Two-dimensional transitional metal dichalcogenide heterostructures : interface optical properties

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**NANYANG
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**TWO-DIMENSIONAL TRANSITIONAL METAL
DICALCOGENIDE HETEROSTRUCTURES: INTERFACE
OPTICAL PROPERTIES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY**

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OPTICAL PROPERTIES**

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Abstract

Since the first report of graphene in 2004 [1], atomically thin materials become more and more attractive to researchers due to their unique properties and promising applications. For example, two-dimensional (2D) transitional metal dichalcogenides (TMDCs), such as MoS₂, WSe₂, exhibit band gap transitions from indirect one in bulk to direct one in monolayer [2]. Additionally, monolayer MoS₂ is flexible and tough material with a high Young's modulus, comparable to the stainless steel [3]. There are many applications based on atomically thin TMDCs, including field effect transistors (FETs) [4], photodetectors [5] and so on. Furthermore, band gap engineering of 2D TMDCs by fabricating the heterojunctions including lateral and van der Waals junctions paves the way to study the novel electronic transport [6], interlayer coupling [7] and charge transfer [8].

In this thesis, I will focus on the fabrication and characterization of 2D TMDCs and their heterostructures. First, I will present the fabrication of lateral alloyed heterojunctions of W_xMo_{1-x}S₂/MoS₂ by chemical vapor deposition method. The heterojunctions have been characterized by photoluminescence (PL) and Raman spectra to support our conclusion. In the monolayer heterojunction, the photoluminescence peak shifts continuously from 686.8 nm at triangle center to 633.4 nm at the edge at excitation wavelength of 457 nm. The part of W_xMo_{1-x}S₂ is attested to be composition-graded alloy according to the position dependent PL peaks and we also calculated the composition of this alloy. This heterojunction with a tunable band gap may have potential applications in wide range photodetectors and multi-

color light emitters.

Then, I will present the interlayer coupling of WS₂ bilayers and trilayers, grown by the CVD method. Both the interlayer distance and twisted angle affect the interlayer coupling in 2D TMDCs, and further change the band structures. I will show that random-twisted WS₂ bilayers (except of 0 and 60 degrees) behave as quasi-direct band gap materials due to the weakened interlayer coupling. Theoretical calculation based on the density functional theory shows the enlarged interlayer distance in the twisted bilayer WS₂. A new peak was observed in the PL spectra in the twisted WS₂ bilayer or trilayer, which is contributed to the interlayer exciton which is composed of one electron in the top (bottom) layer and one hole in the bottom (top) layer.

Next, I will show the evident cathodoluminescence (CL) emission from monolayer TMDCs, including WSe₂, MoS₂ and WS₂, in the van der Waals configuration by sandwiched them in two hexagonal boron nitride (hBN) layers. In the hBN/TMDC/hBN heterostructure, e-beam induced e-h pairs can transfer to and be trapped in the middle TMDC layer, leading to increased recombination probability within the TMDC layer. The emission intensity is almost linearly proportional to the thickness of the top or bottom hBN layers. Moreover, I will demonstrate that CL can be applied to study the strain-induced excitonic peak shift in the suspended monolayer TMDCs.

Finally, as a related project, I will present the multiple phase transitions of 1T-TaS₂ induced by an external electrical field at room temperature. The number of electrically driven

phase transitions is proved to depend on the thicknesses of flakes. The threshold of the electric field in the phase transition is also revealed. Additionally, gate tunable phase transitions were realized by combining the TaS₂ and graphene together.

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List of acronyms

AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
BTBT	Band-To-Band Tunneling
CCDW	Commensurate Charge Density Wave
CDW	Charge Density Wave
CL	Cathodoluminescence
CVD	Chemical Vapor Deposition
FETs	Field Effect Transistors
hBN	Hexagonal Boron Nitride
ICCDW	Incommensurate Charge Density Wave
LEDs	Light-Emitting Diodes
MIT	Metal-Insulator Transition
MOCVD	Metal-Organic Chemical Vapor Deposition
NCCDW	Nearly-Commensurate Charge Density Wave
PT	Phase transition
PL	Photoluminescence
PDMS	Polydimethylsiloxane
PMMA	Polymethylmethacrylate
PVA	Polyvinyl alcohol
PPC	Polypropylene carbonate
SEM	Scanning Electron Microscope
SNOM	Scanning Near-field Optical Microscope
TMDCs	Transitional Metal Dichalcogenides
vdW	van der Waals

Chapter 1 Introduction

In the nanomaterial study, structures can be classified in terms of dimensionality in zero-dimensional (0D, quantum dots), one-dimensional (1D, nanowires), two-dimensional (2D, atomically thin flakes), and three-dimensional (3D, bulk) materials. By lowering the dimensionality from 3D one, plentiful new phenomena and physics were revealed. For example, in the light-emitting quantum dots, the emitting wavelength is determined by the size of the quantum dot [9]; While in the group VI transitional metal dichalcogenides (TMDCs), the band gap evolves from indirect one in bulk to direct one, due to the quantum confinement effect and reduced dielectric screening effect [2]. For example, bulk 2H-MoS₂ is a layered material with an indirect band gap (1.9 eV). Inside the single layer, atoms are bonded by covalent bonds. However, different layers are bonded by van der Waals force which is much weaker than covalent force. In monolayer 2H-MoS₂, the band structure evolves to a direct band gap from the indirect band gap in bulk due to the absence of the interlayer coupling.

2D TMDCs materials are layered materials composed of atoms of the transitional metal and chalcogen (Fig. 1.1). The basic properties of the TMDCs are diverse, ranging from insulators such as HfS₂, semiconductors such as MoS₂, semimetals such as WTe₂, to metals such as NbS₂ [10]. Among various 2D materials, semiconducting TMDCs has attracted scientists' interests due to their unique electronic and optical properties, like sizable band gap and potential optoelectronic applications.

H	MX ₂ M = Transition metal X = Chalcogen																He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Figure 1.1 The group of layered TMDCs are highlighted in the periodic table. [10]

2D group VI TMDCs (MX_2 , M=Mo, or W, X=S, Se, or Te) are semiconducting layered materials where lateral layers are bonded by the van der Waals (vdW) force in the direction of c-axis. Since the interlayer vdW bond is weaker than the covalent bond, it is possible to thin down these TMDCs to monolayers (see Fig. 1.2). Such a thin layer of TMDC makes scientists to investigate novel phenomena, including band structure evolution, valley polarization [11]. Recently, heterostructures composed of different 2D TMDCs attract researchers' attention because of their unique properties. For example, the interlayer coupling and charge transfer were studied in vertically stacked TMDC heterostructures [12, 13]. Atomically thin p-n junction [14] were also achieved in the lateral TMDC heterostructure by chemical vapor deposition (CVD) method.

Figure 1.2 Side (a) and top (b) views of 2H MX₂ structure.

In this chapter, I will introduce the fabrications of 2D TMDCs and their heterostructures (both vertical and lateral heterostructures), and the related optical and electronic properties.

1.1 Fabrication of 2D materials: top-down and bottom-up methods

There are kinds of methods to fabricate 2D materials, which can be roughly classified: top-down and bottom-up methods. One can make an atomically thin 2D material from its bulk material (top-down) by thinning it down; or directly grow it (bottom-up). Typical top-down methods are mechanical exfoliation and liquid exfoliation methods; while bottom-up methods include chemical vapor deposition (CVD), epitaxial deposition, atomic layer deposition (ALD) methods, and so on.

1.1.1 Mechanical exfoliation method

A simple idea to fabricate the 2D material is to thin down its bulk counterpart, but it was a challenge to obtain ultrathin flake via the polishing method. Surprisingly, this difficulty

was conquered when the graphene flake was obtained from graphites by a tape in 2004 [1]. In fact, this method, so called mechanical exfoliation method, can be applied to fabricate all atomically thin 2D materials from their bulk sources. Firstly, the bulk material is transferred to a stripe of a scotch tape. One should use another stripe tape to exfoliate the bulk material on a tape to expose some new, clear and flat surfaces. Then the tape with flakes of 2D materials is pressed on a clean Si/SiO₂ substrate. After removing the tape from the substrate, one can find some thin flakes left on the substrate. Even most of the flakes are thick, there still is a chance to find a few of thin flakes. It requires some experiences, patience and luck to obtain a suitable atomically thin flake. A longer waiting time to detach the tape might increase the yield of thin flakes. Figure 1.3a-b show the scotch tape used in the thesis and the obtained graphene flake. Both monolayer and bilayer were observed in the thin flake.

Figure 1.3 (a) A scotch tape used in this thesis. (b) The optical image of a graphene flake obtained by the mechanical exfoliation method. Both monolayer and bilayer were observed.

In the mechanical exfoliation method, the yield of obtained 2D materials is quite limited, especially for monolayers. Another disadvantage of this method is the small size of obtained 2D materials (maximum tens of micrometers). It is reported that one can obtain hundreds

of micrometers size of monolayer TMDC by evaporating a layer Au on the bulk one [15]. However, this method is limited by the cost of Au and unavoidable contaminations in the Au etching process. Therefore, scientists need to explore other methods to improve the yield and size of 2D materials for future industrial applications.

1.1.2 Liquid exfoliation method

Atomically thin flakes obtained by the mechanical exfoliation method can be applied to investigate its basic properties, such as optical and electronic transporting properties. However, the yield by this method is quite low, which makes it impossible for large scale applications. Liquid exfoliation method [16] can exfoliate layered bulk materials into atomically thin flakes by liquid involving oxidation [17], ion intercalation/exchange, and surface passivation [16]. The most important advantage of liquid exfoliation method is the high yield of 2D materials, which can be prepared into films, quantum dots, and other composites in the commercial applications.

The main liquid method is to deal with layered materials in kinds of solvents by ion intercalation/exchange with following sonication to obtain the ultrathin flakes (Fig. 1.4). Due to the weak interlayer van der Waals bonds, interlayers of 2D materials can be intercalated by N-methylpyrrolidone for graphene [18], Lithium ion solvent for MoS₂ [10]. High yield and large surface area were achieved by this method, making it suitable for applications of energy storage [19]. However, the size of flakes is limited to be below one micrometer because of the flake breaking under the sonication process.

Figure 1.4 Schematic description of the main liquid exfoliation mechanisms. (a) Ion intercalation. (b) Ion exchange. (c) Sonication assisted exfoliation. [16]

1.1.3 CVD method

Two-dimensional materials, such as graphene and monolayer MoS₂, are normally obtained by the mechanical exfoliation method, because it is a straightforward and easy way for the preliminary investigation. However, one of the drawbacks of top-down methods is the limited flake size because the flake is inevitable to break to small pieces in the exfoliation process. The bottom-up methods are promising to realize large scale synthesis of atomically thin materials, by which atomically thin 2D materials are deposited or grown directly on the substrate. The main bottom-up methods include e-beam deposition [20], chemical vapor deposition, epitaxial growth [21] and so on.

Chemical vapor deposition method involves the fabrication of the target material on the substrate surface via the chemical reaction of vapor-phase precursors in the chamber. The

morphology of fabricated materials can be various types, such as thin film, nanowires, or other nanostructures. The quality and morphology are determined by the growth conditions, including temperature, pressure, precursors, growth time and so on. CVD can be classified in terms of the type and control of precursors into traditional CVD, metal-organic CVD (MOCVD), plasma-enhanced CVD, atomic layer deposition. For MOCVD, metal-organic precursors are used to grow single or polycrystalline thin film in vacuum. For plasma-enhanced CVD, the chemical reaction is assisted by plasma generated by the radio frequency rather than thermal energy, which makes chemical reaction possible to occur at low temperature. In atomic layer deposition method, the precursors need to be carefully selected and controlled to realize the layer-by-layer growth in the atomic scale.

Figure 1.5 is a traditional CVD setup which composed of a furnace, a quartz tube, a gas flow meter, a pump with pressure control system. In this system, we can control the precursors, temperature, and pressure to fulfill the growth conditions. Due to the flexible choice of precursors in the traditional CVD, it is suitable to explore the growth of new materials. Therefore, this traditional CVD is extensively studied for the fabrication of 2D materials.

Figure 1.5 A CVD setup used in our lab.

