Growth and characterization of transition metal dichalcogenides: from monolayers to heterostructures

Wang, Xingli

2016

Wang, X. (2016). Growth and characterization of transition metal dichalcogenides: from monolayers to heterostructures. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/66412>

<https://doi.org/10.32657/10356/66412>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**GROWTH AND CHARACTERIZATION OF
TRANSITION METAL DICHALCOGENIDES:
FROM MONOLAYERS TO HETEROSTRUCTURES**

WANG XINGLI

SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

2015

**GROWTH AND CHARACTERIZATION OF
TRANSITION METAL DICHALCOGENIDES:
FROM MONOLAYERS TO HETEROSTRUCTURES**

WANG XINGLI

School of Electrical & Electronic Engineering

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

2015

Dedicated to my family

Acknowledgements

First of all, I would like to express my sincere gratitude and thanks to my supervisor, Professor Tay Beng Kang from Nanyang Technological University, for his patient and helpful guidance through my entire PhD candidature. His insightful discussions and advice have been an invaluable treasure for me. His enthusiasm towards research and life will undoubtedly benefit me throughout my life.

I am grateful to my co-supervisor, Assistant Professor Liu Zheng from Nanyang Technological University, for his valuable discussions and suggestions for my studies. I would also like to thank Professor Pulickel M. Ajayan from Rice University, USA, for his guidance and suggestions for my project. I am also grateful to Assistant Professor Teo Hang Tong Edwin from Nanyang Technological University for his discussions and advice for my work.

I would like to thank Mr. Gong Yongji from Rice University for his dialogue about my project and for his help during my visit to Rice University. I am grateful to the staff and students in Professor Tay's group: Dr. Li Hong, Dr. Li Xiaocheng, Dr. Liu Wenwen, Dr. Lu Congxiang, Dr. Tan Chongwei, Dr. Liang Kun, Dr. Tsang Siuhon, Mr. Chow Waileong, Ms. Tan Dunlin, and Mr. Tay Yingjie Roland, for their help during my project.

Many thanks and appreciations go to Mr. Hasman Bin Hassan, Ms. Neo Bee Geok, and Ms. Teh Hsieh Foong Janet for their technical support in the Nanoelectronics Lab.

Last but not least, I am grateful to my parents, my sisters, my wife and my son. This thesis would never have been completed without their understanding, love and full support in the past years.

Summary

Transition metal dichalcogenides (TMDs) are a large group of two-dimensional (2D) materials in which a layer of metal atoms is sandwiched between two layers of chalcogen atoms. Molybdenum disulfide and diselenide (MoS_2 and MoSe_2) and tungsten disulfide and diselenide (WS_2 and WSe_2) are four TMDs that have been widely explored. As semiconductors with direct band gaps and high carrier mobility, these materials have potential applications in fields such as transistors, optoelectronics, and flexible electronics. However, these films are usually exfoliated from bulk counterpart crystals with adhesive tape, which restricts their applications. The preparation of large area TMD monolayers need to be explored.

On the other hand, these 2D TMD layers can form two different heterostructures: vertical, in which the component layers stack along the (0001) direction of the layers, and lateral, in which different layers are bonded to each other covalently in an atomic plane. These are typically type II heterostructures that can be applied in vertical tunneling, photovoltaic or light-emitting devices. However, the fabrication of these heterostructures is challenging.

In this project, different TMDC monolayers (MoS_2 , MoSe_2 and WS_2) and heterostructures based on MoS_2 and WS_2 (both vertical and lateral) are synthesized with chemical vapor deposition. The qualities of these monolayers or heterostructures are characterized with different methods: Raman, photoluminescence (PL), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning transmission electron microscopy (STEM) and electrical transportation measurement.

(1) Growth and characterization of large, single-crystalline MoS₂ monolayers. In this part, single-crystalline MoS₂ monolayers as large as 1 mm are synthesized with chemical vapor deposition (CVD); these are the largest such monolayers ever synthesized. AFM, Raman and PL spectra prove that the films are uniform monolayers. STEM shows perfect crystalline structure. The electrical characterization of the as-grown monolayer MoS₂ shows a typical N-type channel in the field-effect transistor. Single-crystalline MoS₂'s dependence on the growth recipe for its size is explored as well. The grain size of the MoS₂ monolayers is found to be affected by the growth temperature.

(2) Growth and characterization of MoSe₂ monolayers. In this part, MoSe₂ monolayers are synthesized with CVD growth. AFM, Raman and PL confirmed that the as-grown films are monolayers, and the perfect crystal structure is demonstrated with STEM. The as-synthesized films show a carrier mobility as high as 50 cm²V⁻¹s⁻¹ as an N-type channel, showing potential to be applied in electronic devices.

(3) Growth and characterization of WS₂ monolayers. In this part, WS₂ monolayers are synthesized with CVD using a new growth recipe. The film as grown by sulfuring tungsten powder, whose melting point is decreased by the addition of tellurium. The as-grown monolayers are confirmed with Raman, PL and XPS.

(4) Growth and characterization of vertical WS₂/MoS₂ heterostructures. In this part, vertical WS₂/MoS₂ heterostructures, in which a WS₂ monolayer stacks on top of a MoS₂ monolayer, are synthesized with a one-step CVD. The stacking is

Summary

confirmed by AFM, Raman mapping, PL mapping and element mapping with TEM. The synthesized heterostructures show a new peak at 875 nm in the PL spectrum which is likely due to the coupling between the top WS₂ monolayer and the bottom MoS₂ monolayer. These heterostructures demonstrate high mobility.

- (5) Growth and characterization of lateral WS₂-MoS₂ heterostructures. In this part, WS₂-MoS₂ lateral heterostructure is synthesized with the one-step CVD. The as-grown in-plane heterostructure is observed optically. The formation of monolayer WS₂ and MoS₂ is confirmed with Raman and PL spectra and mappings. The STEM characterization shows a sharp interface between the two monolayers. As WS₂ is a p-type semiconductor and MoS₂ is a typical n-type semiconductor in air, a WS₂-MoS₂ in-plane forms a PN junction with an atomic thickness, which is confirmed by electrical characterization.

Table of Contents

Acknowledgements	I
Summary	I
Table of Contents	IV
List of Figures	VIII
List of Tables	XVII
List of Abbreviations	XVIII
Chapter 1 Introduction	1
1.1 Motivations	1
1.2 Objectives	4
1.3 Main contributions	4
1.4 Organization of the thesis	5
Chapter 2 Transition Metal Dichalcogenide Monolayers and Their Heterostructures	7
2.1 TMD monolayers	7
2.1.1 Crystal structure	7
2.1.2 Vibration properties	9
2.1.3 Band structures	11
2.1.4 Electrical Properties	12
2.1.5 Optical properties	13
2.1.6 Mechanical properties	14
2.1.7 Preparation of TMD monolayers	16
2.2 Heterostructures	24

Table of Contents

2.2.1 Vertical heterostructure	25
2.2.2 Lateral heterostructure	26
Chapter 3 Growth and Characterization of MoS₂ Monolayers	28
3.1 The Growth of MoS ₂ Monolayers with Chemical Vapor Deposition	28
3.2 Characterization of the as-grown MoS ₂ monolayers	29
3.2.1 Optical microscopic characterization of the MoS ₂ monolayer	30
3.2.2 AFM characterization of the MoS ₂ monolayer	31
3.2.3 Raman characterization of the MoS ₂ monolayer	33
3.2.4 PL characterization of the MoS ₂ monolayer	34
3.2.5 XPS characterization of the MoS ₂ monolayer	35
3.2.6 STEM characterization of the MoS ₂ monolayer	37
3.2.7 Electrical transport characterization of the MoS ₂ monolayer	41
3.2.8 Effect of the Growth Temperature on the Size of the Monolayers	43
3.3 Summary	45
Chapter 4 Growth and Characterization of MoSe₂ Monolayers	46
4.1 Growth of the MoSe ₂ monolayer	46
4.2 Characterization of the MoSe ₂ monolayer	47
4.2.1 Optical microscopic characterization of the MoSe ₂ monolayer	47
4.2.2 AFM characterization of the MoSe ₂ monolayer	48
4.2.3 Raman characterization of the MoSe ₂ monolayer	49
4.2.4 PL characterization of the MoSe ₂ monolayer	50
4.2.5 XPS characterization of the MoSe ₂ monolayer	52
4.2.6 STEM characterization of the MoSe ₂ monolayer	53

4.2.7 Electrical transport characterization of the MoSe ₂ monolayer	55
4.3 Summary	56
Chapter 5 Growth and Characterization of WS ₂ Monolayers	57
5.1 Growth of the WS ₂ monolayer	57
5.2 Characterization of the WS ₂ monolayer	58
5.2.1 Optical characterization of the WS ₂ monolayer	58
5.2.2 Raman characterization of the WS ₂ monolayer	59
5.2.3 PL characterization of the WS ₂ monolayer	60
5.2.4 XPS characterization of the WS ₂ monolayer	61
5.3 Summary	62
Chapter 6 Growth and Characterization of WS ₂ /MoS ₂ Vertical Heterostructure	63
6.1 Growth of the WS ₂ /MoS ₂ vertical heterostructure	63
6.2 Characterization of the WS ₂ /MoS ₂ vertical heterostructure	64
6.2.1 Optical microscopic characterization of the WS ₂ /MoS ₂ heterostructure	64
6.2.2 AFM characterization of the WS ₂ /MoS ₂ heterostructure	66
6.2.3 Raman characterization of the WS ₂ /MoS ₂ vertical heterostructure	67
6.2.4 PL characterization of the WS ₂ /MoS ₂ vertical heterostructure	69
6.2.5 Raman and PL characterization of the WS ₂ /MoS ₂ heterostructure stacked by transfer	71
6.2.6 STEM characterization of the WS ₂ /MoS ₂ vertical heterostructure	72
6.2.7 Electrical transport characterization of the WS ₂ /MoS ₂ vertical heterostructure	76
6.3 Summary	77

Table of Contents

Chapter 7 Growth and Characterization of WS₂-MoS₂ Lateral Heterostructure	78
7.1 Growth of the WS ₂ -MoS ₂ lateral heterostructure	78
7.2 Characterization of the WS ₂ -MoS ₂ lateral heterostructure	79
7.2.1 Optical characterization of the WS ₂ -MoS ₂ lateral heterostructure.....	79
7.2.2 AFM characterization of the WS ₂ -MoS ₂ lateral heterostructure	80
7.2.3 Raman characterization of the WS ₂ -MoS ₂ lateral heterostructure	81
7.2.4 PL characterization of the WS ₂ -MoS ₂ heterostructure	82
7.2.5 STEM characterization of the WS ₂ -MoS ₂ lateral heterostructure	85
7.2.6 Electrical transport properties of the WS ₂ -MoS ₂ lateral heterostructure.....	89
7.3 Summary	90
Chapter 8 Conclusions and Recommendations	91
8.1 Conclusions	91
8.2 Recommendations for Further Work	92
8.2.1 Exploration of the effects of other growth parameters	92
8.2.2 Exploration of the growth of other TMD materials	92
8.2.3 Exploration of other TMD heterostructures	92
Author's Publications	94
Bibliography	96

List of Figures

Figure 1-1 Comparison between TMD monolayers and other materials.[11] (a) Comparison of semiconductors' field effect mobility and on/off ratios for electronics. (b) Comparison of field effect mobility and band gap for semiconductors used in current-generation photovoltaic technologies.	1
Figure 1-2 Schematics of heterostructures. (a) Vertical heterostructure based on BN, graphene and TMD monolayers.[22] (b) Lateral heterostructure based on BN and graphene.[23]	2
Figure 2-1 Schematic of TMD crystals.[6] (a) Layered stacking of TMD crystals. (b) Three phases of TMD crystals.	7
Figure 2-2 Schematic of monolayer TMDs.[25, 27] (a) H-phase, (b) T-phase. The top-left figures in (a) and (b) are top views of the structures, the bottom-left figures are side views of the structures, and the right figures are 3D schematics of the structures.	8
Figure 2-3 Raman characterization of TMD crystals with various thicknesses.[36, 37, 42] (a) Four first-order Raman-active modes and one IR-active mode (E_{1u}). (b) Raman spectra of MoS_2 , $MoSe_2$ and WS_2 (from left to right) crystals from monolayer to bulk with a laser of 514.5 nm as illumination. (c) A high-resolution Raman spectra of monolayer WS_2 . The E_{2g}^1 peak is overlapped by the second-order mode 2LA(M) at 352 cm^{-1}	10
Figure 2-4 Band structure crossover of MoS_2 from bulk to monolayer.[46]	12
Figure 2-5 Electrical transport properties of TMD monolayers.[6, 54] (a) Schematic of a FET based on TMD monolayer. (b) I_{ds} - V_g curves recorded from a top-gated device in (a).	13
Figure 2-6 (a) Absorption and (b) PL spectra of MoS_2 flakes with different thicknesses.[28].	14
Figure 2-7 Mechanically exfoliated monolayer crystallites[53] of (a) $NbSe_2$, (b) graphite, (c) $Bi_2Sr_2CaCu_2O_x$ and (d) MoS_2 . Scale bar: $1\text{ }\mu\text{m}$	17
Figure 2-8 Schematic of main liquid exfoliation mechanisms.[99] (a) Ion intercalation-assisted exfoliation. (b) Ion exchange-assisted exfoliation. (c) Sonication or shear-assisted exfoliation.	18

List of Figures

Figure 2-9 Vapor solid deposition of MoS ₂ monolayers.[104].....	19
Figure 2-10 Growth of MoS ₂ thin films by sulfurizing Mo film.[106] (a) Deposition of Mo film by sputtering. (b) Sulfurization of Mo film. (c) Large area of MoS ₂ film. (d) MoS ₂ film on transparent substrate. (e) MoS ₂ films with modulated thickness.	20
Figure 2-11 Growth of MoS ₂ by the thermal decomposition of ammonium thiomolybdate.[110]	21
Figure 2-12 Growth result of large area MoS ₂ film by pulsed laser deposition. (a) Centimeter size MoS ₂ film with controllable thickness on sapphire wafer. (b) Deposition of large area MoS ₂ film on flexible plastic kapton substrate.	22
Figure 2-13 CVD and MOCVD growth of MoS ₂ film. [118, 129] (a) Schematic of the CVD setup for the growth of a MoS ₂ monolayer. (b) Optical image of the CVD growth result. (c) Schematic of the MOCVD setup. (d) Device array fabricated on a 4-inch MoS ₂ film.	23
Figure 2-14 (a) Band alignment of different TMD monolayers.[19] (b) Schematic of the vertical heterostructure of MoS ₂ and WS ₂ monolayers.[136] (c) Schematic of the lateral heterostructure of WS ₂ and MoS ₂ monolayers.[140]	25
Figure 3-1 Schematic of the CVD setup for the growth of MoS ₂ . MoO ₃ powder is located at the center of the furnace with a piece of SiO ₂ /Si wafer suspended above; the sulfur powder is upstream, at the opening of the furnace, where the temperature can reach the 120 °C needed to melt the sulfur.	29
Figure 3-2 Optical images of the as-grown MoS ₂ film. (a) Large domains, which can be observed with the naked eye, appear on the substrate. (b) A triangle, with a size of 1 mm, forms. (c) A polycrystalline polygon appears on the wafer as well. The single-crystalline dome is as large as 500 μm. (d) Continuous-film MoS ₂ forms on the wafer when the films connected. White lines appear along the grain boundaries.	31
Figure 3-3 AFM characterization of the as-grown MoS ₂ film. (a) The topographical image shows that the film is uniform in thickness. (b) A height profile along the red line in (a) shows	

a height step of 0.7 nm, indicating that the as-grown film is a monolayer. (c) The phase image also shows the high uniformity of the as-grown MoS₂ flakes. (d) A phase difference of 2.3 ° is shown along the red line in figure (c).32

Figure 3-4 Raman characterization of the as-grown film. (a) The E_{2g}¹ (in-plane vibration) and A_{1g} (out-of-plane vibration) modes of the MoS₂ layer. (b) A typical Raman spectrum collected from the as-grown film.33

Figure 3-5 Statistics of Raman spectra collected from the as-grown triangle. (a) 91 Raman spectra collected at the red crosses. (b) Statistics of the E_{2g}¹ and A_{1g} peaks and their difference. The E_{2g}¹ peaks are located around 382.7 cm⁻¹, and the A_{1g} peaks are located around 402.7 cm⁻¹; that is a difference of 20 cm⁻¹, indicating that the as-grown large-area film is a uniform monolayer.34

Figure 3-6 Statistics of PL spectra collected from the as-grown film. (a) 91 PL spectra collected from the red crosses. (b) The distribution of the PL peaks (black dots) and corresponding band gaps (blue dots). The band gaps are all around 1.82 eV, indicating that the large-area film is a uniform MoS₂ monolayer. The inset is one of the PL spectra collected. ...35

Figure 3-7 XPS characterization of the as-grown film. (a) The whole XPS spectrum of the CVD-grown MoS₂ film. Four elements appear in the spectrum, including Mo and S from the MoS₂ film and O and Si from the SiO₂/Si substrate. (b) XPS spectrum of Mo 3d. (c) XPS spectrum of S 2p.....37

Figure 3-8 Schematic of the preparation of TEM sample. (a) top view and side view of the as grown MoS₂ flake on SiO₂ wafer. (b) The MoS₂ sample was spincoated with PMMA. (c) The SiO₂ wafer was etched away with KOH solution. (d) The PMMA-MoS₂ film was transferred to a TEM grid. (e) PMMA film was washed away with acetone, and the sample on TEM grid was rinsed with acetone, IPA and DI water. In (a) to (e), the left figures are from top view while the right figures are from side view.38

Figure 3-9 STEM characterization of the as-grown MoS₂ monolayer. (a) Monolayer MoS₂ on a TEM grid covered with holey carbon film after being transferred with the PMMA-assisted

List of Figures

method. (b) ADF image of the monolayer MoS₂ film shows perfect crystalline structure. Inset: electron diffraction pattern of the film indicating that the film is monolayer MoS₂. (c) ADF image with higher magnification. The white dots correspond to molybdenum atoms, and the gray dots correspond to sulfur columns. (d) Intensity line scan along the red box in (c). A sulfur vacancy is observed here. 40

Figure 3-10 Fabrication of TMD based FET device. (a) As-grown TMD monolayers on SiO₂ wafer. (b) The monolayer is covered with patterned photoresist. (c) The TMD flake is patterned to desired pattern. (d) The photoresist is washed away. (e) Metal electrodes are deposited..... 41

Figure 3-11 electrical characterization of MoS₂-based FET. (a) I_{ds}-V_{ds} curves. The back-gate voltage V_{bg} ranges from 0 V to 40 V, with a step of 10 V. The linear dependence indicates Ohmic contact between the electrodes and the channel. (b) I_{ds}-V_{bg} curve. Typical N-type transistor behavior is shown in this figure. The on/off ratio is as high as 10⁸. The inset is an optical image of a FET device. The channel length is 3.7 μm, and the channel width is 20 μm. 43

Figure 3-12 Size's dependence on growth temperature. (a) – (e) MoS₂ grown at 650 °C, 700 °C, 750 °C, 850 °C, and 900 °C, respectively. (f) Plot of size of sample as a function of the growth temperature. 44

Figure 4-1 Schematic of the growth setup. MoO₃ powder (as a Mo source) is placed in a ceramic boat located at the center of the furnace, and the selenium pellets in the other boat at the opening of the furnace serve as a Se source. A mixed gas of Ar and H₂ (15%) is used as the carrier gas. 47

Figure 4-2 Optical images of the CVD-grown MoSe₂ films.[52] (a) After growth, the substrate is covered with many triangles with high coverage. (b) and (c) High magnification optical images of the sample. The size of the triangles ranges from several to more than 100 μm. A triangle with a size as large as 135 μm is found, with many small dots on its surface. (d)

Continuous film formed when small triangles connect. The sizes of the domains are several micrometers.....	48
Figure 4-3 AFM characterization of the CVD-grown MoSe ₂ film.[52] The thickness of the film is verified to be 0.8 nm, indicating that the film is a monolayer.....	49
Figure 4-4 Raman characterization of the CVD-grown film.[52] (a) A MoSe ₂ triangle with a size of about 40 μm is used for the characterization. (b) Raman spectra collected at both the center and edge of the triangle. The similarity of the two spectra indicates the homogeneity of the as-grown film. (c) Raman mapping of the triangle at 239 cm^{-1}	50
Figure 4-5 PL characterization of the CVD-grown MoSe ₂ monolayer film.[52] (a) Optical image of as-grown MoSe ₂ monolayer. (b) PL spectra collected at both the center and the edge of the triangle. The intensity of the peak at the edge is as low as half the intensity of the center, and the peak position is red-shifted; both these effects are attributed to defects at the edge during the growth process. (c) PL intensity mapping of the triangle shows a decrease in intensity at the edge of the triangle. (d) PL peak position mapping shows that the PL peak red-shifts toward the edge.	51
Figure 4-6 XPS characterization of the MoSe ₂ film.[52] (a) Full spectrum of the as-grown MoSe ₂ monolayer. (b) Mo 3d XPS spectrum. (c) Se 3d XPS spectrum.	53
Figure 4-7 STEM characterization of the MoSe ₂ monolayer.[52] (a) Low-magnification image of the MoSe ₂ monolayer on a TEM grid. (b) Magnified TEM image of the transferred MoSe ₂ monolayer film. (c) HAADF-STEM image of MoSe ₂ presenting a perfectly hexagonal crystal lattice. An intensity profile acquired along the red line is shown in the inset. (d) HAADF-STEM image with interface of the MoSe ₂ monolayer (bottom) and bilayer (top).	54
Figure 4-8 Electrical transport measurement of the MoSe ₂ monolayer in a FET device.[52] (a) Optical image of the FET device. S and D stand for the source and drain electrodes, respectively. L and W stand for the length and width of the device channel, respectively. (b) $I_{\text{ds}}-V_{\text{g}}$ curve showing the MoSe ₂ monolayer working as an N-type channel. Inset: $I_{\text{ds}}-V_{\text{ds}}$ curves at different gating voltages.....	56

