in this data and also in the on/off photocurrent test (Figure 2.25c). Therefore, only very small on/off ratio (less than 1) could be obtained. And the photoresponsivity, which is defined as the ratio of the photocurrent and light power, is only 6.5 AW^{-1} . This might be ascribed to the lower quality of the sample, as the drain current under zero gate obtained here is much lower than the previous report. Another reason is the high dark current on the mica substrate due to the lack of gating configuration. It is worth mentioning that the dynamic response time (3.2 ms) and the specific detectivity (10^{11} Jones) in this report (Figure 2.25e and 2.25f) still showed the high potential of $\text{Bi}_2\text{O}_2\text{Se}$ in the photodetector application. By improving the crystal quality and lowering the dark current, the performance of the photodetector based on $\text{Bi}_2\text{O}_2\text{Se}$ could be much improved.

Figure 2.25 The photodetector application of $\text{Bi}_2\text{O}_2\text{Se}$. (a) The optical images of the obtained $\text{Bi}_2\text{O}_2\text{Se}$. (b) The I_d - V_d curve under different light power densities. (c) The on/off photocurrent test of $\text{Bi}_2\text{O}_2\text{Se}$ under different light power densities. (d) The HRTEM image of $\text{Bi}_2\text{O}_2\text{Se}$. (e) The dynamic response time of $\text{Bi}_2\text{O}_2\text{Se}$ photodetector. (f) The power dependence of the photocurrent and specific detectivity of $\text{Bi}_2\text{O}_2\text{Se}$.^[55]

Although a gate configuration can be used to regulate the dark current, it is difficult to realize on f-mica substrate in the photoresponse application. As the 280 nm SiO_2/Si

substrate (Si substrate) possesses inherent back gating, if $\text{Bi}_2\text{O}_2\text{Se}$ can be transferred onto Si substrate, not only the optoelectronic performance could be much improved, but also the applications of $\text{Bi}_2\text{O}_2\text{Se}$ will be broadened since almost all integrated circuits are rooted in the silicon substrate. In the wet transfer of $\text{Bi}_2\text{O}_2\text{Se}$, hydrofluoric acid (HF) becomes the only f-mica etchant, due to the inertness of f-mica and strong electrostatic interaction between the sample and the substrate. Nevertheless, the highly corrosive HF which has the ability to penetrate issues is hazardous to handle. More importantly, since HF is well known as one component of typical buffered oxide etchant (BOE),^[21] $\text{Bi}_2\text{O}_2\text{Se}$ will be inevitably etched by HF during the transfer process. Hence, it is crucial to develop a safe and non-corrosive method to transfer $\text{Bi}_2\text{O}_2\text{Se}$ onto other substrates.

Besides, since $\text{Bi}_2\text{O}_2\text{Se}$ is new discovered, a lot of potential applications should be explored, such as complementary metal-oxide-semiconductor (CMOS) inverters. CMOS inverters provide opposite output logic signal to its input with a high speed at a low power consumption state, which is an essential unit in the integrated circuits (Figure 2.26a).^[119]

Figure 2.26 The CMOS inverter applications of TMDCs. (a) The circuit symbol of CMOS inverter.^[119] (b) The schematic of CMOS inverter based on p-type WSe_2 and n-type K-doped WSe_2 . (c) The FET transfer curve I_D - V_g of the two channels. (d) The V_{OUT} - V_{IN} curves under different V_{DD} . (e) The gain under different V_{DD} . (f) The schematic of CMOS inverter based on p-type MoTe_2 and n-type K-doped MoTe_2 .

n-type MoS₂.^[120]

A lot of trials via using 2D semiconductors to fabricate the CMOS inverters have been made, such as TMDC including MoS₂, WSe₂ and MoTe₂,^[119-122] thanks to their suitable energy bandgap and high mobility. As depicted in Figure 2.26a, a CMOS inverter is formed by a p-type FET and a n-type FET, connected in series and they share the same gate. A V_{DD} was applied at the drain of p-FET and the source of n-FET is grounded (Figure 2.26b). When the gate voltage is applied (noted as the input signal V_{IN}), the output signal (V_{OUT}) is collected at the source of p-FET (or the drain of n-FET). As known to all, when V_{IN} is high, the p-FET has a high resistance while the n-FET has a low resistance. Thus, the voltage drop is almost all at the p-FET and the value of V_{OUT} will be low. Otherwise, when V_{IN} is low, there is nearly no voltage drop at the p-FET, and V_{OUT} will be high. And the gain is defined as the absolute value of the differentiation of the V_{OUT} - V_{IN} curve, which tells how fast the switch happens in the process. The higher the gain is, the faster the CMOS inverter could be operated.

Previously, through chemical doping, CMOS inverters based on p-type and n-type WSe₂ have been reported. For n-type WSe₂, a doping of the electron-donating potassium (K) on the surface (Figure 2.26b) was adopted. The FET transfer I_d - V_g curves show very good symmetry of p-type and n-type behaviors (Figure 2.26c), which means these materials will match well in the inverter. Figure 2.26d shows the V_{OUT} - V_{IN} curve of this inverter. When $V_{DD} = 1$ V, a gain of about 3 has been obtained (Figure 2.26e). For MoTe₂, the ambipolar behavior brings the benefit of free of doping. However, the SiO₂ dielectric hampers the performance of the inverter, in which the gain is only 1.5 at $V_{DD} = 20$ V. In addition, most of the time the ambipolar behavior is not a symmetrical for p-type and n-type, which may be one reason for the low gain. Based on this, p-type WSe₂ and n-type MoS₂ were chosen to fabricate the inverter and a gain of 4.4 at $V_{DD} = 1$ V was achieved (Figure 2.26f).^[120,121]

Nevertheless, there are several questions for these materials in the application of CMOS inverter. First of all, the stability of 2H-MoTe₂ and the doping WSe₂ (K doping) is not convincing. Also, all these samples are prepared by ME method, which is not suitable for

mass production (small size and low yield). Hence, the application of the CVD-grown, stable and high-mobility $\text{Bi}_2\text{O}_2\text{Se}$ to fabricate the CMOS inverters provides a good solution to the current problems.

2.4 Questions to be Answered Based on Literature Review

Firstly, vdW TMDC M/S contacts have shown great advantages in the contact improvement and they are highly possible to be prepared by CVD method. Although CVD method has shown superior advantages in the synthesis of TMDC vdW heterostructures, which are focused on S/S junctions, M/S vdW junctions with an atomically sharp interface were rarely reported. This might be ascribed to the high melting point and low chemical reactivity of the metal oxide precursors and the crystal lattice mismatch between the metallic and semiconducting TMDCs. The selenization method of the vertical metal heterostructure has the drawbacks of bad interface and low crystal quality. To develop a one-step method to produce M/S TMDC vdW heterostructures with high-quality interface becomes challenging but profound.

Secondly, large-area $\text{Bi}_2\text{O}_2\text{Se}$ has been prepared via CVD on mica substrate and proved to be stable in air condition over months. The virtues of high mobility, large area and stability make it attracting in the photodetector application. Although previous report has proved the high potential of this material, there are plenty of room to improve, especially the high dark current and low sensitivity. Although a gate configuration can be used to regulate the dark current, it is difficult to realize on mica substrate. The 280 nm SO_2/Si has inherent back gate function, if the $\text{Bi}_2\text{O}_2\text{Se}$ could be transferred onto it, the performance of the $\text{Bi}_2\text{O}_2\text{Se}$ will be certainly much improved. However, the inertness of mica and the electrostatic interaction between the sample and the substrate make it hard to do the transfer. In consideration of safety, the usage of the corrosive HF acid is hazardous. Moreover, during the transfer, $\text{Bi}_2\text{O}_2\text{Se}$ will be unavoidably etched by HF, which hinders the application of $\text{Bi}_2\text{O}_2\text{Se}$ on substrates other than mica. To improve the performance of photodetector based on $\text{Bi}_2\text{O}_2\text{Se}$, a non-corrosive transfer method needs to be developed. And the improvement in the phototransistor performance of $\text{Bi}_2\text{O}_2\text{Se}$ on Si substrate needs

to be demonstrated.

Thirdly, 2D semiconductor have shown surpassing advantages of high mobility, efficient regulation and high-level integration in the applications of electronics, especially CMOS inverters. While ambipolar TMDC did not have expected performance owing to the asymmetrical behavior of p-type and n-type FET, doped TMDC was limited by the stability of the doping materials. High-mobility and stable $\text{Bi}_2\text{O}_2\text{Se}$ provides a new platform for these applications and also the successful CVD synthesis of large-area $\text{Bi}_2\text{O}_2\text{Se}$ makes it promising for mass production. The dielectric layer dependence of the $\text{Bi}_2\text{O}_2\text{Se}$ based CMOS inverter performance also need to be examined.

References

- [1] C. Qiu, Z. Zhang, M. Xiao, Y. Yang, D. Zhong, L.-M. Peng, *Science* **2017**, 355, 271.
- [2] C. Qiu, F. Liu, L. Xu, B. Deng, M. Xiao, J. Si, L. Lin, Z. Zhang, J. Wang, H. Guo, *Science* **2018**, eaap9195.
- [3] P. S. Peercy, *Nature* **2000**, 406, 1023.
- [4] M. Neisser, S. Wurm, *Adv. Opt. Technol.* **2015**, 4, 235.
- [5] T. Takagahara, K. Takeda, *Phys. Rev. B* **1992**, 46, 15578.
- [6] P. Gargini, presented at GaAs IC Symposium, 2000. 22nd Annual **2000**.
- [7] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666.
- [8] K. S. Novoselov, A. K. Geim, S. Morozov, D. Jiang, M. Katsnelson, I. Grigorieva, S. Dubonos, Firsov, AA, *Nature* **2005**, 438, 197.
- [9] P. Blake, E. Hill, A. Castro Neto, K. Novoselov, D. Jiang, R. Yang, T. Booth, A. Geim, *Appl. Phys. Lett.* **2007**, 91, 063124.
- [10] A. C. Neto, F. Guinea, N. M. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.* **2009**, 81, 109.
- [11] A. K. Geim, K. S. Novoselov, in *Nanoscience and Technology: A Collection of Reviews from Nature Journals*, World Scientific **2010**, 11.
- [12] J. Wang, F. Ma, W. Liang, R. Wang, M. Sun, *Nanophotonics* **2017**, 6, 943.

- [13] D. Lembke, S. Bertolazzi, A. Kis, *Acc. Chem. Res.* **2015**, 48, 100.
- [14] A. K. Geim, *Science* **2009**, 324, 1530.
- [15] A. Grigorenko, M. Polini, K. Novoselov, *Nat. Photonics* **2012**, 6, 749.
- [16] L. Yan, Y. B. Zheng, F. Zhao, S. Li, X. Gao, B. Xu, P. S. Weiss, Y. Zhao, *Chem. Soc. Rev.* **2012**, 41, 97.
- [17] C. K. Chua, M. Pumera, *Chem. Soc. Rev.* **2014**, 43, 291.
- [18] R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, *Nat. Mater.* **2015**, 14, 271.
- [19] X. Wu, M. Sprinkle, X. Li, F. Ming, C. Berger, W. A. de Heer, *Phys. Rev. Lett.* **2008**, 101, 026801.
- [20] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, *Science* **2009**, 324, 1312.
- [21] K. Novoselov, *Rev. Mod. Phys.* **2011**, 83, 837.
- [22] T. Palacios, *Nat. Nanotech.* **2011**, 6, 464.
- [23] F. Xia, T. Mueller, Y.-m. Lin, A. Valdes-Garcia, P. Avouris, *Nat. Nanotech.* **2009**, 4, 839.
- [24] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, *Nature Nanotech.* **2010**, 5, 722.
- [25] S. Niyogi, E. Bekyarova, J. Hong, S. Khizroev, C. Berger, W. de Heer, R. C. Haddon, *J. Phys. Chem. Lett.* **2011**, 2, 2487.
- [26] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. De Arquer, F. Gatti, F. H. Koppens, *Nat. Nanotech.* **2012**, 7, 363.
- [27] B. Sensale-Rodriguez, R. Yan, M. M. Kelly, T. Fang, K. Tahy, W. S. Hwang, D. Jena, L. Liu, H. G. Xing, *Nat. Commun.* **2012**, 3, 780.
- [28] F. Xia, D. B. Farmer, Y.-m. Lin, P. Avouris, *Nano Lett.* **2010**, 10, 715.
- [29] N. E. Staley, J. Wu, P. Eklund, Y. Liu, L. Li, Z. Xu, *Phys. Rev. B* **2009**, 80, 184505.
- [30] H. Sakai, K. Ikeura, M. S. Bahramy, N. Ogawa, D. Hashizume, J. Fujioka, Y. Tokura, S. Ishiwata, *Sci. Adv.* **2016**, 2, e1601378.
- [31] B. Radisavljevic, A. Radenovic, J. Brivio, i. V. Giacometti, A. Kis, *Nat. Nanotech.* **2011**, 6, 147.
- [32] S. Hellmann, M. Beye, C. Sohrt, T. Rohwer, F. Sorgenfrei, H. Redlin, M. Kalläne, M. Marczyński-Bühlow, F. Hennies, M. Bauer, *Phys. Rev. Lett.* **2010**, 105, 187401.

- [33] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotech.* **2012**, 7, 699.
- [34] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, *Nat. Chem.* **2013**, 5, 263.
- [35] L. Yang, K. Majumdar, H. Liu, Y. Du, H. Wu, M. Hatzistergos, P. Hung, R. Tieckelmann, W. Tsai, C. Hobbs, *Nano Lett.* **2014**, 14, 6275.
- [36] H. Fang, M. Tosun, G. Seol, T. C. Chang, K. Takei, J. Guo, A. Javey, *Nano Lett.* **2013**, 13, 1991.
- [37] S. Cho, S. Kim, J. H. Kim, J. Zhao, J. Seok, D. H. Keum, J. Baik, D.-H. Choe, K. J. Chang, K. Suenaga, *Science* **2015**, 349, 625.
- [38] R. Kappera, D. Voiry, S. E. Yalcin, B. Branch, G. Gupta, A. D. Mohite, M. Chhowalla, *Nat. Mater.* **2014**, 13, 1128.
- [39] J. Wang, Q. Yao, C. W. Huang, X. Zou, L. Liao, S. Chen, Z. Fan, K. Zhang, W. Wu, X. Xiao, *Adv. Mater.* **2016**, 28, 8302.
- [40] L. Yu, Y.-H. Lee, X. Ling, E. J. Santos, Y. C. Shin, Y. Lin, M. Dubey, E. Kaxiras, J. Kong, H. Wang, *Nano Lett.* **2014**, 14, 3055.
- [41] A. K. Geim, I. V. Grigorieva, *Nature* **2013**, 499, 419.
- [42] R. Cheng, D. Li, H. Zhou, C. Wang, A. Yin, S. Jiang, Y. Liu, Y. Chen, Y. Huang, X. Duan, *Nano Lett.* **2014**, 14, 5590.
- [43] C.-H. Lee, G.-H. Lee, A. M. Van Der Zande, W. Chen, Y. Li, M. Han, X. Cui, G. Arefe, C. Nuckolls, T. F. Heinz, *Nat. Nanotech.* **2014**, 9, 676.
- [44] H. G. Shin, H. S. Yoon, J. S. Kim, M. Kim, J. Y. Lim, S. Yu, J. H. Park, Y. Yi, T. Kim, S. C. Jun, *Nano Lett.* **2018**, 18, 1937.
- [45] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, Y. Zhang, *Nat. Nanotech.* **2014**, 9, 372.
- [46] A. Barton, R. Yue, S. Anwar, H. Zhu, X. Peng, S. McDonnell, N. Lu, R. Addou, L. Colombo, M. Kim, *Microelectron. Eng.* **2015**, 147, 306-309.
- [47] Z. Wang, Q. Li, F. Besenbacher, M. Dong, *Adv. Mater.* **2016**, 28, 10224.
- [48] L. Yin, K. Xu, Y. Wen, Z. Wang, Y. Huang, F. Wang, T. A. Shifa, R. Cheng, H. Ma, J. He, *Appl. Phys. Lett.* **2016**, 109, 213105.

- [49] D. A. Bandurin, A. V. Tyurnina, L. Y. Gelang, A. Mishchenko, V. Zólyomi, S. V. Morozov, R. K. Kumar, R. V. Gorbachev, Z. R. Kudrynskyi, S. Pezzini, *Nat. Nanotech.* **2017**, 12, 223.
- [50] W. L. Chow, P. Yu, F. Liu, J. Hong, X. Wang, Q. Zeng, C. H. Hsu, C. Zhu, J. Zhou, X. Wang, *Adv. Mater.* **2017**, 29, 1602969.
- [51] Y. Zhao, J. Qiao, Z. Yu, P. Yu, K. Xu, S. P. Lau, W. Zhou, Z. Liu, X. Wang, W. Ji, *Adv. Mater.* **2017**, 29, 1604230.
- [52] J. Wu, Y. Liu, Z. Tan, C. Tan, J. Yin, T. Li, T. Tu, H. Peng, *Adv. Mater.* **2017**, 29, 1704060.
- [53] J. Wu, C. Tan, Z. Tan, Y. Liu, J. Yin, W. Dang, M. Wang, H. Peng, *Nano Lett.* **2017**, 17, 3021.
- [54] J. Wu, H. Yuan, M. Meng, C. Chen, Y. Sun, Z. Chen, W. Dang, C. Tan, Y. Liu, J. Yin, *Nat. Nanotech.* **2017**, 12, 530.
- [55] J. Li, Z. Wang, Y. Wen, J. Chu, L. Yin, R. Cheng, L. Lei, P. He, C. Jiang, L. Feng, *Adv. Funct. Mater.* **2018**, 28, 1706437.
- [56] G. R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y. Son, M. S. Strano, V. R. Cooper, *ACS Nano* **2015**, 9, 11509.
- [57] X. Qian, J. Liu, L. Fu, J. Li, *Science* **2014**, 1256815.
- [58] R. J. Toh, Z. Sofer, J. Luxa, D. Sedmidubský, M. Pumera, *Chem. Commun.* **2017**, 53, 3054.
- [59] G.-B. Liu, D. Xiao, Y. Yao, X. Xu, W. Yao, *Chem. Soc. Rev.* **2015**, 44, 2643.
- [60] H. Zeng, X. Cui, *Chem. Soc. Rev.* **2015**, 44, 2629.
- [61] D. Xiao, G.-B. Liu, W. Feng, X. Xu, W. Yao, *Phys. Rev. Lett.* **2012**, 108, 196802.
- [62] W. Wu, L. Wang, Y. Li, F. Zhang, L. Lin, S. Niu, D. Chenet, X. Zhang, Y. Hao, T. F. Heinz, *Nature* **2014**, 514, 470.
- [63] X. Xu, W. Yao, D. Xiao, T. F. Heinz, *Nat. Phys.* **2014**, 10, 343.
- [64] D. A. Chenet, O. B. Aslan, P. Y. Huang, C. Fan, A. M. van der Zande, T. F. Heinz, J. C. Hone, *Nano Lett.* **2015**, 15, 5667.
- [65] Y.-C. Lin, H.-P. Komsa, C.-H. Yeh, T. Bjorkman, Z.-Y. Liang, C.-H. Ho, Y.-S. Huang, P.-W. Chiu, A. V. Krasheninnikov, K. Suenaga, *ACS nano* **2015**, 9, 11249-11257.

- [66] E. Zhang, Y. Jin, X. Yuan, W. Wang, C. Zhang, L. Tang, S. Liu, P. Zhou, W. Hu, F. Xiu, *Adv. Funct. Mater.* **2015**, 25, 4076.
- [67] H.-P. Komsa, A. V. Krasheninnikov, *J. Phys. Chem. Lett.* **2012**, 3, 3652.
- [68] Y. I. Joe, X. Chen, P. Ghaemi, K. Finkelstein, G. de La Peña, Y. Gan, J. Lee, S. Yuan, J. Geck, G. MacDougall, *Nat. Phys.* **2014**, 10, 421.
- [69] N. R. Pradhan, A. McCreary, D. Rhodes, Z. Lu, S. Feng, E. Manousakis, D. Smirnov, R. Namburu, M. Dubey, A. R. Hight Walker, *Nano Lett.* **2015**, 15, 8377.
- [70] H. Ma, P. Chen, B. Li, J. Li, R. Ai, Z. Zhang, G. Sun, K. Yao, Z. Lin, B. Zhao, *Nano Lett.* **2018**, 6, 3523.
- [71] H. Wang, X. Qian, *Nano Lett.* **2017**, 17, 5027.
- [72] X. Xi, L. Zhao, Z. Wang, H. Berger, L. Forró, J. Shan, K. F. Mak, *Nat. Nanotech.* **2015**, 10, 765.
- [73] Y. Yu, F. Yang, X. F. Lu, Y. J. Yan, Y.-H. Cho, L. Ma, X. Niu, S. Kim, Y.-W. Son, D. Feng, *Nat. Nanotech.* **2015**, 10, 270.
- [74] L. Ma, C. Ye, Y. Yu, X. F. Lu, X. Niu, S. Kim, D. Feng, D. Tománek, Y.-W. Son, X. H. Chen, *Nat. Commun.* **2016**, 7, 10956.
- [75] K. Novoselov, D. Jiang, F. Schedin, T. Booth, V. Khotkevich, S. Morozov, A. Geim, *Proc. Natl. Acad. Sci.* **2005**, 102, 10451.
- [76] X. Tong, E. Ashalley, F. Lin, H. Li, Z. M. Wang, *Nano-Micro Lett.* **2015**, 7, 203.
- [77] A. Nourbakhsh, A. Zubair, R. N. Sajjad, A. Tavakkoli KG, W. Chen, S. Fang, X. Ling, J. Kong, M. S. Dresselhaus, E. Kaxiras, *Nano Lett.* **2016**, 16, 7798.
- [78] D. Kiriya, M. Tosun, P. Zhao, J. S. Kang, A. Javey, *J. Am. Chem. Soc.* **2014**, 136, 7853.
- [79] A. Allain, J. Kang, K. Banerjee, A. Kis, *Nat. Mater.* **2015**, 14, 1195.
- [80] C. Gong, L. Colombo, R. M. Wallace, K. Cho, *Nano Lett.* **2014**, 14, 1714.
- [81] S. Das, H.-Y. Chen, A. V. Penumatcha, J. Appenzeller, *Nano Lett.* **2012**, 13, 100.
- [82] Y. Liu, J. Guo, E. Zhu, L. Liao, S.-J. Lee, M. Ding, I. Shakir, V. Gambin, Y. Huang, X. Duan, *Nature* **2018**, 557, 696.
- [83] K. Novoselov, A. Mishchenko, A. Carvalho, A. C. Neto, *Science* **2016**, 353, aac9439.
- [84] Y. Liu, P. Stradins, S.-H. Wei, *Sci. Adv.* **2016**, 2, e1600069.

- [85] H.-J. Chuang, B. Chamlagain, M. Koehler, M. M. Perera, J. Yan, D. Mandrus, D. Tománek, Z. Zhou, *Nano Lett.* **2016**, 16, 1896.
- [86] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.* **2010**, 22, 3906.
- [87] Y. Kopelevich, P. Esquinazi, *Adv. Mater.* **2007**, 19, 4559.
- [88] M. Katsnelson, K. Novoselov, *Solid State Commun.* **2007**, 143, 3.
- [89] M. I. Katsnelson, *Mater. Today* **2007**, 10, 20.
- [90] K. S. Novoselov, E. McCann, S. Morozov, V. I. Fal'ko, M. Katsnelson, U. Zeitler, D. Jiang, F. Schedin, A. Geim, *Nat. Phys.* **2006**, 2, 177.
- [91] M. Dave, R. Vaidya, S. Patel, A. Jani, *Bull. Mater. Sci.* **2004**, 27, 213.
- [92] I. Naik, A. Rastogi, *Pramana* **2011**, 76, 957.
- [93] P. Yu, J. Lin, L. Sun, Q. L. Le, X. Yu, G. Gao, C. H. Hsu, D. Wu, T. R. Chang, Q. Zeng, *Adv. Mater.* **2017**, 29, 1603991.
- [94] F. Liu, S. Zheng, A. Chaturvedi, V. Zólyomi, J. Zhou, Q. Fu, C. Zhu, P. Yu, Q. Zeng, N. D. Drummond, *Nanoscale* **2016**, 8, 5826.
- [95] X. Zhu, Y. Sun, S. Zhang, H. Lei, L. Li, X. Zhu, Z. Yang, W. Song, J. Dai, *Solid State Commun.* **2009**, 149, 1296.
- [96] X. Wang, F. Xia, *Nat. Mater.* **2015**, 14, 264.
- [97] T. Roy, M. Tosun, X. Cao, H. Fang, D.-H. Lien, P. Zhao, Y.-Z. Chen, Y.-L. Chueh, J. Guo, A. Javey, *ACS Nano* **2015**, 9, 2071.
- [98] F. Ceballos, M. Z. Bellus, H.-Y. Chiu, H. Zhao, *ACS nano* **2014**, 8, 12717-12724.
- [99] A. Dankert, S. P. Dash, *Nat. Commun.* **2017**, 8, 16093.
- [100] K. Zhang, T. Zhang, G. Cheng, T. Li, S. Wang, W. Wei, X. Zhou, W. Yu, Y. Sun, P. Wang, *ACS Nano* **2016**, 10, 3852.
- [101] Y. Kim, A. R. Kim, J. H. Yang, K. E. Chang, J.-D. Kwon, S. Y. Choi, J. Park, K. E. Lee, D.-H. Kim, S. M. Choi, *Nano Lett.* **2016**, 16, 5928.
- [102] A. R. Kim, Y. Kim, J. Nam, H.-S. Chung, D. J. Kim, J.-D. Kwon, S. W. Park, J. Park, S. Y. Choi, B. H. Lee, *Nano Lett.* **2016**, 16, 1890.
- [103] Y. Gong, S. Lei, G. Ye, B. Li, Y. He, K. Keyshar, X. Zhang, Q. Wang, J. Lou, Z. Liu, *Nano Lett.* **2015**, 15, 6135.