CVD method has been used to grow graphene including flakes, films even monolayer with the CH_4 precursor. The substrate is critical for large scale monolayer graphene and Cu is proved to be a good candidate for monolayer graphene growth [22]. Beyond the graphene, other 2D materials were also grown by CVD method. For example, Y. Lee, et al. firstly reported that monolayer MoS_2 sheets were grown on Si/SiO_2 substrates by CVD (Fig. 1.6) [23]. Sulfur and MoO_3 were used as the precursors. To promote the growth, the substrates were treated by aqueous reduced graphene oxide, PTAS or PTCd solution. Monolayer MoS_2 flakes were obtained but the shapes of obtained flakes are irregular.

Figure 1.6 Schematic setup of a traditional CVD method. [23]

Later reports show that the promoters are unnecessary for 2D TMDC growth [24]. One can identify quality and thickness of MoS₂ by the shape and optical contrast. The most common seen shape is the triangle (Fig. 1.7), which is consistent with the lattice structure of MoS₂. The growth results are very sensitive to the experimental parameters such as precursors, temperature, and substrate. Nucleation is another key factor of monolayer TMD growth. In fact, the growth conditions for TMD growth are very strict and the reproducibility is a big issue for CVD method. The protective gas at the growth process is also important for 2D materials. MoS₂ and WS₂ flakes can be grown in N₂ or Ar gas, while H₂ or mixture with H₂ is necessary for the successful growth of MoTe₂ and WTe₂ flakes. Adding seeding promoters might help to form nucleation center to improve the yield of 2D materials [25].

The quality of TMDC flake grown by the traditional CVD method is inhomogeneous according to PL mapping [26], which might be attributed to the ratio change of the precursors at the growth process. N. Peimyoo, *et al.* reported the successful growth of uniform WS₂ by separately heating the sulfur source to stabilize the flow of sulfur vapor [27]. Besides of the triangle shape, the hexagonal shape WS₂ was reported with the region-dependent photoluminescence [28]. It was explained that the hexagonal WS₂ monolayer was divided into three sulfur-vacancy regions and three W-vacancy regions in the growth process.

Figure 1.7 Optical image of MoS₂ grown by CVD method. [29]

In the traditional CVD method, large-scale monolayer graphene can be grown but large scale and high quality 2D TMDC films are not easy to be obtained. It might be due to the poor controllability of reaction gases by heating solid precursors in the growth process. The precursors are flowed to substrates automatically with the protective gas and precise control of the precursor amount is impossible. K. Kang, *et al.* reported a MOCVD method to successfully grow wafer-scale 2D TMDCs including MoS₂ and WS₂ (Fig. 1.8) [30]. The Mo and W sources come from metal-organic precursors Mo(CO)₆ and W(CO)₆, and S source comes from (C₂H₅)₂S. By precisely controlling the precursors and growth conditions, wafer-scale uniform TMDCs films were obtained. Even the films are polycrystalline, the electron mobility still keeps to be $\sim 30 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which makes it suitable for commercial applications

Figure 1.8 Schematic growth setup of the MOCVD. [30]

1.2 Optical and electrical properties of atomically thin 2D TMDCs

One astonishing property of semiconducting 2D TMDCs is the band gap crossover from indirect band gap in bulk to direct band gap in monolayer, such as MoS₂ and WS₂. This feature makes monolayer TMDCs as an efficient luminescent material compared to the bulk ones.

1.2.1 Photoluminescence and Raman spectra of 2D TMDCs

It is well known that bulk MoS₂ is indirect band gap material. According to *ab initio* calculation, the monolayer MoS₂ has a direct band gap [31]. The valence band at Γ point is sensitive to the interlayer interaction while the one at K point is insensitive to the interlayer interaction. When the interlayer interaction disappears in the monolayer MoS₂, the valence band at Γ point drops below the one at K point, turning out to be a direct band gap structure (see Fig. 1.9).

Figure 1.9 Calculated band structure evolution of MoS₂ with different thickness of (a) bulk MoS₂, (b) quadrilayer MoS₂, (c) bilayer MoS₂, and (d) monolayer MoS₂. [32]

The calculation results have been verified experimentally in monolayer MoS₂ in 2010 (see Fig. 1.10) [2]. We can see the PL intensity of monolayer MoS₂ is much higher than the one of bilayer, which evidences the band structure transition from indirect one to direct one (monolayer) and makes them suitable for light-emitting applications.

Figure 1.10 Photoluminescence spectra of monolayer and bilayer MoS₂. [2]

The band gap of MoS₂ is not only affected by its thickness but also the induced strain

[33]. There are several techniques to induce a strain to 2D materials, including bending (Fig. 1.11a), elongating a flexible substrate and stretching samples by using a piezoelectric substrate and so on. An in-plane strain cause the Raman mode E_{2g}^1 splitting into two subpeaks in monolayer MoS₂, due to the breaking of in-plane symmetry (Fig. 1.11c). Also, this strain can induce PL peak redshift and evolution from direct band gap to indirect one in monolayer MoS₂ (Fig. 1.11c) [34], which also can be confirmed by the theoretical calculation. J. Feng, *et al.* [35] have proposed a model to create a solar energy funnel by inducing a center strain on the monolayer MoS₂, which can concentrate the generated carrier following the smooth varying band gap. A sufficient strain even causes a transition from indirect to direct band gap in bilayer WSe₂ [36]. Therefore, those reports pave the way to study strain-engineering band structure and energy conversion.

Figure 1.11 Strain induced PL peak redshift in monolayer MoS₂. (a) Schematic of the in-plane strain applied on the monolayer MoS₂. (b) Raman spectra and (c) PL spectra with different strength of the applied strain. [34]

Although monolayer MoS₂ has a direct band gap, the PL quantum yield is still low [2]. It is attributed to the defect-mediated nonradiative recombination. M. Amani, *et al.* reported that a surface treatment of monolayer MoS₂ by a nonoxidizing organic superacid ((bis(trifluoromethane) sulfonamide) can boost the quantum yield of monolayer MoS₂ to nearly unity (~1, Fig. 1.12) [37]. It may result from the suppression of defect-mediated nonradiative recombination and enhancement of minority carrier properties. Another approach to enhance PL intensity in monolayer TMDCs is the coupling with plasmonic structures [38]. By carefully designing the plasmonic structures, PL enhancement factor can reach ~20 000 in monolayer WSe₂ on plasmonic hybrid structure [39].

Figure 1.12 PL enhancement by surface treatment. (a) Comparison of PL spectra of as exfoliated and treated MoS₂. (b)-(c) the corresponding PL mapping show the giant enhancement of PL intensity. Insets are the optical image of MoS₂. [37]

Due to the quantum confinement and reduced screening effect in monolayer, the exciton is tightly bound in 2D surface. The exciton binding energy in monolayer semiconductor is extremely larger than the one of 3D semiconductors. For example, the exciton binding energy

is measure to be ~ 0.7 eV at monolayer WS_2 by a two-photon excitation spectroscopy and the exciton is Wannier type (Fig.1.13) [40]. Due to the spin-orbital coupling, the valence band of monolayer MoS_2 splits into two bands which correspond to the exciton A and B in the PL and absorbance spectra [2]. Also, the trion (charged exciton) in monolayer MoS_2 has been studied by tuning the carrier density and type [41]. The large binding energy of trion makes it possible to survive even at room temperature.

Figure 1.13. The plots are modulus squared of the real space exciton wave function of monolayer WS_2 at 1s (a), 2p (b), 2s (c) states. [40]

Raman spectroscopy is another powerful tool to study 2D materials. For example, two vibrational modes of A_{1g} and E_{2g}^1 are the basic signatures of MoS_2 [42]. One can identify the monolayer MoS_2 from the bulk MoS_2 easily by measuring the difference between these two modes, because the peak position of A_{1g} shifts red and the one of E_{2g}^1 shifts blue in monolayer due to the absence of the interlayer interaction (Fig. 1.14) [43]. High order Raman scattering with spin-orbital coupling can be excited by a 325 nm UV laser [44]. Shear and breathe modes have also been revealed in the low frequency Raman spectroscopy [45].

Figure 1.14. Raman spectra of MoS₂ with different thickness. [43]

Due to the strong spin-orbital coupling, the valence band (conduction band) of MoS₂ splits into two subbands, which correspond to exciton A and B. In monolayer MoS₂, the valleys are energy-degenerate. However, owing to inversion symmetry broken, the spin angular momentum at the valley of K point in Brillouin zone is opposite to that at K' point. The valley polarization can be achieved by the optical pumping with a circularly polarized light, suggesting the possible applications in valley-based electronics and optoelectronics [46]. PL intensity at σ^+ circularly polarized light excitation is stronger than the one at σ^- circularly polarized light excitation in monolayer MoS₂ in Figure 1.15 which provides a platform for the study of integrated spintronic and valleytronic applications [47].

Figure 1.15 PL spectrum of monolayer MoS₂ at the σ^+ (red line) and σ^- (blue line) polarizations. The black curve is the net degree of polarization. [46]

1.2.2 Electronic transport of 2D TMDCs

According to the scaling limits of Moore's law [48], it requires the exploration of new materials and device geometries for next generation semiconductor device. Two-dimensional material seems to be the promising candidate for future electronic device. For example, graphene possesses an ultrahigh mobility of $\sim 10^6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ when sandwiched into two hBN layers [49]. However, the on/off ratio of FETs based on graphene is low because the absence of the band gap in graphene. To improve the on/off ratio, the semiconducting TMDCs are good candidates thank to their intrinsic band gap properties. However, the mobility of TMDCs ($0.1\sim 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) are quite low compared to the one of graphene [50]. The record of mobility of the monolayer MoS₂ is $\sim 200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which were obtained in a dual gated device (Fig. 1.16) [4]. However, the mobility is overestimated because the real capacitance in the dual-gate device is the coupling of the capacitances of both top and bottom gates.

Figure 1.16 Monolayer MoS₂ transfer characteristic for the FET with 10 mV V_{ds} at room-temperature. Backgate voltage V_{bg} is applied to the substrate and the top gate is disconnected. Inset: I_{ds} – V_{ds} curve acquired for V_{bg} values of 0, 1 and 5 V. [4]

As well as a high mobility, high on/off ratio and switch speed are the critical parameters for FET device. FETs based on 2D TMDCs, such as MoS₂ and WS₂, have a high on/off ratio thank to the band gap of 2D TMDCs. In metal-oxide-semiconductor field-effect transistors, subthreshold swing (SS, represents inverse slope of the current by one decade under a gate voltage) at room temperature is theoretically limited to be ~60 mV/dec due to the thermionic emission of charge carrier injection. One promising candidate to overcome the SS limit is tunneling FETs, in which carriers are injected to the channel by band-to-band tunneling (BTBT) instead of the thermionic emission [51]. An average of 31.1 mV/dec was achieved with a minimum of 3.9 mV/dec in MoS₂/Ge heterostructure due to BTBT (Fig. 1.17) [52]. By applying different gate voltage, one can tune the carrier types of 2D materials and design novel functional devices. For example, electroluminescence was observed in monolayer

MoS₂ device with top gates [53].

Figure. 1.17 Drain current as a function of gate voltage for three different drain voltages of 0.1 V, 0.5 V and 1 V. [52]

1.3 Heterostructures based on 2D TMDCs

Van der Waals heterostructure [54] or vertical heterostructure, based on atomically thin two-dimensional (2D) materials gives a way to study various phenomena and applications such as interlayer coupling [55, 56], light-emitting diodes (LEDs) [57], and tunnel diodes [58, 59]. In atomically thin 2D materials, carriers are confined to a very thin plane like a quantum well. This natural advantage of 2D materials open an easy path to investigate some quantum phenomena such as resonant tunneling, as demonstrated in the heterostructure based on graphene/few layers hexagonal boron nitride (hBN)/graphene [59]. Different from the metallic graphene with a Dirac point, 2D transitional metal dichalcogenides, such as MoS₂, MoSe₂, WS₂, WSe₂, are gapped semiconductors. The artificial heterostructure formed by stacking different TMDCs will allow us to develop many applications such as p-n junction

[60], field effect transistors [61] and LEDs . Another type of the heterostructure is the lateral heterostructure in which different 2D materials connect only at the boundaries which allows researchers to achieve atomically thin p-n junction.