List of Figures

Figure 5-1 Schematic of the setup for the growth of the WS ₂ monolayer.....	58
Figure 5-2 Binary phase diagram of tungsten-tellurium. The region marked by the red arrow shows that tungsten is somewhat soluble in tellurium liquid at 750 °C.....	58
Figure 5-3 Optical microscopic image of the as-grown WS ₂ monolayer.....	59
Figure 5-4 Raman spectrum of the WS ₂ monolayer.	60
Figure 5-5 PL spectrum of the WS ₂ monolayer.....	61
Figure 5-6 XPS characterization of the WS ₂ monolayer. (a) Full XPS spectrum of the sample. (b) XPS spectrum of W 4f. No tellurium is found in the sample.	61
Figure 6-1 Schematic for the growth of the WS ₂ /MoS ₂ vertical heterostructure. For the reaction, the system is heated up to 850 °C and kept at 850 °C for 20 min before cooling down naturally to room temperature; 60 sccm of Ar is used as carrier gas and to provide an inert environment.....	64
Figure 6-2 Optical images of the growth result of the WS ₂ /MoS ₂ vertical heterostructure at low magnification.[134].....	65
Figure 6-3 Optical images of the as-grown flakes at higher magnification.[134] The small (top) layers are in various shapes, but the bottom layers are usually triangles.	66
Figure 6-4 AFM characterization of the as-grown flakes.[134] (a) Height topography of the sample. (b) Height profile along the red line in (a), which moves across the two steps.	67
Figure 6-5 Raman characterization of the vertical heterostructure.[134] (a) Optical image of the vertical heterostructure sample. (b) Raman spectra collected at positions 1, 2, 3 and 4, as labeled in (a). (c) Raman mapping at 384 cm ⁻¹ . (d) Raman mapping at 357 cm ⁻¹	69
Figure 6-6 PL characterization of the vertical heterostructure.[134] (a) Optical image of the vertical heterostructure. (b) PL spectra collected at the positions labelled as 1, 2, 3 and 4 in (a). (c) PL peak intensity profiles along the black line in (a). (d) and (e) PL mapping images at 680 nm and 875 nm, respectively.....	71

Figure 6-7 Raman and PL characterizations of the transferred WS₂/MoS₂ heterostructure.[134]

(a) Optical image of the transferred vertical heterostructure. (b) Raman spectra collected at positions labelled as 1, 2 and 3 in (a). (c) PL spectra of the as-grown and transferred WS₂/MoS₂ vertical heterostructures, respectively. The peak at 875 nm disappears in the PL spectrum collected at the transferred vertical heterostructure.72

Figure 6-8 STEM-ADF image and EELS mapping of the as-grown WS₂/MoS₂ vertical heterostructure.[134] (a) Low-magnification ADF image of the sample. The image is displayed in a false-color scale so that the MoS₂ monolayer is blue, the WS₂ monolayer is green, and the WS₂/MoS₂ vertical heterostructure is orange. (b) Magnified image of the region highlighted in (a), shown in grayscale. (c) ADF image intensity profile along the dashed yellow line in (b). (d) Tungsten O-edge and molybdenum N-edge fine structures extracted from the EELS spectra acquired at the highlighted blue and green regions in (b), respectively. (e) Mo, W, and S elemental mapping from the same region shown in (b). (f) Z-contrast image of the bilayer. The brighter columns stand for overlapping columns of W and S₂, and the dim columns are the overlap of Mo and S₂. A substitution of a W atom with a Mo atom in the WS₂ layer is pointed out with a green arrow. Below: image intensity profile acquired along the dashed yellow line in the top image. (g) ADF image of the WS₂/MoS₂ vertical heterostructure at the edge of the step. The edge of the step is pointed out with a green dashed line, and the orientation of the MoS₂ and WS₂ atomic layers are demonstrated by two triangles. Inset: the FFT diffraction pattern of the ADF image. (h) Schematic of the WS₂/MoS₂ vertical heterostructure with 2H stacking.74

Figure 6-9 Electrical transport characterization.[134] (a) A typical STEM image of a FET device from the WS₂/MoS₂ bilayer stacks. (b) A typical plot of gating voltage versus the source/drain currents of the CVD-grown WS₂/MoS₂ bilayer, transferred WS₂/MoS₂ bilayer, and the MoS₂ monolayer, demonstrating that the CVD-grown WS₂/MoS₂ bilayer has the best performance. The V_{ds} is fixed at 0.5 V.77

List of Figures

Figure 7-1 Schematic image of the CVD setup for the growth of the WS ₂ -MoS ₂ lateral heterostructure.	78
Figure 7-2 Optical images of the as-grown lateral heterostructures.[134] (a) Optical image of a single heterostructure flake. The central part and surrounding area can be distinguished by the weak color contrast. (b) Enlarged image showing a sharp interface between the two domains. (c) A heterostructure film forms when different flakes merge together.	79
Figure 7-3 AFM characterization of the lateral heterostructure.[134] (a) The height topography shows a continuous and uniform film. (b) The height profile shows that the as-grown heterostructure is a monolayer.	80
Figure 7-4 Raman characterization of the as-grown lateral heterostructure. [134] (a) Optical microscope image of a piece of the as-grown lateral heterostructure. (b) Raman spectra from the points labeled in (a). (c) Raman mapping of figure (a) at 381 cm ⁻¹ , showing that the center of the flake is a uniform MoS ₂ domain. (d) Raman mapping at 352 cm ⁻¹ , showing that the surrounding part is a uniform WS ₂ domain.	82
Figure 7-5 PL characterization of the as-grown lateral heterostructure.[134] (a) Optical image of an as-grown flake. (b) PL spectra collected at points 1-5 in (a). (c) PL spectra collected at points 3 and 6 and the superposition of the spectra at points 1 and 5. (d) PL intensity mapping at 630 nm showing that the surrounding parts consist of monolayer WS ₂ . (e) PL intensity mapping at 680 nm showing that the center part is the monolayer MoS ₂ domain. (f) PL mapping at 650 nm showing high intensity along the interface between the MoS ₂ and WS ₂ domains. (g) PL microscope image of the flake showing high intensity along the interface, similar to the PL mapping at 650 nm.	84
Figure 7-6 ADF-STEM characterization of the lateral heterostructure.[134] (a) Low-magnification ADF-STEM image of the interface between the MoS ₂ and WS ₂ domain. (b) Line intensity profile integrated along the white dashed rectangle in (a), where the width of the intensity change is estimated to within 1 nm. (c) Z-contrast STEM image of the in-plane boundary between the MoS ₂ and WS ₂ domains. The yellow dashed lines indicate the	

roughness of the interface. (d) Atomic mapping of the Mo and W atoms' distribution in (c). (e) W concentration estimated along the axis perpendicular to the yellow dashed line (the overall direction of the interface), which averages the W concentration in each individual atomic plane. The width of the boundary is estimated to be within four unit cells. The Mo concentration in the WS₂ side is 0.2%, and the W concentration in the MoS₂ side is about 7.4%.86

Figure 7-7 ADF-STEM characterization of the interface boundary between the WS₂ and MoS₂ domains.[134] (a) A sharp boundary along the interface between the WS₂ and MoS₂ domains. The orange and pink dashed lines show the armchair and zigzag directions, respectively. (b) A boundary along the zigzag direction between the two domains. (c) A boundary along the armchair direction between the two domains. The right parts of (b) and (c) show the atomic models of these two structures. (d) A boundary along both the zigzag and armchair directions forms a nearly 90 ° corner between the two domains.....88

Figure 7-8 Electrical characterization of the lateral heterostructure.[134] (a) Optical image of a PN junction device. The scale bar is 10 μm. (b) I-V curves with and /without illumination....90

List of Tables

List of Tables

Table 2-1 Crystal constants of H-phase MoS ₂ , MoSe ₂ and WS ₂ monolayers.[25]	9
Table 2-2 Band gaps of MoS ₂ , MoSe ₂ and WS ₂ bulk crystals and monolayers.[46, 52]	12
Table 2-3 Mechanical properties of MoS ₂ , WS ₂ , graphene and several other materials.[84, 85]	15

List of Abbreviations

2D	Two dimensional
TMD	Transition Metal dichalcogenide
BN	Boron Nitride
MoS ₂	Molybdenum disulfide
MoO ₃	Molybdenum trioxide
Se	Selenium
Te	Tellurium
W	Tungsten
WS ₂	Tungsten disulfide
MoSe ₂	Molybdenum diselenide
CVD	Chemical vapor deposition
MOCVD	Metal organic chemical vapor deposition
FET	Field effect transistor
I _{ds}	Current pass the source and drain electrodes
V _{ds}	Voltage difference between the source and drain electrodes
V _{bg}	Voltage difference between the source and back gate
C _{ox}	Capacitance per unit area
L	Length of the channel
W	Width of the channel
AFM	Atomic force microscope
STEM	Scanning transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
PL	Photoluminescence
μ _{FE}	Filed effect mobility

Chapter 1 Introduction

1.1 Motivations

Two dimensional (2D) materials ranging from semimetal graphene to semiconductor transition metal dichalcogenide (TMD) monolayers and insulator hexagonal boron nitride (h-BN) have shown many good properties and promising applications in electronic, flexible and other devices since the discovery of atomic graphene in 2004.[1-7] The European Commission has granted ten years of support (valued at 1 billion euros) to this field as one of its “Future and Emerging Technologies.” [8] TMD monolayers, as semiconductors with a band gap ranging from 1.0 to 2.1 eV, have shown high mobility, high on/off ratios and high breaking strength (as summarized in figure 1-1), which make them promising for applications in field effect transistors, optoelectronics and flexible devices.[3, 5-7, 9-11]

Figure 1-1 Comparison between TMD monolayers and other materials.[11]

(a) Comparison of semiconductors' field effect mobility and on/off ratios

for electronics. (b) Comparison of field effect mobility and band gap for semiconductors used in current-generation photovoltaic technologies.

2D monolayers can also be stacked vertically or stitched together laterally to fabricate heterostructures (figure 1-2), which can be used as tunneling devices, photocurrent generators, atomically thin circuits, etc.[12-15] As semiconductor TMD monolayers are intrinsically either N-type or P-type direct semiconductors,[6, 16-18] heterostructures based on TMD monolayers can form typical PN junctions. Calculations and primary experiments have shown potential applications in photovoltaics, optoelectronics, and so on.[19-21]

Figure 1-2 Schematics of heterostructures. (a) Vertical heterostructure based on BN, graphene and TMD monolayers.[22] (b) Lateral heterostructure based on BN and graphene.[23]

Although TMD monolayers and heterostructures have been demonstrated as potential candidates for future electronics, some issues about their preparation should be solved before they are applied in large-scale practical devices:

- (1) Preparation of large-area single-crystalline TMD monolayers is lacking. The preparation methods for TMD monolayers range from top-down methods, including manual mechanical exfoliation with adhesive tape and liquid exfoliation, to bottom-up methods, including various CVD and metal organic CVD. With these methods, monolayers can be prepared with high-yield or large-area poly-crystal. However, so far the sizes of the single crystal monolayers are still in the range of micrometers. The grain boundaries damage the performance of the films in electronic devices. Preparations of larger single crystals are still required, and the relationship between the size and growth recipe need to be explored.
- (2) Growth of more kinds of TMD monolayers is required. Calculations show that more than 40 kinds of TMD monolayers are available, and each shows different performance. For example, the mobility of a hafnium diselenide monolayer is calculated to be $3500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, ten times higher than that of MoS_2 .^[24] However, experimentally, most of the preparations are focused on the growth of MoS_2 films. The growth methods of some other TMD films, such as MoSe_2 and WS_2 , are required.
- (3) Growth methods of TMD heterostructures are lacking. Some work has been reported on the growth of heterostructures, which are mainly based on graphene and other 2D materials; the growth of TMD heterostructures is in need of further exploration.

1.2 Objectives

The main objectives of this PhD study are to explore the growth of different semiconducting TMD monolayers and heterostructures using the CVD method.

The goals of this study are to

- explore the effect of the growth recipes on the domain size of single-crystal monolayers.
- develop new recipes for the growth of different TMD monolayers.
- explore the growth of TMD-based heterostructures.

1.3 Main contributions

The main contributions of my thesis can be summarized as the following:

- With an optimized temperature, single-crystalline MoS₂ monolayers with a size of as large as 1 mm were synthesized. This was the largest single-crystal MoS₂, and in fact the largest TMD, monolayer that had ever been synthesized. The dependence of size on temperature should also be applicable to the growth of other 2D materials.
- The growth of MoSe₂ and WS₂ monolayers were explored. MoSe₂ monolayers with high mobility were synthesized by the reduction of MoO₃ with selenium powder and hydrogen gas (H₂). The WS₂ monolayers were grown with a new recipe in which tungsten powder was used as the metal source. The melting of tungsten powder was successfully accelerated by the addition of tellurium

powder. This growth also paved the way for the synthesis of both a WS₂/MoS₂ vertical heterostructure and a WS₂-MoS₂ lateral heterostructure.

- Both the WS₂/MoS₂ vertical heterostructure and the WS₂-MoS₂ lateral heterostructure were synthesized with a one-step CVD method for the first time. More interestingly, the growth was easily controlled by adjusting the growth temperature. The PN junction between these two semiconductors was observed as expected. This provided a novel platform for fundamental study and for potential applications.

1.4 Organization of the thesis

This thesis is organized in the following chapters:

- Chapter 1 introduces the motivations, objectives, major contributions and organization of this thesis.
- Chapter 2 reviews TMD monolayers' properties, characterization and preparation methods. The properties and fabrication of heterostructures are also included in this chapter.
- In chapter 3, MoS₂ monolayers with a size as large as 1 mm are synthesized with CVD. The as-grown films are observed and characterized with an optical microscope, AFM, Raman, PL, STEM and electrical transport characterization. The relationship between the domain size and growth temperature is explored.
- In chapter 4, MoSe₂ monolayers are synthesized with CVD. These monolayers are confirmed by Raman, PL, and STEM. The composition of the film is characterized with XPS, and the monolayers' electrical performance is also measured.

- In chapter 5, WS₂ monolayers are deposited with a new recipe in which the tungsten powder is sulfurized. The growth result is confirmed by Raman, PL and XPS.
- In chapter 6, WS₂/MoS₂ vertical heterostructures are synthesized with one-step CVD. The vertical heterostructure is confirmed by AFM, Raman, PL, and STEM. The electrical properties of the vertical heterostructure are also characterized. .
- In chapter 7, WS₂-MoS₂ lateral heterostructures are synthesized with one-step CVD. The lateral heterostructure films are characterized by Raman, PL, and STEM. The PN junction between the WS₂ and MoS₂ domains is confirmed by electrical characterization.
- Chapter 8 concludes all the work presented in this thesis and recommends some possible work related to this project.

Chapter 2 Transition Metal Dichalcogenide Monolayers and Their Heterostructures

This chapter reviews the structures, properties, possible applications and preparation of TMD monolayers (mainly MoSe_2 , MoS_2 and WS_2) and heterostructures (both vertical and lateral).

2.1 TMD monolayers

2.1.1 Crystal structure

TMDs consist of transition metal atoms (such as tungsten and molybdenum) and chalcogen atoms (sulfur, selenium and tellurium). Similar to graphite, TMD crystals have a layered structure (figure 2-1(a)) in which TMD monolayers stack along the direction out of the plane, with weak van der Waals interaction.[6] Three bulk phases (2H, 3R and 1T, as shown in figure 2-1(b)) exist based on the composition monolayers and their stacking orders.

Figure 2-1 Schematic of TMD crystals.[6] (a) Layered stacking of TMD crystals. (b) Three phases of TMD crystals.

Unlike graphene, in which the monolayer consists of only one atomic layer, a TMD monolayer consists of metal atoms sandwiched between two layers of chalcogen atoms. In a basic crystal TMD cell, one metal atom is surrounded by six chalcogen atoms with chemical bonds in a prismatic column structure (H phase) (figure 2-2(a)) belonging to the P-6M2 (D_{3h}) point group or an octahedral structure (T phase) (figure 2-2(b)) belonging to the P-2M1 (D_{3d}) point group.[25-27] These phases can be observed and characterized with STEM and electron diffractions. It has been demonstrated that the H phase can be transformed to the T phase by Li^+ ion intercalation and that it can be converted back to the H phase by annealing at 300 °C.[27-35] Usually, the H phase is more stable and preferred from the view of formation energy.[25, 34] As a result, the monolayers grown by CVD are usually H-phase instead of T-phase, and the following discussion of this thesis will be focused on H phases.

Figure 2-2 Schematic of monolayer TMDs.[25, 27] (a) H-phase, (b) T-phase. The top-left figures in (a) and (b) are top views of the structures, the bottom-left figures are side views of the structures, and the right figures are 3D schematics of the structures.

The crystal constants of H-phase MoS_2 , $MoSe_2$ and WS_2 monolayers are listed in table 2-1.[25] Obviously, the differences of the crystal parameters between MoS_2 and

WS₂ are less than 0.7%, which will lead to mere strain when heterostructures form between these monolayers.

Table 2-1 Crystal constants of H-phase MoS₂, MoSe₂ and WS₂ monolayers.[25]

	phase	a (Å)	d _{M-X} (Å)	d _{X-X} (Å)	θ (deg)
MoS ₂	H	3.11	2.37	3.11	81.62
MoSe ₂	H	3.24	2.50	3.32	83.05
WS ₂	H	3.13	2.39	3.13	81.74

2.1.2 Vibration properties

Four first-order Raman-active modes and one IR-active mode (E_{1u}) appear in the unit cell of the TMD bulks (figure 2-3(a)).[36-38] Among the four Raman-active modes, the E_{2g}¹ and A_{1g} modes are usually accessible in the range from 100 cm⁻¹ to 400 cm⁻¹; the E_{2g}² mode occurs at very low frequencies, and the E_{1g} mode is forbidden in back-scattering geometry of a basal plane.[39, 40] When the thickness decreases from bulk to monolayer, on one hand, the A_{1g} mode softens because the interlayer van der Waals interactions increase the effective restoring forces acting on the atoms. On the other hand, the E_{2g}¹ mode stiffens, perhaps due to the influence of stacking-induced structural changes. [36, 37, 41] In the case of WS₂, it should be noted that the E_{2g}¹ peak around 355 cm⁻¹ overlaps with the strongest second-order mode, 2LA(M) at 352 cm⁻¹ (figure 2-3(c)), which depends on the layer numbers as well, when a laser of 514.5 nm is used as an illumination source.[42-44] As the vibration frequencies of the E_{2g}¹ (2LA[M] for WS₂) and A_{1g} modes and their differences shift as a function of the

thickness, Raman can be an effective method to determine the layer numbers of the TMD crystals.[36, 37, 41, 43, 45]

Figure 2-3 Raman characterization of TMD crystals with various thicknesses.[36, 37, 42] (a) Four first-order Raman-active modes and one IR-active mode (E_{1u}). (b) Raman spectra of MoS₂, MoSe₂ and WS₂ (from left to right) crystals from monolayer to bulk with a laser of 514.5 nm as illumination. (c) A high-resolution Raman spectra of monolayer WS₂. The E_{2g}^1 peak is overlapped by the second-order mode 2LA(M) at 352 cm⁻¹.

2.1.3 Band structures

Besides the vibration, the band structures of MoS₂, MoSe₂ and WS₂ also show a relationship with the crystal thicknesses.[46-51] It is well known that bulk MoS₂, MoSe₂ and WS₂ are indirect bandgap semiconductors in the range from 1.1 eV to 1.3 eV. However, these semiconductors become direct semiconductors, and their band gaps increase to about 2.0 eV when the thicknesses decrease from bulk to monolayers (summarized in table 2-2). As an example, the change of MoS₂ band structures with different thicknesses is shown in figure 2-4.[46] This crossover is due to the quantum confinement effect. Calculations based on density functional theory demonstrate that the states of the conduction band at the K point originate from the *d* orbitals of the Mo atoms, which are located in the middle of the monolayer and remain relatively stable during the interlayer interaction. However, near the Γ point, the states come from the hybridization of both the *d* orbital of Mo atoms and the *p_z*-orbitals of S atoms, which are sensitive to the interlayer interaction. When the thickness decreases, the direct excitonic states near the K point remain unchanged, but the states at the Γ point shift. As a result, the band structure transits from indirect to direct with an increased band gap. All MoS₂, MoSe₂ and WS₂ structures undergo a similar transformation.[46, 48, 52]

Figure 2-4 Band structure crossover of MoS₂ from bulk to monolayer.[46]

Table 2-2 Band gaps of MoS₂, MoSe₂ and WS₂ bulk crystals and monolayers.[46, 52]

	MoS ₂	MoSe ₂	WS ₂
Band gap in bulk (eV)	1.2	1.1	1.3
Band gap in monolayer (eV)	1.9	1.5	2.1

2.1.4 Electrical Properties

Unlike graphene, which is a semimetal and cannot be tuned with a gate in a field effect transistor (FET), semiconducting TMD monolayers show good application in FETs.[53-61] A typical FET based on MoS₂ is shown in figure 2-5.[6, 54] This kind of device can be easily fabricated with lithography and is compatible with silicon-based device fabrication. The MoS₂-based FET shows a typical N-type conduction, with an on/off ratio as high as 10⁸, a mobility as high as 60 cm²V⁻¹s⁻¹ and low off-state conductance with the thinnest channels, promising low power consuming and effective switch and showing advantage over graphene in FET devices.[54] MoSe₂ monolayer-based FETs show similar intrinsic N-type transportation behaviors while WS₂

monolayers show ambipolar conduction in FETs.[55, 62] The conduction can be easily tuned by doping or gate engineering.[63-65] It has also been proven that the FETs based on MoS₂ are immune to short-channel effects with a channel length of 100 nm.[66, 67] These TMD monolayers show good potential to be applied in logical devices; however, the low yield of large-area monolayers restricts their application.