- [104] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, *Nat. Mater.* **2014**, 13, 1135.
- [105] T. Zhang, B. Jiang, Z. Xu, R. G. Mendes, Y. Xiao, L. Chen, L. Fang, T. Gemming, S. Chen, M. H. Rummeli, *Nat. Commun.* **2016**, 7, 13911.
- [106] S. Li, S. Wang, D.-M. Tang, W. Zhao, H. Xu, L. Chu, Y. Bando, D. Golberg, G. Eda, *Appl. Mater. Today* **2015**, 1, 60.
- [107] J. Shi, X. Wang, S. Zhang, L. Xiao, Y. Huan, Y. Gong, Z. Zhang, Y. Li, X. Zhou, M. Hong, *Nat. Commun.* **2017**, 8, 958.
- [108] S. Zhao, T. Hotta, T. Koretsune, K. Watanabe, T. Taniguchi, K. Sugawara, T. Takahashi, H. Shinohara, R. Kitaura, *2D Materials* **2016**, 3, 025027.
- [109] M. Zhang, Y. Zhu, X. Wang, Q. Feng, S. Qiao, W. Wen, Y. Chen, M. Cui, J. Zhang, C. Cai, *J. Am. Chem. Soc.* **2015**, 137, 7051.
- [110] J. Yuan, J. Wu, W. J. Hardy, P. Loya, M. Lou, Y. Yang, S. Najmaei, M. Jiang, F. Qin, K. Keyshar, *Adv. Mater.* **2015**, 27, 5605.
- [111] W. Ge, K. Kawahara, M. Tsuji, H. Ago, *Nanoscale* **2013**, 5, 5773.
- [112] K. Keyshar, Y. Gong, G. Ye, G. Brunetto, W. Zhou, D. P. Cole, K. Hackenberg, Y. He, L. Machado, M. Kabbani, *Adv. Mater.* **2015**, 27, 4640.
- [113] X. Li, M.-W. Lin, J. Lin, B. Huang, A. A. Puretzky, C. Ma, K. Wang, W. Zhou, S. T. Pantelides, M. Chi, *Sci. Adv.* **2016**, 2, e1501882.
- [114] W. Zhang, Z. Huang, W. Zhang, Y. Li, *Nano Res.* **2014**, 7, 1731.
- [115] L. Li, J. Kim, C. Jin, G. J. Ye, D. Y. Qiu, H. Felipe, Z. Shi, L. Chen, Z. Zhang, F. Yang, *Nat. Nanotech.* **2017**, 12, 21.
- [116] L. Li, F. Yang, G. J. Ye, Z. Zhang, Z. Zhu, W. Lou, X. Zhou, L. Li, K. Watanabe, T. Taniguchi, *Nat. Nanotech.* **2016**, 11, 593.
- [117] L. Li, G. J. Ye, V. Tran, R. Fei, G. Chen, H. Wang, J. Wang, K. Watanabe, T. Taniguchi, L. Yang, *Nat. Nanotech.* **2015**, 10, 2091.
- [118] J. Zhou, J. Shi, Q. Zeng, Y. Chen, L. Niu, F. Liu, T. Yu, K. Suenaga, X. Liu, J. Lin, *2D Mater.* **2018**, 5, 025019.
- [119] M. Tosun, S. Chuang, H. Fang, A. B. Sachid, M. Hettick, Y. Lin, Y. Zeng, A. Javey, *ACS Nano* **2014**, 8, 4948.

- [120] J. Y. Lim, A. Pezeshki, S. Oh, J. S. Kim, Y. T. Lee, S. Yu, D. K. Hwang, G. H. Lee, H. J. Choi, S. Im, *Adv. Mater.* **2017**, 29, 1701798.
- [121] A. Pezeshki, S. H. Hosseini Shokouh, P. J. Jeon, I. Shackery, J. S. Kim, I.-K. Oh, S. C. Jun, H. Kim, S. Im, *ACS Nano* **2015**, 10, 1118.
- [122] Y. F. Lin, Y. Xu, S. T. Wang, S. L. Li, M. Yamamoto, A. Aparecido-Ferreira, W. Li, H. Sun, S. Nakaharai, W. B. Jian, *Adv. Mater.* **2014**, 26, 3263.

hapter 3

Experimental Methodology

This chapter is going to introduce the typical process of the CVD method, and the rational for the synthesis of 2D vdW heterostructures, followed by the working principles of the characterization techniques, which includes optical microscopy, Raman spectroscopy, AFM, SEM, XPS, STEM, and their application in the material characterization and the analyses of typical data obtained, and how these techniques were applied in the material characterization of this thesis, and finally the FET device fabrication process and measurement system.

3.1 The Rational for the CVD Synthesis of 2D Materials

Chemical vapor deposition (CVD) is a deposition method used to produce high-quality, high-performance thin film materials. It is famous for the microfabrication process of the wafer in the semiconductor industry. In general, the CVD process is the vaporization and reaction of the volatile precursors followed by the nucleation and growth of the product and deposition on the substrate. Several parameters, such as the pressure, growth temperature, gas flow rate and substrates, are essential for the processes. As discussed before, the advantages of this CVD method are large-scale production, high quality and good control of the thickness.^[1-3] In the preparation of the heterostructures, the preponderance of this method is more predominant, especially in the lateral (in-plane) heterostructures. For the vertical (vdW) heterostructures, the advantages of CVD method in large area, high-quality interface and good control of interlayer orientation^[4-7] are surpassing when compared with the mechanical exfoliation and liquid exfoliation methods.

Figure 3.1 CVD processes of the TMDC growth. Up: the chamber model, indicating the location of the precursors and the substrate. Down: the reaction mechanism of MoO₃ and S to produce MoS₂.

As shown in Figure 3.1, in the synthesis of TMDCs, the chalcogen elementary substances

(sulfur, selenium and tellurium) are placed in the upstream and located at suitable temperature zone while metal precursors (metal powders, metal oxides and metal halides) are placed in the central zone of the chamber. The substrates (SiO_2/Si , mica, sapphire, STO, glass and so on) are either placed at the top of the metal precursors (facing down) or at the downstream. Figure 3.1 depicts the CVD growth processes of MoS_2 which includes two routines: (i) The vaporization of Mo precursors is followed by the reaction with the evaporated sulfur to form MoS_2 and then the deposition on substrate. (ii) Mo precursors are adsorbed on substrate first and reacted with sulfur to form the MoS_2 nucleus and then the nucleus grows into the triangular MoS_2 . For the step-by-step growth, after the growth of the first material is finished, the sample is taken out and serves as the substrate for the growth of the second material.^[4] However, the sample may be contaminated when taken out, which will lead to lower quality of the interface. For the one-step growth of vdW heterostructures, two metal precursors are placed in the chamber at the same time. And the mechanism of this one-step method is the sequential growth of the two individual materials due to the difference of the growth temperature.^[6]

In this thesis, Nb_2O_5 and NaCl with a ratio of about 9:1 were used as metal precursors for both the growth of NbS_2 and $\text{NbS}_2/\text{MoS}_2$ vdW heterostructure on Si substrate. In the preparation of the heterostructure, MoO_3 was used to grow MoS_2 and the one-step atmospheric pressure CVD method was adopted in order to get a high-quality interface. In the preparation of $\text{Bi}_2\text{O}_2\text{Se}$ on mica, Bi_2Se_3 and Bi_2O_3 are used as precursors and a low-pressure method was adopted in order to get higher vacuum of the chamber.

3.2 Characterization Techniques

This section will introduce the characterization techniques used in this thesis, which include Optical Microscopy (OM), Atomic Force Microscopy (AFM), Raman Spectroscopy and Photoluminescence Spectroscopy (PL), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Scanning Transmission Microscopy (STEM).

3.2.1 Optical Microscopy

The OM is a type of microscopes which uses visible light and a lenses system to magnify the image of small objects. Most of the time, the order of magnification is $\times 5$ to $\times 100$ (objective lens), since the resolution (R) is limited by the numerical aperture ($N.A.$) and the wavelength of the visible light (λ): $R = 0.61 \times (\lambda / N.A.)$. The numerical aperture is defined as $N.A. = n \times \sin \mu$, in which n is the refractive index of the medium, and μ is half of the angle of the focused light beam (Figure 3.2a). As it is summarized, when μ is up to 90° , the $N.A.$ is equal to 1. And for the visible light, the shortest wavelength is 405 nm. Hence, the resolution for the OM in air is 247 nm. By immersed the OM in oil, the $N.A.$ could be increased to 1.25, and thus, the resolution could be improved to 197 nm,^[8] which is widely adopted in the microfabrication of the chips in the semiconductor Fabs. That is also why even higher magnification lens is used, the resolution still could not be improved further.

Figure 3.2 The working principles of OM. (a) The Numeric Aperture (N.A.) (b) The mechanism of the contrast of the layered materials.^[9] (c) OM image of exfoliated monolayer MoS_2 . (d) The contrast profile of the line marked in (c).^[10] (e) The statistics of the contrast and the layer number.^[11]

On the other hand, a good contrast of sample on substrate is significant for layered materials. As shown in Figure 3.2b, the incident light will be reflected by the sample (R) and the bare substrate (R_0). Hence, the contrast is defined by $C=(R-R_0)/R_0$, and the contrast difference (C_D) between sample and substrate (C_D) is defined as $C_D=C-C_s$.^[11] As now most of the OM is equipped with the charge coupled devices (CCD) optical system, live imaging of this contrast could be easily achieved. Since the contrast is quantified, it could be used to determine the thickness of the sample preliminarily. For example, Figure 3.2c shows an optical image of monolayer MoS₂ and the contrast line profile is shown in Figure 3.2d. From Figure 3.2e, it can be seen that in certain range the contrast difference can be used to determine the thickness, such as 1 layer to 3 layers. However, as it is not a linear relationship between the thickness and the contrast difference. Therefore, for more accurate value of the thickness, AFM should be used instead.

In this thesis, OM was applied to take optical images of all the samples and used to locate the sample in the transfer, Raman test and device measurement.

3.2.2 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is used to obtain the thickness of the sample and to see the roughness of the surface. The working principle of Atomic Force Microscopy is measuring the atomic interaction between the sample and the cantilever via monitoring the deflection of a cantilever-tip when scanning across the sample surface. As shown in Figure 3.3a, the cantilever is fastened on a piezoelectric tube controlled by a computer and a laser that reflects off the back of the cantilever and onto a quadrant photodiode was used to record the deflection of the cantilever (Figure 3.3b). The signal of the position on the quadrant photodiode was then translated into the height profile of the sample surface, based on which the AFM topography can be produced (Figure 3.3c). The cantilever tip tapers to a very sharp point, typically less than 10nm radius of curvature. Hence the resolution of AFM could be as low as sub-nanometer, which is quite suitable for the characterization of 2D materials. AFM provides three types of working modes, contact mode, tapping mode and the non-contact (cantilever at a fixed height). As an example, the AFM topography of

CVD-grown MoS₂ is shown in Figure 3.3b and by extracting the height profile of the line, the thickness of about 0.72 nm could be obtained.^[1] Besides, via statistically analyzing all the line height profiles, the surface roughness of the sample could be acquired.

Figure 3.3 The working principle of AFM. (a) Schematic illustration of the AFM working principle. (b) Cantilever deflection. (c) Three working modes of AFM: contact mode, tapping mode and non-contact mode. (d) AFM topography of CVD-grown MoS₂. (e) The height profile of the line marked in (c).^[1]

In this thesis, AFM was used to determine the thickness of NbS₂ and Bi₂O₂Se. The AFM was conducted on an Asylum Research Cypher S model with a tapping mode.

3.2.3 Raman and Photoluminescence Spectroscopy

Raman spectroscopy is an optical technique used to observe vibrational, rotational, and

other low-frequency modes, which is widely used in material science to identify molecules by the structural fingerprint. As shown in Figure 3.4a, when shined with a monochromatic light, the electron will be excited from ground state to a virtual excited state. Later in the recombination, elastic radiation without energy shift is called Rayleigh scattering while the inelastic radiation with photon energy shifted up and down is called Raman scattering. The energy shift is caused by the interaction between laser light and molecular vibrations, phonons or other excitations. It is the energy shift of the photons that gives the information of vibrational modes, which could be used to identify molecules. Need to note that the application of laser light as light sources makes Raman spectroscopy more powerful in the material science because basically the signal of Raman scattering is weak compared with the strong Rayleigh scattering. Also, complementary to infrared spectroscopy (IR), they provide information of the vibrational modes with different symmetries.

Figure 3.4 The working principle of Raman spectroscopy. (a) The Rayleigh (elastic) and Raman (inelastic) scattering. (b) The active Raman vibrational modes of monolayer 2H TMDC. (c) The phonon dispersion curves of monolayer MoS_2 .^[12] (d) The Raman spectrum of WS_2 .^[2]

For monolayer 2H TMDC, there are four types of Raman active vibrational modes: A'_1 , E' , E'' , E' (LA/TA), as shown in Figure 3.4b. And their phonon dispersion curves are

calculated and presented in Figure 3.4c.^[12] Typically, the Raman spectrum of monolayer WS₂ is shown in Figure 3.4d,^[2] in which all the A_{1g} , E_{2g}^1 , E_{2g}^2 , $2LA$ modes could be found. Apart from identify molecules including the doping, the layer-number evolution of phonons in the Raman spectra of TMDC could be used to identify the layer numbers. In addition, it also could be extensively used to investigate the layer doping, interlayer coupling, spin-orbit splitting and external perturbations.^[12]

In this thesis, Raman spectrum was used to identify molecules of MoS₂, NbS₂ and Bi₂O₂Se. And the Raman spectrum was used to prove the coexistence of MoS₂ and NbS₂ in the heterostructure and further examine the growth mechanism of the heterostructure. Raman spectra were recorded by a *Witec* system equipped with 100x objective lens under 532 nm laser excitation. The grating for the NbS₂/MoS₂ experiment is 1800 lines/mm while that for the Bi₂O₂Se is 1200 lines/mm.

Photoluminescence (PL) is light emission after the absorption of photons, which is initiated by photoexcitation process that excites electrons to a higher energy level, followed by the relaxation processes in which photons are re-radiated. PL was widely used in the exciton dynamics (inter-band transition in the heterostructure, fast photogenerated carrier separation and binding energy of excitons), bandgap engineering (2D semiconductor doping), valley spintronics and so on. As the PL is closely related to the band structure of the targeted molecules, here the band structure of TMDC will be introduced first.

As discussed before, when the layer number of TMDC is decreased, not only the symmetry of the crystal is changed, but also the interactions between the layers. Especially when the thickness comes to single layer, the quantum confinement effect will become prominent. One important property is the change happened in the value and types of the energy band gap. For example, the MoS₂ bulk sample has an energy band gap (E_g) of 1.2 eV, while that of monolayer counterpart is increased to 1.9 eV (Figure 3.5a).^[13] Via analyzing the band composition in the DFT simulation, it could be figured out that what's happened during the thinning process. As presented in Figure 3.5b, the conduction and valence bands near K point in the first Brillouin Zone (BZ) are predominantly from the d orbitals of the metal

atoms (d_{xz} and $d_{x^2-y^2}$ for the valence band and d_{z^2} for the conduction band) in both monolayer and multilayer MoS₂.^[14] This is because the metal atoms are sandwiched in the center of X-M-X, which is insensitive to the interlayer hopping as the thickness increases. However, very different with this, the local minima located at Q point (middle point between the K and Γ points) and the local maximum at Γ point (Figure 3.5b), which are mainly composed of the p_z orbitals from the X atoms, are very sensitive to the interlayer hopping originated from the closer distance of the p_z orbitals in the multilayer MoS₂. Hence, the thickness plays a significant role in the E_g of MoS₂ and also other TMDCs.

And this change of the band composition could also account for another significant change, which is the crossover from indirect band gap in multilayer and bulk MoS₂ to direct band gap in monolayer MoS₂. As it could be seen from Figure 3.5a, for bilayer and bulk MoS₂, the conduction band minimum (CBM) is located at Q point and the valence band maximum (VBM) is located at Γ point, because the interlayer hopping of the p_z orbitals from the X atoms make major contribution. This leads to an indirect band gap of the bilayer and bulk MoS₂. While in the monolayer MoS₂, the role of the d orbitals from metal atoms comes to become more significant. As a result, both the CBM and VBM are shifted to K points, in which CBM is mainly from d_{z^2} orbital and VBM is mainly from d_{xz} and $d_{x^2-y^2}$ orbitals, leading to a direct band gap.

PL spectrum provides firm evidence for both the value change and the crossover from indirect to direct band gap. As shown in Figure 3.6a, the PL intensity of monolayer MoS₂ is four orders of magnitude higher than that of bulk MoS₂, which is a feature of the direct-gap semiconductor.^[15] This is because the requirement of the momentum conservation in optical transitions is waived for semiconductors with direct band gap. From Figure 3.6b, PL peaks provide the E_g of MoS₂ with various thicknesses. It could be seen that the E_g of MoS₂ increases from 1.35 eV to 1.9 eV when the thickness is reduced from 6 layers to monolayer and all the values are larger than that of the bulk counterpart. All these PL results show good consistency with the DFT calculation result.

Figure 3.5 The DFT simulation of band formation of MoS₂. (a) DFT simulation of MoS₂ bulk, bilayer and monolayer (H-type stacking). For bulk and multilayer MoS₂, an indirect band gap is predicted and for monolayer MoS₂, a direct band gap is predicted. The E_g of bulk and monolayer MoS₂ are calculated to be 1.2 eV and 1.9 eV respectively.^[13] (b) DFT simulation analysis of the band composition of monolayer MoS₂ (1H). The CBM and VBM are located at K points, and they are mainly composed of the d orbitals from the metal atoms (CBM is mainly from d_{z^2} orbital and VBM is mainly from d_{xz} and $d_{x^2-y^2}$ orbitals). While the Q and Γ points are predominantly from the p_z orbitals from the X atoms. Hence, they play a significant role in the multilayer and bulk MoS₂ as the p_z orbitals are more sensitive to the interlayer hopping when the thickness is increased.^[14]

Further, it is known that d orbitals from heavy metals will have strong spin orbital coupling (SOC). As discussed above, for monolayer MoS₂, the main compositions of the CBM and VBM located at K points are from the d orbitals of the metal atoms. Interestingly, the $d_{x^2-y^2}$ and d_{xy} orbitals at VBM are split by SOC while the d_{z^2} orbital is not affected

(Figure 3.6c).^[16] Hence, there will be two direct inter-band optical transitions which are noted as A and B excitons. This has also been verified by the PL spectrum (Figure 3.6d), which show two obvious peaks related to A and B excitons respectively.^[17] This splitting characteristic provides a platform to explore the application of MoS₂ in spintronics.

Figure 3.6 Verification of the band structure by PL spectrum. (a) PL density of MoS₂ with various thicknesses. The PL density of monolayer MoS₂ is four orders of magnitude higher than the bulk counterpart, which is a virtue of the direct-gap semiconductor. (b) PL peak values of MoS₂ with various thickness. The E_g of MoS₂ is decreased from 1.9 eV to 1.3 eV when the thickness increases from monolayer to bulk, which show good consistency with the DFT calculation.^[15] (c) d orbitals split by SOC. The $d_{x^2-y^2}$ and d_{xy} orbitals located at VBM near the K points are split by SOC while the affection of the d_{z^2} orbital located at CBM by SOC is small.^[16] (d) The clear A and B excitons in PL of monolayer MoS₂.^[17]

In this thesis, PL spectrum was used to characterize the optical properties of MoS₂ and NbS₂/MoS₂ heterostructure, in which the fast separation of photogenerated carriers is expected. PL spectra were recorded by a Witec system equipped with 100x objective lens and the gating of 300 lines/mm under 532 nm laser excitation.

3.2.4 X-ray Photoelectron Spectroscopy

Figure 3.7 The working principle of XPS. (a) Schematic of the XPS characterization process. (b-c) The XPS characterization of MoS₂. Binding energy peaks of Mo ($3d_{3/2}$ and $3d_{5/2}$) and S ($2p_{3/2}$ and $2p_{1/2}$).^[18]

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique to determine the elemental composition, chemical valence state and the ratio of the elements within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the material being analyzed (Figure 3.7a). As the wavelength of X-ray is ranging from 0.01 nm to 10 nm, the depth of the measurement is limited at the top 0 to 10 nm of the sample surface. That is the reason why XPS is called the surface characterization technique. However, this depth is enough for the 2D materials as most of the time the thickness of 2D

materials is less than 10 nm. One demanding requirement of XPS is the high vacuum ($\sim 10^{-8}$ millibar) or ultra-high vacuum (UHV; $< 10^{-9}$ millibar) conditions, which makes this technique costly.

Figure 3.8 The XPS characterization of TMDCs. (a) The binding energy of Nb (valence state of 4+) in NbSe₂, used to characterize the stability. (b) The shift of the binding energy of Mo in MoS₂ after doped with Nb. (c-d) The shift of the binding energy of Mo (3d) and W (4f) in MoS₂/WS₂ heterostructure.

In the characterization of TMDC, XPS is used to characterized: (i) The elemental compositions. For example, in MoS₂, two binding energy peaks from Mo (232.2 eV and 230 eV) could be assigned to 3d_{3/2} and 3d_{5/2} (Figure 3.7b). Also, the binding energy peaks of sulfur (2p_{3/2} and 2p_{1/2}) could be obtained as well (Figure 3.7c).^[18] (ii) The valence state of the element. This is mainly used to characterize the stability of the tested

material. For example, in NbSe₂, the valence state of Nb is +4 (Figure 3.8a) while it is changed to +5 when oxidized to Nb₂O₅.^[19] This is also applicable to metals in the same group (V and Ta). (iii) The ratio of the elements. This is used to characterize the defect concentration in the few-layer sample, the surface state in the multilayer materials and the doping ratio in the doped TMDC. The ratio could be given via integrating the area of the peaks of each element. Note that the detection limit of XPS is 0.1% (1 part per thousand, or 1000 ppm). Hence, for the doping of TMDC, it is hard to detect the doping ratio if the doping is lower than 0.5% (the lowest value reported up to now).^[20] Besides, for doping TMDC and TMDC vdW heterostructure, the binding energy will have a small shift due to the redistribution of the charge density as shown in the WS₂/MoS₂ (Figure 3.8c and 3.8d).^[21] For the characterization of vdW heterostructure, one more concern is the beam size of X-ray. As it is ranging from 10 μm to 5 mm for monochromatic beam, and the sample size is always small for the exfoliation method. Hence, it is not easy to locate the sample in the chamber.

In this thesis, XPS were used to determine the NbS₂ and MoS₂ in the NbS₂/MoS₂ heterostructure and the ratio of anion (S) to cations (Nb + Mo). XPS tests were carried out via a PHI Quantera II spectrometer with a monochromatic Al-K α radiation ($h\nu = 1486.6$ eV), calibrated with C 1s core level (binding energy: 284.8 eV).

3.2.5 Scanning Electron Microscopy

In addition to light and atomic force microscopy (OM and AFM), electron microscope is one more powerful microscope that produces images by the interaction of sample with a focused beam of electrons. When the primary electron beam interacts with atoms in the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen, which is known as the interaction volume (Figure 3.9a). The interaction volume extends from less than 100 nm to approximately 5 μm into the surface and its size depends on the electron's landing energy, the atomic number of the specimen and the specimen's density.

Figure 3.9 The electron-specimen interaction volume. The interactions between the electron and sample are shown on the right.

The energy exchange between the electron beam and the sample (Figure 3.9b) produces different kinds of high-energy electrons by: (i) elastic scattering, which is called back scattered electrons (BSE), used to determine the crystal phase and grain boundary. (ii) inelastic scattering, which is featured by the emission of secondary electrons (SE), used to obtain the topography information. Besides, if the vacancy caused by the kick-out of SE is filled by the outer level electrons, characteristic X-rays will be emitted, which could be used in energy-dispersive X-ray spectroscopy (EDS) to acquire the composition information. If this energy is transferred to another outer level electron which escape from the atoms, these escaping electrons are called Auger electrons (AE). (iii) Transmitted electrons (TE) and the elastic, inelastic and incoherent elastic scattering electrons. These electrons pass through the thin sample (thinner than 100 nm) and used for TEM, STEM and electron energy loss spectroscopy (EELS), which will be discussed later. Apart from these, there are some electrons absorbed by the sample and other types of electromagnetic emission, such as continuum X-rays, cathodoluminescence (CL) and so on. (Figure 3.9a).