1.3.1 Vertical heterostructures

To fabricate a vertical 2D heterostructure, dry transfer is a most popular method, where the 2D materials are exfoliated on a transparent Polydimethylsiloxane (PDMS) film [62] or Polymethylmethacrylate (PMMA) films [63]. Pick-up method based on the dry transfer method is commonly used as 2D materials can be easily obtained and identified on the Si/SiO₂ substrates. For example, graphene can be picked up and transferred by a PPC (polypropylene carbonate)/PDMS film from a substrate and keep a clear interface [64]. Another one is the wet pick up method which was reported to realize a fast and large scale transfer but water is unavoidable to contact the samples [65].

The most interesting part of vertical heterostructures is to tune and investigate the interlayer coupling between different 2D materials. Figure 1.18 show the strong interlayer coupling and interlayer exciton [55] in the vertical MoS₂/WSe₂ heterostructure. A new emission peak at ~1.55 eV appears in the heterojunction part, which originates from the interlayer excitonic transition between the top and bottom layers. This interlayer exciton is composed of one electron (hole) in MoS₂ layer and one hole (electron) in WSe₂ layer. Furthermore, the lifetime of the interlayer exciton in MoSe₂/WSe₂ heterostructure was proved to be ~1.8 ns at 20 K [66], which is an order of magnitude longer than that of the

intralayer exciton.

Figure 1.18 (a) Optical image of MoS₂/WSe₂ vertical heterostructure. (b) PL spectra of three regions in (a). (c) Schematic model to explain the formation of the interlayer exciton. [55]

The heterostructure is also a perfect platform to investigate the carrier dynamics of 2D materials. The charge transfer between different layers was investigated in the vertical heterostructure with a loose contact and photo blinking was observed in the MoSe₂/WS₂ heterostructure owing to the interlayer carrier transfer (Fig. 1.19) [67]. The emission intensity varying with time implies the switch of bright, neutral and dark states, which is different from the normal two states in 0D or 1D system.

Figure 1.19 Optical image (a) of a WS₂/MoSe₂ bilayer heterostructure and the fluorescence image of the bright, neutral and dark emission states of WS₂ (b-d). [67]

1.3.2 Lateral heterostructures

In the lateral heterostructure, different 2D materials are connected at a lateral level. Until now, only CVD method can be applied to fabricated lateral heterostructure (see Fig. 1.20). So far, in-plane heterostructure TMDCs such as MoS_2/WS_2 [12], WS_2/WSe_2 [68] and $\text{MoSe}_2/\text{WSe}_2$ [13] have been synthesized in one step by CVD method. However, the drawback of the one-step method is that the boundaries of the heterostructure is not very sharp because the different precursors are not well separated. M. Li, *et al.* reported a two-step CVD growth method and finally achieved the atomically thin p-n junction [14].

Figures 1.20 Schematic of lateral epitaxial growth lateral heterostructure. [68]

Figure 1.21 shows the tow-step growth $\text{MoS}_2/\text{WSe}_2$ lateral p-n junction. It clearly shows the rectifying and photovoltaic effects. The width of depletion region of this lateral junction is measured to be ~ 320 nm[14]. Due to the atomically thin thickness, the depletion region is strongly affected by the substrate and circumstance.

Figure 1.21 (a) Optical image for the WSe₂/MoSe₂ p-n junction device. (b) Electrical transport curves (I versus V) with and without light exposure. [14]

Furthermore, the lateral heterostructure can be clearly identified by PL mapping (Fig. 1.22) [13]. The PL peaks at center and edge parts correspond to excitonic emissions of MoSe₂ and WSe₂, respectively. In the junction part the PL peak contains both emissions from MoSe₂ and WSe₂ because the laser spot illuminates on two materials at the same time. The brighter emission at the junction part may be attributed to the trapping of excitons by defects or enhanced radiative recombination at the interface.

Figure 1.22 PL mapping and spectra of MoSe₂/WSe₂ heterojunction. [13]

1.4 Motivation and objectives of this thesis

Two-dimensional materials have shown their potential applications in many fields, such as FETs, energy storage, and medical therapy [69]. Heterostructures based on 2D materials become attractive to researchers because the artificial structures in atomic scale can be used

to explore novel phenomenon and properties. Lateral heterostructures of TMDCs grown by the CVD method can be applied in p-n diodes and LEDs. By the CVD method, not only heterostructure with a sharp interface but alloyed heterostructure could be fabricated. The composition-graded structure may let us to tune the band gap of the 2D material and explore new applications. I will focus on the CVD growth of lateral heterostructures in one step growth and study their composition and optical properties.

Van der Waals interaction dramatically affects the properties of 2D materials and their heterostructures. Interlayer coupling and charge transfer are very interesting topics in van der Waals heterostructures. In fact, interlayer interaction is affected by not only the 2D materials in heterostructures but also the twisted angle. It is not difficult to fabricate twisted sample by the dry transfer method. But the interlayer coupling is hard to control due to the inhomogeneous interface contact. Post annealing is necessary to improve the interface contact. Another way to prepare twisted sample is the CVD method. For example, twisted MoS₂ bilayers have been reported [7] that interlayer coupling is obviously affected by the twist angle. As the twisted sample is grown at a high temperature, the interlayer coupling is assumed to be intrinsic, which is different from the transferred sample. I will explore the interlayer coupling of WS₂ bilayers and trilayers by the CVD method.

Van de Waals heterostructure, a complex system of different 2D materials, has shown its remarkable capabilities in plentiful applications, such as tunneling LEDs, correlated blinking, FETs. It shows fruitful unique properties which are absent in the isolated 2D

materials. Photoluminescence is the most common way to study optical properties of 2D TMDCs, but the spatial resolution is limited by the spot size of a laser. It restricts researchers to study 2D TMDCs at the minimum resolution of the sub micro-meter scale. A luminescence technique with a higher resolution (nanoscale) is required to investigate details of optical properties of 2D TMDCs, for example the emission of defects and edges. Cathodoluminescence spectroscopy is a powerful tool to realize nanoscale emission study because a high energy electron beam can be focused on the size of the nanometer scale. However, CL spectroscopy is applied to study the bulk system and merely in atomically thin materials due to their extremely low excitation volume. For example, CL spectroscopy has been used to study intrinsic and defect-induced emissions of thick hBN and MoS₂ flakes [70, 71]. So far, there is no report about the CL emission from monolayer TMDCs. I will try to apply CL technique in studying monolayer TMDCs by sandwiching the monolayer into two hBN layers and successfully observed CL emissions from monolayer TMDCs in this thesis.

Chapter 2 Monolayer $W_xMo_{1-x}S_2/MoS_2$ lateral heterostructures

Band gap engineering of TMDCs monolayer for their potential optical applications such as photodetectors can be realized by applying strain [34], stacking of different TMDCs [72], and doping. Fabricating heterojunctions of TMDCs is another route to tune the optical and electrical properties. Theories have predicted some interesting physical properties of vertical stacked 2-D heterostructures with respect to individual monolayers [72]. For example, vertical stacked graphene/ WS_2 /graphene trilayers have shown enhanced photon absorption and electron-hole creation, making them promising in efficient flexible photovoltaic device [73]. Graphene/h-BN heterostructures have been fabricated on lithographically patterned h-BN atomic layers [74]. Position dependent photoluminescence of monolayer WS_2 has been reported [26] which may be caused by the impurity and defects. 2D TMDCs alloy materials were theoretically predicted to be stable under ambient conditions [75]. Selenium-doped MoS_2 monolayer [76] and $MoS_{2x}Se_{2(1-x)}$ alloy [77] were directly grown by CVD method to tune the monolayer band gap. Mechanical exfoliated $Mo_{1-x}W_xS_2$ [78] and $Mo_{1-x}W_xSe_2$ [79] monolayer alloys have also been obtained with a continuous tuning of their band gaps.

In this chapter, I will introduce the one-step CVD growth of a $W_xMo_{1-x}S_2$ monolayer alloy with position-dependent composition. Both PL and Raman mapping results show that the triangle sample is in-plane composition-graded alloy that changes gradually from MoS_2 -dominated phase in the center region to WS_2 -dominated phase near the edge. Such alloy

monolayers differ from the recently reported MoS_2 – WS_2 heterojunction which has a distinct interface between the two phases [12]. Realization of such single-crystal monolayers with inhomogeneous band gaps could be important to the application in wideband photodetections and multi-color light emissions.

2.1 CVD synthesis of $\text{W}_x\text{Mo}_{1-x}\text{S}_2/\text{MoS}_2$ lateral heterostructures

Our sample was grown by CVD method (see setup in Fig. 2.1a) similar to previous reported procedure [80]. MoO_3 and WO_3 powder were dispersed into ethanol, and then dropped onto different places of Si/SiO₂ (285 nm SiO₂) surfaces. The Si/SiO₂ substrates were put into a one-end-sealed small quartz tube, and the small tube was then pushed into the center of a 25 mm-diameter quartz tube.

Fig. 2.1 (a) CVD setup for the growth of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloy monolayers. (b) SEM image of a general view of the obtained sample.

Then, 0.2 g sulfur was put at the edge of quart tube. First, the tube was flushed by Ar

gas flow at 200 sccm for 15 min in order to eliminate air, then maintained at an atmospheric pressure with continuous Ar flow at 10 sccm. The furnace was then ramped to 550 °C in 10 min, then to 850 °C at a rate of 5 °C/min and finally maintained at 850 °C for 10 min. After the growth, the furnace was switched off and cooled down to room temperature naturally. $W_xMo_{1-x}S_2$ samples were found near to the WO_3 source.

Scanning Electron Microscope (SEM) characterization was conducted using Field Emission Scanning Electron Microscope with Energy Dispersive X-ray Analysis (JEOL JSM-6700F). Atomic force microscopy (AFM) and scanning near-field optical microscope (SNOM) were measured by a scattering-type system (Neaspec) at an excitation wavelength of 11.2 μm . Photoluminescence mapping at excitation wavelength of 532 nm and 457 nm were obtained from a WITEC CRM200 Raman system with 150 line mm^{-1} grating. Raman mapping at excitation wavelength of 457 nm was measured on a WITEC CRM200 Raman system with 1800 line mm^{-1} grating. Raman spectra at excitation wavelength of 532 nm were obtained from a Renishaw Invia Raman microscope.

As the melting point of WO_3 (1473 °C) is much higher than that of MoO_3 (800 °C), MoS_2 is expected to grow first followed by WS_2 during the increase of furnace temperature. A typical SEM image of the as-synthesized sample is shown in Fig. 2.1b, in which we can find numerous triangle-shaped crystals. Some triangles can be identified to compose of a small triangle around with a big triangle as shown by the red dash square in Fig. 2.1b.

Microscopic optical image of one typical monolayer triangle shows homogeneous

contrast (Fig. 2.2a). However, in SEM image taken from the same triangle (Fig. 2.2b), a contrast between the center and edge part can be inspected and a small triangle at the center is spotted. This contrast indicates that the big triangle contains two kinds of materials. As both MoO_3 and WO_3 were used as the precursor, this triangle should contain both elements. From AFM measurement, the height of this triangle was determined to be about 0.7 nm which is uniform from the edge to the center (Fig. 2.2b). Figure 2.2c is the AFM image of one triangle. There is only a very slight difference between the center and the edge part. Therefore we may conclude that this triangle is a single layer. In other words, the heterostructure is formed in a lateral direction.

Figure 2.2d is a SNOM phase image of the same triangle in Fig. 2.2c recorded using an incident laser of 11.2 μm . The signal of scattering-type SNOM is related to dielectric constant of materials [79]. The contrast of two colors in one triangle is another evidence of the heterostructure, in addition to the SEM image. Note that the intensity of SNOM signal of some triangles is continuous from center to edge, rather than a shape contrast, which is consistent with a mixed composition from the center to edge. Figure 2.3 shows that two triangles are connected at the edge parts. The SNOM image tells us that the compositions of the center and edge parts of both two triangles are different. Therefore, SNOM is a reliable tool to compare the compositions of different materials.

Fig. 2.2 (a) Microscopic optical image of one $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ triangle and (b) the corresponding SEM image. A small triangle in the center region is visible. AFM height signal following the dashed line confirms the monolayer. (c) AFM image of one triangle, and (d) the corresponding SNOM phase image. The different contrast between the center and the edge indicates the composition difference.

Fig. 2.3. (a) SEM image of two triangles. (b) SNOM mapping of the two triangles indicating that the composition of each triangle at the center and edge region is different.