Figure 2-5 Electrical transport properties of TMD monolayers.[6, 54] (a) Schematic of a FET based on TMD monolayer. (b) I_{ds} - V_g curves recorded from a top-gated device in (a).

2.1.5 Optical properties

Strong peaks appear in the absorption and PL spectra of a TMD monolayer.[28, 48, 51, 52, 58, 68, 69] The absorption and PL spectra of thin MoS₂ flakes are shown in figure 2-6. Due to the strong spin-orbital coupling, the top of the valence bands split while the bottom of conducting band remains. As a result, the absorption and PL peaks split in the absorption and PL spectra corresponding to the A and B excitons, respectively; however, the B peaks are usually very weak relative to the A peaks due to the lower transition frequency.[48, 70] Similar phenomena have been observed in MoSe₂ and WS₂ monolayers as well. [51, 68, 71-74]

Figure 2-6 (a) Absorption and (b) PL spectra of MoS₂ flakes with different thicknesses.[28]

As the PL intensity decreases dramatically when the thickness increases from monolayer to bilayer, the PL method has been used to effectively distinguish the monolayers from other flakes. [48, 58, 69, 75-77]

When photons with energy larger than the band gap are absorbed, electron-hole pairs form, and the extra carriers lead to the FET devices' current dramatic increase. In this way, these devices work as photo detectors with high sensitivity.[57-59, 78-80] On the other hand, light emitting transistors have also been demonstrated based on TMD monolayers. [62, 81, 82]

2.1.6 Mechanical properties

Layered materials show high strength due to the strong chemical bonds between atoms. Although bulk layered materials are often used as solid lubricants due to the weak van der Waals interaction between neighboring layers, their monolayer counterparts have shown high break strength because of the strong chemical bond

between atoms in the layers. The Young's modulus of MoS₂ and WS₂ monolayers are listed in table 2-3, with several other materials for comparison.[83-85]

Table 2-3 Mechanical properties of MoS₂, WS₂, graphene and several other materials.[84, 85]

Materials	Young's Modulus (GPa)	Breaking Strength (GPa)
MoS ₂ monolayer	270	16 – 30
MoS ₂ bulk	238	
WS ₂ monolayer	272	
Graphene	1000	130
Stainless steel ASTM-A514	205	0.9
PDMS	0.3-0.87	2.24
Polyimide	2.5	0.231
Kevlar 49	112	3

It has been demonstrated that a MoS₂ monolayer breaks when the strain reaches 6% to 11%, and this material shows an average breaking strength of $15 \pm 3 \text{ Nm}^{-1}$

(corresponding to 23 GPa), which is almost 30 times higher than that of stainless steel.[84] The WS₂ monolayers show similar strength. In addition to their electrical properties, these TMD monolayers show good performance in flexible devices.[86-92]

2.1.7 Preparation of TMD monolayers

TMD monolayers have been prepared by various methods, including top-down methods (mechanical exfoliation and liquid exfoliation of bulk crystals) and bottom-up methods (vapor solid deposition, sulfurizing/selenizing metal thin films, CVD, and so on), as summarized in the following part.

Mechanical exfoliation of bulk crystals

Since the discovery of graphene in 2004,[1] the mechanical exfoliation method has been widely used to prepare high-quality monolayer 2D materials with adhesive tapes from their bulk counterparts. This is due to the material's weak interlayer van der Waals interaction and its strong intralayer covalent bonds. Several samples are shown in figure 2-7. With this method, fundamental physics research has been conducted on various 2D materials, including TMD monolayers. [53, 54, 57, 60-62, 66, 78, 93-97] Although the method can easily provide various monolayers with high quality, it is time-consuming, and the size is usually small (from several micrometers to tens of micrometers) with a low yield, which means the method is not suitable to large-scale applications.

Figure 2-7 Mechanically exfoliated monolayer crystallites[53] of (a) NbSe₂, (b) graphite, (c) Bi₂Sr₂CaCu₂O_x and (d) MoS₂. Scale bar: 1 μm.

Liquid exfoliation of bulk crystals

Bulk crystals can also be exfoliated in the proper solution by ultra-sonication or shear exfoliation, with or without the intercalation of small ions (summarized in figure 2-8).[98-103] With these methods, various kinds of 2D material monolayers or few-layers have been prepared with high yield; these can be used in composites. However, most of the samples are few-layers, and their sizes are usually below 1 μm, limiting their application in electrical devices. It should be noted that the H-phase TMD crystals will change to T phase if ions are used to intercalate the bulk crystals before exfoliation.[28, 29]

Figure 2-8 Schematic of main liquid exfoliation mechanisms.[99] (a) Ion intercalation-assisted exfoliation. (b) Ion exchange-assisted exfoliation. (c) Sonication or shear-assisted exfoliation.

Vapor solid deposition

The 2D bulk crystals can decompose into the component metal and chalcogen atoms when heated to a properly high temperature, and these metal and chalcogen atoms will diffuse and react with each other to form monolayer flakes on substrates in a low temperature zone as shown in figure 2-9. High-quality MoS₂ monolayer flakes have been deposited with this method.[104] The near-unity valley polarization indicates that the sample is as good as the one by mechanical exfoliation. However, this method requires high decomposition temperatures and a high vacuum, so it is not suitable to all 2D materials.

Figure 2-9 Vapor solid deposition of MoS₂ monolayers.[104]

Sulfurization or selenization of metal thin films

The sulfurization or selenization of metal thin films is a direct way to synthesize TMD films (figure 2-10).[105-109] With this method, Mo or W thin films deposited with a sputtering or e-beam vapor deposition are sulfurized or selenized at high temperatures. Wafer-scale continuous TMD films can be achieved easily, and the thickness of the TMD films can be controlled by tuning the thickness of the metal films.[106] However, the uniformity of the film thickness is difficult to control due to the challenge of depositing a thin metal film with uniform thickness. The grain sizes in these films are usually on the scale of tens of nanometers, the grain boundaries lower the carrier mobility dramatically, and the on/off ratio is low, all of which restrict its practical application.[105]

Figure 2-10 Growth of MoS₂ thin films by sulfurizing Mo film.[106] (a) Deposition of Mo film by sputtering. (b) Sulfurization of Mo film. (c) Large area of MoS₂ film. (d) MoS₂ film on transparent substrate. (e) MoS₂ films with modulated thickness.

Thermal Decomposition of Chemical Precursor

A precursor ammonium thiomolybdate [(NH₄)₂MoS₄] can decompose into MoS₂ when it is heated to 500 °C. Therefore, it can be used to grow a MoS₂ monolayer (shown in figure 2-11).[110-112] For this growth, wafers are dipped into the dimethylformamide (DMF) solution of (NH₄)₂MoS₄, and a thin film forms when the sample is pulled out from the solution slowly. After baking at 120 °C for 15min, the wafer can be annealed at 500 °C, and a thin film of MoS₂ will form on top of the wafer.

The sample shows an N-type material with a carrier mobility on the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which can be improved to $4.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ if it is sulfurized further at 1000°C . Although a high-quality MoS_2 monolayer can be grown with the two-step method, it is still challenging to get a wafer-scale film due to the difficulty of getting a uniform precursor film.

Figure 2-11 Growth of MoS_2 by the thermal decomposition of ammonium thiomolybdate.[110]

Pulsed Laser Deposition

Pulsed laser deposition (PLD) is another effective method for the preparation of MoS_2 film with large area.[113-116] For the deposition, a rotating MoS_2 target is ablated with pulsed laser (KrF laser with a wavelength of 248 nm is often used), the duration of which is usually of several tens of nanoseconds (25 ns to 30 ns). The growth substrate is kept several centimeters away from the target, and the substrate is usually heated up to several hundreds of Celsius degrees to anneal the deposited film for better crystalline structure. With this method, MoS_2 with centimeter size can be easily deposited, and the thickness of the film can be well controlled from monolayer to multi-layers with the laser pulse numbers.[115] The composition of the as-deposited MoS_2 is consistent to the target used.[114] Another advantage of the PLD is that the

MoS₂ film can be deposited on various substrates, including metal substrates (such as Ag, Ni, Cu) and polymer substrate,[113] which is not suitable in the CVD growth. However, the quality of the deposited film is not so good, which may be due to the small grain size in the film.

Figure 2-12 Growth result of large area MoS₂ film by pulsed laser deposition. (a) Centimeter size MoS₂ film with controllable thickness on sapphire wafer. (b) Deposition of large area MoS₂ film on flexible plastic kapton substrate.

Chemical Vapor Deposition

CVD is most widely used for the growth of 2D materials. For the growth of TMD films, metal oxides, metal chlorides, and sulfur or selenium are used as precursors (figure2-13).[44, 52, 58, 69, 75, 76, 117-122] During growth, these precursors vaporize and react with each other at high temperatures, and TMD monolayers deposit on various target substrates.[118, 119, 123, 124] It has been proven that nucleation and growth is sensitive to the substrates and that nucleation seeds will accelerate the nucleation.[111, 118, 125, 126] For the growth of selenides, hydrogen is required as a reducing agent to assist in the reduction of the metal oxides.[52, 127, 128] As demonstrated, the TMD monolayers deposited with the CVD method can be as good

as the ones that use mechanical exfoliation. The mobility can reach $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and above, with on/off ratios above 10^6 . [52, 123, 129] With this method, a single-crystal MoS_2 monolayer with a size of $120 \text{ }\mu\text{m}$ can be grown, and continuous polycrystalline films with a size of 2 inches can be synthesized. [117] Recently, 4-inch wafer-scale MoS_2 and WS_2 monolayer (polycrystalline) films have been obtained with metal-organic precursors. [129]

Figure 2-13 CVD and MOCVD growth of MoS_2 film. [118, 129] (a) Schematic of the CVD setup for the growth of a MoS_2 monolayer. (b) Optical image of the CVD growth result. (c) Schematic of the MOCVD setup. (d) Device array fabricated on a 4-inch MoS_2 film.

Among these growth methods, CVD, which has been used for the growth of wafer-scale graphene,[130] is the most promising method for preparing large single-crystal TMD monolayers with high quality. However, this method requires further effort to explore the proper growth recipe. On the other hand, as the focus is largely on the growth of MoS₂ monolayers, the growth of other TMD monolayers needs further exploration.

2.2 Heterostructures

Heterostructures, which consist of two or more layers of different semiconductor materials, have been utilized to engineer the properties of semiconducting materials by manipulating the strain at the interface and the electronic band alignment of the neighboring materials. Heterostructures have become key building blocks for high-speed and photonic devices. However, the heterostructures consisting of layered TMD monolayers have only recently begun being studied.[13, 89, 131-137] Calculations have proven that a staggered (type-II) heterostructure will form when MoX₂ and WX₂ monolayers (“X” stands for “S or Se”) contact each other (figure 2-14(a)).[19, 138, 139] These type-II heterostructures are suitable for water-splitting, photovoltaics, and optoelectronics because free electrons and holes will be spontaneously separated.

Figure 2-14 (a) Band alignment of different TMD monolayers.[19] (b) Schematic of the vertical heterostructure of MoS₂ and WS₂ monolayers.[136] (c) Schematic of the lateral heterostructure of WS₂ and MoS₂ monolayers.[140]

Due to the anisotropic of dimension, especially along the in-plane direction and out-plane direction, layered materials can stack in the direction out of the plane to form a vertical heterostructure (figure 2-14(b)), or they can be stitched in the plane to form a lateral heterostructure (figure 2-14(c)).

2.2.1 Vertical heterostructure

Vertical heterostructures of 2D layered materials, also known as van der Waals heterostructures,[132, 133] have recently been fabricated as quantum tunneling devices and atomic PN junctions; these need further study.[12, 89, 136] So far, all these heterostructures are fabricated by the dry-transfer method.[20, 131, 136, 141, 142] Various monolayers can be easily exfoliated from their bulk counterparts with adhesive tape and then transferred to target substrates, just like Lego toys. It is easy to

fabricate various vertical heterostructures with different 2D monolayers. However, there are drawbacks of such methods:

- (1) Contamination between neighboring layers is inevitable. Atoms or molecules absorb the surfaces of newly exfoliated 2D materials and remain there during the stacking. These absorptions affect the material's performance.
- (2) The stack orientation cannot be controlled. Although the stack order can be precisely controlled with the transfer method, the stack orientation so far is still impossible to control, which leads to a low repeatability.
- (3) The process has a low yield and is time-consuming. Usually, it will take several weeks to fabricate one desired device with the transfer method.

New fabrication methods with precise control and high yield are required.

2.2.2 Lateral heterostructure

In addition to vertical heterostructures, monolayers can be stitched together in-plane with chemical bonds to form lateral heterostructures.[14, 15] Unlike vertical heterostructures, which can be physically stacked with the transfer method, lateral heterostructures can only be synthesized with chemical reactions. These lateral heterostructures can be fabricated with atomic thickness, as has been demonstrated by Liu et al., who deposited growth after the growth of BN.[14, 15] Recently, the lateral heterostructures of $\text{WSe}_2\text{-MoSe}_2$, $\text{WSe}_2\text{-WS}_2$, $\text{MoSe}_2\text{-MoS}_2$ and $\text{WSe}_2\text{-MoS}_2$ have been grown with two-step CVD growth.[21, 143, 144] Furthermore, a CMOS inverter based on the $\text{WSe}_2\text{-WS}_2$ lateral heterostructure, as demonstrated by Duan's group, shows a high voltage gain.[21]

In this project, MoS_2 and WS_2 monolayers are chosen as the building blocks for the fabrication of both vertical and lateral heterostructures. These monolayers were chosen for the following reasons:

- (1) Intrinsically, in air, MoS_2 is a typical N-type semiconductor, and WS_2 is a typical P-type semiconductor. These two monolayers will form a PN heterojunction, which is of great interest for the fundamental research.
- (2) From the point of view of material growth, only three elements (sulfur, tungsten and molybdenum) are involved in the heterostructures, which makes the process easier than the growth of $\text{WS}_2/\text{MoSe}_2$ or $\text{WSe}_2/\text{MoS}_2$. The heterostructures based on $\text{WSe}_2/\text{MoSe}_2$ are also excluded here, as sulfides grow in a much more mature manner than selenides do.

Chapter 3 Growth and Characterization of MoS₂ Monolayers

In this part, monolayer MoS₂ is synthesized with CVD. The as-grown MoS₂ films are as large as 1 mm, which can be observed easily with the naked eye. AFM, Raman and PL spectra confirm that the as-grown films are monolayers. The uniformity of the large-area film is confirmed with Raman and PL spectra. STEM shows the film's perfect crystalline structure. The growth temperature is found to significantly affect the size of the single-crystal domain.

3.1 The Growth of MoS₂ Monolayers with Chemical Vapor Deposition

MoS₂ monolayers are grown with the CVD method. For a typical growth as shown in figure 3-1, molybdenum trioxide (MoO₃) powder is used as molybdenum source (1 mg, 99% purity, Sigma), and sulfur powder (1 g, 99.9%, Sigma) is used as a sulfur source. For growth, the MoO₃ powder is loaded in a ceramic boat while the S powder is loaded in another one. Both boats are put into a quartz tube (diameter: 2 inches). The MoO₃ boat is put at the center of the furnace with a piece of SiO₂/Si wafer suspended above it with the polished side down. The sulfur boat is placed at the upwind end of the furnace, where it can reach 120 °C during the growth. The SiO₂/Si wafer is used as the growth substrate. Usually, the thickness of the SiO₂ layer is 270 nm, which provides a good contrast between the as-grown films and the substrate, and also act as the dielectric layer when a FET is fabricated on the wafer directly, without transfer. Argon is used as a carrier gas to purge the tube before the reaction and push the sulfur gas into the tube during the reaction. A flow rate of 60 standard cubic centimeters per minute (sccm) is used during the reaction. After being sealed, the system is heated to 850 °C with a heating rate of 50 °C/min and allowed to cool down

naturally after staying at 850 °C for 20 min. During the growth, the MoO₃ powder sublimates and is sulfurized by the sulfur gas following the reaction:

MoS₂ is formed on the SiO₂/Si substrate.

Figure 3-1 Schematic of the CVD setup for the growth of MoS₂. MoO₃ powder is located at the center of the furnace with a piece of SiO₂/Si wafer suspended above; the sulfur powder is upstream, at the opening of the furnace, where the temperature can reach the 120 °C needed to melt the sulfur.

3.2 Characterization of the as-grown MoS₂ monolayers

The as-grown MoS₂ monolayers are characterized by optical microscope, Raman, PL, XPS and STEM to confirm that they are MoS₂ monolayers and to evaluate their qualities. The electrical transport properties of these monolayers are evaluated by fabricating FETs on these monolayers.

3.2.1 Optical microscopic characterization of the MoS₂ monolayer

Figure 3-2 shows the as-grown result. Obviously, many triangles and polygons appear on the wafers (figure 3-2(a)) due to the good optical contact with the 270 nm SiO₂ substrate. Unlike the small triangles reported before by other groups, which can only be observed with the help of a microscope, these triangles and polygons are so large that they can be distinguished with the naked eye. With the help of an optical microscope, the sizes of the triangles are measured, and they range from several to several hundred micrometers. The triangles are usually uniform. The largest triangle is found to be 1 mm, as shown in figure 3-2(b). This is the largest single-crystal MoS₂ monolayer and also the largest TMD monolayer that has been ever synthesized. Besides triangles, many polygons appear as well (figure 3-2(c)). Unlike the triangles, which are uniform over the whole domain, white lines often appear on the polygons. These polygons form when two or more domains meet during the growth. As nucleation centers appear on the substrate randomly at the beginning of the growth and with random orientation, these polygons are usually polycrystalline, and grain boundaries appear between neighboring domains. As many defects exist along these domains, the grain boundaries are usually so active for nucleation that the second (or thicker) layers appear along the grain boundaries, which are white under the optical microscope. Sometimes, when all different domains grow together, the substrate is fully covered with a continuous film (figure 3-2(d)).

Figure 3-2 Optical images of the as-grown MoS₂ film. (a) Large domains, which can be observed with the naked eye, appear on the substrate. (b) A triangle, with a size of 1 mm, forms. (c) A polycrystalline polygon appears on the wafer as well. The single-crystalline dome is as large as 500 μm. (d) Continuous-film MoS₂ forms on the wafer when the films connected. White lines appear along the grain boundaries.

3.2.2 AFM characterization of the MoS₂ monolayer

The thickness of the as-grown monolayer is measured with AFM. In order to not damage the film during the thickness measurement, the tapping mode is adopted. The result is shown in figure 3-3. The as-grown MoS₂ film is very uniform in the height mode (figure 3-3(a)) with the false color contrast. A height profile (figure 3-3(b)) across the substrate of the MoS₂ film indicates its thickness is 0.7 nm, confirming it is a monolayer. A white dashed line with a height of 2 nm appears between the MoS₂

domain and the spare substrate area; this may be second or third layers that have appeared along the edge of the films due to the high activity at the edge. The phase image of the sample confirms the uniformity of the film as well with a phase difference of 2.3° (figure 3-3(c) and (d)).

Figure 3-3 AFM characterization of the as-grown MoS_2 film. (a) The topographical image shows that the film is uniform in thickness. (b) A height profile along the red line in (a) shows a height step of $0.7\ \text{nm}$, indicating that the as-grown film is a monolayer. (c) The phase image also shows the high uniformity of the as-grown MoS_2 flakes. (d) A phase difference of 2.3° is shown along the red line in figure (c).

3.2.3 Raman characterization of the MoS₂ monolayer

Raman is an effective method to characterize 2D materials, such as graphene and MoS₂. [36, 41, 145] For MoS₂, two typical peaks appear in the Raman spectra, the A_{1g} mode (due to the out-of-plane vibration) and the E_{2g}¹ mode (due to the in-plane vibration), as shown in figure 3-4(a). [36] As these two modes of vibration are related to the layer number, the difference between the peaks can be used to monitor the layer numbers. In a typical Raman spectrum of MoS₂ monolayer, the E_{2g}¹ peak is located at 384 cm⁻¹, and the A_{1g} peak is located at 403 cm⁻¹; the difference (Δ) between these two peaks is about 19 cm⁻¹. However, in a Raman spectrum of a bulk MoS₂, the E_{2g}¹ peak red shifts to 382 cm⁻¹, and the A_{1g} peak blue shifts to 408 cm⁻¹, with a peak difference of 26 cm⁻¹. In order to further confirm the thickness of the as-grown MoS₂, a Raman spectrum is collected (figure 3-4(b)). It is obvious that the E_{2g}¹ peak is at 382.6 cm⁻¹ and the A_{1g} peak is at 402 cm⁻¹, with a difference between the two peaks of 19.4 cm⁻¹. This indicates that the as-grown MoS₂ film is a monolayer, [36, 41] which is consistent with the AFM measurement result.

Figure 3-4 Raman characterization of the as-grown film. (a) The E_{2g}¹ (in-plane vibration) and A_{1g} (out-of-plane vibration) modes of the MoS₂ layer.

(b) A typical Raman spectrum collected from the as-grown film.

In order to check the uniformity of the as-grown film, 91 spectra are collected at different places, as shown in figure 3-5(a). This figure shows that all the E_{2g}^1 peaks are around 382.7 cm^{-1} and that the A_{1g} peaks are around 402.7 cm^{-1} , with a difference of 20 cm^{-1} . The small difference indicates that the large triangle is a uniform monolayer. The small shift of the peaks may be due to the local strain induced during the cooling process, as the thermal expansion coefficient of MoS_2 is three times larger than that of the SiO_2 substrate.

Figure 3-5 Statistics of Raman spectra collected from the as-grown triangle.

(a) 91 Raman spectra collected at the red crosses. (b) Statistics of the E_{2g}^1 and A_{1g} peaks and their difference. The E_{2g}^1 peaks are located around 382.7 cm^{-1} , and the A_{1g} peaks are located around 402.7 cm^{-1} ; that is a difference of 20 cm^{-1} , indicating that the as-grown large-area film is a uniform monolayer.