Figure 3.10 The schematic setup of SEM. The working principle is described on the right.

In scanning electron microscopy (SEM), electrons are emitted by the filament in the electron gun and accelerated by electric field to the anode and focused by a series of lens and apertures into a spot (Figure 3.10). In a wave form, the de Broglie wavelength^[22] of electron can be calculated by $\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{m_e v} \sqrt{1 - \frac{v^2}{c^2}}$, where h is plank constant, p is the momentum, m_e is static electron mass, v is the electron speed, c is the light speed. The speed of electron could be calculated by $v = \sqrt{\frac{2eV}{m_e}}$, where e is the electron unit charge, V is the accelerating voltage. Here, if the accelerating voltage is 30 kV, v is much smaller than the light speed c , then $\lambda = \frac{h}{m_e v}$. Theoretically, the resolution of SEM is determined by the accelerating voltage of which the highest value now is 30 kV, producing a point resolution of 0.4 nm.

The most common mode of SEM is the detection of SE. As the detected number of SE depends on the sample topography, through scanning the sample and collecting SE, an image which displays the topography of the sample surface is created. Hence, SEM is widely used in the characterization of conductive sample morphology. Another mode is the EDS used to determine the composition and the ratio of each element. However, in terms of the accuracy, SEM EDS is much lower than XPS which is preferred in the characterization of chemical compositions.

In CVD-grown TMDCs, SEM is rarely used as OM work quite well for the morphology characterization. However, when it comes to the metal/semiconductor heterostructure, owing to the difference in conductivity, the two components have quite distinct contrasts in SEM images, which could be used to identify the heterostructure.

In this thesis, SEM is used to identify the NbS₂/MoS₂ heterostructure and evaluate the surface morphology of the transferred Bi₂O₂Se on Si substrate. And the EDS setup was used to determine the ratio of Bi to Se in the transferred Bi₂O₂Se. Also, it was used to develop the electrode pattern via electron beam lithography (EBL) when fabricating devices, which will be discussed later. SEM and EDS characterizations were performed under the *JOEL JSM-7600F system* with an accelerating voltage of 15 kV.

3.2.6 Scanning Transmission Electron Microscopy

In the interaction volume, there are some high-energy electrons transmit through the specimen. In conventional TEM, the fluorescent screen below the sample collects the signals from these electrons (Figure 3.11). As deduced above, $\lambda = \frac{h}{m_e v} \sqrt{1 - \frac{v^2}{c^2}}$ and $v = \sqrt{\frac{2eV}{m_e}}$, if $V = 100$ kV, λ is 0.04 Å. Hence, the wavelength is comparable with the crystal lattice parameter, the inelastic scattering (electron-electron) and elastic scattering (electron-nucleus) electrons could provide the information of crystal lattices. However, in practice, even 200 kV was applied, it is hard to achieve 2 Å, which is limited by the quality of the electromagnetic lens.

Figure 3.11 The schematic setup of TEM. The working principle is described on the right.

Two possible solutions are provided. As the elastic scattering electrons are used to create the image and they are close to the beam center, a lot of apertures are used to limit the electron beam. However, even the electron wavelength is much smaller the width of the aperture, there are still Fraunhofer diffraction phenomenon^[23] in this case (Figure 3.12b). The peak width of the beam is given by $\theta_{\omega} = 1.22 \times \frac{\lambda}{\omega}$, where λ is the electron wavelength and ω is the width of the aperture. From the equation, as ω decreases, θ_{ω} will increase. Hence, there should be a trade-off between the initial beam size and the diffraction effect in decreasing ω .

Figure 3.12 Three major types of electrons in TEM and the Fraunhofer diffraction effect. (a) Three major types of electrons in TEM: transmitted, elastic and inelastic scattering electrons. (b) the Fraunhofer diffraction effect.^[24]

Another method is to decrease the electron wavelength, one of the operating mode is STEM. In STEM, the electron beam is focused to a fine spot with a size of 0.05-0.2 nm, which then scans over the sample. The scan is conducted in a raster way that at each point sample illuminated with the beam parallel to the optical axis. However, the spherical aberration of the lens made the beam cannot be focused on the focal plane (Figure 3.13a), which also lead to a larger spot size (Figure 3.13d). This could be solved by adding an aberration corrector (such as the quadrupole-octupole corrector) to STEM, which serves like a concave lens. With the addition of the aberration corrector, the beam has become more converged (Figure 3.13b). As a result, the beam size becomes smaller (Figure 3.13e) which could also be verified by the enhanced intensity line profiles (Figure 3.13c). This aberration correction enables electron beams to be focused to diameter of sub-Angstrom, which allows images with sub-Angstrom resolution to be acquired. Up to now, advanced aberration-corrected STEMs have since been developed with the resolution of sub-50 pm. Hence, it is now possible to identify atoms and molecules with unprecedented clarity.

In addition to the size and intensity of the electron probe, the aberration corrector also increases the scattering angle, which provides chances to obtain more information, such as

the annular dark-field (ADF) imaging and electron energy loss spectroscopy (EELS). According to the Bragg's law^[25] $2d \sin \theta = \lambda$, in which d is the lattice spacing of the crystal and θ is the scattering angle. Take metal as example, the typical value of d is 2 Å, and the wavelength at the accelerating voltage of 100 kV is 0.04 Å. Thus, $\sin \theta$ is about 0.01 and the corresponding angle is 0.572° or 10.0 mrad. In aberration-corrected STEM, this value could be increased to higher angle (even larger than 50 mrad). Therefore, more detectors are available, including the ADF and HAADF (high angle ADF) detector (Figure 3.13f).

Figure 3.13 The aberration correction of STEM. (a) The spherical aberration of STEM. (b) The addition of aberration corrector to the STEM. (c) The comparison of the peak width and intensity of electrons with and without aberration correction. (d-e) The electron spots with and without aberration correction.^[26] (f) More detectors in aberration-corrected STEM.

ADF imaging is a method of mapping samples by collecting scattered electrons from an annulus around the main beam with an annular detector. This annular design has two advantages: First, the annular design improves the collection efficiency of the elastic electrons. As it avoids the main beam, which has much higher intensity, the intensity of the

elastic electrons will be a problem. That's the reason the name of dark field comes from. However, it excludes the interference from the low-angle inelastic electrons. And as these high-angle elastic electrons are originated from the Rutherford scattering,^[27] the contrast is proportional to the square of the atomic number (Z^2). Hence, not only the contrast has been greatly improved, this method can also provide information of chemical composition.

Figure 3.14 The applications of STEM in the characterization of TMDC. (a) The characterization of different metal elements in the doped TMDC.^[29] (b) The determination of grain boundaries in the in-plane TMDC heterostructure.^[30] (c) The moiré pattern of TMDC vdW heterostructure observed in STEM.^[5] (d-e) The identification of TMDC with 2H, 1T, 1T' and 1T'' phases and the intensity line profiles.^[31]

Second, the hollow center in the annular detector allows the pass of the inelastic electrons which could be collected by the EELS detector at the same time. In EELS, the inner-shell electron ionizations are particularly useful for detecting the elemental components of a material. Need to mention that EELS test provides a complementary method to measure

the light atoms (low atomic number, from Carbon to Zinc). In terms of energy resolution, it is better to choose EELS for 1 eV while EDS is better for a few tens of eV.^[28]

In the characterization of TMDCs, aberration-corrected STEM has been used in many applications. (i) The characterization of different metal elements in the doped TMDC. As the contrast is related to the atomic numbers (Z-contrast), it is easy to distinguish these elements in a doped TMDCs. In Figure 3.13a, the bright spots are W atoms due to higher atomic number while the darker are Mo atoms.^[29] (ii) The determination of the grain boundaries in the in-plane heterostructure. This because of the obvious contrast difference on two sides (Figure 3.13b).^[30] (iii) The verification of the vdW heterostructure. Due to different crystal lattice parameters, the vdW heterostructure will show moiré pattern, which could be clearly seen in the STEM image (Figure 3.13c).^[5] (iv) The identification of crystal with different phases. 2H MoS₂ is trigonal prism while 1T MoS₂ is octahedron. STEM provide the capability to view the differences of the stacking orders among 2H, 1T, 1T' and 1T'' directly (Figure 3.13d-e).^[31] And the intensity line profile helps to confirm the difference of these two stacking orders (Figure 3.13d).

In this thesis, STEM was used to characterize the stacking order of NbS₂/MoS₂ vdW heterostructure. ADF-STEM images were obtained using a probe-corrected Titan ChemiSTEM (FEI, USA) which was operated at an accelerating voltage of 200 kV. The convergent semi-angle for illumination was set to be about 21.4 mrad with a probe current of 79 pA. The collection angle is about 43.4 to 200 mrad for ADF-STEM imaging. The atomic-resolution ADF-STEM images were processed with an improved Wiener filtering method to partly increase the signal-to-noise ratio for a better illumination. STEM-ADF image simulations were carried out using QSTEM software,^[32] with the input parameters being set according to the experimental conditions. False-color images were performed by ImageJ to improve visual inspection.

It was also used to characterize the crystal lattices of Bi₂O₂Se and to verify the etching effect of HF acid to Bi₂O₂Se. ADF-STEM imaging was carried out on an aberration-corrected JEOL ARM-200F equipped with a cold field emission gun, operating at 80 kV,

and an ASCOR probe corrector. The convergent semi-angle of the probe was set at about 30 mrad. ADF-STEM images were collected using a half-angle range from about 68 to 280 mrad. A dwell time of $19 \mu\text{s pixel}^{-1}$ was set for single-scan imaging. EDS mapping was conducted under the Oxford X-Max 100TLE SDD EDS system.

3.3 Device Fabrication and Measurement

Figure 3.15. The device fabrication (EBL) processes.

After the successful production of the desired material, the electrical and optoelectrical properties are evaluated by fabricating the FET devices. As discussed before, SEM could also be applied in develop electrode pattern in the electron beam lithography, which is a widely used method in the device fabrication. The processes are shown in Figure 3.14: First, a layer of electron sensitive resist was spin-coated on the surface. After the electrode pattern was draw in the software, the resist was exposed selectively to the electron beam according to the pattern, which will change the solubility of the resist. When immersed in the developer solution, the exposed area was washed out when the other area was unchanged. Then, the metal was evaporated and deposited on the surface. Finally, in a lift-off process, the metal on the unchanged resist will be washed out, leaving the metal on the exposed area serve as electrodes.

The advantages of EBL are the custom patterns and the higher resolution (sub-10 nm), compared to the photolithography (visible light resolution, 197nm). However, the disadvantage is also obvious, the requirement vacuum and thus, low yield and high cost. Hence, even now deep ultraviolet (DUV) and extreme ultraviolet (EUV) light have been brought into the production of 10 nm and 7nm processing, EBL is not suitable for mass production.

The EBL model in this thesis is Nova nanoSEM 230 with digital pattern generator Nabity-NPGS. After the pattern was developed in MIBK/IPA, metal contacts (3 nm Cr/55 nm Au) were deposited by Kurt J. Lesker Nano 36 Thermal Evaporator. Electrical and photoresponse properties of the FETs were measured in the MicroXact Probe Station by Agilent B1500A Semiconductor Device Parameter Analyzer. The rise and decay time of the light response was measured by Tektronix MDO 3052 Mixed Domain Oscilloscope and Stanford Research SR540 Chopper Controller.

References

- [1] Y. H. Lee, X. Q. Zhang, W. Zhang, M. T. Chang, C. T. Lin, K. D. Chang, Y. C. Yu, J. T. W. Wang, C. S. Chang, L. J. Li, *Adv. Mater.* **2012**, 24, 2320.
- [2] C. Cong, J. Shang, X. Wu, B. Cao, N. Peimyoo, C. Qiu, L. Sun, T. Yu, *Adv. Opt. Mater.* **2014**, 2, 131.
- [3] X. Wang, Y. Gong, G. Shi, W. L. Chow, K. Keyshar, G. Ye, R. Vajtai, J. Lou, Z. Liu, E. Ringe, *ACS Nano* **2014**, 8, 5125.
- [4] Y. Gong, S. Lei, G. Ye, B. Li, Y. He, K. Keyshar, X. Zhang, Q. Wang, J. Lou, Z. Liu, *Nano Lett.* **2015**, 15, 6135.
- [5] T. Zhang, B. Jiang, Z. Xu, R. G. Mendes, Y. Xiao, L. F. Chen, L. W. Fang, T. Gemming, S. L. Chen, M. H. Rummeli, L. Fu, *Nature Commun.* **2016**, 7, 13911.
- [6] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, *Nat. Mater.* **2014**, 13, 1135.
- [7] X. Li, M.-W. Lin, J. Lin, B. Huang, A. A. Puretzky, C. Ma, K. Wang, W. Zhou, S. T. Pantelides, M. Chi, *Sci. Adv.* **2016**, 2, e1501882.

- [8] J. J. Cargille, *New York Microscopical Society Yearbook* **1985**.
- [9] D. Abergel, A. Russell, V. I. Fal'ko, *Appl. Phys. Lett.* **2007**, 91, 063125.
- [10] M. Benameur, B. Radisavljevic, J. Heron, S. Sahoo, H. Berger, A. Kis, *Nanotechnology* **2011**, 22, 125706.
- [11] H. Li, J. Wu, X. Huang, G. Lu, J. Yang, X. Lu, Q. Xiong, H. Zhang, *ACS Nano* **2013**, 7, 10344.
- [12] X. Zhang, X.-F. Qiao, W. Shi, J.-B. Wu, D.-S. Jiang, P.-H. Tan, *Chem. Soc. Rev.* **2015**, 44, 2757.
- [13] A. Kuc, N. Zibouche, T. Heine, *Phys. Rev. B* **2011**, 83, 245213.
- [14] G. Liu, *Phys. Rev. B* **2013**, 88, 085433.
- [15] A. T. MoS, *Phys. Rev. Lett.* **2010**, 105, 136805.
- [16] J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones, G. Aivazian, J. Yan, D. G. Mandrus, D. Xiao, W. Yao, *Nat. Commun.* **2013**, 4, 1474.
- [17] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, 10, 1271.
- [18] Y. Kim, H. Bark, G. H. Ryu, Z. Lee, C. Lee, *J. Phys.: Condens. Matter* **2016**, 28, 184002.
- [19] H. Wang, X. Huang, J. Lin, J. Cui, Y. Chen, C. Zhu, F. Liu, Q. Zeng, J. Zhou, P. Yu, *Nat. Commun.* **2017**, 8, 394.
- [20] J. Suh, T.-E. Park, D.-Y. Lin, D. Fu, J. Park, H. J. Jung, Y. Chen, C. Ko, C. Jang, Y. Sun, *Nano Lett.* **2014**, 14, 6976.
- [21] H. Fang, C. Battaglia, C. Carraro, S. Nemsak, B. Ozdol, J. S. Kang, H. A. Bechtel, S. B. Desai, F. Kronast, A. A. Unal, *Proc. Natl. Acad. Sci.* **2014**, 111, 6198.
- [22] R. P. Feynman, *QED: The Strange Theory of Light and Matter*, Princeton University Press, **2006**.
- [23] M. Born, E. Wolf, *Cambridge U. Press, Cambridge, UK* **1999**, 890.
- [24] D. B. Williams, C. B. Carter, in *Transmission Electron Microscopy*, Springer **1996**, p. 3-17.
- [25] W. H. Bragg, W. L. Bragg, *Proc. R. Soc. Lond. A* **1913**, 88, 428.
- [26] N. Dellby, L. Krivanek, D. Nellist, E. Batson, R. Lupini, *Microscopy* **2001**, 50, 177.

- [27] E. Rutherford, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1911**, 21, 669.
- [28] C. C. Ahn, *Transmission electron energy loss spectrometry in materials science and the EELS atlas*, John Wiley & Sons, **2006**.
- [29] Y. Gong, Z. Liu, A. R. Lupini, G. Shi, J. Lin, S. Najmaei, Z. Lin, A. L. Elías, A. Berkdemir, G. You, *Nano Lett.* **2013**, 14, 442.
- [30] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J.-C. Idrobo, P. M. Ajayan, J. Lou, *Nat. Mater.* **2013**, 12, 754.
- [31] S. S. Chou, N. Sai, P. Lu, E. N. Coker, S. Liu, K. Artyushkova, T. S. Luk, B. Kaehr, C. J. Brinker, *Nat. Commun.* **2015**, 6, 8311.
- [32] C. T. Koch, *Determination of core structure periodicity and point defect density along dislocations*, **2002**.

Chapter 4*

Synthesis and Contact Engineering of MoS₂

Metal/Semiconductor (M/S) vdW contact has shown surpassing advantages in the improvement of M/S contact because of good stability, larger size and clean interface. In the chemical vapor deposition (CVD) synthesis, M/S transitional metal dichalcogenide (TMDC) van der Waals (vdW) heterostructures were less explored due to the high melting points and low chemical reactivity of metal oxide feedstocks and the crystal lattice mismatch. In this work, with the assistance of NaCl, the drawbacks of metal oxide precursors were effectively overcome. Therefore, for the first time, the M/S TMDC vdW heterostructure NbS₂/MoS₂ was synthesized via a one-step halide-assisted CVD method. OM, SEM and XPS offered firm evidences of the M/S vdW heterostructure. This one-step method provides the high crystal quality and clean interface of the NbS₂/MoS₂ heterostructure, which was confirmed by STEM characterization. A growth mechanism was proposed that MoS₂ finished the growth first and subsequently served as a superior substrate for the growth of NbS₂, which was verified by Raman mapping. The PL and device measurement provided physical supports of the M/S heterostructure.

*This section was published as **Qundong Fu**, Xiaowei Wang, Jiadong Zhou, Juan Xia, Qingsheng Zeng, Danhui Lv, Chao Zhu, Xiaolei Wang, Yue Shen, Xiaomin Li, Younan Hua, Fucui Liu*, Zexiang Shen, Chuanhong Jin*, and Zheng Liu*. One-Step Synthesis of Metal/Semiconductor Heterostructure NbS₂/MoS₂, *Chem. Mater.*, **2018**, 30 (12), 4001–4007.

4.1 Introduction

Van de Waals (vdW) heterostructures,^[1, 2] vertically stacked by diverse two-dimensional (2D) components, have shown great potentials on novel physical applications^[3-5] and next

generation optoelectronic devices such as atomically thin P-N junction.^[6-9] Benefiting from the weak interlayer vdW interaction, engineering of vdW heterostructures can be realized via controlling the chemical components,^[7, 10-12] layer numbers^[13] and interlayer stacking orders,^[14] leading to a transition of designing new materials from a traditionally methodology-driven motivation to the one driven by the function of materials. Thanks to the atom-thin nature, various physical properties, and numerous analogues in the family (>40),^[15] 2D transitional metal dichalcogenides (TMDCs) have been employed to construct the artificial vdW heterostructures^[11, 16] with unique functionalities.

Chemical vapor deposition (CVD) has become a dominant method to synthesize the TMDC vdW heterostructures with large size, such as ReS₂/WS₂^[17] and MoSe₂/WSe₂.^[10] However, up to now, only a hand of TMDC vdW heterostructures have been prepared by this method, and nearly all of them are focused on Semiconductor/Semiconductor (S/S) vdW heterostructures,^[7, 10, 17, 18] leaving Metal/Semiconductor (M/S) counterparts less explored. This may be primarily ascribed to the following reasons: 1) High melting points and low chemical reactivity of metal oxides (e.g. Nb₂O₅ and Ta₂O₅), make metallic TMDCs hard to prepare.^[19] 2) Crystal lattice parameter mismatch.^[18] It is relatively easier to grow vdW heterostructures for two components that have the same crystal structure, e.g. 2H-MoS₂ and 2H-WS₂. Yet for different crystal structures, e.g. 2H and 1T, the two components should be meticulously selected to achieve the epitaxial growth.

The fast separation of the photogenerated charge carriers in M/S heterostructures, due to the variant electrical features, makes 2D M/S vdW heterostructures^[20] very fascinating in the optoelectronic and photocatalytic applications.^[21-23] Recently, a two-step CVD method concerning the selenization of sequent deposited Nb₂O₅ and WO₃ to produce M/S NbSe₂/Nb_xW_{1-x}Se₂ was adopted reluctantly owing to the drawbacks of Nb₂O₅ as metal precursors.^[24] As known, such method will lead to interlayer alloying, bring relative high defect and grain boundary concentration,^[25] and finally result in a poor interface. Therefore, to synthesize M/S vdW heterostructures with a high-quality interface becomes challenging but profound as it is the key basis to understand the physical properties of M/S vdW heterostructures.^[26]

Here, the synthesis of high-quality 2D TMDC M/S vdW heterostructure NbS₂/MoS₂ was demonstrated by one-step halide-assisted CVD method, which provides a sharp atomic M/S interface. Firstly, through mixing the metal oxide precursor with the alkaline metal halide salt,^[27] a 20 μm single crystalline monolayer niobium disulfide (NbS₂) was successfully produced, as confirmed by the Atomic Force Microscopy (AFM). Raman spectrum of few-layer sample with a size up to 60 μm reveals the 3R-stacking order of the obtained NbS₂. Further by developing the growth recipe, the 2D M/S TMDC vdW heterostructure NbS₂/MoS₂ was obtained, which was substantiated by Optical Microscopy (OM), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) tests. Scanning Transmission Electron Microscopy (STEM) characterization provided firm evidence of the high quality of this NbS₂/MoS₂ heterostructure, and the periodic superlattice originated from well-aligned orientation affirmed the clean interface of the obtained heterostructure. STEM further revealed the R-type stacking order between the MoS₂ and NbS₂ layer, which is favored in pristine CVD-grown NbS₂. With the aid of OM and Raman characterization, it could be figured out that, due to the difference of growth temperature, only when the growth of MoS₂ is completed, NbS₂ begins the epitaxial growth on MoS₂. Photoluminescence (PL) spectra and FET device measurements provided the physical property support of this M/S vdW heterojunction. This is the first time that high-quality 2D M/S TMDC vdW heterostructure has been prepared by one-step CVD method. Our work is believed to speed up the syntheses of other M/S TMDC vdW heterostructures and provide a platform for the research into the TMDC M/S interface.

4.2 Experimental Methods

4.2.1 CVD Synthesis of NbS₂

Figure 4.1 Schematic of the CVD setup for the synthesis of NbS₂.

Atmospheric Pressure CVD Chamber is schematically depicted in Figure 4.1, in which, detailly, the heating setup is a Lindberg/Blue M Mini-Mite tube furnace (TF55035C-1, digital, single segment), and the fused quartz tube is 1000 mm long with an Outside Diameter (O.D.) of 1 inch. Mixed powders of Nb₂O₅ and NaCl with a ratio around 9:1 were used as metal precursor, placed in an alumina crucible and located in the zone where temperature was ramped to 800 °C in 16 min and hold for 10 min, while sulfur feedstock was placed at the upstream of the mixture with temperature ranging from 120 °C to 200 °C. Under the carrier gas of 60~80 sccm Ar, sulfur vapor was flowed in and reacted with metal mixture, and then layered NbS₂ will be deposited on the substrate (285nm SiO₂/Si), which was placed 3~5 mm above the metal precursor with the polished side facing down. After the reaction is finished, the furnace was naturally cooled down to room temperature.

4.2.2 CVD Synthesis of NbS₂/MoS₂

The same growth temperature (800 °C), gas flow rate (60 sccm Ar), and CVD setup were used for the synthesis of NbS₂/MoS₂. To first grow MoS₂, MoO₃ powder was put at the upper stream of the metal mixture of Nb₂O₅ and NaCl with a distance of 1.5 cm (Figure 4.3). Unlike the control of thickness via gas flow rate in intrinsic NbS₂, the holding time at the temperature of 800 °C was regulated from 6 min to 12 min, to achieve different coverage of NbS₂ on MoS₂.

4.2.3 XPS, SEM and Raman Characterizations

XPS tests were carried out via a PHI Quantera II spectrometer with a monochromatic Al-K α radiation ($h\nu = 1486.6$ eV), calibrated with C 1s core level (binding energy: 284.8 eV). SEM characterization was performed under the *JOEL JSM-7600F system* with an accelerating voltage of 15 kV. Raman spectra were recorded by a *Witec* system equipped with 100x objective lens and a grating of 1800 lines/mm under 532 nm laser excitation.