2.2 Raman spectra of lateral heterostructures

It is further realized that this monolayer is not a MoS_2 - WS_2 two-phase heterojunction, but a $\text{W}_x\text{Mo}_{1-x}\text{S}_2$ alloy with varying composition. The first evidence can be provided by

Raman result. Figure 2.4a is the optical image of one triangle alloy taken by the Raman CCD, and Fig. 2.4b show the Raman spectra recorded from six points marked in Fig. 2.4a. We can clearly see that the E_{2g}^1 mode and A_{1g} mode shift from point 1 (at the edge) to point 6 (at the center). Fig. 2.4c-d show Raman intensity mappings of the peak centered at 356 cm^{-1} (E_{2g}^1 mode of WS_2) and at 384 cm^{-1} (E_{2g}^1 mode of MoS_2), respectively. The mappings by the A_{1g} mode in Figs. 2.4e-f show similar results. Based on these Raman mapping images, one may conclude that our sample is composed of MoS_2 - WS_2 two-phase heterojunction with a sharp interface. In fact, it has been reported that the Raman spectra of $W_xMo_{1-x}S_2$ alloy by exfoliation still look similar to the one of MoS_2 even when the x value reaches 0.42 [78]. It is important to note that the Raman spectrum at each point in Fig. 2.4b is different from each other. At point 1, the Raman shift of E_{2g}^1 mode is 356.1 cm^{-1} and the A_{1g} mode is 418.2 cm^{-1} . From point 1 to point 3, the intensity of A_{1g} mode is unchanged, but the intensity of E_{2g}^1 mode decreases. At the center region (point 6), The E_{2g}^1 mode of MoS_2 locates at 384.5 cm^{-1} and the A_{1g} at 404.0 cm^{-1} . The difference between the two modes is 19.5 cm^{-1} which corresponds to the monolayer MoS_2 [81]. At point 5, the difference of E_{2g}^1 mode (383.1 cm^{-1}) and A_{1g} mode (406.2 cm^{-1}) becomes 23.1 cm^{-1} which is larger than the one of single layer. At point 4, which is the transition region between WS_2 and MoS_2 , the Raman spectrum shows three peaks which are mixed with vibration modes of WS_2 and MoS_2 . Our Raman spectra of six points at Fig. 2.3b correspond very well to that of $W_xMo_{1-x}S_2$ alloy obtained by mechanical exfoliation [78]. Therefore, it can be inferred that our sample is an alloy structure,

rather than a distinction heterojunction.

Fig. 2.4 Raman characterization with the excitation wavelength of 457 nm. (a) Optical image of one triangle. (b) Raman spectra collected from 6 points in (a). Raman intensity mappings of the E_{2g}^1 mode of (c) WS_2 and (d) MoS_2 . Raman intensity mapping of the corresponding A_{1g} mode of (e) WS_2 and of (f) MoS_2 .

To further confirm the alloy composition, Raman spectra were also measured using the excitation wavelength of 532 nm (see Fig. 2.5) [31]. Point 1 and point 2 show WS_2 like Raman spectra. However, compared to pure WS_2 , two additional peaks are present between the E_{2g}^1 and A_{1g} modes of WS_2 . We propose that Mo doping is responsible for two additional peaks. Raman spectrum of Point 3 is composed of peaks from both MoS_2 and WS_2 but the later becomes very weak. At the central region, Point 4 shows MoS_2 like Raman spectrum but the A_{1g} mode is broader than that of pure MoS_2 . These data further corroborate that our sample is composed of $W_xMo_{1-x}S_2$ alloy with different composition from center to the edge of the triangle.

Figure 2.5 Raman spectra obtained with an excitation wavelength of 532 nm. The presence of two new peaks at point 1 and point 2 proves that our sample is not pure WS₂. Inset image are PL mapping (left) and optical image (right).

2.3 PL spectra of lateral heterostructures

We now present and discuss the PL results. Due to the transition from indirect band gap of bulk materials to direct band gap of monolayer, both MoS₂ and WS₂ have strong PL emissions only in monolayers but with different PL peak positions (band gap of MoS₂~1.85 eV and WS₂~1.98 eV) [2, 82]. Figure 2.6a is one selected triangle used for PL characterization at an excitation wavelength of 532 nm. As the PL intensity of WS₂ monolayer is approximately two orders of magnitude that of MoS₂ in our samples, the center of the triangle appears dark (Fig. 2.6b). The difference in PL intensity in our sample could result from the different defect concentrations between the center region and edge part. In general, the photoluminescence emission intensity of monolayer WS₂ is drastically higher than that of monolayer MoS₂. And this has been attributed to higher concentration of defects

or unintentional doping in the monolayer MoS₂ compared to WS₂ [27, 82]. By mapping selectively the fitted PL intensity of the MoS₂ spectra (Fig. 2.6c), we can clearly see that center region of the triangle is close to MoS₂. As for the mapping of the fitted peak intensity of WS₂ [31], the image becomes undistinguishable from Fig. 2.6b, which is not surprising since the PL intensity of WS₂ is much stronger than that of MoS₂.

Fig. 2.6 Photoluminescence characterization. (a) Optical image of one W_xMo_{1-x}S₂ triangle. (b) Panchromatic PL image showing the intensity distribution. (c) PL intensity mapping of MoS₂ fitting from (b). (d) PL spectra collected from six points indicated in (a). Inset shows the PL spectra at point 5 and point 6 with peak fitting. (e) PL peak position as a function of the position, together with data of pure WS₂ and pure MoS₂. The calculated x value of the Mo_xW_{1-x}S₂ monolayer alloy is also plotted.

Figure 2.6d shows the PL spectra selected from the six points, which present the position-dependent peak position and intensity. Consistent to the mapping, the PL intensity drops dramatically from point 1 to point 6, and the peak position simultaneously shifts from

633.6 to 687.4 nm. At point 5 and point 6, the PL spectra are characteristics of MoS₂ (see the two peaks in inset of Fig. 2.6d); however peak A shifts red compared to the pure MoS₂ monolayer that we will discuss later.

To show the shift more clearly, the normalized spectra were presented in Fig. 2.7. It has been shown that the PL peak position of TMDCs alloy can shift continuously by tuning the composition of different elements [77, 79]. Therefore, it is reasonable that the PL shift of our sample results from the composition inhomogeneity at different positions of individual triangle.

Figure 2.7 Normalized PL spectra obtained by the excitation wavelength of 532 nm.

Similar PL spectra were obtained by excitation with a shorter-wavelength (457nm) laser line in Fig. 2.8a. A shorter wavelength laser allowed us to observe another excitonic emission peak B. It is clear that another exciton peak (peak B) shifts with location in the same trend with peak A (Fig. 2.8b).

Figure 2.8 (a) PL spectra obtained by the excitation wavelength of 457 nm. (b) Enlarged view of Peak B to illustrate the shift.

2.4 Band gap evolutions of the lateral heterostructure

Position dependent PL of pure WS₂ monolayer has been reported previously [26, 80], in which the blue shift was observed only near the edge and the shift was due to variation of the W to S atomic ratio [80]. The PL redshift in our study originates from composition inhomogeneity from the edge region to the center; possible reason for this composition inhomogeneity is that WS₂ and MoS₂ are doped into each other during the growth. Peak A and peak B of MoS₂ and WS₂ are the direct excitonic transitions at the Brillouin zone K point from conduction band to valence band [32], due to spin-orbit coupling in valence band. The position of peak A of pure MoS₂ in our sample is 675.4 nm, and 625.0 nm for pure WS₂ at the excitation wavelength of 532 nm. The peak A position from the six points all deviate

from that of pure MoS₂ or WS₂, corresponding to different ratios of Mo to W in the W_xMo_{1-x}S₂ alloy. The redshift at point 6 with respect to the pure MoS₂ can be explained by the Bowling effect in the monolayer W_xMo_{1-x}S₂ alloy [78]. Empirically, the PL peak position can be correlated to the composition according to equation [78]:

$$E_{W_xMo_{1-x}S_2} = xE_{WS_2} + (1 - x)E_{MoS_2} - bx(1 - x) \quad (1)$$

The bowling factor b makes the equation nonlinear, which is what we see in our results (Fig. 2.6e). In order to estimate the composition of the alloy, a reasonable value of b is needed. We assume the bowling factor to be 0.34 by setting the highest value of the above quadratic equation equal to our observed value of 687.4 nm (at point 6). Then, the composition at all six points are calculated and plotted in Fig. 2.6e. Point 0 and point 7 represent the pure WS₂ and pure MoS₂. We can see that x decreases gradually from the edge region to the center. It is proposed that the composition variation stems from a change in the precursor concentration during the growth temperature rises up. Because of its lower melting point, MoO₃ sublimates first and give rise to the initial growth of MoS₂-dominating composition near the center region. Subsequently, further increasing temperature induces the growth of WS₂-dominating composition near the edge region. Hence, Mo_xW_{1-x}S₂ alloy monolayer with inhomogeneous PL is obtained after the whole growth.

2.5 Summary

In conclusion, we have realized Mo_xW_{1-x}S₂ monolayer alloy with in-plane inhomogeneous photoluminescence using the conventional CVD method. SNOM and

Raman characterization reveal that the monolayers are composed of MoS_2 and WS_2 . It is proposed that MoS_2 grows first at the center followed by growth of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ along the edge of MoS_2 . PL results show that the monolayer possesses position-dependent band gap from center to edge, based on which the composition of the alloy has been calculated. $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloy with different band gap may have interesting applications as photodetectors and multi-color light emitters.

Chapter 3 Coupling and interlayer exciton in twist-stacked WS₂ bilayers and trilayers

Van der Waals interaction between atomic layers in two-dimensional materials affects their physical properties such as evolution of band structure from indirect band gap (bulk) to direct band gap (monolayer) in MoS₂ [2]. Vertical twisted 2-D materials are good platforms to study vdW coupling, such as twisted graphene bilayer [83], transitional metal dichalcogenides bilayer [84], and vertical heterostructures [12, 68]. Some interesting phenomena were reported in twisted graphene bilayers such as Van Hove singularities [85], Dirac electrons localization [83], and Hofstadter's butterfly [86].

In vertical stacked MoS₂/WS₂ heterostructure which was fabricated by transferring MoS₂ flakes to WS₂ flakes, a new photoluminescence peak emerged after annealing in vacuum which is dictated by charge transfer and band normalization between the WS₂ and MoS₂ layers [56]. Also, indirect band gap peak of 15 ° twisted MoS₂ grown by chemical vapor deposition method has a smaller redshift due to the larger interlayer distance compared to the ones of AA and AB stacked MoS₂ [87]. Although WS₂ has a similar atomic structure to MoS₂, very different properties have been shown, such as larger valence band splitting of WS₂ (0.41eV) [26] than MoS₂ (0.16eV) [2, 32]. Also, the degree of circular polarization of A exciton emission under near-resonant excitation is around 95% in WS₂ bilayer [85] in contrast to 10–30% in MoS₂ bilayer [88].

In this chapter, we demonstrate the observation of WS₂ bilayers and trilayers with

various twist angles on quartz plates by CVD method. The twisted bilayers have much intensive PL compared to both monolayers and untwisted bilayers (AA and AB stacked bilayers) and the absence of indirect transition peak. As is known, bilayer WS₂ is an indirect band gap material. In our experiment, the twisted bilayer WS₂ has a much stronger PL intensity and absence of indirect emission peak which is similar to monolayer WS₂. On the other hand, both PL peak position and intensity are different with monolayer one. Therefore, we considered that the twisted bilayer WS₂ has a quasi-direct band gap as a result of weakened coupling due to enlarged interlayer distance.

3.1 Synthesis of random twisted WS₂ bilayers and trilayers

Our samples were growth by CVD method at 1100 °C using the setup shown in Fig. 3.1a. Quartz plate was covered on the top of a sapphire boat which was placed in a 25 mm diameter quartz tube and put at the center of furnace. WO₃ powder as a precursor was spread on a piece of Si wafer and put on the bottom of the sapphire boat. Another precursor 0.1 g sulfur powder was put in a quartz boat and placed on the outside of furnace. The furnace was flowed by 200 sccm pure Ar for 30 min then 20 sccm Ar when furnace started heating. The furnace was heated up to 1100 °C at the rate of 20 °C/min. When temperature reached to 1100 °C sulfur powder was pushed to the edge of the furnace by a magnet so that sulfur powder became melting and supplied S vapor to the center of the furnace. After 20 min growth, the furnace cool down naturally. Growth process is at atmospheric pressure.