3.2.4 PL characterization of the MoS_2 monolayer

As monolayer MoS_2 is a semiconductor with a direct band gap, a strong emission peak can be observed during the photoluminescence measurement. As thickness

increases, the band gap decreases from 1.8 eV for the monolayer to 1.2 eV for the bulk MoS₂; the band gap becomes indirect, and the PL emission peak becomes much weaker, leading to red shift.[48, 146, 147] In this case, PL is an efficient method to measure the thickness of the MoS₂ film. Here, 91 PL spectra are collected at the same positions of the sample labeled in figure 3-6(a). A typical PL spectrum is shown in figure 3-6(b). Obviously, a strong peak is located at 680 nm in the spectrum, corresponding to a band gap of 1.82 eV; this indicates that the MoS₂ film is a monolayer.[48, 146] The peak positions of the other 90 PL spectra and the corresponding band gaps are listed in figure 3-6(b). All these peaks are around 677 nm, corresponding to a band gap of 1.83 eV, which verifies that the as-grown MoS₂ film is a uniform monolayer.

Figure 3-6 Statistics of PL spectra collected from the as-grown film. (a) 91 PL spectra collected from the red crosses. (b) The distribution of the PL peaks (black dots) and corresponding band gaps (blue dots). The band gaps are all around 1.82 eV, indicating that the large-area film is a uniform MoS₂ monolayer. The inset is one of the PL spectra collected.

3.2.5 XPS characterization of the MoS₂ monolayer

X-ray photoelectron spectroscopy (XPS) is a technique to analyze the surface elemental composition, chemical state and electronic state. When materials are illuminated with a beam of X-ray (usually the K-alpha line of aluminum is used as the X-ray source), the electrons with specific kinetic energy (E_{kinetic}) can escape from the surface layers (to a depth up to 10 nm) of the materials. According to the conservation of energy equation

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi),$$

in which, E_{binding} is the electron binding energy of the emitted electrons, E_{photon} is the energy of the X-ray photons, and ϕ is the work function, the E_{binding} can be calculated as other items are known. Because E_{binding} is determined by the atom category and their electron configuration, XPS is useful to analyze the surface elemental composition and their chemical and electronic states.

Here, XPS is used here to confirm the composition and binding of the as-grown film. The characterization result is shown in figure 3-7. Four elements appear in the full spectrum (figure 3-7(a)): molybdenum and sulfur from the as-grown film and silicon and oxygen from the SiO_2/Si substrate. The Mo $3d$ spectrum (figure 3-7(b)) consists of two peaks located at 232.9 eV and 229.9 eV, corresponding to the element's $d_{3/2}$ and $d_{5/2}$ core levels, respectively. The S $2p$ spectrum (figure 3-7(c)) has two peaks at 164 eV and 162.8 eV, corresponding to the $2p_{1/2}$ and $2p_{3/2}$ core levels, respectively, in agreement with the value obtained from other MoS_2 films.[118] The atomic ratio of S to Mo was calculated to be 2.1, indicating that the CVD-grown MoS_2 is reasonably stoichiometric.

Figure 3-7 XPS characterization of the as-grown film. (a) The whole XPS spectrum of the CVD-grown MoS₂ film. Four elements appear in the spectrum, including Mo and S from the MoS₂ film and O and Si from the SiO₂/Si substrate. (b) XPS spectrum of Mo 3d. (c) XPS spectrum of S 2p.

3.2.6 STEM characterization of the MoS₂ monolayer

In order to characterize the crystalline quality of the MoS₂ film with a transmission electron microscope (TEM), a piece of film is transferred to a TEM grid covered with QUANTIFOIL brand holey carbon film using poly(methyl methacrylate) (PMMA). After growth, the substrate with the MoS₂ on top is located on a vacuum pit (figure 3-8(a)). A drop of PMMA solution is placed on the sample and spin-coated at a speed of 3000 rpm for 1 min. The sample is then heated up to 120 °C for 5 min to vaporize the solvent and allow the PMMA to solidify to a continuous film (figure 3-8(b)). The

sample with the PMMA film on top is then cut into small pieces, each with a size of about $3 \times 3 \text{ mm}^2$, and then immersed in KOH solution (concentration: 1M) overnight. As the SiO_2/Si substrate is etched away by the KOH solution, the MoS_2 film (with the PMMA as a supporting film) floats on the solution (figure 3-8(c)). This floating hybrid film is scooped up with a piece of clean Si or a glass wafer and is transferred into deionized water to wash away the ions, such as K^+ . After it is rinsed three times, the hybrid film is scooped up with a TEM grid covered with QUANTIFOIL brand holey carbon film and heated to 80°C for 5 min to remove the water so that the film can contact the TEM grid intimately (figure 3-8(d)). Then, the TEM grid with the hybrid film is immersed in acetone solution to wash away the PMMA film. After three rinses in the acetone wash, the TEM grid is washed gently with deionized water and dried naturally (figure 3-8(e)).

Figure 3-8 Schematic of the preparation of TEM sample. (a) top view and side view of the as grown MoS_2 flake on SiO_2 wafer. (b) The MoS_2 sample was spincoated with PMMA. (c) The SiO_2 wafer was etched away with KOH solution. (d) The PMMA- MoS_2 film was transferred to a TEM grid. (e) PMMA film was washed away with acetone, and the sample on TEM grid was rinsed

with acetone, IPA and DI water. In (a) to (e), the left figures are from top view while the right figures are from side view.

After transfer, the MoS₂ film is observed with an optical image of the grid, as shown in figure 3-9(a). A triangle with a size of about 200 μm is successfully transferred to the TEM grid. The transferred MoS₂ is characterized with an aberration-corrected STEM operated at 60 kV. An atomic annular dark field (ADF) image, also known as a Z-contrast image, is shown in figure 3-9b. A perfect hexagonal structure can be observed in the image. A fast Fourier transform (FFT) diffraction pattern is shown in the inset of figure 3-9(b), which indicates that the as-grown film is a perfect MoS₂ film. An ADF image with higher resolution is shown in figure 3-9(c). Two kinds of dots can be observed in the images: clear white dots corresponding to the molybdenum atoms (due to their heavy weight) and blurry gray dots corresponding to the columns of S atoms.[119, 148] An intensity scan along the red box indicated in figure 3-9(c) shows that the S vacancy appeared in the film (figure 3-9(d)).

Figure 3-9 STEM characterization of the as-grown MoS₂ monolayer. (a) Monolayer MoS₂ on a TEM grid covered with holey carbon film after being transferred with the PMMA-assisted method. (b) ADF image of the monolayer MoS₂ film shows perfect crystalline structure. Inset: electron diffraction pattern of the film indicating that the film is monolayer MoS₂. (c) ADF image with higher magnification. The white dots correspond to molybdenum atoms, and the gray dots correspond to sulfur columns. (d) Intensity line scan along the red box in (c). A sulfur vacancy is observed here.

3.2.7 Electrical transport characterization of the MoS₂ monolayer

In order to evaluate the electrical quality of the as-grown film, FETs are fabricated based on the MoS₂ film using the standard lithography method. Briefly, photoresist was spincoated on the as-grown MoS₂ monolayers (figure 3-10(a)), and patterned into rectangle (figure 3-10(b)) with a glass mask with Cr pattern with standard UV lithography. Then the MoS₂ flakes were patterned into rectangle with O₂ plasma etching (figure 3-10(c)) and the photoresist was washed away (figure 3-10(d)). With another round of standard UV-lithography, including spincoating photoresist, patterning, developing, electrode patterns were fabricated on the MoS₂ pattern. With e-beam deposition and lift-off, metal electrodes of 20 nm titanium and 50 nm gold were fabricated (figure 3-10(e)). In this way, TMD based FET device is prepared.

Figure 3-10 Fabrication of TMD based FET device. (a) As-grown TMD monolayers on SiO₂ wafer. (b) The monolayer is covered with patterned photoresist. (c) The TMD flake is patterned to desired pattern. (d) The photoresist is washed away. (e) Metal electrodes are deposited.

For the electrical measurement, the deposited metal electrodes are used as source and drain, while the highly doped Si substrate is used as global back gate to control the

Fermi level of the channel (the TMD layer), with the SiO₂ layer used as dielectric layer. The potential of the source electrode is selected as a reference, and the voltage difference applied between the source and drain electrode is defined as V_d, while the voltage difference between the source and the global back gate (the Si substrate) is V_g. The current goes through the source and drain electrodes is I_d. The curves of I_d-V_d and I_d-V_g are recorded for the performance analysis of the transistors. The mobility of the transistors in this manuscript refers to the field effect mobility μ_{FE} , which is defined as an effective approximation of mobility extracted from a transfer curve *i.e.* a plot of I_d vs gate voltage V_g,

$$\mu = dI_{ds}/dV_{bg} \times L/(WC V_{ds}),$$

where C is the capacitance per unit area of the gate dielectric (1.26×10^{-4} F/m² for 270 nm SiO₂), L and W are the length and width of the channel, respectively. The on/off ratio is defined as the ratio of on-state to off-state current.

A typical device is shown as the inset in figure 3-11(b). The channel length (L) is measured to be 3.7 μ m, and the channel width (W) is 20 μ m. The linear I_{ds}-V_{ds} curves at different back-gate voltages from 0 V to 40 V, with a step of 10 V (figure 3-10(a)), indicate Ohmic contact between the electrodes and the monolayer MoS₂. The I_{ds}-V_{bg} curve shows a typical N-type channel performance, which is consistent with previous reports.[54, 149] The high on/off ratio of 10⁸ indicates a possible application in a low-energy logic circuit. With the equation

$$\mu = dI_{ds}/dV_{bg} \times L/(WC V_{ds}),$$

in which the capacitance per unit area between the channel and the back gate (C) is 1.26×10^{-4} F/m², and the drain-source voltage (V_{ds}) is 0.1 V, the carrier mobility of the

monolayer is calculated to be $1.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is consistent with the reported values of grown MoS₂ monolayer films.[118, 119]

Figure 3-11 electrical characterization of MoS₂-based FET. (a) I_{ds} - V_{ds} curves. The back-gate voltage V_{bg} ranges from 0 V to 40 V, with a step of 10 V. The linear dependence indicates Ohmic contact between the electrodes and the channel. (b) I_{ds} - V_{bg} curve. Typical N-type transistor behavior is shown in this figure. The on/off ratio is as high as 10^8 . The inset is an optical image of a FET device. The channel length is $3.7 \text{ } \mu\text{m}$, and the channel width is $20 \text{ } \mu\text{m}$.

3.2.8 Effect of the Growth Temperature on the Size of the Monolayers

It is found that the size of the as-grown film is affected by the growth temperature (figure 3-11). In this part, MoS₂ films are synthesized from 650 °C to 900 °C. When temperature increases from 650 °C to 850 °C, the size of the triangles increase from several micrometers to about 1 mm. When temperature increases further, the size decreases. A similar trend was also observed by J. Shi et al.[150] It should be noted that the as-grown MoS₂ monolayer decomposes at high temperature during growth.[104] As a result, the size of the grains is determined by competition between

MoS₂'s growth rate (R_g) and decomposition rate (R_d). Obviously, R_g decreases during growth because the sources, especially the Mo source, will be consumed gradually. In the meantime, if one assumes that grain sizes increase during growth, R_d increases throughout the synthesis because the grain size of the MoS₂ becomes larger. At the beginning of the growth, MoS₂'s grain size is small, and R_d is much smaller than R_g . The MoS₂ grain size continues to increase. When R_d equals R_g , MoS₂ reaches a maximum size, which remains constant dynamically. For higher temperature, both R_d and R_g increase. Because R_g is much higher than R_d , the grain size increases with temperature at first. However, as R_d increases faster than R_g , it soon equals R_g at this higher temperature. As a result, the final grain size decreases. Obviously, no monolayer appears when the temperature increases beyond the melting point of MoS₂. Thus, only at a critical temperature ($T_c = 850\text{ }^{\circ}\text{C}$ here), can one get the largest MoS₂. This mechanism should be suitable to the growth of other TMDs as well.

Figure 3-12 Size's dependence on growth temperature. (a) – (e) MoS₂ grown at 650 °C, 700 °C, 750 °C, 850 °C, and 900 °C, respectively. (f) Plot of size of sample as a function of the growth temperature.

3.3 Summary

Large-area MoS₂ monolayers are synthesized with the CVD method. The as-grown films are confirmed to be MoS₂ monolayer using AFM, Raman, and PL. The STEM characterization shows the perfect crystalline structure of the monolayer MoS₂. The electrical characterization shows that the as-grown MoS₂ film is a typical N-type channel material with a carrier mobility of 1.0 cm²V⁻¹s⁻¹. It is proven that the size of the grown MoS₂ film is affected by the growth temperature. With an optimized growth recipe, the largest single-crystal can reach 1 mm, which is not only the largest monolayer single-crystal MoS₂ but also the largest monolayer single-crystalline TMD.

Chapter 4 Growth and Characterization of MoSe₂ Monolayers

In this part, a molybdenum diselenide (MoSe₂) monolayer film is synthesized with CVD, similar to the process used to grow monolayer MoS₂, and characterized with optical microscope, AFM, Raman, PL and STEM. The electrical transport properties of the as-grown monolayers are also measured.

4.1 Growth of the MoSe₂ monolayer

For the growth of the MoSe₂ monolayer, molybdenum trioxide (MoO₃) powder (1 mg, 99.9%, Sigma) is used as the Mo source, and selenium pellets (1 g, 99.9%, Sigma) are used as the Se source, as shown in figure 4-1. The MoO₃ powder is put in a ceramic boat, which is located at the center of the thermal tube furnace. A piece of SiO₂/Si wafer is suspended above the ceramic boat, with its polished surface down. Selenium is put in another ceramic boat, which is located at the opening of the furnace, where the temperature reaches 220 °C during the growth. A mixed gas (50 sccm) of argon and hydrogen (15%) works as a carrier gas. Hydrogen is necessary for the growth of MoSe₂. [128] The furnace is heated to 750 °C in 15 min. After a reaction of 20 min, the system is cooled down naturally.

Figure 4-1 Schematic of the growth setup. MoO₃ powder (as a Mo source) is placed in a ceramic boat located at the center of the furnace, and the selenium pellets in the other boat at the opening of the furnace serve as a Se source. A mixed gas of Ar and H₂ (15%) is used as the carrier gas.

4.2 Characterization of the MoSe₂ monolayer

4.2.1 Optical microscopic characterization of the MoSe₂ monolayer

The growth result is shown in figure 4-2. After growth, many triangles appear on the wafer, with sizes ranging from several to more than 100 μm (figure 4-2(a)). The wafer is covered with MoSe₂ monolayers with high coverage (figure 4-2(b)). A large triangle with a size of 135 μm appears on the wafer (figure 4-2(c)), with many small triangles surrounding it. Continuous films form occasionally (figure 4-2(d)), and many small dots appear on the film. The domains are only several micrometers large.

Figure 4-2 Optical images of the CVD-grown MoSe₂ films.[52] (a) After growth, the substrate is covered with many triangles with high coverage. (b) and (c) High magnification optical images of the sample. The size of the triangles ranges from several to more than 100 μm. A triangle with a size as large as 135 μm is found, with many small dots on its surface. (d) Continuous film formed when small triangles connect. The sizes of the domains are several micrometers.

4.2.2 AFM characterization of the MoSe₂ monolayer

AFM is used to measure the thickness of the as-grown film. The measurement is conducted with the tapping mode, and the result is shown in figure 4-3. The MoSe₂ surface is flat, and many dots appear on the substrate, which should be the nucleation centers. A height scan is performed along the red line in figure 4-3(a), showing that the

height of the as-grown film is only 0.8 nm (figure 4-3(b)), which verifies that the MoSe₂ film is a monolayer.

Figure 4-3 AFM characterization of the CVD-grown MoSe₂ film.[52] The thickness of the film is verified to be 0.8 nm, indicating that the film is a monolayer.

4.2.3 Raman characterization of the MoSe₂ monolayer

A triangle with a size of about 40 μm is analyzed at both the center and edge of the triangle with Raman method (figure 4-4(a)). The Raman spectra are collected with a Renishaw Raman system with an incident laser of 514.5 nm. Similar to the results of the MoS₂ film's Raman spectrum, two typical peaks appear in both spectra: a sharp one at 239 cm⁻¹ corresponding to the A_{1g} mode of the MoSe₂ (the out-of-plane vibration mode) and a broad peak at 301 cm⁻¹ corresponding to the E_{2g} mode (the in-plane vibration mode); this confirms that the film is MoSe₂ (figure 4-4(b)).[68] The nearly identical peak position and the relative intensity of the spectra at the center and edge of the triangle suggest a high homogeneity in the as-grown MoSe₂. The uniformity of the film is also confirmed by Raman intensity mapping of the A_{1g} (239 cm⁻¹) mode (figure 4-4(c)).

Figure 4-4 Raman characterization of the CVD-grown film.[52] (a) A MoSe₂ triangle with a size of about 40 μm is used for the characterization. (b) Raman spectra collected at both the center and edge of the triangle. The similarity of the two spectra indicates the homogeneity of the as-grown film. (c) Raman mapping of the triangle at 239 cm⁻¹.

4.2.4 PL characterization of the MoSe₂ monolayer

PL is another efficient method to characterize the MoSe₂ monolayer. Typical PL spectra are collected at both the center and the edge of the MoSe₂ triangle shown in figure 4-5(a). Only a strong peak around 840 nm is present in both PL spectra, corresponding to a band gap of 1.48 eV (figure 4-5(b)); this is in good agreement with the reported 1.5 eV value for monolayer MoSe₂. [68] The strong PL peak at 840 nm indicates that the as-grown MoSe₂ is a monolayer. It should be noted that, under the same measurement conditions, the PL spectrum collected at the edge is weaker than that at the triangle center; the spectrum also shows a red-shift. This is also verified by PL intensity mapping (figure 4-5(c)), in which the center of the triangle is much brighter than the edge, and by PL peak position mapping (figure 4-5(d)), which shows a red-shift of the PL peak position from the center to the edge of the triangle. A similar phenomenon has also been observed in tungsten disulfide (WS₂), although in that case,

the edges had the higher intensity.[82] For the WS₂ study, the low PL intensity resulted from defects within the crystal that can quench the intrinsic PL or act as non-radiative recombination sites.[82] Thus, the decrease of the PL intensity here can be attributed to defects, especially Se vacancies, which are more common around the edges during CVD growth. The red-shift of the PL peak position from the center to the edge should also be due to these defects.

Figure 4-5 PL characterization of the CVD-grown MoSe₂ monolayer film.[52] (a) Optical image of as-grown MoSe₂ monolayer. (b) PL spectra collected at both the center and the edge of the triangle. The intensity of the peak at the edge is as low as half the intensity of the center, and the peak position is red-shifted; both these effects are attributed to defects at the edge during the growth process. (c) PL intensity mapping of the triangle shows a decrease in intensity at the edge of the triangle. (d) PL peak position mapping shows that the PL peak red-shifts toward the edge.

4.2.5 XPS characterization of the MoSe₂ monolayer

XPS is used to measure the elemental composition and bonding within the as-grown films. The spectra are shown in figure 4-6. Four different elements appear in the full spectra (figure 4-6(a)), including Mo and Se from the MoSe₂ monolayer and Si and O from the SiO₂ substrate. More information about the stoichiometry and bonding are provided in the enlarged 3*d* spectra of Mo and Se (figure 4-6(b) and (c)). Two peaks, at 228.3 eV and 231.5 eV, appear in Mo's 3*d* spectrum; these correspond to the 3*d*_{5/2} and 3*d*_{3/2} core levels, respectively, indicating the reduction of Mo atoms from Mo⁶⁺ to Mo⁴⁺. One peak, at 54.0 eV, is present in Se's 3*d* spectrum; this peak can be divided into two smaller peaks at 53.9 eV and 54.7 eV, which correspond to the 3*d*_{5/2} and 3*d*_{3/2} core levels, respectively.[151, 152] The atomic ratio of Mo/Se is calculated to be 1:1.97 based on the XPS spectrum, suggesting that the as-grown MoSe₂ is reasonably stoichiometric.

Figure 4-6 XPS characterization of the MoSe₂ film.[52] (a) Full spectrum of the as-grown MoSe₂ monolayer. (b) Mo 3d XPS spectrum. (c) Se 3d XPS spectrum.

4.2.6 STEM characterization of the MoSe₂ monolayer

TEM and aberration-corrected STEM are used to characterize the crystal quality of the as-grown MoSe₂ film. A piece of MoSe₂ film is transferred to a QUANTIFOIL brand TEM grid covered with holey carbon film using the PMMA-assisted method, as was done for the transfer of the MoS₂ film. A continuous film after the transfer proves that the as-grown film is of high quality (figure 4-7(a)). Some folds and small particles appear on the film, likely caused during the transfer (figure 4-7(b)). A perfect

hexagonal arrangement of Mo atoms and Se columns can be observed clearly in the high-angle annular dark field (HAADF) STEM images with atomic resolution (figure 4-7(c)). An intensity profile along the red line in figure 4-7(c) is shown in the inset. The Se_2 columns show higher intensity than the Mo atoms due to the columns' heavier atomic weights. A domain of bilayer is also observed in the transferred sample in the STEM image (figure 4-7(d)), which also shows a perfect crystal structure.

Figure 4-7 STEM characterization of the MoSe_2 monolayer.[52] (a) Low-magnification image of the MoSe_2 monolayer on a TEM grid. (b) Magnified TEM image of the transferred MoSe_2 monolayer film. (c) HAADF-STEM image of MoSe_2 presenting a perfectly hexagonal crystal lattice. An intensity profile acquired along the red line is shown in the inset. (d) HAADF-STEM image of MoSe_2 showing a domain of bilayer material.