4.2.4 Transfer and STEM Characterization and Image Simulation

The TEM samples were prepared with a poly (methyl methacrylate) (PMMA) based transfer method. First, the Si wafer with the as-grown CVD samples were spin-coated with PMMA at 3,000 r.p.m. for 60 s and then baked at 150 °C for 3 min. Afterward, PMMA-coated sample was peeled off by etching away the underneath SiO₂ in 1% HF solution. Next, the floating PMMA film was transferred to the distilled water and scooped up by a TEM grid. The TEM grid was heated at 50 °C for 5 hours, and then submerged into acetone for about 24 h to remove PMMA. Finally, the TEM grid was rinsed by isopropyl alcohol (IPA) and dried in air.

ADF-STEM images were obtained using a probe-corrected Titan ChemiSTEM (FEI, USA) which was operated at an accelerating voltage of 200 kV. The convergent semi-angle for illumination was set to be about 21.4 mrad with a probe current of 79 pA. The collection angle is about 43.4 to 200 mrad for ADF-STEM imaging. The atomic-resolution ADF-STEM images were processed with an improved Wiener filtering method to partly increase the signal-to-noise ratio for a better illumination. STEM–ADF image simulations were carried out using QSTEM^[28] software, with the input parameters being set according to the experimental conditions. False-color images were performed by ImageJ to improve visual inspection.

4.2.5 Devices Fabrication and Measurement

After the synthesis of the sample on silicon substrate, the sample was then spin-coated with PMMA. The electrode patterns were then defined by the EBL (Nova nanoSEM 230 with digital pattern generator Nabity-NPGS). After the pattern was developed in MIBK/IPA,

metal contacts (3 nm Cr/55 nm Au) were deposited by Kurt J. Lesker Nano 36 Thermal Evaporator. Electrical and photoresponse properties of the FETs were measured in the MicroXact Probe Station by Agilent B1500A Semiconductor Device Parameter Analyzer.

4.3 Results and Discussions

4.3.1 Halide-assisted CVD Synthesis and Characterization of NbS₂

At first, the synthesis of intrinsic NbS₂ was demonstrated. The CVD setup is depicted in Figure 4.1: under the gas flow of argon, the gaseous sulfur was introduced to the central high temperature zone (800 °C) and reacted with the evaporated metal precursors (mixture of niobium pentoxide, Nb₂O₅ and sodium chloride, NaCl). NbS₂ layers were then deposited on the 285 nm SiO₂/Si substrate. By using argon gas with the flow rate of 60 standard cubic centimeter per minute (sccm), monolayer NbS₂ with the size up to 20 μm was synthesized, shown in Figure 4.2a. To the best of our knowledge, this is the largest monolayer single-crystal NbS₂ that has ever been produced by CVD method. As proposed in the previous report,^[27, 29] the reaction between Nb₂O₅ and NaCl, forming a metal oxychloride at high temperature, which leads to a lower melting point and higher chemical reactivity than Nb₂O₅, contributes to this better result.

AFM height topography (inset of Figure 4.2a) shows that the thickness of the as-grown NbS₂ is about 1.1 nm, which confirms the monolayer nature of our sample. Further by applying different flow rates, the synthesis of bilayer (Figure 4.2b) and tri-layer (Figure 4.2c) NbS₂ could also be achieved, which has a largest area (60 μm) with a thickness around 3.0 nm. In order to confirm the crystal quality and stacking order of this sample, Raman spectra using a 532nm laser as light source were performed. As shown in Figure 4.2d, three peaks at 311.2 cm⁻¹, 343 cm⁻¹, and 381.2 cm⁻¹ were found to be the characteristic peaks of 3R NbS₂, corresponding to the E₁, E₂ and A₁ vibration modes.^[30] This result fits very well with the spectra reported previously.^[31, 32] Worth to mention, the reported phonon stiffening and softening features of E₂ and A₁ modes from thicker to thinner NbS₂,^[33] which results from the dielectric screening of long-range Coulomb interactions, could also be

observed in our result (Figure 1e and 1f). The origin of the peak located at 179.4 cm^{-1} is still unclear, which might come from higher-order Raman processes.

Figure 4.2 Synthesis of large-area layered NbS₂ single crystal. (a-c) Optical images of one, two and three layered NbS₂, inset of (a) shows AFM and the thickness of 1.1 nm indicates the monolayer nature of (a). All the scale bars are 10 μm. (d-f) Raman spectra of samples with different thicknesses (one, two and three layers). (e, f) Zoom-in of E₂ and A₁ peaks in (d), present the phonon stiffening and softening characteristics.

4.3.2 CVD Synthesis and Characterization of NbS₂/MoS₂

Figure 4.3 Schematic of the CVD setup for the synthesis of NbS₂/MoS₂. The distance between MoO₃ and Nb₂O₅ is around 1.5 cm. Both are placed in the alumina crucible and located at the high-temperature zone (center) of the furnace.

The successful synthesis of high-quality NbS₂ atomic layer sheds light on the fabrication of the 2D TMDC M/S vdW heterostructures. As MoS₂ shares the same anionic atom with NbS₂, it was chosen as the substrate to achieve the epitaxial growth of NbS₂, forming the 2D TMDC M/S vdW heterostructure NbS₂/MoS₂ (schematically presented in Figure 4.4a). In order to grow MoS₂, MoO₃ powder was placed at the up flow of the Nb₂O₅/NaCl mixtures, leaving a distance about 1.5 cm (Figure 4.3). Under the growth temperature of 800 °C and 60 sccm argon gas, this vertical stacking heterostructure was successfully obtained (Figure 2b). As can be seen from Figure 4.4b and 4.4f, the distinct contrasts between NbS₂ and MoS₂ in both OM and SEM images, which results from different light absorption and conductivity, confirm that this is a vertical NbS₂/MoS₂ heterostructure rather than a bilayer MoS₂.

To further ascertain this, XPS test was performed at the thicker area (region 2 marked in Figure 4.4b). As shown in Figure 4.4c-e, the peaks at 228.8 eV and 232.0 eV are ascribed to the 3d_{5/2} and 3d_{3/2} orbitals from Mo,^[34] and 203.2 eV and 206.0 eV are attributed to Nb 3d_{5/2} and 3d_{3/2} core levels,^[35] while 162.9 eV and 164.1 eV are corresponded to S 2p_{3/2} and 2p_{1/2} core levels. All these peaks match very well with the reported data. Besides, by integrating the areas of the peaks, the obtained ratio of the anion S to the cations (Nb and Mo), which is 2.125, further demonstrates the stoichiometry of this NbS₂/MoS₂ heterostructure. Hence, with the aid of OM, SEM, and XPS, 2D M/S vdW heterostructure NbS₂/MoS₂ was successfully identified.

Figure 4.4 NbS₂/MoS₂ vdW heterostructure. (a) Schematic of NbS₂/MoS₂ vdW heterostructure. OM (b) and SEM (f) images, show the evident contrast between NbS₂ and MoS₂ owing to the difference in light absorption and conductivity. Scale bar: 10 μ m. (c-e) XPS peaks of Mo 3d (c), Nb 3d (d) and S 2p (e) from NbS₂/MoS₂ vdW heterostructure on SiO₂/Si substrate. The ratio of anion (S) to cations (Mo and Nb) is 2.125, via performing peak area integration, which shows good stoichiometry in this heterostructure.

To further determine the atomic structure and stacking of the 2D NbS₂/MoS₂ vdW heterostructure, annular dark-field (ADF) imaging in an aberration-corrected scanning transmission electron microscope (STEM) was conducted. Figure 4.5a shows the morphology of the as-transferred sample in a low-magnification Z-contrast image. In STEM's Z-contrast image, the intensity is directly related to the atomic number and the thickness of the sample,^[36] which can therefore be used to discriminate different atoms and thickness.

Figure 4.5 Intensity line profiles of few-layer NbS₂/MoS₂ sample. (a) ADF-STEM image of NbS₂ and MoS₂ bilayer structure. Scale bar: 0.5 μm; (b) Intensity profiles obtained along arrows of three typical positions in (a).

Figure 4.6 Atomic structure of the NbS₂/MoS₂ vdW heterostructure. (a) Low-magnification ADF-STEM image of the sample, where the monolayer area was MoS₂, and the bilayer area was monolayer (1L) NbS₂ grown on top of 1L MoS₂; (b) ADF-STEM image acquired from the bilayer area in (a), shows the periodic Moiré pattern. Scale bar: 5 nm; (c) FFT pattern obtained from (b). In the magnified view of the FFT pattern (the inset in black dash line), the reciprocal lattices of

NbS₂ and MoS₂ are marked by green and orange circles, respectively; (d) Top view and side view of the atomic model of the NbS₂/MoS₂ vdW heterostructure with an R-type stacking orientation. (e) The atomic-resolution ADF-STEM image recorded at the lower right corner of (b). (f) The simulated STEM image based on an R-type stacking model in (d), which is consistent with (e). Scale bar of (e) and (f): 2 nm. The supercell of the NbS₂/MoS₂ heterostructure is demarcated by the red dashed rhombuses in (b, d, e and f), with a lattice constant around 6.6 nm.

Figure 4.7 Atomic structure of the NbS₂ and MoS₂ heterostructure. (a) ADF-STEM image of NbS₂ and MoS₂ bilayer structure; (b) FFT pattern obtained from (a). (c and d) Inverse FFT images of 1L NbS₂ and MoS₂ in (a). (e and f) Close-ups of the regions highlighted by small square box in c and d. Insets are their corresponding atomic structures with green balls representing Nb, orange ones for Mo and yellow ones for S. The triangle which connect metal atoms represent their orientations. Scalebars for (a) and (c-d) are both 5 nm.

As Mo (Z=42) and Nb (Z=41) have very close atomic number, a NbS₂ monolayer would exhibit almost the same contrast as monolayer MoS₂. Therefore, by analysing the intensity and comparing it with that of the vacancy area, it can be firstly distinguished that different layer numbers (1L, 2L and 3L) of the sample in specific area. Figure 4.5a is the low

magnification STEM-ADF image of as-transferred few-layer NbS₂/MoS₂ sample on a TEM grid, from which intensity line profiles along the three arrows can be extracted. From the corresponding step-like intensity profiles in Figure 4.5b, it can be differentiated that the darkest region in Figure 4.5a is the vacancy, whereas the other brighter regions with different contrast indicate 1L, 2L and 3L samples.

Furthermore, the detailed atomic structure of different areas can be revealed by high-resolution STEM Z-contrast imaging and corresponding fast Fourier transform (FFT) pattern. Figure 4.6b is a large scale ADF image of the bilayer region, from which it can be observed Moiré pattern with a periodicity of around 6.6 nm, highlighted by the red dashed rhombus. The corresponding FFT image of Figure 4.6b shows two different sets of hexagonally arranged spots. Careful analysis of these spots reveals their lattice constants (parameter: a): one corresponding to NbS₂ of 3.33 Å while the other corresponding to MoS₂ of 3.21 Å, within instrumental error.^[37] In addition, the two sets of well-aligned spots in Figure 4.6c demonstrate that the NbS₂ and MoS₂ layers are aligned with no twist angle.

Figure 4.7a and 4.7b show the NbS₂/MoS₂ heterostructure and its fast Fourier transform (FFT). Two separated sets of spots due to different lattice constants of NbS₂ and MoS₂ could be clearly seen in Figure 4.7b, which make it feasible to separate the lattice information of two different crystals by applying inverse FFT. In order to further resolve the stacking order of the bilayer heterostructure, inverse FFT of both NbS₂ and MoS₂ were applied respectively. Two inverse FFT images of 1L NbS₂ and MoS₂ layers are shown in Figure 4.7c and 4.7d, and their zoom-in images are displayed in Figure 4.7e and 4.7f, with their structure models in the inset which is determined by Z contrast imaging mechanism. These inverse FFT images straightforwardly present that two layers have the same orientation and therefore the R-type stacking order of the bilayer heterostructure was preliminarily confirmed.

Figure 4.8 Comparison of the experimental image (b) with simulation images of H-type (a) and R-type (c) stacking structures.

Figure 4.9. Quantitative analysis of intensity profiles (along lines in region 1, 2 and 3) and comparison of experimental images (center) with simulation images of H-type (left) and R-type (right) stacking structure. As a result, the simulation image of R-type stacking is consistent with experimental image quantitatively, while the simulated H-type stacking image is apparently different from the experimental image.

To provide more consolidate evidence of the R-type stacking order, the experimental image (Figure 4.8b) were compared with the simulation results of both R-type (Figure 4.8c) and H-type (Figure 4.8a) stacking NbS₂/MoS₂ bilayer models via a reported method.^[38] Here three regions which are marked with dashed square were chosen, from which the line profiles of the intensities will be extracted and compared. From intensity profiles of these three regions (Figure 4.9 a-c), it could be clearly seen the simulation image of R-type stacking is consistent with experimental image quantitatively, while the simulated H-type stacking image is apparently different. This confirms the R-type stacking order between NbS₂ and MoS₂ in our heterostructure.

4.3.3 Possible Mechanism for the Growth of NbS₂/MoS₂

From Figure 4.10a and 4.10b, it could be found that the second-layer NbS₂ started the growth from one or two triangle corners, leaving the other uncovered. This is not like a one-step growth behavior, but more like a two-step process. Via regulating the time for growth, different morphologies of this heterostructure can be achieved: (1) NbS₂ on the top firstly nucleates and grows at the corners of bottom-layer MoS₂ (Figure 4.11b); (2) Then top-layer NbS₂ at these corners grows up and merges at the edge, while the core of MoS₂ on the bottom remains uncovered (Figure 4.11c); (3) Finally, the growth of NbS₂ continues and achieves the full coverage of the bottom MoS₂ (Figure 4.11d).

On the basis of these observations, the possible mechanism for the heterostructure growth could be understood as follows (schematically shown in Figure 4e-h): Firstly, MoS₂ nucleates at low temperature (650-750°C) and grows into a monolayer single-crystal triangle. The growth of MoS₂ takes about several minutes until the precursors MoO₃ have been consumed. Then the growth temperature is increased to 800°C, the growth of NbS₂ is initiated. The second-layer NbS₂ preferably nucleates at the corner of the triangular MoS₂ owing to its defects-rich nature,^[10] and then grows inward the central part, finally forms the vertical NbS₂/MoS₂ heterojunction. Worth to mention, this behavior is different with one-step synthesis of WS₂/MoS₂ vertical heterojunction,^[7] where WS₂ starts the growth from the center of growing MoS₂ on the bottom. This might be ascribed to the lower

chemical reactivity of Nb₂O₅ in comparison with WO₃, and thus higher growth temperature. Hence, NbS₂ will grow after MoS₂ finishes the growth while WS₂ starts earlier.

Figure 4.10 Optical images of NbS₂/MoS₂ vdW heterostructure with different morphologies. (a) NbS₂ starts the growth at one triangular corner of the bottom MoS₂. XPS spectra were taken from the area marked with a dash circle; (b) NbS₂ initiates the growth at two corners of MoS₂ triangle on the bottom; (c) NbS₂ begins to grow at the edge of the bottom MoS₂, inward the center, forming a Type-I structure; (d) The grain boundary crossing growth behavior of NbS₂ on two adjacent triangular MoS₂. All of above provide solid support on the mechanism that MoS₂ finishes the growth first and serves as a competitive substrate for the growth of NbS₂. All the scale bars are 10 μm.

Several interesting phenomena will help to understand this process: (1) NbS₂ may start the nucleation along the edge, which is also defect-rich, and then form a type-I like structure defined in the previous report^[10] (Figure 4.10c). This further strengthens that the growth of NbS₂ initiates only after the growth of MoS₂ comes to an end; (2) Another interesting growth behavior is the grain boundary crossing, shown in Figure 4.10d, which would not happen in the growth of second-layer MoS₂ between two adjacent MoS₂ triangles. Both

support the growth mechanism proposed above: The bottom-layer MoS₂ grows first due to the low nucleation temperature, then the second-layer NbS₂ nucleates and grows from the defect-rich corners or edges of the as-grown MoS₂, inward the center, finally forms the M/S vdW heterostructure NbS₂/MoS₂.

Figure 4.11 Proposed mechanism for the vertical heterostructure growth: At first, MoS₂ grows and forms a full triangle. (a) Optical image and (e) schematic structure of MoS₂; (b) and (f) NbS₂ on the top nucleates and grows at the corners of bottom-layer MoS₂; (c) and (g) Then top-layer NbS₂ at these corners grows up and merges at the edge, while the core of MoS₂ on the bottom remains uncovered; (d) and (h) Finally, the growth of NbS₂ continues and achieves the full coverage of the bottom MoS₂. Scale bar: 10 μm .

In order to further examine the mechanism aforementioned, Raman spectra and mapping were carried out using a 532nm laser. The characteristic E₁, E₂, and A₁ peaks of pure NbS₂, could be found at 306.7 cm⁻¹, 342.7 cm⁻¹, and 377.6 cm⁻¹ (red spectrum in Figure 4.12b), respectively. The two characterized, in-plane E₂ and out-of-plane A₁ vibration modes of pure MoS₂ are located at 382.0 cm⁻¹ and 402.6 cm⁻¹ (black spectrum in Figure 4.12b, the frequency difference is 20.6 cm⁻¹, indicating a monolayer MoS₂^[39]), which were collected from the NbS₂ uncovered area of the heterostructure. The blue curve in Figure 4.12b shows the Raman spectrum of the NbS₂/MoS₂ vdW heterostructure, in which all the characteristic peaks from MoS₂ and NbS₂ can be found. One interesting thing should be noted that two

adjacent peaks, A₁ peak of NbS₂ and E₂ peak of MoS₂ are overlapped and merged into one peak at 379.2 cm⁻¹ in this spectrum.

Figure 4.12 Raman spectra and mapping analysis of NbS₂/MoS₂ vdW heterostructure. (a) Optical image of NbS₂/MoS₂ vdW heterostructure, scale bar: 5 μm ; (b) Raman spectra taken from pristine NbS₂ (red curve), NbS₂/MoS₂ vdW heterostructure (blue curve) and the exposed MoS₂ (black curve). Raman mapping at 342.7 cm⁻¹ (c) (E₂ mode of NbS₂) and 402.6 cm⁻¹ (d) (A₁ mode of MoS₂) further confirm that NbS₂ is seated at one corner of bottom-layer MoS₂, scale bar: 3 μm .

The multipeak fitting analysis was performed to figure out the individual peaks (Figure 4.13), in which the A₁ peak of NbS₂ is located at 377.1 cm⁻¹ and E₂ peak of MoS₂ is located at 380.1 cm⁻¹. Figure 4.12c and 4.12d present the Raman mapping of the area (marked with a square in Figure 4.12a) of the NbS₂/MoS₂ vdW heterostructure. Raman mapping from NbS₂ E₂ peak located at 342.7 cm⁻¹ shows the NbS₂ sitting at one corner of MoS₂, as shown in Figure 4.12c, while Raman mapping collected from MoS₂ A₁ peak located at 402.6 cm⁻¹ confirms the single-crystal MoS₂ triangle (Figure 4.12d). These mappings match very

well with the optical image in Figure 4.12a. All the Raman tests further consolidate the mechanism which is proposed above.

Figure 4.13. Multipeak fitting analysis of the Raman peak of NbS₂/MoS₂ at 379.2 cm⁻¹. It is revealed that this peak is formed by the overlap of A₁ peak of NbS₂ located at 377.1 cm⁻¹ and E₂ peak of MoS₂ located at 380.1 cm⁻¹.

Figure 4.14 Photoluminescence (PL) characterization of the NbS₂/MoS₂ heterostructure. (a) Optical image. (b) PL mapping of area marked with dashed rectangle in (a), shows the PL of MoS₂ was quenched in the heterostructure (region 2). (c) PL single spectra of pure MoS₂, region 1 and 2 in (a). The small change in PL of pure MoS₂ and 1 indicates low dopant ratio of Nb in MoS₂ (region 1 in (a)).

4.3.4 Physical Properties Characterizations of NbS₂/MoS₂

The physical properties of the NbS₂/MoS₂ heterostructure, such as optical properties and device performances, were also evaluated. PL single spectra and mapping were conducted on the pure MoS₂ and heterostructure (region 1 and 2 in Figure 4.14a) respectively. From Figure 4.14b, it clearly shows that in region 2 (heterostructure), the PL of the bottom-layer MoS₂ has been quenched because of the fast charge transfer process,^[40] which confirms the high quality of metal/semiconductor interface. It is noted that the small change in PL single spectrum (Figure 4.14c) of the pure MoS₂ and uncovered MoS₂ (region 1) indicates a low dopant ratio (less than 0.5%) of Nb in the bottom-layer MoS₂.^[41]

To evaluate the quality of the interface, two-terminal devices were fabricated (the detailed process is described in the experiment part). Need to note that as shown in Figure 4.15a, the partially covered sample was patterned three electrodes to compare all the three types of contacts, Au/NbS₂ (electrode 1 and 2), NbS₂/MoS₂ and Au/MoS₂ (electrode 2 and 3). From Figure 4.15b, the FET I_d - V_d curves were measured between electrode 1 and 2 under different gate voltages to see the Au/NbS₂ contact. The good linearity of the I_d - V_d curve shows a good contact between Au and NbS₂. The drain current is up to 80 μ A without any gating, indicating a good conductivity of NbS₂. Besides, the drain current cannot be tuned by the gate voltage. This further confirm the metallic property of NbS₂. The Contacts of NbS₂/MoS₂ and Au/MoS₂ were compared via measure the I_d - V_d curve between electrode 2 and 3. As shown in Figure 4.15b, when the drain is applied at electrode 2 while the source at 3, a clear current rectification behavior with a rectification factor of around 5 can be observed. This reveals that there is a Schottky barrier between NbS₂ and MoS₂, which is larger than the barrier between Au and MoS₂. This is consistent with the prior report^[42] and the origin of the barrier should be the difference in work functions of the two materials (4.81 eV for NbS₂ and 4.53eV for MoS₂). Later, gate voltages were applied to see the change of the barrier height. As shown in Figure 4.15c, as the gate voltage was changed from 0V to 10 V, 30V and 50 V, the rectification factor is decreased from 5 to 3.75, 2.5 and 2, indicating a reduced Schottky barrier. This 2D Schottky junction provides new configuration in the 2D electronic applications. Furthermore, by choosing new 2D metallic TMDC with lower work function, the Fermi level pinning is highly possible to be eliminated.

Figure 4.15 Device performance of NbS₂/MoS₂. (a) Optical image of the device. Three electrodes were patterned on the partially covered sample to compare the contacts. (b) FET I_d - V_d curve measured between electrode 1 and 2 (Au/NbS₂ contact). (c) FET I_d - V_d curve measured between electrode 2 and 3 (comparison of NbS₂/MoS₂ and Au/MoS₂ contact). (d) FET I_d - V_d curves measured between electrode 2 and 3 under various gate voltages.

4.4 Conclusions

In conclusion, the syntheses of both largest area monolayer (20 μm) and few-layer (60 μm) NbS₂, and for the first time, the preparation of 2D M/S TMDC vdW heterostructure NbS₂/MoS₂ are reported here, which is benefited from the contribution of sodium chloride on the reduction of melting point and the improvement of chemical reactivity of Nb₂O₅. Also, it is the difference in chemical reactivity between NbS₂ and MoS₂ precursors that results in the sequent growth, leading to the formation of this vertical heterostructure. TEM characterization offers firm evidence that shows the high quality, R-type stacking order and clean interface of the obtained NbS₂/MoS₂ heterostructure. PL characterization and

device measurement provided physical property supports of this M/S heterostructure. It is believed that this work could be developed into the syntheses of other 2D TMDC M/S heterostructures and will accelerate the research in the TMDC M/S interface. Since the mobility of CVD-grown MoS₂ is low, most of which is less than $1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, in the next section of this thesis, the focus will be shifted to the air-stable CVD-grown Bi₂O₂Se with a higher mobility ($450\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

References

1. Geim, A. K.; Grigorieva, I. V., *Nature* **2013**, 499, (7459), 419-425.
2. Shi, Y. M.; Zhou, W.; Lu, A. Y.; Fang, W. J.; Lee, Y. H.; Hsu, A. L.; Kim, S. M.; Kim, K. K.; Yang, H. Y.; Li, L. J.; Idrobo, J. C.; Kong, J., *Nano Lett.* **2012**, 12, (6), 2784-2791.
3. Georgiou, T.; Jalil, R.; Belle, B. D.; Britnell, L.; Gorbachev, R. V.; Morozov, S. V.; Kim, Y. J.; Gholinia, A.; Haigh, S. J.; Makarovskiy, O.; Eaves, L.; Ponomarenko, L. A.; Geim, A. K.; Novoselov, K. S.; Mishchenko, A., *Nat. Nanotechnol.* **2013**, 8, (2), 100-103.
4. Hunt, B.; Sanchez-Yamagishi, J. D.; Young, A. F.; Yankowitz, M.; LeRoy, B. J.; Watanabe, K.; Taniguchi, T.; Moon, P.; Koshino, M.; Jarillo-Herrero, P.; Ashoori, R. C., *Science* **2013**, 340, (6139), 1427-1430.
5. Xu, W. G.; Liu, W. W.; Schmidt, J. F.; Zhao, W. J.; Lu, X.; Raab, T.; Diederichs, C.; Gao, W. B.; Seletskiy, D. V.; Xiong, Q. H., *Nature* **2017**, 541, (7635), 62-67.
6. Lee, C. H.; Lee, G. H.; van der Zande, A. M.; Chen, W. C.; Li, Y. L.; Han, M. Y.; Cui, X.; Arefe, G.; Nuckolls, C.; Heinz, T. F.; Guo, J.; Hone, J.; Kim, P., *Nat. Nanotechnol.* **2014**, 9, (9), 676-681.
7. Gong, Y.; Lin, J.; Wang, X.; Shi, G.; Lei, S.; Lin, Z.; Zou, X.; Ye, G.; Vajtai, R.; Yakobson, B. I., *Nat. Mater.* **2014**, 13, (12), 1135-1142.
8. Yu, W. J.; Li, Z.; Zhou, H.; Chen, Y.; Wang, Y.; Huang, Y.; Duan, X. *Nat. Mater.* **2013**, 12, (3), 246-252.
9. Liu, F.; Chow, W. L.; He, X.; Hu, P.; Zheng, S.; Wang, X.; Zhou, J.; Fu, Q.; Fu, W.; Yu, P., *Adv. Funct. Mater.* **2015**, 25, (36), 5865-5871.