Optical images are taken on Nikon microscope with a 100× objective lens. Bilayer WS₂

with twist angles of 0° , 13° , 30° , 41° , 60° , and 83° were observed as shown in Fig. 3.1b-g. The twist angle is defined by rotation of upper layer related to the lower layer at counter-clockwise direction. We can see that the smaller upper monolayer WS_2 triangle is twisted to different angles in related to the bigger lower monolayer WS_2 in each sample.

Figure 3.1 (a) CVD setup for the growth of WS_2 bilayers. (b)-(g) Optical images of the twisted WS_2 bilayers with twist angles of 0° , 13° , 30° , 41° , 60° and 83° , respectively. The twist angle is defined by the rotation of top triangle with respect to the bottom one in the counter-clockwise direction.

3.2 Extremely strong PL intensity in twisted WS_2 bilayers

PL at 532 nm and 457 nm excitation wavelength is conducted on a WITEC CRM200

Raman system with 150 line mm^{-1} grating. Raman mapping at excitation wavelength of 457

nm is measured on a WITEC CRM200 Raman system with 1800 line mm⁻¹ grating. Raman spectra at 532 nm is measured on a Renishaw Invia Raman microscope. Absorbance spectra is measured on JASCO Microspectrophotometer with a 5 μ m spot size.

Monolayer WS₂ is a direct band gap material whereas WS₂ bilayers with AA or AB stacking is known to have an indirect band gap due to the interlayer electronic coupling [89]. However, as the symmetry between upper and lower layer is broken, the random twisted WS₂ bilayer samples are expected to have interlayer distance and degree of coupling different from the AA-stacked (0° twist) WS₂ bilayer. Figure 3.2 shows the absorbance spectra of monolayer, 0° and 30° twisted bilayer WS₂. Surprisingly, the peak position of exciton A at 30° twisted bilayer is almost same to monolayer one rather than 0° bilayer. This trend implied that the band structure of 30° twisted bilayer tends to evolve from AA stacked bilayer to monolayer, which is attested in the following PL spectra. One should notices that there is another peak near to the exciton A at 30° twisted bilayer WS₂, which is still unclear and need further investigation.

Figure 3.2 Absorbance spectra of monolayer, 0° bilayer and 30° twisted bilayer WS₂.

Photoluminescence can provide useful information on the band gap structure and direct or indirect band gap transition. Figure 3.3a shows the PL spectra of the twisted WS₂ bilayers. PL spectra of the WS₂ bilayer with 0° and 60° twist angle (viz., AA and AB stacking) show two dominating peaks that correspond to direct transition peak A and indirect transition peak I. This is well within expectation and proves that the 0° and 60° twisted WS₂ bilayers are indirect band gap materials. However, for the random twisted WS₂ bilayers (13°, 30°, 41°, and 83°) the PL spectra are very different. Firstly, the PL intensity is much stronger than that of AA or AB stacked bilayer. For example, PL intensity of 30° twisted WS₂ bilayer is about 22 times stronger than the 0° sample. Secondly, the indirect transition peak I seen in the AA or AB stacked bilayers is absent in random twisted bilayers. Thirdly, a small peak A_I shows up in the PL spectra of random twisted bilayers. All these PL features indicate prove that the random twisted WS₂ bilayer has a different band structure from AA or AB stacking WS₂ bilayers. To show clearly the changes of PL spectra, we fit the PL curves by Lorentz function and plot as a function of the twisting angle in Fig. 3.3b. As can be seen, the PL curves in random twisted WS₂ bilayers are composed of three peaks (peak A, peak A_I, and peak I). Note that Peak A and peak A_I are also observed in the absorbance spectrum in Fig. 3.3c. Peak I is absent in the absorbance spectrum, which corroborates the assignment of indirect transitions.

Figure 3.2 Photoluminescence and Raman results of twisted WS₂ bilayers at the excitation wavelength of 532 nm. (a) PL spectra of the random twisted WS₂ bilayers as a comparison to the 0° and 60° twisted bilayers, and monolayer (1L). Note the stronger PL intensity of A exciton and disappearance of indirect transition peak I in the random twisted bilayers. (b) Summary of PL peaks position obtained by Lorentz fitting of the PL curves in (a). (c) Absorbance spectrum of the 30° twisted bilayer showing the peak A and A_I. (d) Raman spectra of all bilayer samples showing the redshift and broadening of the A_{1g} mode and blueshift of 2LA mode (E_{2g}¹ mode is merged into 2LA).

Phonon vibrations in 2-D TMDCs are very sensitive to interlayer coupling and are useful in identifying the layer number of TMDCs [42]. We also investigated Raman spectra of our samples in Fig. 3.3d. The out-of-plane vibration mode A_{1g} of the random twisted bilayers both redshifts and broadens with respect to the 0° and 60° bilayers. The longitudinal acoustic phonon (2LA) shifts blue in random twisted bilayers. The in-plane mode E_{2g}¹ which is merged into the 2LA mode peak may have the same trend with 2LA. The broadening and redshift of A_{1g} mode in random twisted WS₂ bilayers has a similar trend with the monolayer WS₂, which proves that interlayer mechanical coupling of random twisted bilayers is weaker than the AA or AB stacked bilayers.

To further verify our results, we also measured the PL spectra of our samples at excitation wavelength of 457 nm. The result is presented in Fig. 3.4a. Similar to the result by 532 nm excitation, PL spectra of the random twisted WS₂ bilayers show that there bilayers are quasi-direct band gap materials. Both Raman modes of E_{2g}^1 and A_{1g} can be seen in Fig. 3.4b since the 2LA mode becomes much weaker at 457 nm excitation. We can clearly see that E_{2g}^1 of random twisted bilayers blueshifts compared to the ones of 0° and 60° bilayers. This can be more clearly seen from the summary of both peak shift and Raman intensity ratio of E_{2g}^1 to A_{1g} modes in Fig. 3.4c. The peak difference, $\omega(A_{1g}) - \omega(E_{2g}^1)$, of the random twisted bilayer is smaller than the AA or AB stacked bilayer. Also, the intensity ratio of two modes in the random twisted bilayer is near to that of monolayer, which implies that the mechanical coupling in the random twisted bilayer is weaker than that of AA or AB ones.

Figure 3.4 Photoluminescence and Raman results of twisted WS₂ bilayers at excitation wavelength of 457 nm. (a) PL spectra of the bilayers, showing the large intensity of peak A and absence of peak I in the random twisted bilayers. (b) Raman spectra. (c) Peak position difference and the intensity ratio of A_{1g} to E_{2g}^1 . Data from monolayer (1L) is included.

3.3 Indirect band gap evolution in twisted WS₂ trilayers

In addition to twisted bilayers, twisted trilayer WS₂ were also observed with twist angle of 30°, 0°, and 60° (see Fig. 3.5a-c). In this case, the bottom layer has an AA stacking configuration on top of which a new layer grow with twisted symmetry. PL spectra of the trilayer WS₂ are shown in Fig. 3.5d.

Figure 3.5 Optical images and PL spectra of twisted WS₂ trilayers at excitation wavelength of 457 nm. (a)-(c) Optical images of the trilayers with twist angle of 30°, 0°, and 60°. Scale bars are 10 μ m. (d) PL spectra. A new peaks A_I presents in the 30° twisted trilayer. Red curve is the absorbance spectrum of 30° twisted trilayer in (a). (e) Raman spectra

Different from twisted bilayer WS₂, trilayer WS₂ with 30° twisted angle does have a strong indirect peak I which also shifts blue with respect to the ones of 0° and 60° twist angles. Interestingly, the new peak A_I also appears at slightly higher energy position than peak A, which is similar to the case of twisted bilayers. Again, this new peak was also observed in the absorbance spectrum of 30° twisted trilayer (see inset in Fig. 3.5d), indicative

of its excitonic nature. Raman spectra of twisted trilayer are shown in Fig. 3.5e. As expected, the E_{2g}^1 mode of 30 ° twisted trilayer has a weaker Raman intensity than the ones of 0 ° and 60 °. Peak positions of both E_{2g}^1 and A_{1g} modes have no obvious shift in the twisted trilayers.

3.4 Theoretical calculation and explanation

In order to understand the coupling evolution of twisted WS_2 bilayer, we conducted *ab initio* calculations on the band structure and interlayer distance at different twist angles. Our calculations were based on density functional theory (DFT) within the local density approximation formulated by Perdew and Wang (PWC) [26] as implemented in the DMol3 code [27, 28]. Because the weak interactions are not well described by the standard exchange-correlation functional, the DFT-D (D stands for dispersion) approach within the OBS scheme was adopted for the vdW corrections [29], DFT Semi-core Pseudopotentials (DSPP), which induce some degree of relativistic correction into the core, were used for the core treatment. Moreover, double numerical atomic orbital plus polarization was chosen as the basis set, with the global orbital cutoff of 4.6 Å. The k-point was set to $9 \times 9 \times 1$ for the structural optimization and $15 \times 15 \times 1$ for the electronic properties calculations, and the smearing value was 0.005 Ha (1 Ha = 27.2114 eV). The convergence tolerance of energy, maximum force, and maximum displacement were set to 1.0×10^{-5} Ha, 0.002 Ha Å, and 0.005 Å, respectively. A large vacuum of 30 Å was used to prevent the interaction and artificial dipole moment effects from neighboring cells in the direction normal to the WS_2 surface.

First, we calculated the band structure of monolayer WS_2 . Figure 3.6 shows that

monolayer WS_2 is a direct band gap material of 2.01 eV as the lowest energy transition happens at K point. The spin-orbital coupling is not considered in the calculation.

Figure 3.6 Side (a) and top (b) views of monolayer WS_2 and the corresponding band structure (c).

Then, we moved to calculate the band structures of bilayer WS_2 . As we discussed, there are AA and AB stacking types in bilayer. For AA stacking type WS_2 , we took the atomic structure in Fig. 3.7 as an example. The sulfur atom at the top layer is aligned to the sulfur atom at the bottom layer. Also, the Mo atom at the top layer is aligned to the Mo atom at the bottom layer with a rotation 60° at the center of sulfur atom. The band structure clearly shows that the AA stacked bilayer WS_2 is an indirect band gap material with an indirect band gap of 1.65 eV. This is because Γ point has the highest energy at valence band and the lowest energy transition happens at different k vector. A phonon is necessary to assist this transition.

Figure. 3.7 Side (a) and top (b) views of AA stacked bilayer WS₂ and the corresponding band structure (c).

Figure. 3.8 Side (a) and top (b) views of AB stacked bilayer WS₂ and the corresponding band structure (c).

For AB stacking type WS₂, we took the atomic structure in Fig. 3.8 as an example. The sulfur atom at the top layer is aligned to the Mo atom at the bottom layer. Also, the Mo atom

at the top layer is aligned to the sulfur atom at the bottom layer with a rotation 60° at the center of sulfur atom. Similarly, the band structure of AB stacked bilayer WS_2 is an indirect band gap material with an indirect band gap of 1.24 eV. So we know both AA and AB stacked bilayer WS_2 are indirect band gap materials.

Then we calculated the band gap with different twist angles in bilayer WS_2 . The result of band gap and interlayer distance as a function of twist angle is plotted in Fig. 3.9. The values do not exactly match experiment data, because partially of the different twist angles used in the ideal atomic model; Nevertheless, we are more interested in the trend. The interlayer distance is about 0.627 nm of 27.8° twisted WS_2 bilayers which is larger than the ones of AA (0.593 nm) and AB (0.595 nm) stacking configurations. The increased interlayer distance of random twisted bilayers, which is due to the steric repulsion effect [87], may explain the broadening and redshift of A_{1g} modes in Fig. 3.3d. In addition, Figure 3.9 also shows that the random twisted bilayers have an evidently larger indirect band gap than AA or AB stacked one. For example, the indirect band gap of 27.8° twisted bilayer increased by 0.35 eV compared to the AA stacked one. Such a larger blueshift may clarify the PL spectra of our samples in Fig. 3.3a. Fitting of the PL curve show that the indirect peak (1.83 eV) of 30° twisted bilayer has a 0.15 eV blueshift compared to the one (1.70 eV) of AA stacking bilayer. Both the enlarged interlayer distance and blueshift of indirect band gap prove the weakened interlayer couplings in random twisted bilayers, which are manifested by their extraordinary PL spectra.