(d) HAADF-STEM image with interface of the MoSe₂ monolayer (bottom) and bilayer (top).

4.2.7 Electrical transport characterization of the MoSe₂ monolayer

The electrical performance of the as-grown MoSe₂ monolayers is characterized by fabricating FETs on the film with e-beam lithography. The MoSe₂ film is first patterned into small rectangles with e-beam lithography, and electrodes of titanium (3 nm) and gold (35 nm) are deposited with e-beam evaporation. The FET's channel length and width are designed to be 10 μm and 2 μm , respectively (figure 4-8(a)). The FET device is annealed at 120 $^{\circ}\text{C}$ for 2 h under vacuum after the electrode deposition. A typical $I_{\text{ds}}\text{-}V_{\text{bg}}$ curve, as shown in figure 4-8(b), features typical N-type behavior, which is in good agreement with reports from exfoliated samples.[57] The film's carrier mobility is estimated with the equation

$$\mu = (dI_{\text{ds}}/dV_{\text{bg}}) [L/(WCV_{\text{ds}})],$$

in which the channel length (L) is 10 μm , the channel width (W) is 2 μm and the gate capacitance per unit area (C) is $1.26 \times 10^{-4} \text{ F/m}^2$. Here, 0.5 V was used for the V_{ds} . The linear $I_{\text{ds}}\text{-}V_{\text{ds}}$ curves (inset in figure 4-8(b)) indicate that Ohmic contacts are formed between MoSe₂ and the metal electrodes. The on/off ratio is calculated to be higher than 10^6 , and the electron mobility is within $20\text{--}80 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with an average mobility of $50 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The high mobility and high on/off ratio prove that the CVD-grown MoSe₂ samples are of high quality and suitable to the application in FET devices.

Figure 4-8 Electrical transport measurement of the MoSe₂ monolayer in a FET device.[52] (a) Optical image of the FET device. S and D stand for the source and drain electrodes, respectively. L and W stand for the length and width of the device channel, respectively. (b) I_{ds} - V_g curve showing the MoSe₂ monolayer working as an N-type channel. Inset: I_{ds} - V_{ds} curves at different gating voltages.

4.3 Summary

MoSe₂ monolayers are successfully synthesized by CVD. The AFM, PL and (S)TEM characterizations verify that the as-grown films are monolayers. The Raman and XPS characterizations prove that the monolayer is MoSe₂, and the ratio of Mo/Se was calculated to be 1:1.97, indicating a stoichiometric composition of the CVD-grown film. The as-grown film works as an N-type channel, and the average mobility is as high as $50 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, indicating that the as-grown MoSe₂ monolayers are of high quality.

Chapter 5 Growth and Characterization of WS₂ Monolayers

In this chapter, a WS₂ monolayer is grown with the CVD method and characterized with Raman, PL, and XPS.

5.1 Growth of the WS₂ monolayer

The setup for the growth of WS₂ is shown in figure 5-1. Tungsten powder (99.99%, 10 mg, Sigma Aldrich) and sulfur powder (99%, 500 mg, Sigma Aldrich) are used as tungsten and sulfur sources, respectively. Tellurium powder (99.99%, 100 mg, Sigma Aldrich) is used to accelerate the melting of the tungsten powder. Tungsten and tellurium powders are scattered on a SiO₂/Si wafer, which is located at the center of the furnace, and sulfur powder is placed in another ceramic boat at the edge of the furnace. The tellurium powder here is used to lower the melting temperature of the tungsten source for the reaction. According to the phase diagram (figure 5-2), tungsten can be absorbed in liquid tellurium at 450 °C. In this way, the melting point of tungsten decreases from 3422 °C to 450 °C, facilitating the reaction. For the growth of WS₂ monolayers, the system is heated up to 750 °C in 15 min and kept at 750 °C for another 20 min before cooling down to room temperature naturally. A carrier gas flow of 100 sccm of argon is used to provide an inert atmosphere and push the sulfur gas into the furnace.

Figure 5-1 Schematic of the setup for the growth of the WS_2 monolayer.

Figure 5-2 Binary phase diagram of tungsten-tellurium. The region marked by the red arrow shows that tungsten is somewhat soluble in tellurium liquid at 750 °C.

5.2 Characterization of the WS_2 monolayer

5.2.1 Optical characterization of the WS_2 monolayer

The as-grown flakes are shown in figure 5-3. Obviously, many triangles appear on the wafer; these are WS_2 monolayers, as proven by the Raman and PL characterizations shown later in the chapter. Some polygons also form when the two or

more domains merge during growth. The size of the flakes ranges from several micrometers to tens of micrometers. Besides the monolayers, small bilayers and bright dots appear at the centers of the some flakes. These may be due to sources left from the growth.

Figure 5-3 Optical microscopic image of the as-grown WS₂ monolayer.

5.2.2 Raman characterization of the WS₂ monolayer

Raman is an effective method to evaluate the quality and thickness of WS₂ flakes. Here, Raman characterization is performed on the as-grown flakes with a laser of 514.5 nm and a power of 20 mW at room temperature as an excitation source. A typical Raman spectrum is shown in figure 5-4. Two main peaks appear at 356.8 cm⁻¹ and 418.5 cm⁻¹, corresponding to the 2LA(M) and A_{1g} modes of the WS₂ monolayer, respectively, indicating that the as-grown flakes are a WS₂ monolayer.[42, 44]

Figure 5-4 Raman spectrum of the WS₂ monolayer.

5.2.3 PL characterization of the WS₂ monolayer

PL characterization has been widely used to characterize the layered semiconducting TMDs. PL characterization is performed on the as-grown flakes with a laser of 514.5 nm as excitation source using a Renishaw inVia system. A typical PL spectrum is shown in figure 5-5. Only one strong peak appears at 631 nm in the PL spectrum; this corresponds to a band energy of 1.97 eV, proving that the flake is a WS₂ monolayer. [44, 51]

Figure 5-5 PL spectrum of the WS₂ monolayer.

5.2.4 XPS characterization of the WS₂ monolayer

Figure 5-6 XPS characterization of the WS₂ monolayer. (a) Full XPS spectrum of the sample. (b) XPS spectrum of W 4*f*. No tellurium is found in the sample.

The as-grown flakes are characterized with XPS. Four elements appear in the full spectrum (figure 5-5(a)): oxygen, silicon, tungsten and sulfur. The oxygen and silicon should be from the SiO₂/Si substrate, and the tungsten and sulfur should be from the as-grown flakes. Interestingly, no tellurium is found in the sample, especially in the

enlarged zone in figure 5-5(b), despite the system's resolution. This may be because telluride is unstable in a sulfur atmosphere. The W $4f$ spectrum consists of two peaks located at 32.4 eV and 34.5 eV; these peaks corresponding to the $f_{7/2}$ and $f_{5/2}$ core levels of W, respectively, which corresponds with the values obtained from other WS₂ films.

5.3 Summary

WS₂ monolayers are synthesized with CVD using tungsten powder and sulfur powder as sources. The WS₂ monolayers are confirmed with Raman and PL spectra. No telluride appears in the sample even though tellurium powder is used to facilitate the melting of the tungsten powder. The growth of the WS₂ monolayer paves the way for the growth of heterostructures based on the WS₂ and MoS₂ monolayers.

Chapter 6 Growth and Characterization of WS₂/MoS₂ Vertical Heterostructure

Heterostructures have been applied in the semiconductor industry for a long time. However, traditional heterostructures are based on bulk materials, such as GaAs/AlGaAs. Recently 2D-material-based heterostructures stacked out-of-plane have been fabricated using the transfer method; these heterostructures have shown novel properties. However, the transfer method has problems. First, the interfaces between neighboring layers are easily contaminated during exfoliation and transfer. In addition, the stacking orientation is uncontrolled and time-consuming. It usually takes several weeks to get a single desired stacking heterostructure. A way to synthesize heterostructures directly would be desirable. Here, a vertical heterostructure based on WS₂ and MoS₂ monolayers is synthesized with a one-step CVD.

6.1 Growth of the WS₂/MoS₂ vertical heterostructure

The vertical heterostructure based on WS₂ and MoS₂ monolayers is grown with the CVD method, as shown in figure 6-1. For the growth of this vertical heterostructure, sulfur powder (1 g, 99%, Sigma) is placed in a ceramic boat located at the end of the furnace for use as a sulfur source. Molybdenum trioxide (MoO₃) powder (1 mg, 99.9%, Sigma) is placed in another ceramic boat along with a piece of SiO₂/Si wafer; which is located at the center of the furnace. A mixture of tungsten and tellurium powders is scattered on the SiO₂/Si wafer as a tungsten source.

Figure 6-1 Schematic for the growth of the WS₂/MoS₂ vertical heterostructure. For the reaction, the system is heated up to 850 °C and kept at 850 °C for 20 min before cooling down naturally to room temperature; 60 sccm of Ar is used as carrier gas and to provide an inert environment.

For the growth of the heterostructure, the system is heated to 850 °C at a heating rate of 50 °C/min and cooled down to room temperature naturally after reacting at 850 °C for 20 min. Before the reaction, the tube is purged with an argon flow of 200 sccm to push out any oxygen or moisture in the tube and to provide an inert environment for growth. During the reaction, a gas flow of 60 sccm Ar is used to carry the sulfur gas into the tube.

6.2 Characterization of the WS₂/MoS₂ vertical heterostructure

6.2.1 Optical microscopic characterization of the WS₂/MoS₂ heterostructure

After a 20-min reaction, many flakes appeared on the SiO₂/Si wafer, as shown in figure 6-2. Although many monolayer flakes look light in color, similar to the growth results of monolayer MoS₂ or MoSe₂ (figures 3-2 and 4-2), more bilayer flakes appeared on the wafer; these are dark in color with an obvious contrast. It can be seen

from the optical images at low magnification that the wafer is highly covered with the bilayer flakes and that the bottom layer of the bilayers are about 10 μm while the top layers are smaller, usually only several micrometers in size.

Figure 6-2 Optical images of the growth result of the WS₂/MoS₂ vertical heterostructure at low magnification.[134]

At higher magnification (figure 6-3), the shapes of the bottom (large) layers are usually triangles (for individual domains) or polygons (when two or more domains merge during growth), similar to the shapes from the monolayer sample. The top layers are usually smaller, with a size of about 5 μm . The morphologies are random, as some follow the shape of the bottom layers while others are polygons.

Figure 6-3 Optical images of the as-grown flakes at higher magnification.[134] The small (top) layers are in various shapes, but the bottom layers are usually triangles.

6.2.2 AFM characterization of the WS₂/MoS₂ heterostructure

The thickness of the bilayer flakes is characterized with AFM, in the tapping mode. Obviously, two steps can be observed in the height topography (figure 6-4(a)). The top and bottom layers are continuous and uniform in thickness. A height profile crossing the step edges of the heterostructure is shown in figure 6-4(b). It shows that the thicknesses of the top and bottom layers are 0.8 nm and 0.7 nm, respectively, corresponding to the thickness of the monolayer TMDs and confirming that the heterostructure is composed of two monolayers.

Figure 6-4 AFM characterization of the as-grown flakes.[134] (a) Height topography of the sample. (b) Height profile along the red line in (a), which moves across the two steps.

6.2.3 Raman characterization of the WS₂/MoS₂ vertical heterostructure

In order to confirm that the heterostructure is composed of a WS₂ monolayer and a MoS₂ monolayer (instead of two WS₂ monolayers or two MoS₂ monolayers) the as-grown flakes are characterized with Raman. A laser source with a wavelength of 514.5 nm is used as the incident source. Four spectra (figure 6-5(b)) are collected randomly, with two from the large film only and two from the bilayer region, as shown in figure 6-5(a). It is obvious that only two peaks appear in spectra 1 and 2, which were collected from the large film only. The peaks are located at 384 cm⁻¹ and 405.3 cm⁻¹, which correspond to the E_{2g}¹ and A_{1g} vibration modes of the MoS₂ monolayer, confirming that the large-area film is a MoS₂ monolayer.[36, 41] However, in spectra 3 and 4, in addition to the two peaks of the MoS₂ monolayer, another two peaks appear at 356.8 cm⁻¹ and 418.5 cm⁻¹, which can be assigned to the overlapping 2LA(M) and E' modes and to the A₁' mode of the WS₂ monolayer, respectively.[42, 43] As the large

bottom layer is confirmed to be a MoS₂ monolayer, the two peaks of the WS₂ monolayer should be attributed to the small top layer, verifying that the small top layer is a WS₂ monolayer. In order to characterize the uniformity of the monolayers, Raman mapping is performed on the sample as well. Figure 6-5(c) is the Raman mapping at 384 cm⁻¹, in which a large, bright triangle ring encircles a small, triangular dim area, indicating that the large triangle is a MoS₂ monolayer. The dim triangle's center is due to the small, top WS₂ monolayer's coverage of the center. In figure 6-5(d), the Raman mapping is performed at 357 cm⁻¹, corresponding to a WS₂ mapping. Only a bright triangle appears at the center, corresponding to the bilayer region only, and the surrounding area is dark black, meaning that no WS₂ appears around it. These Raman mappings confirm that the small, top layer is a pure WS₂ monolayer and that the bottom, large layer is a pure MoS₂ monolayer.

Figure 6-5 Raman characterization of the vertical heterostructure.[134] (a) Optical image of the vertical heterostructure sample. (b) Raman spectra collected at positions 1, 2, 3 and 4, as labeled in (a). (c) Raman mapping at 384 cm⁻¹. (d) Raman mapping at 357 cm⁻¹.

6.2.4 PL characterization of the WS₂/MoS₂ vertical heterostructure

PL is another effective method to characterize the TMDs. Here, PL is also applied to characterize the vertical heterostructure of WS₂/MoS₂. Similar to the Raman characterization, four PL spectra are collected from a bilayer sample, as shown in figure 6-6(a). In spectra 1 and 2, which are collected from the monolayer region, there is only one strong peak at 680 nm, corresponding to a band gap of 1.82 eV. This can be attributed to the direct excitonic transition energy in a MoS₂ monolayer, confirming

that the large monolayer region is only MoS₂. [28, 48, 146] In spectra 3 and 4, another two peaks appear at 630 nm and 875 nm, respectively. The 680 nm peak confirms the existence of the MoS₂ monolayer in the bilayer region. The peak at 630 nm (corresponding to 1.97 eV) is attributed to the direct excitonic transition energy of the WS₂ monolayer, verifying that the WS₂ monolayer exists in the bilayer region. The peak at 875 nm (1.42 eV) is observed in such a heterostructure for the first time. The peak intensity of 875 nm is comparable to that of its individual component monolayers, indicating a possible direct excitonic transition at the energy range, as predicted by previous theoretical studies. [138] PL mapping is performed on the as-grown film. Notably, localized enhancement of the PL intensity at 680 nm is observed near the step between the monolayer and bilayer regions (figure 6-6(d)), and the edge of the large monolayer triangle shows similar PL intensity to the bilayer region. This enhancement near the step edges is also demonstrated by the PL peak intensity-line profile across the step edges (figure 6-6(c)). It is also illustrated by the PL spectra collected from the region near the step (point 1) and the edge of the MoS₂ monolayer (point 2), which show an obvious intensity difference. This step enhancement of the PL peak intensity is likely due to interaction between the MoS₂ and WS₂ monolayers. This interaction is different from the edge-enhanced or homogenous PL responses that have been reported previously in monolayer TMDs. The PL intensity mapping is also performed at 875 nm. This peak is localized in the bilayer region, as shown in figure 6-6(e). The peak is also demonstrated by the peak intensity-line profile (figure 6-6(c)).

Figure 6-6 PL characterization of the vertical heterostructure.[134] (a) Optical image of the vertical heterostructure. (b) PL spectra collected at the positions labelled as 1, 2, 3 and 4 in (a). (c) PL peak intensity profiles along the black line in (a). (d) and (e) PL mapping images at 680 nm and 875 nm, respectively.

6.2.5 Raman and PL characterization of the WS₂/MoS₂ heterostructure stacked by transfer

Raman and PL spectra are collected on a stacked WS₂/MoS₂ heterostructure made by the transfer method (figure 6-7) for comparison. These Raman spectra are almost identical to the WS₂/MoS₂ bilayer made from direct growth (figure 6-7(b)); however, the PL peak at 875 nm (from the interlayer coupling) disappears in the PL spectrum of the transferred bilayer sample. The absence of this peak may be due to interlayer

contamination caused during the transfer, which blocks the interaction between the monolayers. These results demonstrate the advantage of directly synthesizing heterostructures with this one-step CVD method, as no sample transfer is required, and there is no contamination between the layers.

Figure 6-7 Raman and PL characterizations of the transferred WS₂/MoS₂ heterostructure.[134] (a) Optical image of the transferred vertical heterostructure. (b) Raman spectra collected at positions labelled as 1, 2 and 3 in (a). (c) PL spectra of the as-grown and transferred WS₂/MoS₂ vertical heterostructures, respectively. The peak at 875 nm disappears in the PL spectrum collected at the transferred vertical heterostructure.

6.2.6 STEM characterization of the WS₂/MoS₂ vertical heterostructure

ADF imaging and element mapping via electron energy-loss spectroscopy (EELS) in an aberration-corrected STEM were performed to further explore the atomic structure of the stacked WS₂/MoS₂ bilayer. Figure 6-8(a) shows the morphology of a piece of the as-grown WS₂/MoS₂ heterostructure after it is transferred to a TEM grid in a low-magnified ADF image. Since the intensity of an ADF image is determined by the thickness and atomic weight of the sample, a WS₂ monolayer should be brighter than a MoS₂ monolayer, and the image intensity of the bilayer heterostructure should

be roughly as high as the sum of the intensities of its component monolayers. The ADF-TEM image (figure 6-8(a)) is displayed in a false-color scale to highlight different regions in the sample. The continuous bilayer heterostructure (in orange) covers most of the sample, and both the MoS₂ monolayer domain (in blue) and the WS₂ monolayer domain (in green) appear along some broken edges, which are induced intentionally. A magnified ADF image of the highlighted square region in figure 6-8(a) is shown in figure 6-8(b). The image intensity-line profile in figure 6-8(c) shows a clear contrast step across the two atomic layers, demonstrating the presence of separate MoS₂ and WS₂ monolayers instead of a homogeneous Mo_xW_{1-x}S₂ alloy. The chemical identity of each individual layer is further confirmed by EELS. EELS spectra collected from the individual MoS₂ and WS₂ monolayers (the green and blue squares, respectively, in figure 6-8(b)) show distinct, fine structures for the molybdenum N-edge in MoS₂ and the tungsten O-edge in WS₂ (figure 6-8(d)). Element mapping of Mo, W and S (figure 6-8(e)) from the region shown in figure 6-8(b) demonstrates unambiguously that MoS₂ and WS₂ are segregated into two different atomic layers, which compose the heterostructure in the bilayer region.

Figure 6-8 STEM-ADF image and EELS mapping of the as-grown WS₂/MoS₂ vertical heterostructure.[134] (a) Low-magnification ADF image of the sample. The image is displayed in a false-color scale so that the MoS₂ monolayer is blue, the WS₂ monolayer is green, and the WS₂/MoS₂ vertical heterostructure is orange. (b) Magnified image of the region highlighted in (a), shown in grayscale. (c) ADF image intensity profile along the dashed yellow line in (b). (d) Tungsten O-edge and molybdenum N-edge fine structures extracted from the EELS spectra acquired at the highlighted blue and green regions in (b), respectively. (e) Mo, W, and S elemental mapping from the same region shown in (b). (f)

Z-contrast image of the bilayer. The brighter columns stand for overlapping columns of W and S₂, and the dim columns are the overlap of Mo and S₂. A substitution of a W atom with a Mo atom in the WS₂ layer is pointed out with a green arrow. Below: image intensity profile acquired along the dashed yellow line in the top image. (g) ADF image of the WS₂/MoS₂ vertical heterostructure at the edge of the step. The edge of the step is pointed out with a green dashed line, and the orientation of the MoS₂ and WS₂ atomic layers are demonstrated by two triangles. Inset: the FFT diffraction pattern of the ADF image. (h) Schematic of the WS₂/MoS₂ vertical heterostructure with 2H stacking.

Figure 6-8(f) shows an ADF-TEM image of a bilayer region of WS₂/MoS₂. Bright and dim atomic columns appear alternately in a hexagonal lattice structure in the image; the bright column consists of a W atom aligned with a S₂ column, and the dim column consists of a Mo atom aligned with a S₂ column, which indicates that the WS₂ and MoS₂ monolayers stack with a 2H order, as shown in the schematic image in figure 6-8(h). A similar arrangement is also observed at the step edge of the heterostructure (figure 6-8(g)). The perfect 2H stacking of the heterostructure demonstrates the advantage of the CVD growth method (relative to the mechanical transfer method) in controlling the stacking orientation with which the orientation of the heterostructure is uncontrolled. Trace substitution of W atoms with Mo atoms in the WS₂ layer is also observed occasionally, as indicated by reduced brightness at the W atomic site (labeled by green arrows in figure 6-8(f) and the corresponding intensity-line profile). Substitutions of Mo atoms are observed as well. However, all these substitutions are at very low concentrations and thus have a minimal effect on the properties of the component monolayers.