10. Gong, Y.; Lei, S.; Ye, G.; Li, B.; He, Y.; Keyshar, K.; Zhang, X.; Wang, Q.; Lou, J.; Liu, Z., *Nano Lett.* **2015**, 15, (9), 6135-6141.
11. Doan, M.-H.; Jin, Y.; Adhikari, S.; Lee, S.; Zhao, J.; Lim, S. C.; Lee, Y. H., *ACS Nano* **2017**, 11, (4), 3832-3840.
12. Kozawa, D.; Carvalho, A.; Verzhbitskiy, I.; Giustiniano, F.; Miyauchi, Y.; Mouri, S.; Castro Neto, A.; Matsuda, K.; Eda, G., *Nano Lett.* **2016**, 16, (7), 4087-4093.
13. Wang, J.; Yao, Q.; Huang, C. W.; Zou, X.; Liao, L.; Chen, S.; Fan, Z.; Zhang, K.; Wu, W.; Xiao, X., *Adv. Mater.* **2016**, 28, (37), 8302-8308.
14. Heo, H.; Sung, J. H.; Cha, S.; Jang, B. G.; Kim, J. Y.; Jin, G.; Lee, D.; Ahn, J. H.; Lee, M. J.; Shim, J. H.; Choi, H.; Jo, M. H., *Nat. Commun.* **2015**, 6, 7372.
15. Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H., *Nat. Chem.* **2013**, 5, (4), 263-275.
16. Fang, H.; Battaglia, C.; Carraro, C.; Nemsak, S.; Ozdol, B.; Kang, J. S.; Bechtel, H. A.; Desai, S. B.; Kronast, F.; Unal, A. A., *P. Natl. Acad. Sci.* **2014**, 111, (17), 6198-6202.
17. Zhang, T.; Jiang, B.; Xu, Z.; Mendes, R. G.; Xiao, Y.; Chen, L. F.; Fang, L. W.; Gemming, T.; Chen, S. L.; Rummeli, M. H.; Fu, L., *Nat. Commun.* **2016**, 7, 13911.
18. Li, X.; Lin, M.-W.; Lin, J.; Huang, B.; Piretzky, A. A.; Ma, C.; Wang, K.; Zhou, W.; Pantelides, S. T.; Chi, M., *Sci. Adv.* **2016**, 2, (4), e1501882.
19. Zhou, J.; Liu, F.; Lin, J.; Huang, X.; Xia, J.; Zhang, B.; Zeng, Q.; Wang, H.; Zhu, C.; Niu, L., *Adv. Mater.* **2017**, 29, (3), 1603471.
20. Koma, A.; Sunouchi, K.; Miyajima, T., *Microelectron. Eng.* **1984**, 2, (1-3), 129-136.
21. Dutta, S. K.; Mehetor, S. K.; Pradhan, N., *J. Phys. Chem. Lett.* **2015**, 6, (6), 936-944.
22. Cui, X.; Lee, G.-H.; Kim, Y. D.; Arefe, G.; Huang, P. Y.; Lee, C.-H.; Chenet, D. A.; Zhang, X.; Wang, L.; Ye, F., *Nat. Nanotechnol.* **2015**, 10, (6), 534-540.
23. Zhao, M.; Ye, Y.; Han, Y.; Xia, Y.; Zhu, H.; Wang, S.; Wang, Y.; Muller, D. A.; Zhang, X., *Nat. Nanotechnol.* **2016**, 11, (11), 954-959.
24. Kim, A. R.; Kim, Y.; Nam, J.; Chung, H. S.; Kim, D. J.; Kwon, J. D.; Park, S. W.; Park, J.; Choi, S. Y.; Lee, B. H.; Park, J. H.; Lee, K. H.; Kim, D. H.; Choi, S. M.; Ajayan, P. M.; Hahm, M. G.; Cho, B., *Nano Lett.* **2016**, 16, (3), 1890-1895.
25. Zhan, Y. J.; Liu, Z.; Najmaei, S.; Ajayan, P. M.; Lou, J., *Small* **2012**, 8, (7), 966-971.

26. Amin, B.; Kaloni, T. P.; Schreckenbach, G.; Freund, M. S., *Appl. Phys. Lett.* **2016**, 108, (6), 063105.
27. Li, S.; Wang, S.; Tang, D.-M.; Zhao, W.; Xu, H.; Chu, L.; Bando, Y.; Golberg, D.; Eda, G., *Appl. Mater. Today* **2015**, 1, (1), 60-66.
28. Koch, C. T., *Determination of core structure periodicity and point defect density along dislocations*. Arizona State University: Phoenix, AZ, 2002.
29. Wang, H.; Huang, X.; Lin, J.; Cui, J.; Chen, Y.; Zhu, C.; Liu, F.; Zeng, Q.; Zhou, J.; Yu, P., *Nat. Commun.* **2017**, 8, 394.
30. McMullan, W. G.; Irwin, J. C., *Solid State Commun.* **1983**, 45, (7), 557-560.
31. Yanase, T.; Watanabe, S.; Weng, M.; Wakeshima, M.; Hinatsu, Y.; Nagahama, T.; Shimada, T., *Cryst. Growth Des.* **2016**, 16, (8), 4467-4472.
32. Ge, W. Y.; Kawahara, K.; Tsuji, M.; Ago, H., *Nanoscale* **2013**, 5, (13), 5773-5778.
33. Zhao, S. H.; Hotta, T.; Koretsune, T.; Watanabe, K.; Taniguchi, T.; Sugawara, K.; Takahashi, T.; Shinohara, H.; Kitaura, R., *2D Mater.* **2016**, 3, (2), 025027.
34. Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F., *Nat. Mater* **2012**, 11, (11), 963-969.
35. Ettema, A.; Haas, C., *J. Phys.: Condens. Matter* **1993**, 5, (23), 3817-3826.
36. Nellist, P. D.; Pennycook, S. J., *Scanning Transmission Electron Microscopy: Imaging and Analysis*. Springer: 2011.
37. Wilson, J.; Yoffe, A., *Adv. in Phys.* **1969**, 18, (73), 193-335.
38. Zhang, C.; Chuu, C.-P.; Ren, X.; Li, M.-Y.; Li, L.-J.; Jin, C.; Chou, M.-Y.; Shih, C.-K., *Sci. Adv.* **2017**, 3, (1), e1601459.
39. Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D., *Adv. Funct. Mater.* **2012**, 22, (7), 1385-1390.
40. Niu, L.; Liu, X.; Cong, C.; Wu, C.; Wu, D.; Chang, T. R.; Wang, H.; Zeng, Q.; Zhou, J.; Wang, X., *Adv. Mater.* **2015**, 27, (47), 7800-7808.
41. Sasaki, S.; Kobayashi, Y.; Liu, Z.; Suenaga, K.; Maniwa, Y.; Miyauchi, Y.; Miyata, Y., *Appl. Phys. Express* **2016**, 9, (7), 071201.
42. Shin, H.G., Yoon, H.S., Kim, J.S., Kim, M., Lim, J.Y., Yu, S., Park, J.H., Yi, Y., Kim, T., Jun, S.C. and Im, S., *Nano lett*, **2018**, 18(3), 1937-1945.

Chapter 5*

Synthesis and Phototransistor Application of Bi₂O₂Se

Two-dimensional (2D) materials have been considered as intriguing building blocks for next generation optoelectronic devices. However, their photoresponse performance still needs to be improved for practical applications. Here, ultrasensitive 2D phototransistors are reported employing CVD-grown 2D Bi₂O₂Se transferred onto silicon substrates with a non-corrosive transfer method. The as-transferred Bi₂O₂Se preserved high quality in contrast to the serious quality degradation in HF-assisted transfer. The phototransistors showed a responsivity of 3.5×10^4 AW⁻¹, a photoconductive gain of more than 10^4 , and a time response in the order of sub-millisecond. With back gating of the silicon substrate, the dark current could be reduced to several pA. This yields an ultrahigh sensitivity with specific detectivity of 9.0×10^{13} Jones, which is one of the highest values among 2D material photodetectors and two orders of magnitude higher than that of other CVD-grown 2D materials. The high performance of the phototransistor shown here together with the developed unique transfer technique are promising for the development of novel 2D material based optoelectronic applications.

*This section was published as **Qundong Fu**, Chao Zhu, Xiaoxu Zhao, Xingli Wang, Apoorva Chaturvedi, Chao Zhu, Xiaowei Wang, Qingsheng Zeng, Jiadong Zhou, Fucui Liu*, Stephen Pennycook, Tay Beng Kang, Hua Zhang, and Zheng Liu*. Ultrasensitive Phototransistor Based on 2D Bi₂O₂Se on Silicon Substrates, *Adv. Mater.*, **2018**.

5.1 Introduction

Two dimensional (2D) materials have shown great potential for high-performance electronic devices, thanks to their dangling-bond-free surface and atomic thickness which bring merits of high carrier mobility, efficient channel current regulation and higher degree of vertical integration.^[1-5] Many 2D semiconducting materials have shown outstanding phototransistor performances, such as MoS₂,^[6-8] WSe₂,^[9, 10] GaTe^[11, 12] and SnSe₂,^[13-15] because of their suitable energy bandgap and high mobility. Recently, a new type of 2D semiconductor Bi₂O₂Se has been prepared by chemical vapor deposition (CVD) with large area on fluorine mica substrate (f-mica, KMg₃(AlSi₃O₁₀)F₂).^[16-17] The merits of high mobility and superior air stability make it promising for optoelectronic applications.^[18-19]

However, the high dark current and small on/off ratio limit the performances of the photodetector based on Bi₂O₂Se on f-mica substrate.^[20] Although a gate configuration can be used to regulate the dark current, it is difficult to realize on f-mica substrate in the photoresponse application. As the 280 nm SiO₂/Si substrate (Si substrate) possesses inherent back gating, if Bi₂O₂Se can be transferred onto the Si substrate, not only the optoelectronic performance could be much improved, but also the applications of Bi₂O₂Se will be broadened since almost all integrated circuits are rooted in the silicon substrate. In the wet transfer of Bi₂O₂Se, hydrofluoric acid (HF) becomes the only f-mica etchant, due to the inertness of f-mica and strong electrostatic interaction between the sample and the substrate. Nevertheless, the highly corrosive HF which has the ability to penetrate issues is hazardous to handle.^[21] More importantly, since HF is well known as one component of typical buffered oxide etchant (BOE),^[22] Bi₂O₂Se will be inevitably etched by HF during the transfer process.

Here, high-quality Bi₂O₂Se on 280 nm SiO₂/Si substrate (Si substrate) was obtained and high-performance Bi₂O₂Se based phototransistor was demonstrated, via developing a non-corrosive transfer method. Firstly, high-quality Bi₂O₂Se was synthesized on f-mica and the etching effect of HF acid during the transfer processes was verified. Based on this, a polystyrene (PS)-assisted non-corrosive transfer method^[23] was developed to transfer the

$\text{Bi}_2\text{O}_2\text{Se}$ crystal onto the Si substrate. The as-transferred $\text{Bi}_2\text{O}_2\text{Se}$ retained a high quality and showed high phototransistor performances: (i) high photoresponsivity of $3.5 \times 10^4 \text{ AW}^{-1}$; (ii) high photoconductive gain of 8×10^4 ; (iii) fast response timescale of 0.308 ms for the rise and 0.448 ms for the decay times and (iv) high specific detectivity of 9.0×10^{13} Jones. Moreover, by applying a negative gate voltage, the dark current can be lowered to the order of pA, which is four orders of magnitude less than the value at zero gate voltage.^[20]

5.2 Experimental Methods

5.2.1 CVD Synthesis of $\text{Bi}_2\text{O}_2\text{Se}$ on f-mica

Figure 5.1 Schematic of the CVD setup for the synthesis of $\text{Bi}_2\text{O}_2\text{Se}$ on f-mica.

The CVD process is schematically depicted in Figure 5.1. In detail, the setup is a split tube furnace with interconnected control system (1-Zone, 1200°C) and we used 1200 mm long fused quartz tubes with an outside diameter (O.D.) of 50 mm. Powders of Bi_2Se_3 and Bi_2O_3 were used as precursors, placed in two alumina crucibles and Bi_2O_3 was located in the central zone while Bi_2Se_3 was located in the upstream with a distance of 8 cm. The f-mica substrate was placed downstream with a distance of 12 cm. The chamber was first pumped down to 6.0×10^{-2} Torr, and then 170 sccm (standard cubic centimeter per minute) Ar was introduced to reach a pressure of 350-400 Torr. The chamber was heated to 620°C in 25 min and held for 40 min. After that the furnace was cooled down naturally to room temperature and the chamber was refilled with Ar gas to reach atmospheric pressure.

5.2.2 AFM, SEM EDS and Raman Characterizations

AFM was conducted under the Asylum Research Cypher Scanning Probe Microscope system with a tapping mode. SEM EDS characterization was performed under the JOEL JSM-7600F system with an accelerating voltage of 15 kV. Raman spectra were recorded by a Witec Raman system equipped with 100x objective lens and a grating of 1200 lines/mm under 532 nm laser excitation.

5.2.3 Transfer of $\text{Bi}_2\text{O}_2\text{Se}$ Onto Cu Grid and STEM Characterization

The TEM samples were prepared with a poly (methyl methacrylate) (PMMA) based transfer method. First, the f-mica substrates with the as-grown CVD samples were spin-coated with PMMA at 3,000 r.p.m. for 60 s and then baked at 150 °C for 5 min. Afterward, PMMA-coated sample was peeled off by etching away the underneath f-mica in 2% HF solution. Next, the floating PMMA film was transferred to the DI water and scooped up by a TEM grid. The TEM grid was dried at 50 °C for 30 mins, and then submerged into acetone for about 24 h to remove PMMA. Finally, the TEM grid was rinsed by isopropyl alcohol (IPA) and dried in air.

ADF-STEM imaging was carried out on an aberration-corrected JEOL ARM-200F equipped with a cold field emission gun, operating at 80 kV, and an Advanced STEM Corrector (ASCOR) probe corrector. The convergent semi-angle of the probe was set at about 30 mrad. ADF-STEM images were collected using a half-angle range from about 68 to 280 mrad. A dwell time of 19 $\mu\text{s pixel}^{-1}$ was set for single-scan imaging. EDS mapping was conducted using the Oxford X-Max 100TLE Silicon Drift Detectors (SDD) EDS system.

5.2.4 PS-assisted Transfer of $\text{Bi}_2\text{O}_2\text{Se}$ Onto Si Substrate

The as-transferred $\text{Bi}_2\text{O}_2\text{Se}$ was prepared with a PS assisted transfer method. First, the f-mica substrate with the as-grown $\text{Bi}_2\text{O}_2\text{Se}$ was spin-coated with PS at 3,500 r.p.m. for 60

s and then baked at 85 °C for 15 min. After the edge of f-mica was cut away, PS-coated sample was peeled off by a drop of DI water. Next, the floating PS film was transferred onto Si substrate. The Si substrate was dried at 80 °C for 1 h and then heated at 150 °C for 30 mins to improve the contact between the sample and the Si substrate. Then the Si substrate was immersed into toluene for 24 h to remove PS and then into acetone for 5h to remove organic residuals. Finally, the Si substrate was dried by floating nitrogen.

5.2.5 Devices Fabrication and Measurement

After the Bi₂O₂Se was transferred onto the silicon substrate, the sample was then spin-coated with PMMA. The electrode patterns were then defined by the Electron-beam Lithography (EBL) (Nova nanoSEM 230 with digital pattern generator Nabity-Nanometer Pattern Generation System (NPGS)). After the pattern was developed in Methyl Isobutyl Ketone (MIBK)/IPA, metal contacts (3 nm Cr/55 nm Au) were deposited by Kurt J. Lesker Nano 36 Thermal Evaporator. Electrical and photoresponse properties of the FETs were measured in the MicroXact Probe Station by Agilent B1500A Semiconductor Device Parameter Analyzer. The rise and decay time of the light response was measured by Tektronix MDO 3052 Mixed Domain Oscilloscope and Stanford Research SR540 Chopper Controller.

5.3 Results and Discussions

5.3.1 Synthesis and Characterization of Bi₂O₂Se on f-mica

As depicted in Figure 5.2a, layered Bi₂O₂Se belongs to the I4/mmm space group, where oxygen atoms form a tetragonal lattice and the upper and lower bismuth atoms are stacked at different sets of tetragonal interstitial sites, forming a [Bi₂O₂]²⁺ layer. Meanwhile selenium atoms which are filled in the other set of sites bind the upper and lower [Bi₂O₂]²⁺ layers with weak electrostatic force, giving an interlayer spacing of about 0.61 Å. Large-area single crystalline Bi₂O₂Se samples were prepared via a low-pressure chemical vapor deposition method (Figure 5.1).^[17] Briefly, in a 2-inch quartz tube, bismuth selenide and

bismuth oxide powders were placed in the high-temperature zone while the f-mica was put at the downstream low-temperature zone. Under a pressure of 400 Torr, the growth temperature was elevated to 620 °C in 25 min and held for 40 min, and then cooled down to room temperature naturally.

Figure 5.2 Synthesis and characterization of $\text{Bi}_2\text{O}_2\text{Se}$. (a) Crystal structure of $\text{Bi}_2\text{O}_2\text{Se}$. (b) Optical image of square $\text{Bi}_2\text{O}_2\text{Se}$ on f-mica. The size is around 100 μm . (c) AFM topography of the as-grown $\text{Bi}_2\text{O}_2\text{Se}$. The thickness is around 5.2 nm, which is consistent with an eight-layer sample. (d) Raman spectrum of $\text{Bi}_2\text{O}_2\text{Se}$ with the characteristic A_{1g} peak at 159.1 cm^{-1} .

As shown in Figure 5.2b, $\text{Bi}_2\text{O}_2\text{Se}$ sample up to 100 μm was obtained with a square morphology, indicating the tetragonal crystal group of $\text{Bi}_2\text{O}_2\text{Se}$. As determined by atomic force microscopy (AFM, Figure 5.2c), the surface of the as-grown sample is clean and homogeneous and the thickness is around 5.2 nm, which corresponds to an eight-layer sample. The characteristic A_{1g} peak of $\text{Bi}_2\text{O}_2\text{Se}$ can be found at $\sim 159.1 \text{ cm}^{-1}$ in the Raman spectrum (Figure 5.2d), which shows good consistency with the prior reports.^[24-25]

Figure 5.3 STEM characterization of $\text{Bi}_2\text{O}_2\text{Se}$. (a) Low magnification ADF-STEM image. (b) The atomic-resolution ADF-STEM image of $\text{Bi}_2\text{O}_2\text{Se}$ shows tetragonally arranged atoms. (c) FFT pattern of (b). Squarely arranged spots indicate the crystal space group of $I4/mmm$. (d-f) EDS mappings of elements Bi (d), Se (e) and O (f) in $\text{Bi}_2\text{O}_2\text{Se}$ sample show uniform distribution of the three elements.

To further determine the atomic structure and chemical composition, annular dark-field (ADF) imaging and energy-dispersive X-ray spectroscopy (EDS) mapping were conducted on an aberration-corrected scanning transmission electron microscope (STEM) system. Figure 5.3b shows the ADF-STEM image of the square atom lattice while Figure 5.3c is the corresponding fast Fourier transform (FFT) of Figure 5.3b. The square arrangement of spots, (200), (110) and (110) in Figure 5.3c confirms the $I4/mmm$ space group of $\text{Bi}_2\text{O}_2\text{Se}$. As shown in Figure 5.3d-5.3f, EDS element mappings demonstrate the uniform distribution of elements Bi, Se and O. All the results confirm the high quality of our CVD-grown $\text{Bi}_2\text{O}_2\text{Se}$.

Figure 5.4 Demonstration of the etching effect of HF acid. (a) Schematic of normal transfer process using HF acid. (b-g) Changes of optical images and Raman spectra of $\text{Bi}_2\text{O}_2\text{Se}$ with the HF treatment for different times. (b-c) Initial state. (d-e) Partial etching and disappearance of the Raman peak at 30 s. (f-g) Almost full etching and nearly disappearance of the Raman peak at 90 s.

5.3.2 PS-assisted Transfer of $\text{Bi}_2\text{O}_2\text{Se}$ onto Si substrate

As discussed above, the inertness of f-mica and the electrostatic interaction between the $\text{Bi}_2\text{O}_2\text{Se}$ and f-mica make it hard to do the transfer. The normal transfer process using HF acid as the substrate etchant is schematically depicted in Figure 5.4a. Firstly, PMMA was spin-coated on the surface and $\text{Bi}_2\text{O}_2\text{Se}$ together with PMMA was separated from f-mica as the substrate was etched by HF. This process will take about half an hour. After transferred to the desired substrate, PMMA was removed by acetone, leaving the uncovered $\text{Bi}_2\text{O}_2\text{Se}$. However, usage of the corrosive HF acid is hazardous. Besides, as HF is well known as a component of BOE, the $\text{Bi}_2\text{O}_2\text{Se}$ will definitely be etched during the above process. To demonstrate the etching effect of HF, the etching process of $\text{Bi}_2\text{O}_2\text{Se}$ was tracked by immersing samples in the 2% HF acid. Figure 5.4b shows the untreated $\text{Bi}_2\text{O}_2\text{Se}$ flake, while Figure 5.4d and 5.4f show the same sample after HF treatment for 30 s and 90 s, respectively. As shown in Figure 5.4d and 5.4f, a high-quality square $\text{Bi}_2\text{O}_2\text{Se}$ was partially etched after 30 s treatment and almost fully etched after 90 s treatment. The

etching effect was also verified by Raman spectra shown in Figure 5.4c, 5.4e and 5.4g. It turns out that the Raman signal was significantly weakened after 30 s and nearly vanished after 90 s.

Figure 5.5 STEM of the etched $\text{Bi}_2\text{O}_2\text{Se}$. (a) Low magnification ADF-STEM image shows non-uniform contrast, which indicates the non-flat surface brought by the etching effect. (b) Nanopores in $\text{Bi}_2\text{O}_2\text{Se}$ after the transfer using HF acid and magnified images (c) and (d). The evidence that nanopores exist in ADF-STEM images under different magnifications further verifies that $\text{Bi}_2\text{O}_2\text{Se}$ has been etched by HF acid during the transfer process.

To elaborate this etching effect, the HF-assisted transferred sample was investigated under aberration-corrected STEM. From Figure 5.5a, the nonuniform contrast in the low magnification image indicates the partial etching of this sample. In addition, nanopores found in both the low and high magnification images (Figure 5.5b-5.5d) further confirmed that $\text{Bi}_2\text{O}_2\text{Se}$ had been etched by HF acid during the transfer process. Therefore, a non-corrosive transfer method is highly demanded to transfer $\text{Bi}_2\text{O}_2\text{Se}$ onto other substrates.

Figure 5.6 PS-assisted transfer of $\text{Bi}_2\text{O}_2\text{Se}$. (a) Schematic of PS-assisted transfer process. (b-g) Changes of optical images and Raman spectra of $\text{Bi}_2\text{O}_2\text{Se}$ with the DI water treatment at different times. (b-c) Initial state. (d-g) No obvious changes could be observed after the DI water treatment with 2 h and 24 h, which indicates good stability during this process.

Figure 5.7 Characterization of the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$. (a) Optical image and (b) SEM image shows the uniform contrast, indicating the success of the developed non-corrosive method. (c) Raman spectrum of the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$ on the Si substrate. (d) FET I_d - V_g curve of the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$. The mobility is calculated to be about $107 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is the same order with the prior reports.