Figure 3.9 Calculated interlayer distance and indirect band gap energy as a function of different twist angles in WS₂ bilayers.

In the growth of random twisted bilayers, it is found that temperature and nucleation are important factors in our experiments. Random twisted WS₂ bilayers were found at high growth temperature (1100 °C) while only AA and AB stacking bilayers were observed at a lower temperature (850 °C). Most likely, the top layer tends to grow following the nucleus orientation and overcome the angle mismatch with the bottom layer at a high temperature. In addition, the twist angles are random and we found no preference of certain twist angle in our experiments. This is consistent with both experimental (similar PL and Raman spectra) and theoretical modelling results (similar interlayer distances and indirect band gaps). It would be interesting to be able to control the growth of different twist angles, for example, by tuning the growth temperature and precursor concentration, which will be our future study.

Twisted TMDCs bilayer is good platform to study many-body phenomena, such as interlayer exciton [84] and trion [90]. Due to the spin and layer pseudospin coupling in

TMDCs AB stacking bilayer, interlayer hopping energy is twice of spin-orbital coupling (SOC) strength [90]. In other words, interlayer hopping is greatly suppressed due to spin-layer locking effect. However, the larger interlayer distance and symmetry breaking in the random twisted WS_2 bilayer make interlayer hopping possible to form an interlayer exciton. The PL peak fitting of 30° twisted WS_2 bilayer is shown in Fig. 3.7a. The peak A_I (1.98 eV) is supposed to result from the interlayer exciton transition and peak A (1.90 eV) from the well-known intralayer excitonic transition. Both peaks are clearly observed in the absorbance spectra, which implies that these two peaks originates from excitonic transitions.

Figure 3.10 (a) Lorentz fitting of the PL spectra of the 30° twisted WS_2 bilayer (black line) showing the peak A, peak A_I , and peak I. (b) Schematics of intralayer exciton state and interlayer exciton state in the twisted WS_2 bilayer.

Figure 3.7b illustrates the interlayer exciton and intralayer exciton in the twisted WS₂ bilayer, in which the binding energy of interlayer exciton is lower than that of intralayer one [8, 66]. The binding energy of interlayer exciton A_I is about 80 meV less than the one of intralayer exciton A ($E_{A_I} - E_A = 1.98 \text{ eV} - 1.9 \text{ eV}$). In this random twisted bilayer, the weaker interlayer coupling allows carrier to transfer from one layer to the other and form interlayer electron-hole pairs.

3.5 Summary

WS₂ bilayers with different twist angles have been grown by CVD method at high temperature (1100 °C) and are employed for the study of interlayer coupling. It is found that these random twisted WS₂ bilayers possess a quasi-direct band gap PL characteristics with much higher intensity than the non-twisted AA or AB stacked bilayers. This extraordinary PL results from weakened interlayer coupling between the twisted bilayers due to increased interlayer distance. Calculation reveals that random twisted bilayers have larger interlayer distance and blueshift of indirect transition energy compared to AA or AB stacked bilayer. In addition to the A excitonic transition peak, another peak A_I has been observed in PL spectra of both random twisted bilayers and trilayers. We attribute this peak A_I to the interlayer excitonic transition. These random twisted WS₂ bilayers with adjustable interlayer coupling could be a suitable platform to investigate optoelectronic and spin-valley properties.

Chapter 4 Giant enhancement of cathodoluminescence of monolayer TMDCs

4.1 Introduction

Cathodoluminescence, photon emission excited by a high-energy electron beam, is widely applied in the analysis of mineral compositions [91], light emitting diodes [92], surface plasmon mapping [93]. Compared to photoluminescence excited by light, CL offers a much higher excitation energy allowing the study of wide band gap materials including diamond [94] and hexagonal boron nitride [95]. Due to a small excitation hotspot CL has been extensively used to study nanostructures including hyper-spectral imaging of plasmonic gratings [96], nanoparticles [97], nano-antenna [98], quantum well [99], three-dimensional nanoscale visualization of metal-dielectric nanoresonators [100] and nanoscale light sources [101].

The basic setup of a CL spectroscopy is shown in Fig. 4.1, which is quite similar to a scanning electron microscope. A high speed electron beam from an electron gun hits the sample in vacuum and excites various types of signal including back-scattered electrons, secondary electrons, Auger electrons, X-ray, cathodoluminescence (light), and so on. Back-scattered electrons and secondary electrons are used to image samples. The excited CL signal can be collected by a spectrometer via inserting a parabolic mirror. As the energy of the incident electron is much higher than the band gap of materials, the wavelength range of detectable CL signal is almost unlimited from infrared to ultra violet.

Figure 4.1 Schematic setup of a cathodoluminescence spectroscopy

One advantage of CL compared to PL is its high spatial resolution. The spot size of an electron beam is much smaller than the one of a laser because the diffraction limit of a high speed electron is smaller than the one of a photon from a laser. For example, CL spectroscopy has been used to realize the 3D nanoscale visualization of metal-dielectric nanoresonators [100]. Figure 4.2 shows that the 3D nanostructure is reconstructed by the CL spectroscopy at the nanoscale resolution. Moreover, CL spectroscopy can be applied in many research fields. X. Fu, *et al.* [102] reported that the exciton drift in a bended ZnO wire was observed by CL spectroscopy, which proved that CL spectroscopy was a powerful tool to study exciton dynamics. Ultra violet single photon emission (4.1 eV) from an hBN flake (wide band gap material) was found by CL technique [70], which is attributed to a point defect. Therefore, we can investigate 2D materials by CL spectroscopy in nanoscale resolution and wide spectral ranges which are not easy realized by PL spectroscopy.

Figure 4.2 Schematics, SEM and CL mapping at a wavelength of 850 nm of crescents with orientations of 90 °, 120 ° and 150 °.

In atomic layers of MX_2 , it is challenging to detect the CL signal as the electron-hole creation cross section is extremely small. Moreover, the spatial distribution of electron-hole pairs at the interface, which is near the point of free-electron injection, is close to a 3D spherical shape of a few microns in diameter. Only a small fraction of recombination takes place in the top 2D material and most of them happen in the supporting slab. One potential way to enhance the CL signal is to imbed the thin material in a quantum well structure. For example, the CL emission of a 5 nm InGaN film has been observed in the InGaN/GaN quantum well [103], which is also supported by the Monte Carlo simulation [104, 105]. The excitation volume of InGaN thin film was enlarged by sandwiched it into a quantum well, which gives us a hint to solve the excitation volume problem of 2D materials.

So far only a few reports are available on CL study of 2D materials, including six atomic

layer thick flakes of boron nitride [106]. However, CL from monolayer MX_2 has not reported. In this report we show that CL emissions from monolayer MX_2 (MoS_2 , WS_2 and WSe_2) can be enhanced and efficiently detected in a van der Waals heterostructure, in which the luminescent MX_2 layer is sandwiched between layers of hexagonal boron nitride with higher energy gap (see schematics in Fig. 4.3a). Here the $\text{hBN}/\text{MX}_2/\text{hBN}$ heterostructure can effectively increase the recombination probability of electron-hole pairs in the monolayer MX_2 in such a way that a good fraction of the electrons and holes generated in the hBN layers diffuse to and then radiative recombine in the MX_2 layer, leading to significant enhancement of the emission, comparatively to an isolated layer (Fig. 4.3b).

Figure 4.3 (a) Illustration of cathodoluminescence in an $\text{hBN}/\text{MX}_2/\text{hBN}$ van der Waals heterostructure. (b) Process of the generation, diffusion and recombination of e-h pairs. The minor number of e-h pairs generated in the MX_2 layer is ignored.

To confirm our proposed model, we conducted Monte Carlo Simulation via the software

of Casino 3.3 version [107]. The energy distribution of an electron beam of 5 keV and 20 nm diameter in 60 nm thick hBN layer was obtained (Fig. 4.4a). The electron energy decays and dispersed. When we changed the material of pure hBN to hBN/WSe₂/hBN, we found that the energy distribution was confined below the WSe₂ layer (Fig. 4.4b). The simulation results indicate that electron energy can be confined to narrow band gap TMD layer from the wide band gap hBN layer. However, this simulation is just based on the electron scattering. Diffusion and trapping of Electron-hole pairs are not included in this simulation. Thus we believe the enhancement in the practical condition should be larger than that of simulation.

Fig. 4.4 Energy distribution of 5 keV electron beam at 60 nm thick hBN layer (a) and sandwiched hBN/WSe₂/hBN layers (b).

4.2 Transfer method hBN/ MX₂/hBN heterostructures

Heterostructures of hBN/TMDC/hBN were prepared using a dry transfer technique [62, 64] (see Fig. 4.5). Monolayer TMDCs and hBN flakes were mechanically exfoliated from bulk hBN and TMDCs single crystals synthesized by chemical vapor transport method with Scotch tapes and deposited on 300 nm-thick SiO₂ on Si (SiO₂/Si) substrates. Mono- and few-layer flakes were identified by optical contrast (Nikon optical microscope), Raman

spectroscopy and atomic force microscopy. As adhesion layer, polyvinyl alcohol (PVA) was used as it is water-soluble with a moderate adhesion. A PVA solution (9% weight in water) was spin coated on a PDMS film (~ 0.5 mm thick). After baking at 90 °C on a hot plate, the PDMS/PVA film was attached on a glass slide and the whole stack was mounted on a micromanipulator. Under an optical microscope, the PDMS/PVA stack was aligned to an hBN flake on a SiO₂/Si substrate and brought into contact with the flake underneath. The flake can be easily picked up due to its stronger adhesion to PVA than SiO₂. The procedure was repeated to pick up a monolayer TMDC flake. Then, the hBN/TMDC on the stack was aligned and brought into contact to another hBN flake on a Si/SiO₂ substrate. The PDMS/PVA film was released from the heterostructure on SiO₂/Si by slowly peeling the PDMS film from the PVA film at 70 °C leaving the PVA film on the Si/SiO₂. The PVA film was washed off by dipping in water for half an hour. Fewer bubbles and better contacts were created with the latter approach since the heterostructure was not stretched during the removal of the PDMS film.

Figure 4.5 Schematics of the dry transfer process to fabricate the hBN/TMD/hBN vdW heterostructure.

4.3 Cathodoluminescence of hBN/monolayer WSe₂/hBN heterostructure

Figure 4.6 is the CL spectroscopy that we used in our experiments. A PDMS/PVA film supported the monolayer WSe₂ with top hBN flakes is shown in Figure 4.7a so that the shape of each flake can be clearly seen. In the next step, the hBN/WSe₂ heterostructure was aligned to a large and thick bottom hBN (thickness ~100 nm). Figure 4.7b shows the optical image of the prepared hBN/WSe₂/hBN heterostructure. Some bubbles generated during sample transfer process and enlarged when the sample was put into SEM vacuum chamber, which can be proved by atomic force microscopy topography image. The thickness of the top hBN

layer is around 4.2 nm. Furthermore, the monolayer WSe₂ is clearly identified by Raman mapping, in which the Raman intensities of the vibration mode A_{1g} are less affected by the top hBN layer.

Figure 4.6 The CL spectroscopy composed of SEM, spectrometers, and a CCD.

When CL measurement was done to monolayer MX₂ on Si substrates or freestanding monolayer MX₂, the emissions are too weak to be observable. However, strong emissions from the monolayer WSe₂ can be observed in the hBN/WSe₂/hBN van der Waals heterostructure (acceleration voltage of 5 keV, beam current of 36.2 nA). CL mapping clearly shows the giant enhancement of the emission intensity in the hBN/WSe₂/hBN region (indicated by red color in Fig. 4.7c). The CL signal was only present in the hBN/WSe₂/hBN region (indicated by point 1), but absent in the WSe₂ region without the top hBN layer (point 2). Therefore, both the top and bottom hBN layer are key factors to CL emission of monolayer WSe₂. The CL emission peak around 1.572 eV corresponds to the excitonic

energy of the monolayer WSe₂ (Fig. 4.7d). This CL emission peak is consistent to the photoluminescence emission peak, but with a small redshift of 16.8 meV. The disalignment between CL and PL peak position may be due to the local heating effect by the e-beam, which is consistent to the well-known temperature-induced semiconductor band gap shrinkage [108]. Similar redshifts were also observed from other MX₂ samples in the heterostructure.