6.2.7 Electrical transport characterization of the WS₂/MoS₂ vertical heterostructure

In order to test the electrical transport properties of the vertical heterostructure, back-gate FETs are fabricated with e-beam lithography on the bilayer WS₂/MoS₂ heterostructure film prepared by the CVD method (figure 6-9(a)). For comparison, the same electrical measurements are carried out for monolayer MoS₂ on the same substrate, CVD-grown bilayer MoS₂, and WS₂/MoS₂ bilayer made by the transfer method. The results are summarized in figure 6-9(b), showing the correlation between the source drain resistance and the back-gate voltage of different devices. The on/off ratio of the CVD WS₂/MoS₂ bilayer thin film is larger than 10⁶, and the calculated mobility ranges from 15 to 34 cm²V⁻¹s⁻¹, with an average of 25 cm²V⁻¹s⁻¹. In contrast, the average mobility of the monolayer MoS₂ is about 4.5 cm²V⁻¹s⁻¹, comparable to the results reported for other CVD-grown single crystalline MoS₂ monolayers tested by back-gating configurations. The mobility of the MoS₂ bilayer, with an average of 5.7 cm²V⁻¹s⁻¹, is slightly higher than that of the MoS₂ monolayer. In sharp contrast, the WS₂/MoS₂ bilayer made by the transfer method shows poor FET performance, possibly due to contamination between the layers. Thus, the direct-growth WS₂/MoS₂ bilayer has significantly higher mobility than do the MoS₂ monolayer, the bilayer grown under similar conditions, or the WS₂/MoS₂ bilayer by transfer. This may be due to the modified electronic structure that provides an additional channel for the electrons. The better electrical performance of the grown bilayer WS₂/MoS₂ heterostructure further demonstrates the advantages of this one-step CVD growth method.

Figure 6-9 Electrical transport characterization.[134] (a) A typical STEM image of a FET device from the WS₂/MoS₂ bilayer stacks. (b) A typical plot of gating voltage versus the source/drain currents of the CVD-grown WS₂/MoS₂ bilayer, transferred WS₂/MoS₂ bilayer, and the MoS₂ monolayer, demonstrating that the CVD-grown WS₂/MoS₂ bilayer has the best performance. The V_{ds} is fixed at 0.5 V.

6.3 Summary

In summary, a high-quality vertically stacked WS₂/MoS₂ bilayer heterostructure with large scale and high yield can be achieved through a direct, one-step CVD. The heterostructure is revealed to predominantly use 2H stacking between the WS₂ and MoS₂ layers. The observation of an additional peak in the PL spectra, which is caused by the new direct-band gap from the strong coupling between MoS₂ and WS₂ layers, confirms the theoretical prediction and provides a prototypical example for exploring the interlayer excitonic behavior and band-gap engineering of TMDs' thin layers. This one-step direct growth method may also apply to other heterostructures between different TMD materials, further increasing the diversity of the 2D materials family.

Chapter 7 Growth and Characterization of WS₂-MoS₂ Lateral

Heterostructure

In this part, lateral WS₂-MoS₂ heterostructures are synthesized with one-step CVD, and the structure and the electrical properties of this heterostructure are characterized and evaluated.

7.1 Growth of the WS₂-MoS₂ lateral heterostructure

As shown in figure 7-1, the setup and source for the growth are identical to those of the vertical heterostructure. The only difference is the growth temperature, which was 800 °C for the growth of the vertical heterostructure but is 650 °C here for the growth of the lateral heterostructure. Typically, the setup is heated to 650 °C in 13 min, and it remains at this temperature for 20 min before cooling down to room temperature naturally.

Figure 7-1 Schematic image of the CVD setup for the growth of the WS₂-MoS₂ lateral heterostructure.

7.2 Characterization of the WS₂-MoS₂ lateral heterostructure

7.2.1 Optical characterization of the WS₂-MoS₂ lateral heterostructure

The growth result is characterized with an optical microscope, as shown in figure 7-2. A small pink triangle is surrounded by a larger triangle with a light pink color (figure 7-2(a)). These two triangles can be distinguished due to the weak color contrast, which indicates a composition difference. The small triangle is as large as 20 μm , and the surrounding triangle reaches 40 μm . These triangles are arranged in the same direction. The enlarged optical image of one edge is shown in figure 7-2(b), which shows a sharp interface. Similar to the CVD growth of MoS₂, some of the triangle domains merge together into connected films (figure 7-2(c)). The center parts of each flake are labelled with dashed white circles. Further characterization proves that the center, dark parts are MoS₂ monolayers and that the surrounding parts are monolayers of WS₂. Considering that MoS₂ is an N-type semiconductor and that WS₂ is a P-type semiconductor, this merging behavior opens up the possibility of building up monolayer lateral triodes or even more complicated devices. More interestingly, the outline of MoS₂ and WS₂ are found to always have similar shapes but different sizes. In other words, the interface is always parallel with the edge of the WS₂ contour.

Figure 7-2 Optical images of the as-grown lateral heterostructures.[134] (a)

Optical image of a single heterostructure flake. The central part and

surrounding area can be distinguished by the weak color contrast. (b)

Enlarged image showing a sharp interface between the two domains. (c) A

heterostructure film forms when different flakes merge together.

7.2.2 AFM characterization of the WS₂-MoS₂ lateral heterostructure

The thickness of the lateral heterostructure is characterized with AFM. The height topography (figure 7-3(a)) clearly shows that the samples are continuous and uniform. However, it is difficult to observe the interface between the center parts and the surroundings. This should be due to the similar thicknesses of the WS₂ and MoS₂ monolayers. The height profile (figure 7-3(b)) with a step of 0.8 nm confirms that both the center MoS₂ and the outer WS₂ domains are monolayers, providing strong evidence of the monolayer's in-plane heterostructure.

Figure 7-3 AFM characterization of the lateral heterostructure.[134] (a)

The height topography shows a continuous and uniform film. (b) The

height profile shows that the as-grown heterostructure is a monolayer.

7.2.3 Raman characterization of the WS₂-MoS₂ lateral heterostructure

Figure 7-4(a) is an optical image of the lateral heterostructure, which has a clear interface. There are three marked points for the Raman spectra (figure 7-4(b)). The center layer shows two peaks (at 381.9 cm⁻¹ and 405.3 cm⁻¹), which correspond to the E_{2g}¹ and A_{1g} modes of the MoS₂ monolayer. For the surrounding area, two peaks at 350.8 cm⁻¹ and 416.4 cm⁻¹ appear in Raman spectrum 3, and these can be assigned to the 2LA(M) and A_{1g} modes of the WS₂ monolayer. In the interface area, the peaks from both the MoS₂ and WS₂ monolayers are present. The direct images of the distribution of MoS₂ and WS₂ are given by the corresponding Raman intensity mapping at 381 cm⁻¹ and 351 cm⁻¹ (figures 7-4c and 4d), which confirms that the center part is an MoS₂ monolayer and that the surrounding area is a WS₂ monolayer.

Figure 7-4 Raman characterization of the as-grown lateral heterostructure.

[134] (a) Optical microscope image of a piece of the as-grown lateral heterostructure. (b) Raman spectra from the points labeled in (a). (c) Raman mapping of figure (a) at 381 cm^{-1} , showing that the center of the flake is a uniform MoS_2 domain. (d) Raman mapping at 352 cm^{-1} , showing that the surrounding part is a uniform WS_2 domain.

7.2.4 PL characterization of the WS_2 - MoS_2 heterostructure

PL characterization is performed on the same sample (figure 7-5(a)). PL spectra of the points marked 1 through 5 in figure 7-5(a) are shown in figure 7-5(b); these points run from the surrounding WS_2 area, across the interface, to the center MoS_2 area. The peak positions of points 1 and 5 are 630 nm and 680 nm, respectively. These

correspond to the direct excitonic transition energies of 1.97 eV and 1.82 eV, respectively indicating pristine WS₂ and pristine MoS₂. Points 2 and 4 are still in the WS₂ and MoS₂ areas, respectively, but they are very close to the interface. The peaks shift from 630 nm to 638 nm and from 680 nm to 671 nm. Interestingly, the PL peak at the interface has a broader and stronger PL peak, located at 650 nm. This indicates a strong coupling effect at the interface. A comparison of the PL spectrum at the edge of the interface (point 3), the spectrum at the corner of the interface (point 6), and the superposition of the spectra from pure MoS₂ (point 5) and pure WS₂ (point 1) is exhibited in figure 7-5(c). The obvious difference between these spectra indicates that there is a strong coupling effect near the interface rather than a simple superposition of MoS₂ and WS₂. Notably, the peak intensity at the edge of the interface is much stronger than the intensity at the corner. Figures 7-5(d) and 7-5(e) are PL intensity mappings at 630 nm and 680 nm, respectively; these confirm the distribution of MoS₂ and WS₂. The PL peak intensity mapping at 650 nm (figure 7-5(f)) demonstrates that the 650-nm peak only appears around the interface and that the intensity is much stronger at the edge of the interface than it is at corner, which is in agreement with the PL spectra shown in figure 7-5(c). Similar localized PL intensity enhancement is also observed with the PL microscope (figure 7-5(g)), which is consistent with the PL mapping at 650 nm. This enhancement is likely caused by the coupling effect at the edge of the interface.

Figure 7-5 PL characterization of the as-grown lateral heterostructure.[134]

(a) Optical image of an as-grown flake. (b) PL spectra collected at points 1-5 in (a). (c) PL spectra collected at points 3 and 6 and the superposition of the spectra at points 1 and 5. (d) PL intensity mapping at 630 nm showing that the surrounding parts consist of monolayer WS_2 . (e) PL intensity mapping at 680 nm showing that the center part is the monolayer MoS_2 domain. (f) PL mapping at 650 nm showing high intensity along the interface between the MoS_2 and WS_2 domains. (g) PL microscope image of the flake showing high intensity along the interface, similar to the PL mapping at 650 nm.

7.2.5 STEM characterization of the WS₂-MoS₂ lateral heterostructure

The interface between the MoS₂ and WS₂ domains is further characterized by STEM. Figure 7-6(a) shows the ADF image of the interface's overall morphology between two domains at low magnification, indicating the homogeneity of the film within the individual domain. Since the intensity in the ADF-STEM image directly relates to the atomic number of the imaged species, and since the W domain has a much higher intensity than do the Mo, the W domain can be easily identified by its intensity profile, as indicated in figure 7-6(b). The sharp intensity change across the interface indicates a narrow transition region between the MoS₂ and WS₂ domains, with an estimated width of about 3 nm based on the intensity drop. However, the lateral MoS₂-WS₂ boundaries are indeed atomically sharp along each individual growth direction in the same atomic plane, where the overall interface consists of boundaries in several growth orientations, as will be discussed in the manuscript thesis. Figure 7-6(c) shows the in-plane MoS₂-WS₂ boundary structure with higher magnification. The corresponding atom-by-atom mapping is shown in figure 7-6(d). The overall transition width between the two domains is estimated by the averaged local W concentration integrated along the atomic planes parallel to the overall boundary direction. The result, as shown in figure 7-6(e), indicates that the transition region maintains a width of about 3 nm, which is consistent with the intensity analysis in figure 7-6(b). Such high-quality in-plane boundary structures, in which the composition of one semiconducting monolayer changes completely within several atomic planes, provide a novel platform for exploring the intralayer coupling effect and further demonstrate the advantage of this one-step CVD method. Though substitutions of single tungsten atoms are observed on the MoS₂ side (and vice versa),

the concentration is relatively low ($\sim 5\%$), which has a limited effect on the individual MoS_2 domain.

Figure 7-6 ADF-STEM characterization of the lateral heterostructure.[134]

(a) Low-magnification ADF-STEM image of the interface between the MoS_2 and WS_2 domain. (b) Line intensity profile integrated along the white dashed rectangle in (a), where the width of the intensity change is estimated to within 1 nm. (c) Z-contrast STEM image of the in-plane boundary between the MoS_2 and WS_2 domains. The yellow dashed lines

indicate the roughness of the interface. (d) Atomic mapping of the Mo and W atoms' distribution in (c). (e) W concentration estimated along the axis perpendicular to the yellow dashed line (the overall direction of the interface), which averages the W concentration in each individual atomic plane. The width of the boundary is estimated to be within four unit cells. The Mo concentration in the WS₂ side is 0.2%, and the W concentration in the MoS₂ side is about 7.4%.

Two types of the connections are observed at the interface between the MoS₂ and WS₂ domains, as shown in figure 7-7. The pink and the orange dashed lines show the atomic planes along the zigzag and armchair directions, respectively, which further illustrates that the WS₂ and MoS₂ regions share the same crystal orientation. Such an interface indicates that the WS₂ monolayer grows directly from the MoS₂ edge in what is called lateral epitaxial growth. In figure 7-7(a) and (b), the WS₂ is grown along the zigzag direction of the MoS₂ domain. The WS₂ also grows along the armchair direction of the MoS₂ domain, as observed in figure 7-7(c). The atomic models on the right sides of figure 7-7(b) and (c) show the sharp interfaces along the zigzag and armchair directions, respectively. In some areas, seamless connections appeared along both the zigzag and the armchair directions, and these connections formed a 90 ° angle at the corner, as shown in figure 7-7(d).

Figure 7-7 ADF-STEM characterization of the interface boundary between the WS₂ and MoS₂ domains.[134] (a) A sharp boundary along the interface between the WS₂ and MoS₂ domains. The orange and pink dashed lines show the armchair and zigzag directions, respectively. (b) A boundary along the zigzag direction between the two domains. (c) A boundary along the armchair direction between the two domains. The right parts of (b) and (c) show the atomic models of these two structures. (d) A boundary along both the zigzag and armchair directions forms a nearly 90 °corner between the two domains.

7.2.6 Electrical transport properties of the WS₂-MoS₂ lateral heterostructure

The electrical property of the lateral heterostructure is evaluated in PN junction devices. Figure 7-8(a) shows the configurations of a PN junction device based on the WS₂-MoS₂ lateral heterostructure. Electrodes of 5-nm titanium and 35-nm gold were deposited on top of the junction after the e-beam lithography process. Figure 7-8(b) shows the I-V curves of the junction with and without illumination. When there is no illumination and the junction is forward-biased with a voltage larger than 1.5 eV, the diffusion current is larger than the drifting current. With a bias larger than 1.5 eV, the current increases exponentially. With a reverse bias, the junction shuts down with a reverse current on the order of pico-amperes (pA); in other words, the forward-biased current is two orders of magnitude larger than the reversed-bias current, which gives the WS₂-MoS₂ junction a good rectification character, indicating that it can play the role of a diode in a 2D electronics application. With illumination (532 nm, 1000 mW/cm²), the junction shows strong photo response: a 60 pA photocurrent under +3 V bias and a -30 pA photocurrent under -3 V bias. Obviously, this structure is suitable for use in a photodetector; although the photocurrent is weak, the dark current is two orders of magnitude smaller in this range, and it yields a higher signal-to-noise ratio.

Figure 7-8 Electrical characterization of the lateral heterostructure.[134] (a) Optical image of a PN junction device. The scale bar is 10 μm . (b) I-V curves with and /without illumination.

7.3 Summary

An atomic lateral heterostructure based on WS_2 and MoS_2 monolayers is successfully synthesized with the CVD method. In this heterostructure, the MoS_2 monolayer domains are surrounded by a WS_2 monolayer with a sharp interface that has a width of about 3 nm. This structure is confirmed by Raman, PL and STEM characterization. The STEM images show that the domains are connected along both the zigzag and armchair directions. As the WS_2 and MoS_2 monolayer are intrinsic P-type and N-type semiconductors, respectively, a PN junction forms between the WS_2 and MoS_2 domains; this finding is confirmed by electrical characterization. This structure is also suitable for use as a photodetector, as the current can be two orders of magnitude higher with illumination than that without illumination.

Chapter 8 Conclusions and Recommendations

8.1 Conclusions

The major findings and contributions of this PhD study include the following:

- MoS₂ monolayers with sizes as large as 1 mm are synthesized with CVD. The sizes of the MoS₂ monolayers depend strongly on the growth temperature. The MoS₂ monolayers are of high quality, as confirmed by Raman, PL, STEM and electrical characterizations.
- MoSe₂ monolayers are synthesized with CVD. The AFM, Raman and PL characterizations prove that the as-grown MoSe₂ films are monolayers. STEM presents a perfect hexagonal crystal structure, and XPS shows a Mo/Se ratio of 1:1.97, suggesting that the CVD-grown MoSe₂ is reasonably stoichiometric. These MoSe₂ monolayers show an average mobility of 50 cm²V⁻¹s⁻¹ as N-type channels.
- WS₂ monolayers are grown by sulfurizing tungsten powder. A new recipe for the growth of the WS₂ monolayer is explored. The WS₂ monolayer is confirmed by Raman and PL characterizations. XPS demonstrates that no tellurium appear in the WS₂ monolayer after growth.
- Vertical heterostructures based on WS₂ and MoS₂ monolayers are synthesized with one-step CVD. In this structure, the WS₂ monolayer stacks on top of the MoS₂ monolayer. This structure is confirmed by Raman, PL, and STEM. High carrier mobility has been shown with the vertical heterostructure.
- Lateral heterostructures based on WS₂ and MoS₂ monolayers are synthesized with one-step CVD. In this structure, the MoS₂ monolayer domains are surrounded by WS₂ monolayer domains. The interfaces between neighboring

domains are as narrow as 3 nm. PN junctions form between the WS₂ and MoS₂ domains, as demonstrated by the electrical transport characterization.

8.2 Recommendations for Further Work

8.2.1 Exploration of the effects of other growth parameters

The growth result is determined by the growth recipe parameters. Some groups have also demonstrated the effect of the seed, and the effect of growth temperature is shown in chapter 3. Aside from temperature, other parameters are involved in growth, including the source ratio, carrier gas flow, pressure and so on. How these parameters affect the growth result needs further exploration.

How do these growth parameters affect the growth of other TMD monolayers? Will the same or similar trends appear? These issues will be solved in the future.

8.2.2 Exploration of the growth of other TMD materials

There are more than 40 kinds of TMDs available,[25] and different monolayers have different performances; for example, hafnium diselenide is calculated to have the highest mobility (about ten times higher than the MoS₂ monolayer),[24] and vanadium dichalcogenides show intrinsic ferromagnetic properties.[153, 154] However, most of the research now is focused on MoS₂. More attention should be paid to the growth, characterization and application of other TMD monolayers.

8.2.3 Exploration of other TMD heterostructures

Chapter 8 Conclusions and Recommendations

In this study, both vertical and lateral heterostructures based on MoS₂ and WS₂ monolayers are shown to grow successfully. However, the exploration of these heterostructures should not stop here. In further work, these heterostructures will serve as platforms for both fundamental research studies and device fabrications.

On the other hand, as many other TMD monolayers are available, many combinations of heterostructures remain to be explored. In addition, novel heterostructures based on more than two component monolayers can be created. The growth and characterization of these heterostructures will be explored as well. Simulation and calculation before the experimental work will help target the proper heterostructures and provide theoretical explanation for the phenomena that will be observed.

Author's Publications

Peer-Reviewed Journal Publications

1. C. Zhu, P. Yang, D. Chao, X. Wang, X. Zhang, S. Chen, B. K. Tay, H. Huang, H. Zhang, W. Mai, H. J. Fan, All Metal Nitrides Solid-State Asymmetric Supercapacitors. *Advanced Materials*, (2015).
2. H. Li, A. W. Contryman, X. Qian, S. M. Ardakani, Y. Gong, X. Wang, J. M. Weisse, C. H. Lee, J. Zhao, P. M. Ajayan, J. Li, H. C. Manoharan, X. Zheng, Optoelectronic crystal of artificial atoms in strain-textured molybdenum disulphide. *Nature Communications* 6, (2015); published online.
3. W. Liu, C. Lu, X. Wang, R. Y. Tay, B. K. Tay, High-Performance Microsupercapacitors Based on Two-Dimensional Graphene/Manganese Dioxide/Silver Nanowire Ternary Hybrid Film. *ACS Nano* 9, 1528-1542 (2015).
4. W. Liu, C. Lu, X. Wang, K. Liang, B. K. Tay, In situ fabrication of three-dimensional, ultrathin graphite/carbon nanotube/NiO composite as binder-free electrode for high-performance energy storage. *Journal of Materials Chemistry A* 3, 624-633 (2015).
5. C. Lu, W.-w. Liu, X. Wang, X. Li, C. W. Tan, B. K. Tay, P. Coquet, Solid source growth of Si oxide nanowires promoted by carbon nanotubes. *Applied Surface Science* 314, 119-123 (2014).
6. Y. Gong*, J. Lin*, X. Wang*, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B. I. Yakobson, H. Terrones, M. Terrones, Beng K. Tay, J. Lou, S. T. Pantelides, Z. Liu, W. Zhou, P. M. Ajayan, Vertical and in-plane heterostructures from WS₂/MoS₂

Author's Publications

monolayers. *Nature Materials* 13, 1135-1142 (2014). (* contributed equally to this work)

7. **X. Wang**, Y. Gong, G. Shi, W. L. Chow, K. Keyshar, G. Ye, R. Vajtai, J. Lou, Z. Liu, E. Ringe, B. K. Tay, P. M. Ajayan, Chemical Vapor Deposition Growth of Crystalline Monolayer MoSe₂. *ACS Nano* 8, 5125-5131 (2014).

8. R. Y. Tay, **X. Wang**, S. H. Tsang, G. C. Loh, R. S. Singh, H. Li, G. Mallick, E. H. Tong Teo, A systematic study of the atmospheric pressure growth of large-area hexagonal crystalline boron nitride film. *Journal of Materials Chemistry C* 2, 1650-1657 (2014).

Conference Papers

1. **X. Wang**, W.L. Chow, J. Gusakova, B.K. Tay, Z. Liu, Growth of monolayer molybdenum disulfide and diselenide with chemical vapor deposition, *Nanomeeting* 2015, Minsk, Belarus.

2. **X. Wang**, C. Lu, W.L. Chow, Z. Liu, B.K. Tay, Growth of MoS₂ layers with various shapes and stacks with vapor solid deposition, *Graphene Week 2015*, Manchester, UK.

3. V. Labunov, A. Prudnikava, B. Shulitski, B.K. Tay, **X. Wang**, A. Basaev, V. Galperin, Y. Shaman, Self-Organized Hybrid Nanostructures Composed of the Array of Vertically Aligned Carbon Nanotubes and Planar Graphite Layer, *Nanoelectronics Conference (INEC) 2013*, Singapore

.