Here, a PS-assisted transfer method was developed (schematically presented in Figure 5.6a).^[22] Briefly, PS was first spin-coated on the surface of f-mica and then baked at 80°C

for 15 min. Then the PS film together with $\text{Bi}_2\text{O}_2\text{Se}$ was peeled away from the f-mica under the assistance of deionized (DI) water. The PS film was then placed on the Si substrate and baked at 70 °C for 1 h, and finally washed out by toluene, leaving the $\text{Bi}_2\text{O}_2\text{Se}$ sample on the Si substrate. The more hydrophobic surface property together with the much stiffer film property of the PS film distinguish it with the PMMA film, which make it much easier to peel off from the f-mica substrate.^[23] The superior stability of $\text{Bi}_2\text{O}_2\text{Se}$ in DI water is demonstrated in Figure 5.6b-5.6g. As a striking contrast to the HF acid treatment, no obvious changes can be found in the optical images (Figure 5.6b, 5.6d and 5.6f) and Raman spectra (Figure 5.6c, 5.6e and 5.6g) even after a 24 h DI water treatment.

Figure 5.8 AFM, SEM and EDS characterization of the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$. (a) AFM topography of the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$. The thickness obtained from the height profile is about 7.8 nm. (b) SEM image shows the uniform contrast and flat surface. (c) EDS of the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$ (marked with pink square in (b)). The ratio of Bi to Se is about 1.93, which shows a good chemical stoichiometry.

Figure 5.7a shows the optical image of Bi₂O₂Se on Si substrate after the transfer. Scanning electron microscopy (SEM) image shows a uniform surface of the as-transferred sample (Figure 5.7b). Raman spectrum (Figure 5.7c) presents the characteristic A_{1g} peak at ~159 cm⁻¹, which matches well with that of the sample on f-mica. As presented in Figure 5.8a (AFM), the thickness of this as-transferred sample is about 7.8 nm. The SEM EDS (Figure 5.8c) provides the information of chemical composition, in which the ratio of Bi to Se is around 1.93. This shows very good chemical stoichiometry within the allowed equipment error. All of these demonstrate the robustness of our non-corrosive transfer method.

5.3.3 The Phototransistor Application of Bi₂O₂Se on Si Substrate

To further evaluate the quality of the samples, two-terminal devices were fabricated based on the as-transferred Bi₂O₂Se flakes on the Si substrate to examine the electrical transport and photoresponse properties. Details of the device fabrication processes are described in the experimental section. Figure 5.7d shows the output and transfer curves of the Bi₂O₂Se transistor using SiO₂/Si as a back gate. It can be seen that the transistor exhibits an n-type semiconducting behavior, which is in accordance with previous reports.^[18, 19] The two-terminal field-effect mobility (μ_{2p}) of the device could be calculated by fitting the linear region in I_d - V_g curve using the equation $\mu_{2p} = \frac{dI_d}{dV_g} \times \frac{L}{WC_iV_d}$, where L is the channel length, W is the channel width, C_i is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0\epsilon_r/d$; ϵ_0 is vacuum permittivity, ϵ_r is the relative permittivity, and d is the thickness of SiO₂ layer). The μ_{2p} of the as-transferred Bi₂O₂Se device is calculated as about 107 cm²V⁻¹s⁻¹, which is the same order as the reported value in a Hall mobility measurement.^[16] Suppressing the scattering from the surface by encapsulating a high- κ dielectric layer may further improve the mobility.^[26-28]

Figure 5.9 Photoresponse performances of the transferred Bi₂O₂Se. (a) FET I_d - V_d curves of the transferred Bi₂O₂Se under different light powers. Inset: the optical image of the device. (b-c) The light power dependence of (b) photocurrent (I_{ph}) as a function of bias, (c) the photoresponsivity (R) and photogain (G). The maximum R and G are 3.5×10^4 A/W and 8.0×10^4 respectively. (d) The largest photocurrent (10.7 μ A) obtained in the experiment under the light power of 5.0 nW.

The high field-effect transistor (FET) performance of the as-transferred Bi₂O₂Se and the convenience of the gate tunability on the Si substrate make it attractive for optoelectronic applications. The optoelectronic behavior of Bi₂O₂Se phototransistor was systematically investigated by exploring the photocurrent at different optical powers, applied drain and gate voltages. Figure 5.9a shows the photocurrent at different drain voltages under the excitation of 532 nm light with different powers. The device (inset of Figure 5.9a) can generate photocurrent as high as 3.5 μ A even under the illumination of an incident light power of about 0.1 nW and the bias of 500 mV. As the light power increases from 0.1 nW to 5 nW, the photocurrent increases gradually from 3.5 μ A to 10.7 μ A (Figure 5.9d). The light power dependence of the photocurrent is plotted with a log-log scale (Figure 5.9b),

where the photocurrent can be expressed by a simple power law ($I_{ph} \approx P^{0.30}$). The non-unity exponent is attributed to the complex processes including the electron-hole generation, trapping, and recombination within the semiconductor.^[13] One of the most important parameters for a photodetector is the photoresponsivity (R), which is the ratio of generated photocurrent (I_{ph}) and incident optical power ($R = I_{ph} / PS$, where P is the power density and S is the effective area). Figure 5.9c shows the photoresponsivity acquired at different light powers. The photoresponsivity reaches up to $3.5 \times 10^4 \text{ AW}^{-1}$, which is one of the highest values of reported 2D semiconductors^[13,29-34] and much higher than that of the commercial Silicon device (0.5 AW^{-1}).^[35] The photoconductive gain (G) is another parameter to evaluate the performance of a phototransistor, which is defined by the equation $G = Rhv/\eta q$, where η is the external quantum efficiency (EQE), q is the electron charge, h is Planck's constant, and v is the frequency of the incident light. Assuming $\eta = 100\%$, G is estimated to be 8.0×10^4 (Figure 5.9c). The charge traps by the surface-bound water on the silicon substrate (photovoltaic effect) and the band tail states near the band edge (photoconductive effect) together contribute to the high gain of the phototransistor.^[36-37] Note that under strong light illumination, the recombination rate of the photocarriers will increase and thus the lifetime will decrease, which results in a slight decrease of the gain in Figure 5.9c.^[37]

Figure 5.10 Dynamic time response of Bi₂O₂Se phototransistor. (a) The on/off test of photocurrent under the power of 0.1 nW and the bias of 0.5 V. The photoresponsivity is as high as $3.5 \times 10^4 \text{ AW}^{-1}$. (b-c) The exponential fitting of the dynamic response of photocurrent for the rise (b) and decay (c). The deduced rise (τ_{rise}) and decay (τ_{decay}) time constants are about 0.308 and 0.448 ms.

The response time is a critical factor for high-speed photodetector. Here, the response time was investigated by monitoring the change of the photocurrent while alternatively turning on and off the light illumination using a mechanical chopper (see the experimental section). As shown in Figure 5.10a, the photocurrent changes as a function of time with a good repeatability. In order to investigate the fast response of the photocurrent, the photocurrent change at the initial stage of the light illumination on and off was recorded (Figure 5.10b and 5.10c). The dynamic response of the photocurrent for the rise and decay can be expressed by $I(t) = I_{\text{dark}} + A \exp(t/\tau_{\text{rise or decay}})$,^[38] where A , t and τ are the scaling constant, on or off state duration time and rise or decay time constant, respectively. By fitting the photocurrent trace, the rise and decay time constants of the measured device are figured out to be about 0.308 ms and 0.448 ms, respectively, which is already a very good result for photodetectors based on 2D semiconductors.^[13,29-34] By using a more sensitive measurement technique like ultrafast two-pulse photovoltage correlation measurements,^[39] the response time of Bi₂O₂Se could be improved in consideration of the limitation of the current equipment.

Figure 5.11 Schematic of the Bi₂O₂Se phototransistor on the Si substrate, which provides the convenience of back gating.

Figure 5.12 Gate-tunable photoresponse of the transferred $\text{Bi}_2\text{O}_2\text{Se}$. (a) FET I_d - V_g curve of the transferred $\text{Bi}_2\text{O}_2\text{Se}$ under different light powers. The dark current could be reduced to several pA. (b) The photoresponsivity under different gate voltages, which could be tuned from 10 to 3.6×10^4 AW^{-1} . (c) The specific detectivity and on/off ratio under different gate voltages. (d) The photoconductive gain as a function of light power under different gate voltages.

The gate bias dependence of the photoresponse was also investigated. The silicon based back-gating configuration can be applied to the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$ device for tuning the dark current as well as the photoresponse (Figure 5.11). Figure 5.12a presents the I_d - V_g curves under dark and light illumination, in which significant photocurrent is generated when the gate voltage is changed from 50 V to -50 V. As the light intensity increases, the I_d - V_g transfer curve shifts to the left significantly, owing to the positive gate effect caused by the trapped photogenerated holes in the interface between the $\text{Bi}_2\text{O}_2\text{Se}$ channel and Si substrate. Figure 5.12b shows the gate dependence of the photoresponsivity, which could be tuned from 10 to 3.6×10^4 AW^{-1} under a light power of 0.2 nW and a bias of 0.5 V. Such back-gate tunability is of great importance in phototransistors because it adds an additional

dimension to engineer the photoresponsivity and photoconductive gain for the detection of light in a wide range (Figure 5.12d). The reason for the decrease of the responsivity at high gate voltage might be ascribed to the reducing contribution of the photogating effect on the photocurrent under high electrostatic gating effect.^[37] Furthermore, due to the evident n-type behavior of the sample, the device shows large dark current at zero gating (hundreds of nA), which will cause a high consumption of power at off state. By applying a negative gate voltage, the dark current could be reduced significantly to several pA because of the higher Schottky barrier. As a result, the on/off ratio of the current between the light irradiation and dark state can reach $\sim 10^7$ (Figure 5.12c). The specific detectivity (D^*) is a parameter to evaluate the sensitivity of the photodetector, which is defined by the noise equivalent power (NEP) equation $NEP = (A\Delta f)^{1/2}/D^*$ where A is the effective area of the photodetector and Δf is the electrical bandwidth. When the shot noise from the dark current is the major limiting factor of D^* , D^* can be expressed as $D^* = RA^{1/2}/(2eI_{dark})^{1/2}$.^[40-42] As shown in Figure 5.12c, D^* reaches its maximum value at a gate of -32 V where a much smaller dark current and a relatively large photocurrent contribute jointly to this result. The maximum D^* obtained here is up to 9.0×10^{13} Jones, which is much higher than that of the commercial Silicon device ($\sim 10^{12}$ Jones).^[43] Also, it is one of the highest values among 2D material based photodetectors and two orders of magnitude higher than that of other CVD-grown 2D materials reported.^[13,26-31]

To compare the photodetector performances of the as-transferred Bi₂O₂Se with other 2D semiconductors prepared by CVD and mechanical exfoliation (ME) methods, the photoresponsivity (R/V_d), dynamic response time (τ_{rise}) and specific detectivity (D^*) are summarized in **Table 1**. Here the photoresponsivity was divided by the bias voltage (V_d) to exclude the contribution of V_d to the photocurrent, assuming that the photocurrent increases linearly with V_d . It is noted that our Bi₂O₂Se photodetectors show excellent performance in the photoresponsivity and specific detectivity, both of which are among the highest values in photodetectors based on 2D semiconductors. In addition, the specific detectivity of our Bi₂O₂Se photodetectors is two orders of magnitude larger than that of other CVD-grown 2D materials, which is ascribed to the reduced dark current by the back gating of silicon substrate. In terms of the dynamic response time, although CVD-grown

MoS₂ and SnS₂ have better performances (0.07 ms and 0.005 ms), they are limited their much lower photoresponsivity (less than 0.1 AW⁻¹V⁻¹) and specific detectivity (less than 10¹⁰), which are five and four orders of magnitude smaller than our results (7.0×10⁴ AW⁻¹V⁻¹ and 9.0×10¹³ Jones). Therefore, compared with other 2D semiconductors, our as-transferred Bi₂O₂Se showed overall high photodetector performances.

Table 1. Comparison of phototransistor performance based on the as-transferred Bi₂O₂Se with other 2D semiconductors prepared by CVD or mechanical exfoliation (ME) methods.

Device	Fabrication method	Responsivity/V _d (AW ⁻¹ V ⁻¹)	Detectivity (Jones)	Rise time (ms)	Ref.
MoS ₂	CVD	0.057	1×10 ¹⁰	0.07	29
ReS ₂	CVD	1208	4.44×10 ¹⁰	2	30
SnS ₂	CVD	0.0044	1×10 ⁹	0.005	31
SnSe ₂	CVD	337	1×10 ¹⁰	14.5	13
InSe	ME	15.7	1×10 ¹¹	50	34
In ₂ Se ₃	ME	79	1×10 ¹⁰	18	33
GaTe	ME	55	1×10 ¹²	48	32
Bi ₂ O ₂ Se	CVD	70000	9×10 ¹³	0.308	This work

5.3.4 Direct CVD Synthesis of Bi₂O₂Se on Si Substrate and its Application

Apart from the transfer of CVD-grown Bi₂O₂Se from f-mica to Si substrate, a direct CVD method to synthesize Bi₂O₂Se on Si substrate (direct-method Bi₂O₂Se) was also developed. From Figure 5.13a, a square Bi₂O₂Se could be obtained by direct CVD method. From the AFM topography in Figure 5.13b, the sample surface is uniform. It can be known from the crystal structure that there are many dangling bonds on the surface of Bi₂O₂Se. Therefore, weak electrostatic interaction from f-mica could lower the surface potential of Bi₂O₂Se and samples with a small thickness can be stabilized. On electroneutral Si substrate, the surface potential is high, especially the few-layer samples. Thus, the smallest thickness that can be obtained from the direct CVD is around 51.0 nm (Figure 5.13b), where the much higher thickness contributes to reduce the surface potential. The same as samples on f-mica, the representative A_{1g} Raman peak, 158.5 cm⁻¹, can be found in the Raman spectrum (Figure

5.13c). SEM EDS was also used to determine the element ratio of Bi to Se, which was found to be around 1.98 (Figure 5.13d), indicating a very good chemical stoichiometry of the direct-method $\text{Bi}_2\text{O}_2\text{Se}$ on Si substrate. Hence, direct-method $\text{Bi}_2\text{O}_2\text{Se}$ was identified by All these characterizations.

Figure 5.13 Characterizations of direct-method $\text{Bi}_2\text{O}_2\text{Se}$ on Si substrate. (a) Optical image of direct-method $\text{Bi}_2\text{O}_2\text{Se}$. (b) AFM topography of direct-method $\text{Bi}_2\text{O}_2\text{Se}$. The thickness extracted from the line height profile is around 51.0 nm. (c) Raman spectrum of direct-method $\text{Bi}_2\text{O}_2\text{Se}$. The characteristic A_{1g} peak could be found at 158.5 cm^{-1} . (d) SEM EDS of direct-method $\text{Bi}_2\text{O}_2\text{Se}$. The element ratio of Bi to Se was found to be 1.98.

The transport and photoresponse properties of the direct-method sample were studied in the same method as the transferred sample. Figure 5.14a and 5.14b show the FET I_d - V_g and I_d - V_d transfer curves of the device, in which n-type semiconducting behavior can be clearly observed and the mobility is about $36.9 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$, which is much lower than the sample on f-mica. This indicates the quality of the direct-method sample on Si substrate might not be as good as that on f-mica. The linear relationship in the I_d - V_d curve shows a good contact between the metal electrode and $\text{Bi}_2\text{O}_2\text{Se}$. The photoresponse properties were investigated under different gate voltages and light intensities. Figure 5.14c shows the I_d - V_g curves

under different light intensities. Both the dark drain current and the photocurrent could also be tuned under different gate voltages. As the gate voltages is changed from -60 V to 60 V, the photocurrent could be tuned from 0.14 μA to 9.7 μA under a bias of 0.5 V (Figure 5.14d).

Figure 5.14 The FET and photoresponse performances of the direct-method Bi₂O₂Se. (a-b) FET I_d - V_g and I_d - V_d transfer curves. (c) I_d - V_g curves under various light intensities. (d) On/off photocurrent test under various gate voltages.

In addition, the power dependence of the photoresponse properties was further analyzed in Figure 5.15. As the light intensity increases, the photocurrent ranges from 0.16 μA to 9.7 μA can be generated under the gate voltage of 60 V (Figure 5.15a), which can be expressed by a simple law $I_{ph} \approx P^{0.75}$. As shown in Figure 5.15b, the photoresponsivity (R) increases as the gate voltage is changed from -60 V to 60 V. The maximum R obtained at the gate of 60 V is around $2.5 \times 10^4 \text{ AW}^{-1}$, which is a bit smaller than the as-transferred one. This may be ascribed to the lower quality of direct-method Bi₂O₂Se as some cracks can be found in

the OM image. It should be the difference in the expansion coefficients between the Si substrate and Bi₂O₂Se that results in these cracks of Bi₂O₂Se crystals in the cooling process. The specific detectivity (D^*) also increases as the gate voltage is changed from -60 V to 60 V (Figure 5.15c). The maximum D^* at the gate of 60 V is around 5×10^{10} Jones, which is much lower than the as-transferred sample. As the D^* at the gate voltage of 30 V and 60 V are really close, it seems the value here is the maximum D for this thickness. This should be owing to the large dark current as the sample thickness of direct-method Bi₂O₂Se is much higher (51.0 nm). Moreover, the maximum D^* appears at the gate of 60V, which is very different from the as-transferred sample (Figure 5.15c). Hence, the photodetector performance of the direct-method Bi₂O₂Se still needs to be improved by modifying the Si surface in the future.

Figure 5.15 The power dependence of the photoreponse properties of the direct-method Bi₂O₂Se under various gate voltages. (a) The power dependence of the photocurrent (I_{ph}). (b) The power dependence of the photoresponsivity (R). (c) The power dependence of the specific detectivity (D^*).

5.4 Conclusion

In summary, a non-corrosive method was developed to transfer Bi₂O₂Se onto the Si substrate, and the Bi₂O₂Se film retained a high quality after transfer. Then phototransistor devices based on the as-transferred Bi₂O₂Se on the Si substrate were fabricated. The devices showed overall high performances in photodetection: high responsivity of 3.5×10^4 A W⁻¹, large photoconductive gain of 8×10^4 , and fast response time of 0.308 ms for the rise and 0.448 ms for the decay processes. Benefiting from the gate tunability on Si substrate,

the devices showed a very low dark current as well as high specific detectivity up to 9.0×10^{13} Jones. Such ultrasensitive photodetection is promising for the development of 2D optoelectronic devices. The developed transfer method also opens a wealth of possibilities to integrate high-quality Bi₂O₂Se with the silicon complementary metal-oxide–semiconductors technologies. Also, the Bi₂O₂Se synthesized by the direct CVD method showed high quality and good phototransistor performance. The successful CVD synthesis of Bi₂O₂Se creates lots of opportunities for the electronic applications of this material, such as CMOS inverters, which will be discussed in the next chapter.

References

- [1] M. Liu, X. Yin, E. Ulin-Avila, B. Geng, T. Zentgraf, L. Ju, F. Wang, X. Zhang, *Nature* **2011**, 474, 64.
- [2] B. Radisavljevic, A. Radenovic, J. Brivio, i. V. Giacometti, A. Kis, *Nat. Nanotechnol.* **2011**, 6, 147.
- [3] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.* **2012**, 7, 699.
- [4] F. Liu, W. L. Chow, X. He, P. Hu, S. Zheng, X. Wang, J. Zhou, Q. Fu, W. Fu, P. Yu, *Adv. Funct. Mater.* **2015**, 25, 5865.
- [5] J. Zhou, J. Lin, X. Huang, Y. Zhou, Y. Chen, J. Xia, H. Wang, Y. Xie, H. Yu, J. Lei, *Nature* **2018**, 556, 355.
- [6] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, H. Zhang, *Acs Nano* **2011**, 6, 74.
- [7] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, *Nat Nanotechnol.* **2013**, 8, 497.
- [8] W. Zhang, J. K. Huang, C. H. Chen, Y. H. Chang, Y. J. Cheng, L. J. Li, *Adv. Mater.* **2013**, 25, 3456.
- [9] W. Zhang, M.-H. Chiu, C.-H. Chen, W. Chen, L.-J. Li, A. T. S. Wee, *Acs Nano* **2014**, 8, 8653.
- [10] T. Wang, K. Andrews, A. Bowman, T. Hong, M. Koehler, J. Yan, D. Mandrus, Z. Zhou, Y.-Q. Xu, *Nano Lett.* **2018**, 18, 2766.

- [11] F. Liu, H. Shimotani, H. Shang, T. Kanagasekaran, V. Zólyomi, N. Drummond, V. I. Fal'ko, K. Tanigaki, *Acs Nano* **2014**, 8, 752.
- [12] Z. Wang, K. Xu, Y. Li, X. Zhan, M. Safdar, Q. Wang, F. Wang, J. He, *Acs Nano* **2014**, 8, 4859.
- [13] X. Zhou, L. Gan, W. Tian, Q. Zhang, S. Jin, H. Li, Y. Bando, D. Golberg, T. Zhai, *Adv. Mater.* **2015**, 27, 8035.
- [14] P. Perumal, R. K. Ulaganathan, R. Sankar, Y. M. Liao, T. M. Sun, M. W. Chu, F. C. Chou, Y. T. Chen, M. H. Shih, Y. F. Chen, *Adv. Funct. Mater.* **2016**, 26, 3630.
- [15] X. Zhou, Q. Zhang, L. Gan, H. Li, T. Zhai, *Adv. Funct. Mater.* **2016**, 26, 4405.
- [16] J. Wu, Y. Liu, Z. Tan, C. Tan, J. Yin, T. Li, T. Tu, H. Peng, *Adv. Mater.* **2017**, 29, 1704060.
- [17] J. Wu, C. Tan, Z. Tan, Y. Liu, J. Yin, W. Dang, M. Wang, H. Peng, *Nano Lett.* **2017**, 17, 3021.
- [18] J. Wu, H. Yuan, M. Meng, C. Chen, Y. Sun, Z. Chen, W. Dang, C. Tan, Y. Liu, J. Yin, *Nat. Nanotechnol.* **2017**, 12, 530.
- [19] J. Yin, Z. Tan, H. Hong, J. Wu, H. Yuan, Y. Liu, C. Chen, C. Tan, F. Yao, T. Li, *Nat. Commun.* **2018**, 9, 3311.
- [20] J. Li, Z. Wang, Y. Wen, J. Chu, L. Yin, R. Cheng, L. Lei, P. He, C. Jiang, L. Feng, *Adv. Funct. Mater.* **2018**, 28, 1706437.
- [21] T. G. Mayer, P. L. Gross, *Annals of emergency medicine* **1985**, 14, 149.
- [22] R. Chow, W. Lanford, W. Ke-Ming, R. S. Rosler, *J. Appl. Phys.* **1982**, 53, 5630.
- [23] A. Gurarslan, Y. Yu, L. Su, Y. Yu, F. Suarez, S. Yao, Y. Zhu, M. Ozturk, Y. Zhang, L. Cao, *Acs Nano* **2014**, 8, 11522.
- [24] T. Cheng, C. Tan, S. Zhang, T. Tu, H. Peng, Z. Liu, *J. Phys. Chem. C* **2018**, 122, 19970.
- [25] A. L. Pereira, D. Santamaría-Pérez, J. Ruiz-Fuertes, F. J. Manjón, V. P. Cuenca-Gotor, R. Vilaplana, O. Gomis, C. Popescu, A. Munoz, P. Rodriguez-Hernandez, *J. Phys. Chem. C* **2018**, 122, 8853.
- [26] J. Schrieffer, *Phys. Rev.* **1955**, 97, 641.
- [27] C. Sah, T. Ning, L. Tschopp, *Surf. Sci.* **1972**, 32, 561.