Figure 4.7 Cathodoluminescence of the monolayer WSe₂. (a) Optical image of the hBN/WSe₂ structure on a PDMS/PVA film before the last transfer step. The top hBN and WSe₂ layers can be easily seen. (b) Optical image of the prepared hBN/WSe₂/hBN heterostructure. (c) CL intensity mapping of the hBN/WSe₂/hBN heterostructures. The strong emission is indicated by the red color. 1: hBN/WSe₂/hBN part. 2: WSe₂/hBN part without the top hBN layer. (d) CL spectra of point 1 (red curve) and point 2 (black curve) and PL spectrum of point 1.

Furthermore, the CL intensity is proportional to the electron beam currents and the CL

intensity is unresolvable when the beam current is below 1.9 nA (Fig. 4.8). It is reasonable as the higher beam currents can generate more electron-hole pairs to recombine into photons.

Figure 4.8 Cathodoluminescence of the monolayer WSe₂ as a function of the beam current. Inset is the integrated CL intensity as a function of the beam current, which shows a linear relationship.

4.4 The dependence of cathodoluminescence intensity on hBN thickness

It is found that the emission intensity is strongly dependent on the thicknesses of both top and bottom hBN layers. We fabricated an hBN/WSe₂/hBN sample with a flat bottom hBN layer of 165.3 nm and a top hBN layer with different thickness regions of 3.5, 11.8, and 23.0 nm (see more details in Fig. 4.9a-c). The CL mapping shows clearly the intensity difference between the three thickness regions; highest at the region of 23.0 nm and weakest at the one of 3.5 nm. This can be clearly seen from the CL spectra selected from the three regions (Fig. 4.9d). Each spectrum is the average of 20 points selected from the corresponding region to eliminate intensity inhomogeneity. The dependence of integrated intensity on top hBN thickness is plotted in Fig. 4.9e, which is nearly a linear relationship.

Figure 4.9 Effect of the thickness of the top hBN layer. (a) Optical image of the selected top hBN layer before transfer, which has three thickness regions as indicated, (b) The final sample of hBN/WSe₂/hBN on Si/SiO₂ substrate and (c) the corresponding CL mapping. (d) Spectra collected from three regions of different top hBN thicknesses. Each spectrum is the average of 20 points selected from the same thickness region. (e) The plot of integrated intensity versus the thickness of the top hBN layer.

Furthermore, we found that the intensity has a similar dependence on the thickness of the bottom hBN layer. We prepared another hBN/WSe₂/hBN sample with a flat top hBN layer (20 nm thick), and a bottom hBN layer of four thickness regions of 12.1, 21.6, 36.7, 48.3 nm (see details in Fig. 4.10a-c). The CL mapping can also be identified with four parts corresponding to the four thickness regions. The average spectra selected from each regions also attest this intensity difference (Fig. 4.10d). The difference in peak positions in Fig. 4.9d may be related to spatial-dependent strain and/or heterostructure inhomogeneity. Similar to above where the top hBN layer thickness is varied, the plot of CL intensity as a function of

the thickness of the bottom hBN layer shows a nearly linear relationship (Fig 4.10e). We have also conducted similar tests on other heterostructures and obtained similar trend. Such a strong thickness dependence concords with our notion that the e-h pairs for recombination originate mainly from the hBN layers, in which a larger thickness corresponds to a higher excitation volume.

Figure 4.10 Effect of the thickness of the bottom hBN layer. (a) Optical image of the selected bottom hBN layer before transfer, (b) the finished hBN/WSe₂/hBN sample 3 on Si/SiO₂ substrate and (c) the corresponding CL mapping. (d) Averaged spectra from the four regions of different bottom hBN thicknesses. (e) Plot of integrated intensity versus the bottom hBN layer thickness.

According to calculations, the diffusion lengths for electrons and holes in hBN are in the μm range [109], so the e-h pairs generated in both top and bottom hBN layers in the heterostructure can diffuse to the middle MX₂ layer before recombination. Therefore, it is reasonable that CL intensity has a strong dependence on the thickness of the hBN layers.

Since the CL signal is hard to be observed in monolayer TMDCs, it is hard to estimate the exact enhancement factor in the van der Waals heterostructure. However, we can observe a quite small signal of monolayer WSe₂ on an hBN substrate. The enhancement factor is roughly estimated to be more than 500 when the thicknesses of both top and bottom hBN layers are 19.8 and 123.9 nm (Fig. 4.11). Finally, it is noteworthy that the bottom hBN layer cannot be replaced by the amorphous SiO₂ substrate, as the latter does not provide a flat and perfect van der Waals contact.

Figure 4.11 Enhancement factor in this sample is estimated to be more than 500.

One advantage of CL compared to PL is its high spatial resolution. The van der Waals heterostructure allows us to characterize monolayer TMDCs in nanoscale resolution. Figure 4.12 shows the CL mapping of monolayer WSe₂ sandwiched into two hBN layers. Due to the inhomogeneity of the prepared sample, some twinkles and bubbles were generated. CL mapping tells us the detailed information and ~50 nm resolution can be achieved.

Figure. 4.12 Nanoscale resolution of monolayer WSe₂ in a van der Waals heterostructure via CL mapping. The inhomogeneity of CL intensity is attributed to the local strain variation.

The question is, why both top and bottom hBN layers are necessary for evident CL emission. In our configuration, strong emission from WSe₂ requires that the generated e-h pairs can efficiently diffuse to and be trapped at the interface between the two hBN layers. Because of the potential well, the carriers are transferred to the middle MX₂ which is the recombination center, leading to evident luminescence emission. In case of a single top or bottom hBN layer, the generated e-h pairs are not efficiently confined at the surface of the hBN layer even with a monolayer MX₂. Therefore, the strong CL due to WSe₂ band gap emission is attributed to the both increased excitation volume and efficient interface confinement of e-h pairs in the sandwich configuration.

4.5 Effect of strain

Cathodoluminescence spectroscopy is also powerful in revealing spatial-resolved strain effect in 2D semiconductors. It is known that the band gap shift in MX₂ is sensitive to the

strain, as evidenced in both theoretical calculations [110] and experiments [34, 36]. We investigated the strain-induced peak shift of the monolayer WSe₂ by suspending the hBN/WSe₂/hBN heterostructure sample on holes made on the Si substrate. Array of holes were fabricated by a focused ion beam with diameter of 1 and 2 μm , so that part of the sample is suspended (Fig. 4.13).

Figure 4.13 hBN/WSe₂/hBN sample on located on fabricated holes. (a) Optical image of a Si substrate with holes fabricated by a focused ion beam. The holes have two diameters of 1 and 2 μm . (b) Optical image of the hBN/WSe₂/hBN sample transferred on top of the holes. (c) AFM topography mapping of the sample around holes. Inset: height profile along the line.

Interestingly, the emission intensity of hBN/WSe₂/hBN suspended on the hole is much stronger than the part laid on the substrate at room temperature (Fig. 4.14a). By cooling down the sample, we can identify the exciton and trion peak positions clearly from the spectra. Position-dependent spectra at 10 K (Fig. 4.14b-c) clearly shows that the excitonic peak redshift with a maximum shift of 11.2 meV from the edge to the center of the hole due to strain.

Figure 4.14 Strain effect. (a) CL mapping of the hBN/WSe₂/hBN sample at room temperature. Parts of the samples are suspended on focused-ion beam fabricated holes on the substrate. Inset is the Si substrate with holes before transfer. (b) Enlarged CL mapping at 10 K around a hole. (c) Position-dependent spectra taken from a series of points in (b).

In addition to the strain due to suspension, strain in the thin heterostructures is also inevitably introduced during the transfer process. Such inhomogeneous local strain in the heterostructures is also detectable by CL spectroscopy. Indeed two energy domains were observed from the hBN/WSe₂/hBN (indicated by purple and green colors in Fig. 4.15a) sample in terms of the exciton peak position at 77 K. From the CL spectra from selected points (Fig. 4.15b), two emission peaks can be resolved at both point A and B. The two peaks correspond to the emissions of neutral excitons and trions (charged excitons) [40]. However,

the peak positions of excitons and trions at point A are 1.640 and 1.614 eV, respectively, while 1.657 and 1.623 eV at point B. The peak position difference between point A and B in the heterostructure may be caused by strain, which is possibly generated during the transfer process (e.g., bubbles).

Temperature dependent CL spectra of the point B were plotted in Fig. 4.15c. The peak positions of both excitons and trions are fitted (Fig. 4.15d) according to the semiempirical semiconductor band gap equation [108]:

$$E_g(T) = E_g(0) - S\hbar\omega \left[\coth\left(\frac{\hbar\omega}{2kT}\right) - 1 \right] \quad (2)$$

where $E_g(0)$ is the excitonic energy at 0 K, S is a dimensionless coupling constant and $\hbar\omega$ is an average phonon energy. From the fitting curves, we extract $E_g(0)$ of the exciton and trion of the monolayer WSe₂ to be 1.6652 and 1.6344 eV, respectively. So, the binding energy of the trion is calculated to be 30.8 meV which is consistent with the previous report (30 meV) [64].

Figure 4.15 Temperature dependent CL of hBN/WSe₂/hBN vdW heterostructure. (a) CL wavelength mapping at 78 K. The green and purple correspond to two frequency domains corresponding to the dominating exciton peak, respectively. (b) CL spectra recorded from the two points in (a) showing both excitons and trions. (c) Temperature-dependent CL spectra and (d) plot of the peak positions of the excitons and trions as a function of temperature. Lines are the fittings according to a semiconductor band gap equation.

4.6 Cathodoluminescence of other monolayer semiconductors

In addition to WSe₂, we also performed CL experiments to monolayer WS₂ and MoS₂ in a van der Waals heterostructure (sandwiched by two hBN layers). The emission peak position from the WS₂ heterostructure locates at 1.933 eV (Fig. 4.16a) and that from the MoS₂ in heterostructure at 1.831 eV (Fig. 4.16b). The emission peak positions of both two heterostructures redshift with respect to their photoluminescence peak positions, similar to the case of hBN/WSe₂/hBN. Cathodoluminescence mapping is inhomogeneous at the MoS₂

sample which is most likely due to poor interface contact. Therefore, sandwiching monolayer MX_2 into two hBN layers is a universal approach to study CL emissions of monolayer MX_2 .

Figure 4.16 Cathodoluminescence of monolayer WS_2 and MoS_2 . (a) CL and PL spectra of the monolayer WS_2 in the top-hBN (7.5 nm)/ WS_2 /bottom-hBN (299.4 nm). (b) CL and PL spectra of the monolayer MoS_2 in the top-hBN (13.5 nm)/ MoS_2 /bottom-hBN (168.6 nm). Insets are the corresponding CL intensity mappings. Yellow lines guide the shapes of monolayer TMDs in the van der Waals heterostructures.

4.7 Summary

In summary, for the first time we have obtained evident CL emission from monolayer MX_2 , including WSe_2 , MoS_2 and WS_2 , via a van der Waals configuration. In the hBN/ MX_2 /hBN heterostructure, electron beam induced e-h pairs can transfer to and be trapped in the middle MX_2 layer, leading to increased recombination probability within the MX_2 layer. Moreover, we demonstrate that CL spectroscopy can be applied to study the strain-induced excitonic peak shift in monolayer MX_2 . Because of its high spatial resolution and high beam energy, our demonstration makes CL spectroscopy a powerful technique to the study of 2D materials in various forms such as alloy, heterostructures or defects. The 2D monolayer-based heterostructure may promise potential applications in single-photon emitters, surface-conduction electron-emitter and field emission display technologies.

Chapter 5 Multiple phase transition in 1-T TaS₂

5.1 Introduction

Two-dimensional materials are under the current research focus because of their unique physical properties from bulk their counterparts and their application potentials in optoelectronics, energy conversion and storage, and environment remedy [50, 111]. Semiconducting transitional metal dichalcogenides, such as MoS₂ and WSe₂ with band gap in the visible range [4], are useful in field effect transistors and light emitting diodes. The most studied inorganic TMDC is MoS₂, which exhibits a transition from indirect band gap in bulk to direct band gap when it is thinned to monolayer [2]. In addition, some TMDCs show semi-metallic behavior such as WTe₂ [112]. Phase transition (PT) between metallic state and superconducting state was also observed in 2D NbSe₂ [113]. Metal-insulator transition (MIT) induced by temperature or electrical field have been observed in some 2D materials, such as 1T-TiSe₂ [114] and 1T-TaS₂ [115]. These MITs origin from charge density wave (CDW) switching.