Bibliography

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, *Science*, 306 (2004) 666-669.
- [2] S.Z. Butler, S.M. Hollen, L. Cao, Y. Cui, J.A. Gupta, H.R. Gutiérrez, T.F. Heinz, S.S. Hong, J. Huang, A.F. Ismach, E. Johnston-Halperin, M. Kuno, V.V. Plashnitsa, R.D. Robinson, R.S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M.G. Spencer, M. Terrones, W. Windl, J.E. Goldberger, Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene, *ACS NANO*, 7 (2013) 2898-2926.
- [3] G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, S.K. Banerjee, L. Colombo, Electronics based on two-dimensional materials, *Nat Nano*, 9 (2014) 768-779.
- [4] Ten years in two dimensions, *Nat Nano*, 9 (2014) 725-725.
- [5] A.C. Ferrari, F. Bonaccorso, V. Fal'ko, K.S. Novoselov, S. Roche, P. Boggild, S. Borini, F.H.L. Koppens, V. Palermo, N. Pugno, J.A. Garrido, R. Sordan, A. Bianco, L. Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhanen, A. Morpurgo, J.N. Coleman, V. Nicolosi, L. Colombo, A. Fert, M. Garcia-Hernandez, A. Bachtold, G.F. Schneider, F. Guinea, C. Dekker, M. Barbone, Z. Sun, C. Galiotis, A.N. Grigorenko, G. Konstantatos, A. Kis, M. Katsnelson, L. Vandersypen, A. Loiseau, V. Morandi, D. Neumaier, E. Treossi, V. Pellegrini, M. Polini, A. Tredicucci, G.M. Williams, B. Hee Hong, J.-H. Ahn, J. Min Kim, H. Zirath, B.J. van Wees, H. van der Zant, L. Occhipinti, A. Di Matteo, I.A. Kinloch, T. Seyller, E. Quesnel, X. Feng, K. Teo, N. Rupesinghe, P. Hakonen, S.R.T. Neil, Q. Tannock, T. Lofwander, J. Kinaret, Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems, *Nanoscale*, 7 (2015) 4598-4810.

Bibliography

- [6] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, *Nature Nanotechnology*, 7 (2012) 699-712.
- [7] F.H.L. Koppens, T. Mueller, P. Avouris, A.C. Ferrari, M.S. Vitiello, M. Polini, Photodetectors based on graphene, other two-dimensional materials and hybrid systems, *Nat Nano*, 9 (2014) 780-793.
- [8] Graphene and Human Brain Project win largest research excellence award in history, as battle for sustained science funding continues, http://europa.eu/rapid/press-release_IP-13-54_en.htm, (2013).
- [9] X.F. Song, J.L. Hu, H.B. Zeng, Two-dimensional semiconductors: recent progress and future perspectives, *Journal of Materials Chemistry C*, 1 (2013) 2952-2969.
- [10] H. Schmidt, F. Giustiniano, G. Eda, Electronic transport properties of transition metal dichalcogenide field-effect devices: surface and interface effects, *Chemical Society Reviews*, (2015).
- [11] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Emerging Device Applications for Semiconducting Two-Dimensional Transition Metal Dichalcogenides, *ACS Nano*, 8 (2014) 1102-1120.
- [12] L. Britnell, R.V. Gorbachev, R. Jalil, B.D. Belle, F. Schedin, A. Mishchenko, T. Georgiou, M.I. Katsnelson, L. Eaves, S.V. Morozov, N.M.R. Peres, J. Leist, A.K. Geim, K.S. Novoselov, L.A. Ponomarenko, Field-Effect Tunneling Transistor Based on Vertical Graphene Heterostructures, *Science*, 335 (2012) 947-950.
- [13] M. Buscema, J.O. Island, D.J. Groenendijk, S.I. Blanter, G.A. Steele, H.S.J. van der Zant, A. Castellanos-Gomez, Photocurrent generation with two-dimensional van der Waals semiconductors, *Chemical Society Reviews*, (2015).

- [14] M.P. Levendorf, C.-J. Kim, L. Brown, P.Y. Huang, R.W. Havener, D.A. Muller, J. Park, Graphene and boron nitride lateral heterostructures for atomically thin circuitry, *Nature*, 488 (2012) 627-632.
- [15] Z. Liu, LuluMa, G. Shi, W. Zhou, Y. Gong, S. Lei, X. Yang, J. Zhang, J. Yu, K.P. Hackenberg, A. Babakhani, J.-C. Idrobo, R. Vajtai, J. Lou, P.M. Ajayan, In-plane heterostructures of graphene and hexagonal boron nitride with controlled domain sizes, *nature Nanotechnology*, 8 (2013) 6.
- [16] M. Xu, T. Liang, M. Shi, H. Chen, Graphene-like two-dimensional materials, *Chemical Reviews*, 113 (2013) 3766-3798.
- [17] P. Miro, M. Audiffred, T. Heine, An atlas of two-dimensional materials, *Chemical Society Reviews*, 43 (2014) 6537-6554.
- [18] Y. Guo, D. Liu, J. Robertson, Chalcogen vacancies in monolayer transition metal dichalcogenides and Fermi level pinning at contacts, *Applied Physics Letters*, 106 (2015) 173106.
- [19] J. Kang, S. Tongay, J. Zhou, J. Li, J. Wu, Band offsets and heterostructures of two-dimensional semiconductors, *Applied Physics Letters*, 102 (2013) 012111.
- [20] N. Huo, J. Kang, Z. Wei, S.-S. Li, J. Li, S.-H. Wei, Novel and Enhanced Optoelectronic Performances of Multilayer MoS₂–WS₂ Heterostructure Transistors, *Advanced Functional Materials*, 24 (2014) 7025-7031.
- [21] X. Duan, C. Wang, J.C. Shaw, R. Cheng, Y. Chen, H. Li, X. Wu, Y. Tang, Q. Zhang, A. Pan, J. Jiang, R. Yu, Y. Huang, X. Duan, Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions, *Nat Nano*, 9 (2014) 1024-1030.
- [22] K.S. Novoselov, Nobel Lecture: Graphene: Materials in the Flatland*, *Reviews of Modern Physics*, 83 (2011) 837-849.

Bibliography

- [23] Z. Liu, L. Ma, G. Shi, W. Zhou, Y. Gong, S. Lei, X. Yang, J. Zhang, J. Yu, K.P. Hackenberg, A. Babakhani, J.-C. Idrobo, R. Vajtai, J. Lou, P.M. Ajayan, In-plane heterostructures of graphene and hexagonal boron nitride with controlled domain sizes, *Nat Nano*, 8 (2013) 119-124.
- [24] W.X. Zhang, Z.S. Huang, W.L. Zhang, Y.R. Li, Two-dimensional semiconductors with possible high room temperature mobility, *Nano Research*, 7 (2014) 1731-1737.
- [25] C. Ataca, H. Sahin, S. Ciraci, Stable, Single-Layer MX_2 Transition-Metal Oxides and Dichalcogenides in a Honeycomb-Like Structure, *Journal of Physical Chemistry C*, 116 (2012) 8983-8999.
- [26] H. Zhang, L.M. Liu, W.M. Lau, Dimension-dependent phase transition and magnetic properties of VS_2 , *Journal of Materials Chemistry A*, 1 (2013) 10821-10828.
- [27] M. Chhowalla, H.S. Shin, G. Eda, L.-J. Li, K.P. Loh, H. Zhang, The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets, *Nature chemistry*, 5 (2013) 263-275.
- [28] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, Photoluminescence from chemically exfoliated MoS_2 , *Nano Lett*, 11 (2011) 5111-5116.
- [29] R.A. Gordon, D. Yang, E.D. Crozier, D.T. Jiang, R.F. Frindt, Structures of exfoliated single layers of WS_2 , MoS_2 , and MoSe_2 in aqueous suspension, *Physical Review B*, 65 (2002) 125407.
- [30] D. Voiry, A. Mohite, M. Chhowalla, Phase engineering of transition metal dichalcogenides, *Chemical Society Reviews*, (2015).

- [31] R. Kappera, D. Voiry, S.E. Yalcin, B. Branch, G. Gupta, A.D. Mohite, M. Chhowalla, Phase-engineered low-resistance contacts for ultrathin MoS₂ transistors, *Nat Mater*, 13 (2014) 1128-1134.
- [32] Y.C. Lin, D.O. Dumcenco, Y.S. Huang, K. Suenaga, Atomic mechanism of the semiconducting-to-metallic phase transition in single-layered MoS₂, *Nat Nanotechnol*, 9 (2014) 391-396.
- [33] D. Nasr Esfahani, O. Leenaerts, H. Sahin, B. Partoens, F.M. Peeters, Structural Transitions in Monolayer MoS₂ by Lithium Adsorption, *The Journal of Physical Chemistry C*, 119 (2015) 10602-10609.
- [34] K.-A.N. Duerloo, Y. Li, E.J. Reed, Structural phase transitions in two-dimensional Mo- and W-dichalcogenide monolayers, *Nat Commun*, 5 (2014).
- [35] G. Eda, T. Fujita, H. Yamaguchi, D. Voiry, M. Chen, M. Chhowalla, Coherent Atomic and Electronic Heterostructures of Single-Layer MoS₂, *ACS NANO*, 6 (2012) 7311-7317.
- [36] C. Lee, H. Yan, L.E. Brus, T.F. Heinz, J. Hone, S. Ryu, Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂, *Acs Nano*, 4 (2010) 2695-2700.
- [37] P. Tonndorf, R. Schmidt, P. Bottger, X. Zhang, J. Borner, A. Liebig, M. Albrecht, C. Kloc, O. Gordan, D.R.T. Zahn, S.M. de Vasconcellos, R. Bratschitsch, Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂, *Optics Express*, 21 (2013) 4908-4916.
- [38] M. Yamamoto, S.T. Wang, M.Y. Ni, Y.F. Lin, S.L. Li, S. Aikawa, W.B. Jian, K. Ueno, K. Wakabayashi, K. Tsukagoshi, Strong Enhancement of Raman Scattering from a Bulk-Inactive Vibrational Mode in Few-Layer MoTe₂, in: *Acs Nano*, 2014, pp. 3895-3903.

Bibliography

- [39] G. Plechinger, S. Heydrich, J. Eroms, D. Weiss, C. Schuller, T. Korn, Raman spectroscopy of the interlayer shear mode in few-layer MoS₂ flakes, *Applied Physics Letters*, 101 (2012).
- [40] G. Plechinger, S. Heydrich, M. Hirmer, F.X. Schrettenbrunner, D. Weiss, J. Eroms, C. Schuller, T. Korn, Scanning Raman spectroscopy of few- and single-layer MoS₂ flakes, in: E.A. Dobisz, L.A. Eldada (Eds.) *Nanoengineering: Fabrication, Properties, Optics, and Devices IX*, Spie-Int Soc Optical Engineering, Bellingham, 2012.
- [41] H. Li, Q. Zhang, C.C.R. Yap, B.K. Tay, T.H.T. Edwin, A. Olivier, D. Baillargeat, From Bulk to Monolayer MoS₂: Evolution of Raman Scattering, *Advanced Functional Materials*, 22 (2012) 1385-1390.
- [42] A. Berkdemir, H.R. Gutiérrez, A.R. Botello-Méndez, N. Perea-López, A.L. Elías, C.-I. Chia, B. Wang, V.H. Crespi, F. López-Urías, J.-C. Charlier, H. Terrones, M. Terrones, Identification of individual and few layers of WS₂ using Raman Spectroscopy, *Scientific Reports*, 3 (2013).
- [43] W.J. Zhao, Z. Ghorannevis, K.K. Amara, J.R. Pang, M. Toh, X. Zhang, C. Kloc, P.H. Tan, G. Eda, Lattice dynamics in mono- and few-layer sheets of WS₂ and WSe₂, *Nanoscale*, 5 (2013) 9677-9683.
- [44] C. Cong, J. Shang, X. Wu, B. Cao, N. Peimyoo, C. Qiu, L. Sun, T. Yu, Synthesis and Optical Properties of Large-Area Single-Crystalline 2D Semiconductor WS₂ Monolayer from Chemical Vapor Deposition, *Advanced Optical Materials*, 2 (2014) 131-136.
- [45] Y. Zhao, X. Luo, H. Li, J. Zhang, P.T. Araujo, C.K. Gan, J. Wu, H. Zhang, S.Y. Quek, M.S. Dresselhaus, Q. Xiong, Interlayer Breathing and Shear Modes in Few-Trilayer MoS₂ and WSe₂, *Nano Letters*, 13 (2013) 1007-1015.

- [46] A. Kuc, N. Zibouche, T. Heine, Influence of quantum confinement on the electronic structure of the transition metal sulfide TS_2 , *Physical Review B*, 83 (2011).
- [47] W. Jin, P.-C. Yeh, N. Zaki, D. Zhang, J.T. Sadowski, A. Al-Mahboob, A.M. van der Zande, D.A. Chenet, J.I. Dadap, I.P. Herman, P. Sutter, J. Hone, R.M. Osgood, Direct Measurement of the Thickness-Dependent Electronic Band Structure of MoS_2 Using Angle-Resolved Photoemission Spectroscopy, *Physical Review Letters*, 111 (2013).
- [48] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, Atomically Thin MoS_2 : A New Direct-Gap Semiconductor, *Physical Review Letters*, 105 (2010).
- [49] S. Tongay, J. Zhou, C. Ataca, K. Lo, T.S. Matthews, J. Li, J.C. Grossman, J. Wu, Thermally driven crossover from indirect toward direct bandgap in 2D semiconductors: MoSe_2 versus MoS_2 , *Nano Lett*, 12 (2012) 5576-5580.
- [50] W.J. Zhao, Z. Ghorannevis, L.Q. Chu, M.L. Toh, C. Kloc, P.H. Tan, G. Eda, Evolution of Electronic Structure in Atomically Thin Sheets of WS_2 and WSe_2 , *Acs Nano*, 7 (2013) 791-797.
- [51] H.R. Gutierrez, N. Perea-Lopez, A.L. Elias, A. Berkdemir, B. Wang, R. Lv, F. Lopez-Urias, V.H. Crespi, H. Terrones, M. Terrones, Extraordinary Room-Temperature Photoluminescence in Triangular WS_2 Monolayers, *Nano Letters*, 13 (2013) 3447-3454.
- [52] X. Wang, Y. Gong, G. Shi, W.L. Chow, K. Keyshar, G. Ye, R. Vajtai, J. Lou, Z. Liu, E. Ringe, B.K. Tay, P.M. Ajayan, Chemical Vapor Deposition Growth of Crystalline Mono layer MoSe_2 , *Acs Nano*, 8 (2014) 5125-5131.
- [53] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A.K. Geim, Two-dimensional atomic crystals, *Proceedings of the National Academy of Sciences of the United States of America*, 102 (2005) 10451-10453.

Bibliography

- [54] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Single-layer MoS₂ transistors, *Nature Nanotechnology*, 6 (2011) 147-150.
- [55] D. Ovchinnikov, A. Allain, Y.-S. Huang, D. Dumcenco, A. Kis, Electrical Transport Properties of Single-Layer WS₂, *Acs Nano*, 8 (2014) 8174-8181.
- [56] J. Wang, D. Rhodes, S. Feng, M.A.T. Nguyen, K. Watanabe, T. Taniguchi, T.E. Mallouk, M. Terrones, L. Balicas, J. Zhu, Gate-modulated conductance of few-layer WSe₂ field-effect transistors in the subgap regime: Schottky barrier transistor and subgap impurity states, *Applied Physics Letters*, 106 (2015) 152104.
- [57] S. Larentis, B. Fallahazad, E. Tutuc, Field-effect transistors and intrinsic mobility in ultra-thin MoSe₂ layers, *Applied Physics Letters*, 101 (2012).
- [58] J. Xia, X. Huang, L.-Z. Liu, M. Wang, L. Wang, B. Huang, D.-D. Zhu, J.-J. Li, C.-Z. Gu, X.-M. Meng, CVD synthesis of large-area, highly crystalline MoSe₂ atomic layers on diverse substrates and application to photodetectors, *Nanoscale*, 6 (2014) 8949-8955.
- [59] Y.-H. Chang, W. Zhang, Y. Zhu, Y. Han, J. Pu, J.-K. Chang, W.-T. Hsu, J.-K. Huang, C.-L. Hsu, M.-H. Chiu, T. Takenobu, H. Li, C.-I. Wu, W.-H. Chang, A.T.S. Wee, L.-J. Li, Monolayer MoSe₂ Grown by Chemical Vapor Deposition for Fast Photodetection, *ACS Nano*, 8 (2014) 8582-8590.
- [60] S. Ghatak, A.N. Pal, A. Ghosh, Nature of Electronic States in Atomically Thin MoS₂ Field-Effect Transistors, *Acs Nano*, 5 (2011) 7707-7712.
- [61] B. Radisavljevic, M.B. Whitwick, A. Kis, Small-signal amplifier based on single-layer MoS₂, *Applied Physics Letters*, 101 (2012).
- [62] S. Jo, N. Ubrig, H. Berger, A.B. Kuzmenko, A.F. Morpurgo, Mono- and Bilayer WS₂ Light-Emitting Transistors, *Nano Letters*, 14 (2014) 2019-2025.

- [63] D. Jimenez, Drift-diffusion model for single layer transition metal dichalcogenide field-effect transistors, *Applied Physics Letters*, 101 (2012).
- [64] Y.J. Zhang, J.T. Ye, Y. Matsushashi, Y. Iwasa, Ambipolar MoS₂ Thin Flake Transistors, *Nano Letters*, 12 (2012) 1136-1140.
- [65] M. Fontana, T. Deppe, A.K. Boyd, M. Rinzan, A.Y. Liu, M. Paranjape, P. Barbara, Electron-hole transport and photovoltaic effect in gated MoS₂ Schottky junctions, *Scientific Reports*, 3 (2013).
- [66] H. Liu, A.T. Neal, P.D. Ye, Channel Length Scaling of MoS₂ MOSFETs, *ACS NANO*, 6 (2012) 8563-8569.
- [67] F. Zhang, J. Appenzeller, Tunability of Short-Channel Effects in MoS₂ Field-Effect Devices, *Nano Letters*, 15 (2015) 301-306.
- [68] P. Tonndorf, R. Schmidt, P. Boettger, X. Zhang, J. Boerner, A. Liebig, M. Albrecht, C. Kloc, O. Gordan, D.R.T. Zahn, S.M. de Vasconcellos, R. Bratschitsch, Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂, *Optics Express*, 21 (2013) 4908-4916.
- [69] J. Shaw, H. Zhou, Y. Chen, N. Weiss, Y. Liu, Y. Huang, X. Duan, Chemical vapor deposition growth of monolayer MoSe₂ nanosheets, *Nano Research*, 7 (2014) 511-517.
- [70] E.S. Kadantsev, P. Hawrylak, Electronic structure of a single MoS₂ monolayer, *Solid State Communications*, 152 (2012) 909-913.
- [71] H. Zeng, G.B. Liu, J. Dai, Y. Yan, B. Zhu, R. He, L. Xie, S. Xu, X. Chen, W. Yao, X. Cui, Optical signature of symmetry variations and spin-valley coupling in atomically thin tungsten dichalcogenides, *Sci Rep*, 3 (2013) 1608.
- [72] J.R. Schaibley, T. Karin, H. Yu, J.S. Ross, P. Rivera, A.M. Jones, M.E. Scott, J. Yan, D.G. Mandrus, W. Yao, K.-M. Fu, X. Xu, Population Pulsation Resonances of

Bibliography

Excitons in Monolayer MoSe₂ with Sub-1eV Linewidths, *Physical Review Letters*, 114 (2015) 137402.

[73] N. Kumar, Q. Cui, F. Ceballos, D. He, Y. Wang, H. Zhao, Exciton-exciton annihilation in MoSe₂ monolayers, *Physical Review B*, 89 (2014).

[74] G.B. Liu, W.Y. Shan, Y.G. Yao, W. Yao, D. Xiao, Three-band tight-binding model for monolayers of group-VIB transition metal dichalcogenides, *Physical Review B*, 88 (2013).

[75] Y. Zhang, Y. Zhang, Q. Ji, J. Ju, H. Yuan, J. Shi, T. Gao, D. Ma, M. Liu, Y. Chen, X. Song, H.Y. Hwang, Y. Cui, Z. Liu, Controlled Growth of High-Quality Monolayer WS₂ Layers on Sapphire and Imaging Its Grain Boundary, *ACS nano*, 7 (2013) 8963-8971.

[76] Z.-Q. Xu, Y. Zhang, S. Lin, C. Zheng, Y.L. Zhong, X. Xia, Z. Li, P.J. Sophia, M.S. Fuhrer, Y.-B. Cheng, Q. Bao, Synthesis and Transfer of Large-Area Monolayer WS₂ Crystals: Moving Toward the Recyclable Use of Sapphire Substrates, *ACS Nano*, 9 (2015) 6178-6187.

[77] Y. Liu, H. Nan, X. Wu, W. Pan, W. Wang, J. Bai, W. Zhao, L. Sun, X. Wang, Z. Ni, Layer-by-Layer Thinning of MoS₂ by Plasma, *Acs Nano*, 7 (2013) 4202-4209.

[78] Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, H. Zhang, Single-Layer MoS₂ Phototransistors, *Acs Nano*, 6 (2012) 74-80.

[79] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, Ultrasensitive photodetectors based on monolayer MoS₂, *Nature Nanotechnology*, 8 (2013) 497-501.

[80] W. Zhang, J.K. Huang, C.H. Chen, Y.H. Chang, Y.J. Cheng, L.J. Li, High-gain phototransistors based on a CVD MoS₂ monolayer, *Adv Mater*, 25 (2013) 3456-3461.