- [28] N. P. Butch, K. Kirshenbaum, P. Syers, A. B. Sushkov, G. S. Jenkins, H. D. Drew, J. Paglione, *Phys. Rev. B* **2010**, *81*, 241301.
- [29] D.-S. Tsai, K.-K. Liu, D.-H. Lien, M.-L. Tsai, C.-F. Kang, C.-A. Lin, L.-J. Li, J.-H. He, *ACS Nano* **2013**, *7*, 3905.
- [30] E. Liu, M. Long, J. Zeng, W. Luo, Y. Wang, Y. Pan, W. Zhou, B. Wang, W. Hu, Z. Ni, Y. You, X. Zhang, S. Qin, Y. Shi, K. Watanabe, T. Taniguchi, H. Yuan, H. Y. Hwang, Y. Cui, F. Miao, D. Xing, *Adv. Funct. Mater.* **2016**, *26*, 1938.
- [31] G. Su, V. G. Hadjiev, P. E. Loya, J. Zhang, S. Lei, S. Maharjan, P. Dong, P. M. Ajayan, J. Lou, H. Peng, *Nano Lett.* **2015**, *15*, 506.
- [32] P. Hu, J. Zhang, M. Yoon, X.-F. Qiao, X. Zhang, W. Feng, P. Tan, W. Zheng, J. Liu, X. Wang, J. C. Idrobo, D. B. Geohegan, K. Xiao, *Nano Res.* **2014**, *7*, 694.
- [33] R. B. Jacobs-Gedrim, M. Shanmugam, N. Jain, C. A. Durcan, M. T. Murphy, T. M. Murray, R. J. Matyi, R. L. Moore, B. Yu, *ACS Nano* **2014**, *8*, 514.
- [34] S. R. Tamalampudi, Y.-Y. Lu, U. R. Kumar, R. Sankar, C.-D. Liao, B. K. Moorthy, C.-H. Cheng, F. C. Chou, Y.-T. Chen, *Nano Lett.* **2014**, *14*, 2800.
- [35] C. O. Kim, S. Kim, D. H. Shin, S. S. Kang, J. M. Kim, C. W. Jang, S. S. Joo, J. S. Lee, J. H. Kim, S.-H. Choi, *Nat. Commun.* **2014**, *5*, 3249.
- [36] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. De Arquer, F. Gatti, F. H. Koppens, *Nat. Nanotech.* **2012**, *7*, 363.
- [37] M. M. Furchi, D. K. Polyushkin, A. Pospischil, T. Mueller, *Nano Lett.* **2014**, *14*, 6165.
- [38] A. Grinvald, I. Z. Steinberg, *Anal. Biochem.* **1974**, *59*, 583.
- [39] H. Wang, C. Zhang, W. Chan, S. Tiwari, F. Rana, *Nat. Commun.* **2015**, *6*, 8831.
- [40] X. Gong, M. Tong, Y. Xia, W. Cai, J. S. Moon, Y. Cao, G. Yu, C.-L. Shieh, B. Nilsson, A. J. Heeger, *Science* **2009**, *325*, 1665.
- [41] S. Liu, Z. Wei, Y. Cao, L. Gan, Z. Wang, W. Xu, X. Guo, D. Zhu, *Chem. Sci.* **2011**, *2*, 796.
- [42] P. Hu, L. Wang, M. Yoon, J. Zhang, W. Feng, X. Wang, Z. Wen, J. C. Idrobo, Y. Miyamoto, D. B. Geohegan, *Nano Lett.* **2013**, *13*, 1649.
- [43] J. Wojtas, J. Mikolajczyk, Z. Bielecki, *Sensors* **2013**, *13*, 7570.

Chapter 6*

High-performance CMOS Inverters Based on n-type Bi₂O₂Se and p-type WSe₂

The continuing scaling of silicon-based metal-oxide-semiconductor field-effect transistor is hindered by the serious short channel effect in sub-10 nm channel length. Thanks to the atomic thickness and non-dangling surface, which leads to efficient channel regulation, high level of integration and high mobility, two-dimensional (2D) semiconductors have shown great potential in the electronic and optoelectronic research. Here, the CMOS inverters based on n-type Bi₂O₂Se and p-type WSe₂ have been demonstrated on both f-mica and silicon substrate. On f-mica substrate, under the gating of ion liquid, a gain of 3.5 can be obtained at the supply voltage of only 1.0 V. Dynamic voltage response at the frequency of 100 Hz shows good response with almost no voltage lose. On silicon substrate, the CMOS inverter showed a high gain of 2.2 at the supply voltage of 5.0 V, a high noise margin of 5.2 V_{DD} and a low power consumption at the order of 10⁻⁹ W. Although further optimization is needed to improve the performance of the current device, the high potential of Bi₂O₂Se shown here open a wealthy of possibilities in amounts of promising applications.

*This section is under preparation as **Qundong Fu**, Chao Zhu, Xiaoxu Zhao, Xingli Wang, Apoorva Chaturvedi, Jiadong Zhou, Fucan Liu*, Stephen John Pennycook, Tay Beng Kang, Hua Zhang, and Zheng Liu*. High-performance CMOS Inverters Based on n-type Bi₂O₂Se and p-type WSe₂. **2018**.

6.1 Introduction

As the miniaturization of silicon-based metal-oxide-semiconductor field-effect transistors (MOSFET) continues, the rapid growth of the transistor number on a chip enables lower operating voltage and faster operating speed.^[1,2] Nevertheless, the subsequent short channel effect also becomes destructive to the performance when the channel length is lowered to sub-10 nm regime.^[3,4] Although the multi-gate architectures push the scaling to 7 nm, new methods are highly demanded in the further scaling.^[5,6] As the thickness could be smaller than 1/3 of the gate length, which provides an active channel regulation, ultrathin materials have drawn huge attention.^[7-9] In addition, two dimensional (2D) semiconducting materials possess the merits of high mobility and higher degree of vertical integration.^[10-14] Therefore, 2D electronics and optoelectronics have shown attracted huge interests since then. One of these significant applications is complementary metal-oxide-semiconductor (CMOS) inverter, which is an essential circuit unit providing opposite output logic signal to the input with fast speed and low power consumption. Many 2D semiconductors have shown high CMOS inverter performance, such as MoS₂, WSe₂, MoTe₂,^[15-18] thanks to their suitable energy bandgap and high mobility. However, the stability of either the intrinsic channel material (MoTe₂)^[18] or the doping material (K doped WSe₂)^[16] is not satisfactory.

Recently, a new type of 2D semiconducting material Bi₂O₂Se has been prepared via chemical vapor deposition with a large area.^[19] More importantly, it has been proved to possess high mobility and superior air stability over months.^[20,21] All of these virtues make it a competitive candidate in the application of the CMOS inverter. Here, the CMOS inverters based on n-type Bi₂O₂Se and p-type WSe₂ have been demonstrated on both f-mica and silicon substrate. On f-mica, under the gating of ion liquid, a gain of 3.5 can be obtained at the supply voltage of only 1.0 V. Dynamic voltage response at the frequency of 100 Hz shows good response with almost no voltage lose. On silicon substrate, the CMOS inverter showed a high gain of 2.2 at the supply voltage of 5.0 V, a high noise margin of 5.2 V_{DD} and a low power consumption at the order of 10⁻⁹ W. Although further optimization could improve the performance, the high potential of Bi₂O₂Se proved here sheds light on amounts of promising applications in the future.

6.2 Experimental Methods

6.2.1 CVD Synthesis of $\text{Bi}_2\text{O}_2\text{Se}$ on f-mica

Figure 6.1 Schematic of the CVD setup for the synthesis of $\text{Bi}_2\text{O}_2\text{Se}$ on f-mica.

The CVD process is schematically depicted in Figure 6.1. In detail, the setup is a split tube furnace with interconnected control system (1-Zone, 1200°C) and we used 1200 mm long fused quartz tubes with an outside diameter (O.D.) of 50 mm. Powders of Bi_2Se_3 and Bi_2O_3 were used as precursors, placed in two alumina crucibles and Bi_2O_3 was located in the central zone while Bi_2Se_3 was located in the upstream with a distance of 8 cm. The f-mica substrate was placed downstream with a distance of 12 cm. The chamber was first pumped down to 6.0×10^{-2} Torr, and then 170 sccm (standard cubic centimeter per minute) Ar was introduced to reach a pressure of 350-400 Torr. The chamber was heated to 620°C in 25 min and held for 40 min. After that the furnace was cooled down naturally to room temperature and the chamber was refilled with Ar gas to reach atmospheric pressure.

6.2.2 AFM and Raman Characterizations

AFM was conducted under the Asylum Research Cypher Scanning Probe Microscope system with a tapping mode. Raman spectra were recorded by a Witec Raman system equipped with 100x objective lens and a grating of 1200 lines/mm under 532 nm laser excitation.

6.2.3 Transfer of Bi₂O₂Se onto Cu Grid and STEM Characterization

Figure 6.2 Schematic of the transfer process of Bi₂O₂Se using HF acid for TEM characterization.

The TEM samples were prepared with a poly (methyl methacrylate) (PMMA) based transfer method. First, the f-mica substrates with the as-grown CVD samples were spin-coated with PMMA at 3,000 r.p.m. for 60 s and then baked at 150 °C for 5 min. Afterward, PMMA-coated sample was peeled off by etching away the underneath f-mica in 2% HF solution. Next, the floating PMMA film was transferred to the DI water and scooped up by a TEM grid. The TEM grid was dried at 50 °C for 30 mins, and then submerged into acetone for about 24 h to remove PMMA. Finally, the TEM grid was rinsed by isopropyl alcohol (IPA) and dried in air.

ADF-STEM imaging was carried out on an aberration-corrected JEOL ARM-200F equipped with a cold field emission gun, operating at 80 kV, and an ASCOR probe corrector. The convergent semi-angle of the probe was set at about 30 mrad. ADF-STEM images were collected using a half-angle range from about 68 to 280 mrad. A dwell time of 19 $\mu\text{s pixel}^{-1}$ was set for single-scan imaging. EDS mapping was conducted under the Oxford X-Max 100TLE SDD EDS system.

6.2.4 PS-assisted Transfer of Bi₂O₂Se Onto Si Substrate

The as-transferred Bi₂O₂Se was prepared with a PS assisted transfer method. First, the f-mica substrate with the as-grown Bi₂O₂Se was spin-coated with PS at 3,500 r.p.m. for 60 s and then baked at 85 °C for 15 min. After the edge of f-mica was cut away, PS-coated sample was peeled off by a drop of DI water. Next, the floating PS film was transferred

onto Si substrate. The Si substrate was dried at 80 °C for 1 h and then heated at 150 °C for 30 mins to improve the contact between the sample and the Si substrate. Then the Si substrate was immersed into toluene for 24 h to remove PS and then into acetone for 5h to remove organic residuals. Finally, the Si substrate was dried by floating nitrogen.

6.2.5 Devices Fabrication and Measurement

To fabricate the CMOS inverter, a p-type WSe₂ sample was transferred onto the f-mica or Si substrate using a scotch tape method. Firstly, the WSe₂ sample was exfoliated manually by the scotch tape to few layers and then exfoliated onto a soft substrate polydimethylsilane (PDMS). On the PDMS, WSe₂ was located under the optical microscopy, and transferred to the position near the Bi₂O₂Se flakes on f-mica or Si substrate.

After the transfers of Bi₂O₂Se (onto silicon) and WSe₂ were finished, the samples were then spin-coated with PMMA. As f-mica is insulated, a conductive layer (20 nm thin film of Au or AR-PC 5090.02 conductive protective layer) was spin-coated above the PMMA on f-mica substrate. The electrode patterns were then defined by the EBL (Nova nanoSEM 230 with digital pattern generator Nabity-NPGS). An additional electrode was deposited near the two samples for the purpose of the gating by ion liquid (diethyl methyl (2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl) imide, DEME-TFSI). After the pattern was developed in MIBK/IPA, metal contacts (3 nm Cr/55 nm Au) were deposited by Kurt J. Lesker Nano 36 Thermal Evaporator. As the Electrical and photoresponse properties of the FETs were measured in the MicroXact Probe Station by Agilent B1500A Semiconductor Device Parameter Analyzer.

6.3 Results and Discussions

6.3.1 Synthesis and Characterization of Bi₂O₂Se on f-mica

As depicted in Figure 6.1, layered Bi₂O₂Se belongs to I4/mmm space group, where oxygen atoms form a tetragonal lattice and the upper and lower bismuth atoms are stacked at

different sets of tetragonal interstitial sites, forming a [Bi₂O₂]²⁺ layer. Meanwhile selenium atoms which are filled in the other set of sites bind the upper and lower [Bi₂O₂]²⁺ layers with weak electrostatic force, giving an interlayer spacing about 0.61 Å. Large-area single crystalline Bi₂O₂Se samples were prepared via a low-pressure chemical vapor deposition method (Figure 6.1).^[19] Briefly, in a 2-inch quartz tube, bismuth selenide and bismuth oxide powders were placed in the high-temperature zone while the f-mica was put at the downstream low-temperature zone. Under the pressure of 400 Torr, the growth temperature was elevated to 620 °C in 25 min and held for 40 min, and then cooled down to room temperature naturally.

Figure 6.3 Synthesis and characterization of Bi₂O₂Se. (a) Crystal structure of Bi₂O₂Se. (b) Optical image of square Bi₂O₂Se on f-mica. The size is around 40 μm. (c) AFM topography of the as-grown Bi₂O₂Se. The thickness is around 3.5 nm, which is related to 5-layer sample. (d) Raman spectrum of Bi₂O₂Se with the characteristic A_{1g} peak at 160.6 cm⁻¹.

As shown in Figure 6.3b, Bi₂O₂Se sample with a size of around 40 μm was obtained with a square morphology, indicating the high quality and tetragonal crystal group of Bi₂O₂Se. As determined by atomic force microscopy (AFM, Figure 6.3c), the surface of our sample

is clean and homogeneous and the thickness is around 3.5 nm, corresponding to a 5-layer sample. The characteristic A_{1g} peak of Bi₂O₂Se ($\sim 160.6 \text{ cm}^{-1}$) can be found in the Raman spectrum (Figure 6.3d), which shows good consistency with the prior report.^[19]

Figure 6.4 STEM characterization of Bi₂O₂Se. (a) Low magnification ADF-STEM image. (b) The atomic-resolution ADF-STEM image of Bi₂O₂Se shows tetragonally arranged atoms. (c) FFT pattern of (b). Squarely arranged spots indicate the crystal space group of I4/mmm. (d-f) EDS mappings of elements Bi (d), Se (e) and O (f) in Bi₂O₂Se sample show uniform distribution of three elements.

To further determine the atomic structure and chemical composition, annular dark-field (ADF) imaging and energy-dispersive X-ray spectroscopy (EDS) mapping were conducted on an aberration-corrected scanning transmission electron microscope (STEM) system. Figure 6.4b shows the ADF-STEM image of squarely arranged atom lattice while Figure 6.4c is the corresponding fast Fourier transform (FFT) of Figure 6.4b. The squarely arranged spots (200), (1 $\bar{1}$ 0) and (110) in Figure 6.4c confirm the I4/mmm space group of Bi₂O₂Se. As shown in Figure 6.4d-6.4f, EDS element mappings consolidate the uniform

distribution of elements Bi, Se and O. All the results confirm the high quality of our CVD-grown Bi₂O₂Se.

Figure 6.5 FET performance of Bi₂O₂Se on f-mica. (a) Optical image of the CMOS inverter based on Bi₂O₂Se and WSe₂ device. An additional electrode is for the gate use of ion liquid (IL). (b) The FET I_d - V_d curve of Bi₂O₂Se under different gate voltages. (c) The FET I_d - V_g curve of Bi₂O₂Se.

6.3.2 The CMOS Inverter Application of Bi₂O₂Se on f-mica Substrate

To fabricate CMOS inverter devices, two-terminal devices based on Bi₂O₂Se and WSe₂ were fabricated at the same time and details of the device fabrication processes are described in the method part. Here, ion liquid diethyl methyl (2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl) imide (DEME-TFSI) was used to gate both the Bi₂O₂Se and WSe₂ devices. Therefore, an additional electrode was fabricated near the two devices (Figure 6.5a). The electrical transport property of Bi₂O₂Se FET was examined first. Figure 6.5b and 6.5c show the I_d - V_d and I_d - V_g curves of the Bi₂O₂Se transistor. The good linearity in I_d - V_d curve indicates a good contact between the electrode and Bi₂O₂Se. Under the gate of 2.0 V and the bias of 0.1 V, the device can generate a current as high as 41.0 μA. From the I_d - V_g curve, the transistor exhibits clear n-type semiconducting behavior with on/off ratio of 10^5 , which matches well with previous reports. The field-effect mobility of the device could be calculated by fitting the linear region in I_d - V_g curve using the equation $\mu = \frac{dI_d}{dV_g} \times \frac{L}{WC_iV_d}$, where L is the channel length, W is the channel width, C_i is the capacitance between the channel and the back gate per unit area. The mobility of this Bi₂O₂Se is calculated about $235 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is almost the same as the reported value in a Hall mobility measurement.^[20]

Figure 6.6 FET performances of WSe₂ and Bi₂O₂Se in a CMOS inverter on f-mica substrate. (a) Raman spectrum of WSe₂. (b) The FET Id-Vg curves of WSe₂ (black) and Bi₂O₂Se (blue). Inset: circuit symbol of CMOS inverter.

Meanwhile, the transfer curve of the p-channel WSe₂ which has been verified by Raman spectrum (Figure 6.6a) is shown in Figure 6.6b. Although these two curves show very good symmetry (Figure 6.6b), which is essential for the CMOS inverter, the drain current and mobility of WSe₂ (1.2 μA and 17 cm²V⁻¹s⁻¹) are both a bit smaller than those of Bi₂O₂Se (7.5 μA and 65 cm²V⁻¹s⁻¹). This might affect the CMOS inverter performance. Note that the quality of Bi₂O₂Se may be not as good as the previous one. Nevertheless, this results in a good match of these two materials.

As shown in the inset of Figure 6.6b, two FETs are connected in series while WSe₂ (p-FET) was connected to the drain supply and the source was of Bi₂O₂Se (n-FET) was grounded. As shown in Figure 6.5a, a droplet of IL was dropped at the additional electrode and at the same time covered both the n-type and p-type channels. Thus, the V_{in} signal was provided by this gate electrode and the V_{out} signal was collected at the common electrode of the two FETs. The voltage transfer curves of the CMOS inverter (V_{out} versus V_{in}) under different V_{DD} are shown in Figure 6.7, from which clear signal inversion can be observed with low V_{in} and high V_{out} and vice versa under all the V_{DD} voltages. The voltage gain (G) is a significant parameter to access the switch efficiency of the CMOS inverter, which is defined as the absolute value of $\partial V_{out}/\partial V_{in}$. From Figure 6.7, the gains of 1.3, 2.6 and 3.5 can be obtained at the V_{DD} voltages of 0.2 V, 0.5 V and 1.0 V, respectively. This is already

a very good result at the V_{DD} of only 1.0 V compared to prior reports.^[15,16] Although the further increase of V_{DD} may lead to higher gain, the high voltage will also lead to the quality degradation of the channel materials, which may be ascribed to the contamination of the impurity (H₂O) in the IL.

Figure 6.7 CMOS transfer curves and gains under different V_{DD} . (a) 0.2 V, (b) 0.5 V and (c) 1.0 V. Clear signal inversion can be observed with low V_{in} and high V_{out} and vice versa.

Noise margin is another parameter to evaluate the performance of CMOS inverter, which means the amount of noise that a circuit can withstand. Two types of noise margins which are high-state (NM_H) and low-state (NM_L) are calculated by using the formula $NM_H = V_{OH} - V_{IH}$ and $NM_L = V_{IL} - V_{OL}$, where V_{OH} stands for the minimum high output voltage, and V_{IH} is the minimum high input voltage, and V_{IL} is the maximum low input voltage, and V_{OL} is the maximum low output voltage. V_{IH} and V_{IL} are the input voltages where the slope value of the voltage transfer curve is -1, corresponding to the gain value of 1, while V_{OH} and V_{OL} are the corresponding output voltages, respectively. Here, the noise margins of the inverter are figured out to be $NM_H = 0.52 V_{DD}$ and $NM_L = 0.15 V_{DD}$ for $V_{DD} = 1.0$ V. The reason for the small NM_L should be the fluctuation shown in the gain curve (Figure 6.7c) caused by the reaction with the impurity in the IL. This could also be verified by the power consumption of the CMOS inverter (Figure 6.8), where it is 10^{-10} W at the V_{DD} of 0.2 V (Figure 6.8a) while at the V_{DD} of 1.0 V, it reaches up to 10^{-6} W (Figure 6.8c), indicating a significant increase of the drain current.

Figure 6.8 The power consumption of the CMOS inverter under different V_{DD} . (a) 0.2 V, (b) 0.5 V and (c) 1.0 V.

Figure 6.9 Dynamic switch behaviors of the CMOS inverter under different frequencies. (a) 10 Hz, (b) 100 Hz and (c) 500 Hz.

To test the dynamic response of the CMOS inverter, a square wave of 0 V and 2.5 V was applied to examine the output voltage response. As shown in Figure 6.9a, when the frequency is 10 Hz, the response is good with almost no delay. However, the overshoot and undershoot behavior of ion liquid is evident owing to the slow charging and discharging process of the ion liquid. When the frequency was elevated to 100 Hz and 500 Hz, first small and then obvious delay can be observed. Besides, the voltage lose is also obvious in the 500 Hz test, which is ascribed to the increased current during the dynamic switch process as discussed above.

Therefore, the CMOS inverters based on n-type Bi₂O₂Se and p-type WSe₂ have been demonstrated with a gain of 3.5 at the V_{DD} of only 1.0 V and a dynamic response of 100 Hz without obvious voltage lose. However, the impurity of the ion liquid leads to a high drain current which limits the further improvement of this method. The CMOS inverter on silicon substrate was then fabricated and evaluated.

6.3.3 The CMOS Inverter Application of Bi₂O₂Se on Silicon Substrate

Firstly, a non-corrosive PS-assisted transfer method was developed (Figure 6.10).^[22] Briefly, PS was first spin-coated on the surface of f-mica and then baked at 80 °C for 15min. Then the PS film together with Bi₂O₂Se was peeled away from f-mica under the assistance of DI water. The PS film was then placed on Si substrate and baked at 70 °C for 1 h, and finally washed out by toluene, leaving the Bi₂O₂Se sample on Si substrate.

Figure 6.10 Schematic of the non-corrosive PS-assisted transfer process.

After Bi₂O₂Se and WSe₂ were transferred onto silicon substrate, the device fabrication processes were almost the same as those on f-mica substrate, which are described in the method part. The back-gating configuration on 280 nm SiO₂/Si substrate provide the convenience of the gating for the CMOS inverter. The electrical transport property of Bi₂O₂Se FET was evaluated first. Figure 6.11a shows the FET I_d - V_d curves of the Bi₂O₂Se transistor while Figure 6.11b and 6.11c present I_d - V_g curves of the Bi₂O₂Se and WSe₂ transistors, respectively. The good linearity in I_d - V_d curve indicates a good contact between the electrode and Bi₂O₂Se. Under the gate of 40.0 V and the bias of 1.0 V, the device can generate a current as high as 25.2 μ A. From the I_d - V_g curves, the Bi₂O₂Se transistor exhibits clear n-type semiconducting behavior with the on/off ratio of 10⁶ (Figure 6.11b), while the

WSe₂ transistor shows ambipolar but more p-type behavior with the on/off ratio of 10⁵ (Figure 6.11c). The field-effect mobility of the device could be calculated by fitting the linear region in I_d - V_g curve using the equation $\mu = \frac{dI_d}{dV_g} \times \frac{L}{WC_iV_d}$, where L is the channel length, W is the channel width, C_i is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0\epsilon_r/d$; ϵ_0 is vacuum permittivity, ϵ_r is the relative permittivity, and d is the thickness of SiO₂ layer). The mobility of this Bi₂O₂Se is calculated about 107 cm²V⁻¹s⁻¹, which is a bit smaller than the reported value.^[20]

Figure 6.11 FET performances of WSe₂ and Bi₂O₂Se in a CMOS inverter on Si substrate. (a) The FET I_d - V_d curves of Bi₂O₂Se transistor under different gate voltages. (b-c) The FET I_d - V_g curves of Bi₂O₂Se (b) and WSe₂ (c) transistors.

Meanwhile, the mobility of WSe₂ is calculated to be around 21.7 cm²V⁻¹s⁻¹, a bit higher than that on f-mica. This further confirms that the quality of the ion liquid is not good. The same case as that on f-mica, the drain current and mobility of WSe₂ (1.8 μA and 21 cm²V⁻¹s⁻¹) are still a bit smaller than those of Bi₂O₂Se (25.2 μA and 107 cm²V⁻¹s⁻¹). Note that the quality of the as-transferred Bi₂O₂Se here is as good as the one on f-mica. Hence, a better performance is expected for the CMOS inverter on silicon substrate.

As shown in Figure 6.12, the performance of CMOS inverter based on WSe₂ (p-FET) and Bi₂O₂Se (n-FET) was evaluated in the same method. The voltage transfer curves of the CMOS inverter (V_{out} versus V_{in}) under different V_{DD} are shown in Figure 6.12, from which clear signal inversion can be observed with low V_{in} and high V_{out} and vice versa under all the V_{DD} voltages. From Figure 6.12, the gains of 0.48, 1.3 and 2.2 can be obtained at the V_{DD} voltages of 1.0 V, 3.0 V and 5.0 V, respectively. Compared to 2D inverters using

silicon based back-gating, this value is a very good result.^[18] The further increase of V_{DD} may lead to higher gain, and thus better performance of the CMOS inverter.

Figure 6.12 CMOS transfer curves and gains under different V_{DD} . (a) 1.0 V, (b) 3.0 V and (c) 5.0 V. Clear signal inversion can be observed with low V_{in} and high V_{out} and vice versa.

Figure 6.13 The power consumption of the CMOS inverter under different V_{DD} . (a) 0.2 V, (b) 0.5 V and (c) 1.0 V.

The noise margins of the CMOS inverter on silicon substrate are found to be $NM_H = 5.2 V_{DD}$ and $NM_L = 6.4 V_{DD}$ for $V_{DD} = 5.0$ V. The reason for the large NM_H should be the small applied V_{DD} compared with the gate voltages (Figure 6.12). The better performance of the CMOS inverter could also be seen in the power consumption of the CMOS inverter (Figure 6.13), where it is 10^{-11} W at the V_{DD} of 1.0 V (Figure 6.13a) and keep at the level of 10^{-9} W at the V_{DD} of 5.0 V. This is superior performance in the power consumption.