- [81] O. Salehzadeh, N.H. Tran, X. Liu, I. Shih, Z. Mi, Exciton Kinetics, Quantum Efficiency, and Efficiency Droop of Monolayer MoS₂ Light-Emitting Devices, *Nano Letters*, 14 (2014) 4125-4130.
- [82] N. Peimyoo, J. Shang, C. Cong, X. Shen, X. Wu, E.K. Yeow, T. Yu, Non-Blinking Intense Two-Dimensional Light Emitter: Monolayer WS₂ Triangles, *ACS Nano*, 7 (2013) 10985-10994.
- [83] A. Castellanos-Gomez, M. Poot, G.A. Steele, H.S. van der Zant, N. Agrait, G. Rubio-Bollinger, Mechanical properties of freely suspended semiconducting graphene-like layers based on MoS₂, *Nanoscale research letters*, 7 (2012) 233.
- [84] S. Bertolazzi, J. Brivio, A. Kis, Stretching and Breaking of Ultrathin MoS₂, *Acs Nano*, 5 (2011) 9703-9709.
- [85] K. Liu, Q. Yan, M. Chen, W. Fan, Y. Sun, J. Suh, D. Fu, S. Lee, J. Zhou, S. Tongay, J. Ji, J.B. Neaton, J. Wu, Elastic Properties of Chemical-Vapor-Deposited Monolayer MoS₂, WS₂, and Their Bilayer Heterostructures, *Nano Letters*, 14 (2014) 5097-5103.
- [86] Q. He, Z. Zeng, Z. Yin, H. Li, S. Wu, X. Huang, H. Zhang, Fabrication of flexible MoS₂ thin-film transistor arrays for practical gas-sensing applications, *Small*, 8 (2012) 2994-2999.
- [87] J. Yoon, W. Park, G.Y. Bae, Y. Kim, H.S. Jang, Y. Hyun, S.K. Lim, Y.H. Kahng, W.K. Hong, B.H. Lee, H.C. Ko, Highly Flexible and Transparent Multilayer MoS₂ Transistors with Graphene Electrodes, *Small*, 9 (2013) 3295-3300.
- [88] S. Jiang, X. Yin, J. Zhang, X. Zhu, J. Li, M. He, Vertical Ultrathin MoS₂ Nanosheets on Flexible Substrate as Efficient Counter Electrode for Dye-Sensitized Solar Cells, *Nanoscale*, (2015).

Bibliography

- [89] T. Georgiou, R. Jalil, B.D. Belle, L. Britnell, R.V. Gorbachev, S.V. Morozov, Y.J. Kim, A. Gholinia, S.J. Haigh, O. Makarovsky, L. Eaves, L.A. Ponomarenko, A.K. Geim, K.S. Novoselov, A. Mishchenko, Vertical field-effect transistor based on graphene-WS₂ heterostructures for flexible and transparent electronics, *Nature Nanotechnology*, 8 (2013) 100-103.
- [90] R. Cheng, S. Jiang, Y. Chen, Y. Liu, N. Weiss, H.-C. Cheng, H. Wu, Y. Huang, X. Duan, Few-layer molybdenum disulfide transistors and circuits for high-speed flexible electronics, *Nat Commun*, 5 (2014).
- [91] H.-Y. Chang, S. Yang, J. Lee, L. Tao, W.-S. Hwang, D. Jena, N. Lu, D. Akinwande, High-Performance, Highly Bendable MoS₂ Transistors with High-K Dielectrics for Flexible Low-Power Systems, *ACS Nano*, 7 (2013) 5446-5452.
- [92] G.-H. Lee, Y.-J. Yu, X. Cui, N. Petrone, C.-H. Lee, M.S. Choi, D.-Y. Lee, C. Lee, W.J. Yoo, K. Watanabe, T. Taniguchi, C. Nuckolls, P. Kim, J. Hone, Flexible and Transparent MoS₂ Field-Effect Transistors on Hexagonal Boron Nitride-Graphene Heterostructures, *ACS Nano*, 7 (2013) 7931-7936.
- [93] J. Lee, Z. Wang, K. He, J. She, X.L. Feng, High Frequency MoS₂ Nanomechanical Resonators, *Acs Nano*, 7 (2013) 6086-6091.
- [94] H. Zeng, J. Dai, W. Yao, D. Xiao, X. Cui, Valley polarization in MoS₂ monolayers by optical pumping, *Nat Nanotechnol*, 7 (2012) 490-493.
- [95] D.J. Late, B. Liu, H. Matte, V.P. Dravid, C.N.R. Rao, Hysteresis in Single-Layer MoS₂ Field Effect Transistors, *Acs Nano*, 6 (2012) 5635-5641.
- [96] X. Zou, J. Wang, C.-H. Chiu, Y. Wu, X. Xiao, C. Jiang, W.-W. Wu, L. Mai, T. Chen, J. Li, J.C. Ho, L. Liao, Interface Engineering for High-Performance Top-Gated MoS₂ Field-Effect Transistors, *Advanced Materials*, 26 (2014) 6255-6261.

- [97] J.R. Chen, P.M. Odenthal, A.G. Swartz, G.C. Floyd, H. Wen, K.Y. Luo, R.K. Kawakami, Control of Schottky Barriers in Single Layer MoS₂ Transistors with Ferromagnetic Contacts, *Nano Letters*, 13 (2013) 3106-3110.
- [98] J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, I.V. Shvets, S.K. Arora, G. Stanton, H.Y. Kim, K. Lee, G.T. Kim, G.S. Duesberg, T. Hallam, J.J. Boland, J.J. Wang, J.F. Donegan, J.C. Grunlan, G. Moriarty, A. Shmeliov, R.J. Nicholls, J.M. Perkins, E.M. Grieveson, K. Theuwissen, D.W. McComb, P.D. Nellist, V. Nicolosi, Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials, *Science*, 331 (2011) 568-571.
- [99] V. Nicolosi, M. Chhowalla, M.G. Kanatzidis, M.S. Strano, J.N. Coleman, Liquid Exfoliation of Layered Materials, *Science*, 340 (2013).
- [100] K.R. Paton, E. Varrla, C. Backes, R.J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O.M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S.E. O'Brien, E.K. McGuire, B.M. Sanchez, G.S. Duesberg, N. McEvoy, T.J. Pennycook, C. Downing, A. Crossley, V. Nicolosi, J.N. Coleman, Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids, *Nat Mater*, 13 (2014) 624-630.
- [101] J. Zheng, H. Zhang, S. Dong, Y. Liu, C. Tai Nai, H. Suk Shin, H. Young Jeong, B. Liu, K. Ping Loh, High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide, *Nat Commun*, 5 (2014).
- [102] J. Shen, Y. He, J. Wu, C. Gao, K. Keyshar, X. Zhang, Y. Yang, M. Ye, R. Vajtai, J. Lou, P.M. Ajayan, Liquid Phase Exfoliation of Two-Dimensional Materials by Directly Probing and Matching Surface Tension Components, *Nano Letters*, (2015).
- [103] K.C. Knirsch, N.C. Berner, H.C. Nerl, C.S. Cucinotta, Z. Gholamvand, N. McEvoy, Z. Wang, I. Abramovic, P. Vecera, M. Halik, S. Sanvito, G.S. Duesberg, V.

Bibliography

Nicolosi, F. Hauke, A. Hirsch, J.N. Coleman, C. Backes, Basal-Plane Functionalization of Chemically Exfoliated Molybdenum Disulfide by Diazonium Salts, *ACS Nano*, 9 (2015) 6018-6030.

[104] S. Wu, C. Huang, G. Aivazian, J.S. Ross, D.H. Cobden, X. Xu, Vapor-Solid Growth of High Optical Quality MoS_2 Monolayers with Near-Unity Valley Polarization, *Acs Nano*, 7 (2013) 2768-2772.

[105] Y. Zhan, Z. Liu, S. Najmaei, P.M. Ajayan, J. Lou, Large-area vapor-phase growth and characterization of MoS_2 atomic layers on a SiO_2 substrate, *Small*, 8 (2012) 966-971.

[106] N. Choudhary, J. Park, J.Y. Hwang, W. Choi, Growth of Large-Scale and Thickness-Modulated MoS_2 Nanosheets, *ACS Appl. Mater. Interfaces*, 6 (2014) 21215-21222.

[107] D. Kong, H. Wang, J.J. Cha, M. Pasta, K.J. Koski, J. Yao, Y. Cui, Synthesis of MoS_2 and MoSe_2 Films with Vertically Aligned Layers, *Nano Letters*, 13 (2013) 1341-1347.

[108] H. Hadouda, J. Pouzet, J.C. Bernede, A. Barreau, MoS_2 Thin-Film Synthesis by Soft Sulfurization of a Molybdenum Layer, *Materials Chemistry and Physics*, 42 (1995) 291-297.

[109] Y. Jung, J. Shen, Y. Liu, J.M. Woods, Y. Sun, J.J. Cha, Metal Seed Layer Thickness-Induced Transition From Vertical to Horizontal Growth of MoS_2 and WS_2 , *Nano Letters*, 14 (2014) 6842-6849.

[110] K.K. Liu, W. Zhang, Y.H. Lee, Y.C. Lin, M.T. Chang, C.Y. Su, C.S. Chang, H. Li, Y. Shi, H. Zhang, C.S. Lai, L.J. Li, Growth of large-area and highly crystalline MoS_2 thin layers on insulating substrates, *Nano Letters*, 12 (2012) 1538-1544.

- [111] Y. Shi, W. Zhou, A.Y. Lu, W. Fang, Y.H. Lee, A.L. Hsu, S.M. Kim, K.K. Kim, H.Y. Yang, L.J. Li, J.C. Idrobo, J. Kong, van der Waals epitaxy of MoS₂ layers using graphene as growth templates, *Nano Letters*, 12 (2012) 2784-2791.
- [112] A.S. George, Z. Mutlu, R. Ionescu, R.J. Wu, J.S. Jeong, H.H. Bay, Y. Chai, K.A. Mkhoyan, M. Ozkan, C.S. Ozkan, Wafer Scale Synthesis and High Resolution Structural Characterization of Atomically Thin MoS₂ Layers, *Advanced Functional Materials*, 24 (2014) 7461-7466.
- [113] D.J. Late, P.A. Shaikh, R. Khare, R.V. Kashid, M. Chaudhary, M.A. More, S.B. Ogale, Pulsed Laser-Deposited MoS₂ Thin Films on W and Si: Field Emission and Photoresponse Studies, *ACS Appl. Mater. Interfaces*, 6 (2014) 15881-15888.
- [114] C.R. Serrao, A.M. Diamond, S.-L. Hsu, L. You, S. Gadgil, J. Clarkson, C. Carraro, R. Maboudian, C. Hu, S. Salahuddin, Highly crystalline MoS₂ thin films grown by pulsed laser deposition, *Applied Physics Letters*, 106 (2015) 052101.
- [115] G. Siegel, Y.P. Venkata Subbaiah, M.C. Prestgard, A. Tiwari, Growth of centimeter-scale atomically thin MoS₂ films by pulsed laser deposition, *APL Mater.*, 3 (2015) 056103.
- [116] T.A.J. Loh, D.H.C. Chua, Growth Mechanism of Pulsed Laser Fabricated Few-Layer MoS₂ on Metal Substrates, *ACS Appl. Mater. Interfaces*, 6 (2014) 15966-15971.
- [117] Y.-C. Lin, W. Zhang, J.-K. Huang, K.-K. Liu, Y.-H. Lee, C.-T. Liang, C.-W. Chu, L.-J. Li, Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization, *Nanoscale*, 4 (2012) 6637-6641.
- [118] Y.H. Lee, X.Q. Zhang, W.J. Zhang, M.T. Chang, C.T. Lin, K.D. Chang, Y.C. Yu, J.T.W. Wang, C.S. Chang, L.J. Li, T.W. Lin, Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition, *Advanced Materials*, 24 (2012) 2320-2325.

Bibliography

- [119] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B.L. Yakobson, J.-C. Idrobo, P.M. Ajayan, J. Lou, Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers, *Nature Materials*, 12 (2013) 6.
- [120] A.M. van der Zande, P.Y. Huang, D.A. Chenet, T.C. Berkelbach, Y.M. You, G.H. Lee, T.F. Heinz, D.R. Reichman, D.A. Muller, J.C. Hone, Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide, *Nature Materials*, 12 (2013) 554-561.
- [121] Y.H. Chang, W. Zhang, Y. Zhu, Y. Han, J. Pu, J.K. Chang, W.T. Hsu, J.K. Huang, C.L. Hsu, M.H. Chiu, T. Takenobu, H. Li, C.I. Wu, W.H. Chang, W. Wee, L.J. Li, Monolayer MoSe₂ Grown by Chemical Vapor Deposition for Fast Photodetection, *ACS Nano*, 8 (2014), 8582-8590.
- [122] Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang, L. Cao, Controlled Scalable Synthesis of Uniform, High-Quality Monolayer and Few-layer MoS₂ Films, *Scientific reports*, 3 (2013).
- [123] S.J. Yun, S.H. Chae, H. Kim, J.C. Park, J.-H. Park, G.H. Han, J.S. Lee, S.M. Kim, H.M. Oh, J. Seok, M.S. Jeong, K.K. Kim, Y.H. Lee, Synthesis of Centimeter-Scale Monolayer Tungsten Disulfide Film on Gold Foils, *ACS Nano*, 9 (2015) 5510-5519.
- [124] I. Song, C. Park, M. Hong, J. Baik, H.J. Shin, H.C. Choi, Patternable large-scale molybdenum disulfide atomic layers grown by gold-assisted chemical vapor deposition, *Angewandte Chemie*, 53 (2014) 1266-1269.
- [125] Y.-H. Lee, L. Yu, H. Wang, W. Fang, X. Ling, Y. Shi, C.-T. Lin, J.-K. Huang, M.-T. Chang, C.-S. Chang, M. Dresselhaus, T. Palacios, L.-J. Li, J. Kong, Synthesis and Transfer of Single-Layer Transition Metal Disulfides on Diverse Surfaces, *Nano Letters*, 13 (2013) 130329103804007.

- [126] X. Ling, Y.-H. Lee, Y. Lin, W. Fang, L. Yu, M.S. Dresselhaus, J. Kong, Role of the Seeding Promoter in MoS₂ Growth by Chemical Vapor Deposition, *Nano Letters*, 14 (2014) 464-472.
- [127] B. Liu, M. Fathi, L. Chen, A. Abbas, Y. Ma, C. Zhou, Chemical Vapor Deposition Growth of Monolayer WSe₂ with Tunable Device Characteristics and Growth Mechanism Study, *ACS Nano*, 9 (2015) 6119-6127.
- [128] J.-K. Huang, J. Pu, C.-L. Hsu, M.-H. Chiu, Z.-Y. Juang, Y.-H. Chang, W.-H. Chang, Y. Iwasa, T. Takenobu, L.-J. Li, Large-Area Synthesis of Highly Crystalline WSe₂ Monolayers and Device Applications, *ACS nano*, 8 (2013) 923-930.
- [129] K. Kang, S. Xie, L. Huang, Y. Han, P.Y. Huang, K.F. Mak, C.-J. Kim, D. Muller, J. Park, High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity, *Nature*, 520 (2015) 656-660.
- [130] J.-H. Lee, E.K. Lee, W.-J. Joo, Y. Jang, B.-S. Kim, J.Y. Lim, S.-H. Choi, S.J. Ahn, J.R. Ahn, M.-H. Park, C.-W. Yang, B.L. Choi, S.-W. Hwang, D. Whang, Wafer-Scale Growth of Single-Crystal Monolayer Graphene on Reusable Hydrogen-Terminated Germanium, *Science*, 344 (2014) 286-289.
- [131] R. Cheng, D.H. Li, H.L. Zhou, C. Wang, A.X. Yin, S. Jiang, Y. Liu, Y. Chen, Y. Huang, X.F. Duan, Electroluminescence and Photocurrent Generation from Atomically Sharp WSe₂/MoS₂ Heterojunction p-n Diodes, *Nano Letters*, 14 (2014) 5590-5597.
- [132] K.S. Novoselov, A.H. Castro Neto, Two-dimensional crystals-based heterostructures: materials with tailored properties, *Physica Scripta*, T146 (2012) 014006.
- [133] A.K. Geim, I.V. Grigorieva, Van der Waals heterostructures, *Nature*, 499 (2013) 419-425.

Bibliography

- [134] Y. Gong, J. Lin, X. Wang, G. Shi, S. Lei, Z. Lin, X. Zou, G. Ye, R. Vajtai, B.I. Yakobson, H. Terrones, M. Terrones, Beng K. Tay, J. Lou, S.T. Pantelides, Z. Liu, W. Zhou, P.M. Ajayan, Vertical and in-plane heterostructures from WS₂/MoS₂ monolayers, *Nat Mater*, 13 (2014) 1135-1142.
- [135] X. Zhu, N.R. Monahan, Z. Gong, H. Zhu, K.W. Williams, C.A. Nelson, Charge Transfer Excitons at van der Waals Interfaces, *Journal of the American Chemical Society*, (2015).
- [136] X. Hong, J. Kim, S.-F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, F. Wang, Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures, *Nat Nano*, 9 (2014) 682-686.
- [137] M.Z. Bellus, F. Ceballos, H.-Y. Chiu, H. Zhao, Tightly Bound Trions in Transition Metal Dichalcogenide Heterostructures, *ACS Nano*, 9 (2015) 6459-6464.
- [138] K. Kosmider, J. Fernandez-Rossier, Electronic properties of the MoS₂-WS₂ heterojunction, *Physical Review B*, 87 (2013).
- [139] H. Terrones, F. Lopez-Urias, M. Terrones, Novel hetero-layered materials with tunable direct band gaps by sandwiching different metal disulfides and diselenides, *Scientific Reports*, 3 (2013).
- [140] J. Kang, H. Sahin, F.M. Peeters, Tuning Carrier Confinement in the MoS₂/WS₂ Lateral Heterostructure, *The Journal of Physical Chemistry C*, (2015).
- [141] P.M. Campbell, A. Tarasov, C.A. Joiner, W.J. Ready, E.M. Vogel, Enhanced Resonant Tunneling in Symmetric 2D Semiconductor Vertical Heterostructure Transistors, *ACS Nano*, 9 (2015) 5000-5008.
- [142] L. Wang, I. Meric, P.Y. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe, L.M. Campos, D.A. Muller, J. Guo, P. Kim, J. Hone, K.L. Shepard, C.R.

Dean, One-Dimensional Electrical Contact to a Two-Dimensional Material, *Science*, 342 (2013) 614-617.

[143] C. Huang, S. Wu, A.M. Sanchez, J.J.P. Peters, R. Beanland, J.S. Ross, P. Rivera, W. Yao, D.H. Cobden, X. Xu, Lateral heterojunctions within monolayer MoSe_2 – WSe_2 semiconductors, *Nat Mater*, 13 (2014) 1096-1101.

[144] M.-Y. Li, Y. Shi, C.-C. Cheng, L.-S. Lu, Y.-C. Lin, H.-L. Tang, M.-L. Tsai, C.-W. Chu, K.-H. Wei, J.-H. He, W.-H. Chang, K. Suenaga, L.-J. Li, Epitaxial growth of a monolayer WSe_2 - MoS_2 lateral p-n junction with an atomically sharp interface, *Science*, 349 (2015) 524-528.

[145] A.C. Ferrari, D.M. Basko, Raman spectroscopy as a versatile tool for studying the properties of graphene, *Nat Nano*, 8 (2013) 235-246.

[146] A. Splendiani, L. Sun, Y.B. Zhang, T.S. Li, J. Kim, C.Y. Chim, G. Galli, F. Wang, Emerging Photoluminescence in Monolayer MoS_2 , *Nano Letters*, 10 (2010) 1271-1275.

[147] N. Scheuschner, O. Ochedowski, A.-M. Kaulitz, R. Gillen, M. Schleberger, J. Maultzsch, Photoluminescence of freestanding single- and few-layer MoS_2 , *Physical Review B*, 89 (2014).

[148] W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P.M. Ajayan, B.I. Yakobson, J.-C. Idrobo, Intrinsic Structural Defects in Monolayer Molybdenum Disulfide, *Nano Letters*, 13 (2013) 2615-2622.

[149] D. Lembke, A. Kis, Breakdown of high-performance monolayer MoS_2 transistors, *ACS Nano*, 6 (2012) 10070-10075.

[150] J. Shi, D. Ma, G.-F. Han, Y. Zhang, Q. Ji, T. Gao, J. Sun, X. Song, C. Li, Y. Zhang, X.-Y. Lang, Y. Zhang, Z. Liu, Controllable Growth and Transfer of Mono

Bibliography

layer MoS₂ on Au Foils and Its Potential Application in Hydrogen Evolution Reaction, *Acs Nano*, 8 (2014) 10196-10204.

[151] M. Bougouma, A. Batan, B. Guel, T. Segato, J.B. Legma, F. Reniers, M.P. Delplancke-Ogletree, C. Buess-Herman, T. Doneux, Growth and characterization of large, high quality MoSe₂ single crystals, *Journal of Crystal Growth*, 363 (2013) 122-127.

[152] Y. Gong, Z. Liu, A.R. Lupini, G. Shi, J. Lin, S. Najmaei, Z. Lin, A.L. El ás, A. Berkdemir, G. You, H. Terrones, M. Terrones, R. Vajtai, S.T. Pantelides, S.J. Pennycook, J. Lou, W. Zhou, P.M. Ajayan, Band Gap Engineering and Layer-by-Layer Mapping of Selenium-Doped Molybdenum Disulfide, *Nano Letters*, 14 (2014) 442-449.

[153] K. Xu, P.Z. Chen, X.L. Li, C.Z. Wu, Y.Q. Guo, J.Y. Zhao, X.J. Wu, Y. Xie, Ultrathin Nanosheets of Vanadium Diselenide: A Metallic Two-Dimensional Material with Ferromagnetic Charge-Density-Wave Behavior, *Angew. Chem.-Int. Edit.*, 52 (2013) 10477-10481.

[154] Y. Ma, Y. Dai, M. Guo, C. Niu, Y. Zhu, B. Huang, Evidence of the Existence of Magnetism in Pristine VX₂ Monolayers (X = S, Se) and Their Strain-Induced Tunable Magnetic Properties, *ACS Nano*, 6 (2012) 1695-1701.