6.4 Conclusions

In summary, the CMOS inverters based on n-type Bi₂O₂Se and p-type WSe₂ have been demonstrated both on f-mica substrate and silicon substrate. On f-mica, under the gating of ion liquid, a gain of 3.5 can be obtained at the V_{DD} of only 1.0 V. Dynamic voltage response at the frequency of 100 Hz shows good response with almost no voltage lose. On silicon substrate, the CMOS inverter showed a high gain of 2.2 at the V_{DD} of 5.0 V, a high noise margin of 5.2 V_{DD} and a low power consumption at the level of 10⁻⁹ W. This overcomes the drawbacks of ion liquid. In the future, by encapsulating a high- κ dielectric layer or improving the contact of WSe₂, the CMOS inverter performance could be much improved.

References

- [1] C. Qiu, Z. Zhang, M. Xiao, Y. Yang, D. Zhong, L.-M. Peng, *Science* **2017**, 355, 271-276.
- [2] C. Qiu, F. Liu, L. Xu, B. Deng, M. Xiao, J. Si, L. Lin, Z. Zhang, J. Wang, H. Guo, *Science* **2018**, eaap9195.
- [3] Y. Yazawa, Y. Kobayashi, A. Fukami, T. Nagano, Google Patents, 1989.
- [4] K. K. Young, *IEEE Trans. on Electron Devices* **1989**, 36, 399-402.
- [5] B. A. Anderson, A. Bryant, E. J. Nowak, Google Patents, 2008.
- [6] B. Yu, L. Chang, S. Ahmed, H. Wang, S. Bell, C.-Y. Yang, C. Tabery, C. Ho, Q. Xiang, T.-J. King, presented at International Electron Devices Meeting **2002**.
- [7] B. Radisavljevic, A. Radenovic, J. Brivio, i. V. Giacometti, A. Kis, *Nat. Nanotech.* **2011**, 6, 147.
- [8] K. Novoselov, D. Jiang, F. Schedin, T. Booth, V. Khotkevich, S. Morozov, A. Geim, *Proc. Natl. Acad. Sci.* **2005**, 102, 10451-10453.
- [9] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, 306, 666-669.
- [10] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, *Nat. Mater.* **2014**, 13, 1135.

- [11] X. Wang, F. Xia, *Nat. Mater.* **2015**, 14, 264.
- [12] D. A. Bandurin, A. V. Tyurnina, L. Y. Gelang, A. Mishchenko, V. Zólyomi, S. V. Morozov, R. K. Kumar, R. V. Gorbachev, Z. R. Kudrynskyi, S. Pezzini, *Nat. Nanotech.* **2017**, 12, 223.
- [13] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. De Arquer, F. Gatti, F. H. Koppens, *Nat. Nanotech.* **2012**, 7, 363.
- [14] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, Y. Zhang, *Nat. Nanotech.* **2014**, 9, 372.
- [15] A. Pezeshki, S. H. Hosseini Shokouh, P. J. Jeon, I. Shackery, J. S. Kim, I.-K. Oh, S. C. Jun, H. Kim, S. Im, *ACS Nano* **2015**, 10, 1118-1125.
- [16] M. Tosun, S. Chuang, H. Fang, A. B. Sachid, M. Hettick, Y. Lin, Y. Zeng, A. Javey, *ACS Nano* **2014**, 8, 4948-4953.
- [17] J. Y. Lim, A. Pezeshki, S. Oh, J. S. Kim, Y. T. Lee, S. Yu, D. K. Hwang, G. H. Lee, H. J. Choi, S. Im, *Adv. Mater.* **2017**, 29, 1701798.
- [18] Y. F. Lin, Y. Xu, S. T. Wang, S. L. Li, M. Yamamoto, A. Aparecido - Ferreira, W. Li, H. Sun, S. Nakaharai, W. B. Jian, *Adv. Mater.* **2014**, 26, 3263-3269.
- [19] J. Wu, C. Tan, Z. Tan, Y. Liu, J. Yin, W. Dang, M. Wang, H. Peng, *Nano Lett.* **2017**, 17, 3021-3026.
- [20] J. Wu, Y. Liu, Z. Tan, C. Tan, J. Yin, T. Li, T. Tu, H. Peng, *Adv. Mater.* **2017**, 29, 1704060.
- [21] J. Wu, H. Yuan, M. Meng, C. Chen, Y. Sun, Z. Chen, W. Dang, C. Tan, Y. Liu, J. Yin, *Nat. Nanotech.* **2017**, 12, 530.
- [22] A. Gurarslan, Y. Yu, L. Su, Y. Yu, F. Suarez, S. Yao, Y. Zhu, M. Ozturk, Y. Zhang, L. Cao, *ACS Nano* **2014**, 8, 11522-11528.

Chapter 7

Conclusions and Recommendations for Future Work

This chapter will first give a summary to the research work. Based on this, discussions on the hypotheses will be presented and how the hypotheses have been demonstrated will be illustrated. Furthermore, future work will be provided and recommendations will be proposed.

7.1 Conclusions

This thesis is aimed to improve the performance of 2D materials in electronic and optoelectronic applications, such as high mobility, high sensitivity and high gain.

Firstly, the aim of this work is to improve the FET performance of MoS₂ via contact engineering of metal/semiconductor (M/S) vdW heterostructure with an atomically sharp interface prepared by CVD method. Amounts of methods including phase engineering,^[1] chemical doping,^[2] tunneling layer insertion^[3] and vdW contact^[4] have been developed to improve the M/S contact. Among these methods, vdW contact is of great advantages as other methods are limited by their less-than-perfect stability. Besides, vdW TMDC heterostructure is properly prepared by the chemical vapor deposition (CVD) method with larger size and clean interface. In the CVD synthesis of TMDC vdW heterostructures, there were many successful reports but they were focused on the semiconductor/semiconductor.^[5] While M/S TMDC vdW heterostructures are less explored which might be due to the high melting points and low chemical reactivity of metal oxide feedstocks and the crystal lattice mismatch. In this work, with the assistance of NaCl, the drawbacks of metal oxide precursors are effectively overcome.^[6] Therefore, for the first time, the M/S TMDC vdW heterostructure NbS₂/MoS₂ was synthesized via a one-step halide-assisted CVD method. Compared with the sulfurization of the pre-deposited oxide,^[7] this one-step method provides the high crystal quality and clean interface of the NbS₂/MoS₂ heterostructure. OM, SEM and XPS were used to identify this M/S vdW heterostructure. TEM provided firm evidences of the high crystal quality and the R-type stacking order between the two layers. Via regulating the growth time and tracking the morphology change, the growth mechanism was proposed that MoS₂ finished the growth first and subsequently served as a superior substrate for the growth of NbS₂. Raman mapping was applied to verify this mechanism. The quench of PL (MoS₂) in the heterostructure provided physical support of the M/S structure. The device measurement further revealed a Schottky barrier in the M/S interface and this barrier could be tuned when a gate was applied. In summary, the novel halide-assisted method was developed to prepare M/S TMDC vdW heterostructure with an atomically sharp interface. This provides

an excellent platform for the research of M/S TMDC vdW heterostructures.

Secondly, the aim of this work is to prepare high-mobility $\text{Bi}_2\text{O}_2\text{Se}$ and achieve high photodetector performance of $\text{Bi}_2\text{O}_2\text{Se}$ via transferring the high-quality $\text{Bi}_2\text{O}_2\text{Se}$ onto 280 nm SiO_2/Si substrate (Si substrate) by a non-corrosive method. The inherent back gate configuration on Si substrate is applied to reduce the dark current and then improve the sensitivity of $\text{Bi}_2\text{O}_2\text{Se}$ photodetector. While graphene has a very high mobility but the lack of an energy band gap leads to a high off current and small on/off ratio,^[8] MoS_2 has a suitable bandgap but limited performance even after the device optimization.^[9] Hence, the chasing of high-mobility 2D semiconductors has been a hot research topic in recent years. A new competitive candidate is the $\text{Bi}_2\text{O}_2\text{Se}$ which has suitable band gap and high mobility.^[10] $\text{Bi}_2\text{O}_2\text{Se}$ has been prepared by CVD method on f-mica substrate with large size^[11] and also showed high potential in the photoresponse application.^[12] However, the large dark current curtails its performance regarding on/off ratio and specific detectivity.^[13] Although a gate configuration can be used to regulate the dark current, it is difficult to realize on f-mica substrate in the photoresponse application. As the Si substrate possesses inherent back gating, if $\text{Bi}_2\text{O}_2\text{Se}$ can be transferred onto Si substrate, the optoelectronic performance can be much improved. In the wet transfer of $\text{Bi}_2\text{O}_2\text{Se}$, hydrofluoric acid (HF) becomes the only f-mica etchant, due to the inertness of f-mica and strong electrostatic interaction between the sample and the substrate. Nevertheless, the highly corrosive HF which has the ability to penetrate issues is hazardous to handle. More importantly, the etching effect of HF acid during the transfer process has been verified by OM, Raman and STEM characterizations. Therefore, a non-corrosive PS-assisted method has been developed to transfer $\text{Bi}_2\text{O}_2\text{Se}$ onto Si substrate.^[14] In striking contrast to the quality degradation in the HF-assisted transfer, the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$ retained a high quality. Based on the as-transferred $\text{Bi}_2\text{O}_2\text{Se}$, ultrasensitive 2D phototransistors were demonstrated, which showed a responsivity of $3.5 \times 10^4 \text{ AW}^{-1}$, a photoconductive gain of more than 10^4 , and a time response in the order of sub-millisecond. With the back gating of silicon substrate, the dark current could be reduced to several pA. This yields an ultrahigh sensitivity with the specific detectivity of 9.0×10^{13} Jones, which is one of the highest values among 2D material photodetectors and two orders of magnitude higher than that of other

CVD-grown 2D materials.^[15] Hence, the essential role of the back-gating configuration on Si substrate in improving the photodetector performance has been proved. The high performances of the phototransistor shown here together with the developed unique transfer technique are promising for the development of novel 2D material based optoelectronic applications.

Thirdly, the aim of this work is to improve the performance and stability of the CMOS inverters based on 2D semiconductor. Continuous scaling of silicon-based metal-oxide-semiconductor field-effect transistor is hindered by the serious short channel effect in sub-10 nm channel length.^[16] Thanks to the atomic thickness and non-dangling surface, which leads to efficient channel regulation, high level of integration and high mobility, 2D semiconductors have shown great potential in the electronic and optoelectronic research. One of these significant applications is complementary metal-oxide-semiconductor (CMOS) inverter, which is an essential circuit unit providing opposite output logic signal to the input with fast speed and low power consumption. Many 2D semiconductors have shown high CMOS inverter performance, such as MoS₂, WSe₂, MoTe₂ thanks to their suitable energy bandgap and high mobility.^[17-20] However, the stability of either the intrinsic channel material (MoTe₂) or the doping material (K doped WSe₂) is not satisfactory. As demonstrated, CVD-grown Bi₂O₂Se has the merits of large size, high mobility and superior stability in air, which makes it promising in the application of the CMOS inverter. As Bi₂O₂Se showed n-type semiconducting behavior, WSe₂ was chosen as the p-channel. The CMOS inverters based on n-type Bi₂O₂Se and p-type WSe₂ have been demonstrated with clear signal inversion (low V_{in} and high V_{out} , and vice versa) on both f-mica and silicon substrate. On f-mica substrate, under the gating of ion liquid, a gain of 3.5 can be obtained at the supply voltage of only 1.0 V. Dynamic voltage response at the frequency of 100 Hz shows good response with almost no voltage lose. However, the impurity in ion liquid leads to the serious degradation of the channel material and thus large drain current at the supply voltage of 1.0 V. Since Bi₂O₂Se was transferred onto Si substrate, CMOS inverters were also fabricated on silicon substrate, which showed a high gain of 2.2 at the supply voltage of 5.0 V, a high noise margin of 5.2 V_{DD} and a low power consumption at the order of 10^{-9} W. Further optimization such as the usage of high-mobility p-type

material (black phosphorus), encapsulation of high- κ dielectric layer and improvement of the WSe₂ contact is needed to improve the performance of the current device. Nevertheless, the high potential of Bi₂O₂Se shown here open a wealthy of possibilities in amounts of promising applications.

7.2 Discussions on the Hypotheses

As discussed in chapter 1, the hypothesis of this thesis is the CVD syntheses of M/S TMDC vdW heterostructure NbS₂/MoS₂ and ternary compound Bi₂O₂Se and their improvement in the performance of electronic and optoelectronic applications, such as the mobility, the sensitivity and the gain.

Firstly, the CVD syntheses of M/S TMDC vdW heterostructure NbS₂/MoS₂ and ternary compound Bi₂O₂Se have been demonstrated. In the synthesis of NbS₂/MoS₂ vdW heterostructure, as CVD has been proved successful in the synthesis of semiconductor /semiconductor TMDC vdW heterostructure. The difficulty needed to be overcome is the high melting points and low chemical reactivity of the metal oxide precursors. It has been proved that with the assistance of the NaCl, the melting point of the precursors will be much lower and the chemical reactivity will be much improved. This is because the formation of the metal oxychloride through the reaction of the NaCl and the metal oxides. One more problem may be the crystal lattice mismatch of the two materials. To overcome this, we choose NbS₂ and MoS₂ as the metallic and semiconducting TMDC, which have close crystal lattice parameter. Besides, these two materials share the same anions, which will be much easier to control the growth. More importantly, these two materials have a good separation in the growth temperature, which allows the sequential growth in a one-step process. As a result, the NbS₂/MoS₂ vdW heterostructure was successfully prepared via a halide-assisted one-step method. It was verified by the OM, SEM, XPS, Raman spectrum and STEM characterizations. Also, the physical support from PL mapping and FET current rectification, which will be discussed later. For the synthesis of ternary compound Bi₂O₂Se, as CVD is already successful to synthesize the ternary compound WSSe from the precursors of WS₂ and WSe₂ powers. And different with WSSe which

could be any ratio between S and Se, $\text{Bi}_2\text{O}_2\text{Se}$ has a fixed ratio of O to Se (2:1). Thus, it should be much easier to synthesize $\text{Bi}_2\text{O}_2\text{Se}$ from the precursors of Bi_2O_3 and Bi_2Se_3 powders. Actually, $\text{Bi}_2\text{O}_2\text{Se}$ could also be synthesized by the oxidation of Bi_2Se_3 . However, it turns out some samples are partially oxidized. Hence, high-quality $\text{Bi}_2\text{O}_2\text{Se}$ has been synthesized by the reaction of Bi_2O_3 and Bi_2Se_3 through a low-pressure CVD method. It was verified by the OM, Raman spectrum and STEM characterizations. Hence, the hypothesis here has been proved.

Secondly, the contact engineering via vdW M/S TMDC contact. The high crystal quality and clean interface have been confirmed by the STEM. PL mapping provides the physical support of metal/semiconductor while PL single spectrum proves low interlayer mixing ratio, which further confirms the atomically sharp interface. The current rectification behavior indicates the formation of Schottky barrier and the tunability of the barrier under different gate voltages reveals the elimination of the Fermi level pinning effect. Hence, the hypothesis of contact engineering via vdW M/S contact is also proved. Note that more measurements are required to provide more details of this contact.

Thirdly, the non-corrosive transfer and the better performance originated from the back gate on Si substrate. The CVD-grown $\text{Bi}_2\text{O}_2\text{Se}$ has shown high mobility, superior stability and good responsivity. The high dark of hundreds of nA leads to small on/off ratio and low sensitivity. A gate configuration could be applied to reduced the dark current. However, it is hard to realize on f-mica. Then transfer of $\text{Bi}_2\text{O}_2\text{Se}$ onto substrates with inherent gate architecture such as 280 nm SiO_2/Si (Si substrate) becomes a good solution. In the wet transfer of $\text{Bi}_2\text{O}_2\text{Se}$, hydrofluoric acid (HF) becomes the only f-mica etchant, due to the inertness of f-mica and strong electrostatic interaction between the sample and the substrate. Nevertheless, the highly corrosive HF which has the ability to penetrate issues is hazardous to handle. More importantly, since HF is well known as one component of typical buffered oxide etchant (BOE), $\text{Bi}_2\text{O}_2\text{Se}$ will be inevitably etched by HF during the transfer process. Therefore, a PS-assisted method has been developed to successfully transfer $\text{Bi}_2\text{O}_2\text{Se}$ onto silicon substrate. This is because the high surface energy of PS in contact with DI water, which leads to fast separation of the PS film together with $\text{Bi}_2\text{O}_2\text{Se}$ from f-mica substrate.

As evaluated by the OM, SEM, Raman spectrum, EDS and FET performance, the high quality of Bi₂O₂Se was maintained, which indicates the success of the developed transfer. On Si substrate, the dark current could be reduced to several pA under the back gating of Si substrate. While the photocurrent was kept on the order of μA , the specific detectivity was then elevated to 9×10^{13} Jones, which is one of the highest values among 2D photodetectors and two orders of magnitude larger than that of the CVD-grown 2D materials. Hence, both of the hypotheses have been proved.

Last but not the least, the fabrication of CMOS inverters based on n-type Bi₂O₂Se and p-type WSe₂ and the impact of the dielectric layer to the performance. Bi₂O₂Se has shown n-type semiconducting behavior with high mobility ($235 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and high on/off ratio (10^5), while WSe₂ showed p-type behavior with a mobility of $17 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The CMOS inverters based on n-type Bi₂O₂Se and p-type WSe₂ have been demonstrated with clear signal inversion (low V_{in} and high V_{out} , and vice versa) both on f-mica substrate and Si substrate. On f-mica, under the gating of ion liquid, a gain of 3.5 can be obtained at the V_{DD} of only 1.0 V. Dynamic voltage response at the frequency of 100 Hz shows good response with almost no voltage lose. Since Bi₂O₂Se was transferred onto Si substrate, CMOS inverters were also fabricated on silicon substrate, which showed a high gain of 2.2 at the V_{DD} of 5.0 V, a high noise margin of $5.2 V_{\text{DD}}$ and a low power consumption at the level of 10^{-9} W. Although the symmetry matching is not good for these two materials, the CMOS inverter have been demonstrated. Besides, the Si substrate overcomes the drawbacks of ion liquid which indicates the essential role of the dielectric layer. In the future, by encapsulating a high- κ dielectric layer or improving the contact of WSe₂, the CMOS inverter performance could be much improved.

7.3 Future Work and Recommendations

In the future, many works in this thesis should be carried on and lots of opportunities could also be found.

For the M/S vdW TMDC heterostructure, more device measurements should be conducted. This includes the more detailed I_d - V_g curves under the shining of light to see whether there is any photogenerated voltage. It also includes I_d - V_d curves at different temperatures to calculate the height of Schottky barrier. Otherwise, to measure the I_d - V_d under certain gate voltage but two different temperature or certain temperature but different gate voltages is also possible to see the change of the barrier height. In addition, for the CVD synthesis, different material systems could also be explored, such as TaS₂ and WS₂, which have close crystal lattice parameter but large temperature separation of the growth temperature. And the stability of TaS₂ is better than that of NbS₂. Hence, TaS₂/WS₂ may be a good metal/semiconductor junction system.

For the Bi₂O₂Se photodetector, to reduce the dark current, a layer of PbS quantum dots on the surface may also be effective and simple way.^[21] It has been reported that for the PbS quantum dots on the surface of graphene, when shined a light, the generated holes will be transferred to graphene, leaving the negative charges in the interface. Note that these negative charges served as a negative gate for the device. Hence, when coated on the surface of Bi₂O₂Se, the photoinduced negative gate may reduced the dark current of Bi₂O₂Se, which will improve the total photoresponse performance.

For the CMOS inverters based on Bi₂O₂Se, two main factors need to be improved. On one hand, the performance of p-channel. It clear that the performance of WSe₂ is not satisfactory. Therefore, to use high-mobility p-type 2D semiconductor, such as black phosphorus^[22] and layered tellurene (2D tellurium),^[23] or to improve the contact between the metal electrode and WSe₂^[24] are highly possible to improve the performance of CMOS inverter. On the other hand, the application of high- κ dielectric layer.^[25] This will improve the FET performance of both channel material and thus improve the CMOS inverter performance. Higher gain is expected because of the faster switch of the channel materials encapsulated by high- κ dielectric layer.

References

- [1] R. Kappera, D. Voiry, S. E. Yalcin, B. Branch, G. Gupta, A. D. Mohite, M. Chhowalla, *Nat. Mater.* **2014**, 13, 1128.
- [2] L. Yang, K. Majumdar, H. Liu, Y. Du, H. Wu, M. Hatzistergos, P. Hung, R. Tieckelmann, W. Tsai, C. Hobbs, *Nano Lett.* **2014**, 14, 6275-6280.
- [3] J. Wang, Q. Yao, C. W. Huang, X. Zou, L. Liao, S. Chen, Z. Fan, K. Zhang, W. Wu, X. Xiao, *Adv. Mater.* **2016**, 28, 8302-8308.
- [4] L. Yu, Y.-H. Lee, X. Ling, E. J. Santos, Y. C. Shin, Y. Lin, M. Dubey, E. Kaxiras, J. Kong, H. Wang, *Nano Lett.* **2014**, 14, 3055-3063.
- [5] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, *Nat. Mater.* **2014**, 13, 1135.
- [6] S. Li, S. Wang, D.-M. Tang, W. Zhao, H. Xu, L. Chu, Y. Bando, D. Golberg, G. Eda, *Appl. Mater. Today* **2015**, 1, 60-66.
- [7] A. R. Kim, Y. Kim, J. Nam, H.-S. Chung, D. J. Kim, J.-D. Kwon, S. W. Park, J. Park, S. Y. Choi, B. H. Lee, *Nano Lett.* **2016**, 16, 1890-1895.
- [8] M. Katsnelson, K. Novoselov, *Solid State Commun.* **2007**, 143, 3-13.
- [9] B. Radisavljevic, A. Radenovic, J. Brivio, i. V. Giacometti, A. Kis, *Nat. Nanotech.* **2011**, 6, 147.
- [10] J. Wu, H. Yuan, M. Meng, C. Chen, Y. Sun, Z. Chen, W. Dang, C. Tan, Y. Liu, J. Yin, *Nat. Nanotech.* **2017**, 12, 530.
- [11] J. Wu, C. Tan, Z. Tan, Y. Liu, J. Yin, W. Dang, M. Wang, H. Peng, *Nano Lett.* **2017**, 17, 3021-3026.
- [12] J. Wu, Y. Liu, Z. Tan, C. Tan, J. Yin, T. Li, T. Tu, H. Peng, *Adv. Mater.* **2017**, 29, 1704060.
- [13] J. Li, Z. Wang, Y. Wen, J. Chu, L. Yin, R. Cheng, L. Lei, P. He, C. Jiang, L. Feng, *Adv. Funct. Mater.* **2018**, 28, 1706437.
- [14] A. Gurarslan, Y. Yu, L. Su, Y. Yu, F. Suarez, S. Yao, Y. Zhu, M. Ozturk, Y. Zhang, L. Cao, *ACS Nano* **2014**, 8, 11522-11528.
- [15] C. Xie, C. Mak, X. Tao, F. Yan, *Adv. Funct. Mater.* **2017**, 27, 1603886.
- [16] P. S. Peercy, *Nature* **2000**, 406, 1023.
- [17] A. Pezeshki, S. H. Hosseini Shokouh, P. J. Jeon, I. Shackery, J. S. Kim, I.-K. Oh, S. C. Jun, H. Kim, S. Im, *ACS Nano* **2015**, 10, 1118-1125.

- [18] M. Tosun, S. Chuang, H. Fang, A. B. Sachid, M. Hettick, Y. Lin, Y. Zeng, A. Javey, *ACS Nano* **2014**, 8, 4948-4953.
- [19] J. Y. Lim, A. Pezeshki, S. Oh, J. S. Kim, Y. T. Lee, S. Yu, D. K. Hwang, G. H. Lee, H. J. Choi, S. Im, *Adv. Mater.* **2017**, 29, 1701798.
- [20] Y. F. Lin, Y. Xu, S. T. Wang, S. L. Li, M. Yamamoto, A. Aparecido - Ferreira, W. Li, H. Sun, S. Nakaharai, W. B. Jian, *Adv. Mater.* **2014**, 26, 3263-3269.
- [21] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. De Arquer, F. Gatti, F. H. Koppens, *Nat. Nanotech.* **2012**, 7, 363.
- [22] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, Y. Zhang, *Nat. Nanotech.* **2014**, 9, 372.
- [23] Y. Wang, G. Qiu, R. Wang, S. Huang, Q. Wang, Y. Liu, Y. Du, W. A. Goddard, M. J. Kim, X. Xu, *Nat. Electron.* **2018**, 1, 228.
- [24] M. Yamamoto, S. Nakaharai, K. Ueno, K. Tsukagoshi, *Nano Lett.* **2016**, 16, 2720-2727.
- [25] D. Lembke, S. Bertolazzi, A. Kis, *Acc. Chem. Res.* **2015**, 48, 100-110.