MIT in TaS₂ results from the fundamental instability of the periodical structure, which is described in Peierls' model of one-dimensional chain of atoms [116]. In the 1D chain model, the Fermi point is at $\pm\pi/2a$, which is half of lattice vector of $\pm\pi/a$ (Fig. 5.1a). The system is unstable and the electronic disturbance will open a band gap at $\pm\pi/2a$. Lattice distortion is preferable below the critical temperature to stabilize the lattice structure and open a Mott gap. Figure 5.1b shows the phonon energy is imaginary at $2k_F$ when T equals to

T_{CDW} , which indicates a new lattice structure and phase transition.

Figure 5.1 (a) The plot of 1D band structure for a chain of atoms with one electron per atom site.
(b) Kohn anomaly in the acoustic phonon branch as a function of temperature. [116]

Even a large number of materials undergo Peierls transitions to a CDW state, only a small fraction of these have shown collective charge transport due to CDW motion [117]. The most common CDW materials include TiSe_2 , 1T-TaS_2 , NbSe_2 , NbSe_3 and so on. 1T-TaS_2 experiences two PTs during cooling down process: incommensurate charge density wave (ICCDW) below 550 K to nearly-commensurate charge density wave (NCCDW) around 350 K, and then NCCDW to commensurate charge density wave (CCDW) around 180 K (Fig. 5.2) [115]. With decreasing temperature, lattice distortion of Ta atoms causes the formation of clusters of David stars. Within one David star, 12 Ta atoms tend to move to the center of Ta atom (Fig. 5.3). As a result, only one free electron is left in David star and the rest electron are confined in valence band, leading to an increase in electrical resistance. The NCCDW state exists between CCDW state (completely filled with David stars in crystal) and ICCDW state (no David star in crystal). In the NCCDW state the crystal is partially filled with David

stars.

Figure 5.2 Phase transition of TaS₂ with temperature variation. ICCDW, NCCDW, CCDW states are shown at different temperature.

In addition to the temperature-induced PT, it has been reported that other techniques can also trigger the PT, such as femtosecond pulses [118], electric pulses [119] and gate voltage [111, 120]. These research reveal that there might be several NCCDW states in 1T-TaS₂. In addition, PTs between CCDW and NCCDW states have also been reported using an electric field at 77 K [121]. In the report by G. Liu *et al.* [122] PTs between NCCDW and ICCDW were studied at room temperature, but only at the flake thickness of 6~9 nm. So far there are no reports on the effect of layer thickness to the electrically driven PTs at room temperature.

Figure 5.3 Lattice structure of 1T-TaS₂ and a David star formation.

In this chapter, I will introduce the thickness dependent, electrically driven PTs of 1T-TaS₂ 2D flakes particularly at room temperature. We found that 1T-TaS₂ at NCCDW state at room temperature experiences an obvious electric field-induced PT. The critical electrical field to trigger PT is both thickness and temperature dependent. For relative thicker samples, both double (13~17 nm) and multiple (≥ 17.5 nm) PTs were observed, which implies the existence of several NCCDW' states before the final ICCDW state. To our best knowledge, this is the first time to observe multiple electrically driven PTs in 1T-TaS₂ at room temperature. In addition, we fabricated a TaS₂/graphene hybrid FET device and demonstrated gate-tunable PTs of 1T-TaS₂ layers.

5.2 Electrically driven phase transition of a TaS₂ flake

2D 1T-TaS₂ flakes with different thicknesses were obtained by a classic mechanical exfoliation method with a scotch tape. Thickness is a critical factor for PT from NCCDW state to CCDW state in 1T-TaS₂. Different from bulk materials, transition from NCCDW state to CCDW state is absent in thin flake of 1T-TaS₂ (24 nm) when cooling down sample

[123]. Only NCCDW state exists in the thin film 1T-TaS₂. In our experiment, we focus on PT between NCCDW state and ICCDW state in thin film 1T-TaS₂. A device with thickness of 7.8 nm is fabricated (Fig. 5.4a-b). Electron beam lithography (EBL) was employed to fabricate electrodes patterns of all samples. Then samples were evaporated 5 nm Cr and 80 nm Au by a thermal evaporator, respectively.

Figure 5.4 (a) Optical image of the 7.8 nm thick sample with gold contacts. Scale bar: 10 μm . (b) The AFM height profile is provided.

We do observe the PT induced by electric field at 300 K, as manifested by an abrupt drop of the electric resistance (Fig. 5.5a). Before the abrupt drop in resistance, there are elbows seen in curves. This is similar with CDW sliding in MIT [124]. It is observed that the electric induced PT is temperature dependent; a higher electric field is needed to trigger the PT at lower temperatures (Fig. 5.5a). In the bulk 1T-TaS₂, there should be an PT between NCCDW state and CCDW state around 180 K [118]. However, no CCDW state was observed in our 7.8 nm thick flake around 180 K, which is consistent with previous report [125] and may be due to surface oxidation [126]. Instead there is a so-called super-cooled NCCDW (sc-NCCDW) state [123], in which the discommensuration still exists below the PT

temperature from NCCDW to CCDW state in bulk sample.

We can clearly see the difference of the hysteresis loops between above 210 K and below 180 K in Fig. 5.5a. Final resistance at 180 K or 150 K seems to experience twice abrupt changes before recovering to the initial resistance. PT from final state (ICCDW) to initial state (sc-NCCDW) below 180 K is different from the one (from ICCDW to NCCDW) above 210 K with decreasing the electric field in the backward scan. And the resistance prior to the PT increases with decreasing temperature (see also Fig. 5.5b). The initial resistance goes up with cooling down but without the existence of a CCDW state. The final resistance (after PT) is temperature independent. The critical electric field corresponding to the abrupt change of resistance is temperature dependent (Fig. 5.5c). There are two linear temperature regions between above 210 K and below 180 K, from which one might identify the NCCDW state and sc-NCCDW state.

5.3 Thickness-dependent phase transition of 1T-TaS₂

The CDW transition temperature varies when thickness is thinned down to atomic scale, as observed previously also in 2D TiSe₂ [127]. To investigate the thickness effect of 1T-TaS₂ at room temperature, measurements were performed to samples with different thicknesses (Fig. 5.6) of 5.2, 8.8, 13.8, 17.0, 25.0, and 33 nm. As the 1T-TaS₂ is not stable in air, one should finish the device fabrication quickly and minimize the exposure of sample to air. The device were measured in an ultrahigh vacuum chamber by a probe station.

Figure 5.5 Electrically driven phase transition of a 7.8 nm-thick 1T-TaS₂ flake. (a) Resistance as a function of electric field showing the single PT at different temperatures, and (b) the corresponding plot of temperature dependent resistance. Final resistance after the PT is temperature independent (blue curve). (c) Temperature dependence of the critical electric field to trigger PT. Two linear regions indicate the difference between NCCDW state and sc-NCCDW state. Lines are linear fittings to the data.

Interestingly, it is observed that thinner samples require higher electric fields to trigger the PT (Fig. 5.7a). This may be related to surface impurities [120] and quantum confinement of carriers [128], as surface impurities affect more apparently the transport of 1T-TaS₂ in thinner flakes and electron-electron interaction is subject to the influence of the atomically thin film. Herein, a higher electric field is required to overcome those barriers to trigger transitions in the thinner sample.

Figure 5.6 AFM depth profiles and corresponding topography images of the samples with different thicknesses.

Another interesting phenomenon is that single PT is observed in the samples with thickness less than 8.8 nm, while double and multiple transitions appear in the samples thicker than 13 nm (Fig. 5.7b). For example, at least four transitions were observed in the 25 nm sample. Similar multiple PTs also exist at low temperatures and are reversible (Fig. 5.7c). In the report by Tsen et al [126], several abrupt drops of current with increasing electric field at 150 K have also been observed in 1T-TaS₂, which corresponds to PT between NCCDW and CCDW. However, the multiple PTs in our results occur at room temperature and is related to PT between NCCDW and ICCDW, which is more promising for memory applications with multi-level resistance states.

Figure 5.7 Thickness dependence of the phase transition. (a) Current density as a function of electric field showing PTs of the 1T-TaS₂ flakes with different thicknesses. (b) Thickness dependence of the critical electric field. (c) PT of the 25 nm thick flake at different temperatures, showing clearly multiple transitions that are probably due to electrical screening effect. (d) Schematic of the temperature-dependent PT and electrically driven PT. Multiple NCCDW states may exist in electrically driven PT according to our results.

The origin of this multiple PTs is so far unclear. Actually there are several possible mechanisms to affect the PT of 1T-TaS₂, such as defects pinning, strain [129], and substrates [130]. According to previous study of PT in bulk TaS₂, in NCCDW state, electron-electron interaction is screened by domain boundaries [131] and the screening may prevent transition to CCDW state. The multiple PTs between NCCDW and ICCDW states implies that there may exist several metastable NCCDW' states [123] with different density and area of

domains before reaching to the ICCDW state (Fig. 5.7d). An electric field may decrease the density and area of domains to form metastable NCCDW' states, which corresponds to the occurrence of the second and subsequent PTs. Also, the NCCDW' states may originate from multiple transitions in different layers of the TaS₂ flake at different voltages, as the multiple PTs are observed only in the relatively thick films. The absence of NCCDW' state in the relatively thin sample is still unclear and may be related to the influence of the substrate.

As the contact resistance may be dependent on the applied electric field [132], we conducted the four-probe measurement. It is found that the contact resistance is only around 8% of total resistance regardless of the sample thickness and has little influence on the *I-V* curve during the PT process (Fig. 5.8a-d). Therefore, the contact resistance is not a major factor to the multiple PTs in our samples.

5.4 Reversibility of phase transition of 1T-TaS₂

The above observed PT in 1T-TaS₂ at room temperature is reversible with certain range of the electric field. However, there exists threshold; when the applied electric field is beyond certain values, the transition becomes irreversible. In the 5.2 nm thick sample, when the electric field reaches 31.5 kV/cm, the sample remains at the low-resistance state (ICCDW state) and no transition back to high-resistance state is observed in backward scan (see Fig. 5.9a). This threshold phenomenon and irreversibility are also observed in other thicknesses and at low temperatures (Fig 5.9b-c).

If the voltage increases over the threshold, we observed sample breakdown as shown

by AFM images (Fig. 5.10a-b). An obvious crack track from TaS₂ flake was seen (Fig. 5.10b),

which may be due to Joule heating by the high electric field. We attempted to resume the reversibility by heating the samples (without breaking down) at 150 °C for half hour or cooling down to 30 K. However, it is found that the samples still stay in the low-resistance state. Also, Raman spectra before and after overvoltage show similar results (Fig. 5.10c), implying no structure change at the examined part of samples. Therefore, we propose that the irreversibility at the high electric field is probably related to the sample crack.

Figure 5.10 (a) Electric field threshold of 13.8 nm sample and device breakdown. (b) AFM image shows the detail of sample after breakdown. There is a crack trace near to one electrode. (c) Raman spectra comparison before overvoltage and after overvoltage.

5.5 Phase transition in hybrid 1T-TaS₂/graphene FET device

We attempt to make a PT device based on the TaS₂ 2D flakes. Up to now, the electrically

driven PT of 2D TaS₂ is studied by applying lateral source-drain voltage. Tuning the PT by a third gate terminal in a FET geometry is regarded to interesting and compatible with modern CMOS technology, and could open up new ways for memristive applications. Although the liquid-gate tunable PT in 1T-TaS₂ has been demonstrated [120], it requires Li ion intercalation which is not practical for device applications and also can not be achieved at room temperature. Herein, we combine 2D TaS₂ with graphene into one hybrid FET (Fig. 5.11a-b). A graphene layer was transferred near to TaS₂ flake by the wet transfer method and then connected with TaS₂ by Au [65]. The graphene after transfer shows typical bipolar electronic property (Fig. 5.11c). And the 8.8 nm thick TaS₂ flake exhibits single PT at the current of ~2 mA (Fig. 5.11d). By joining these two materials in series, the hybrid FET device shows an evident PT manifested by an abrupt increase in source-drain current (Fig. 5.11e). As PT in TaS₂ require a relative high electric field, a drain voltage of 3.5 V was applied. The drain current suddenly increases at the gate voltage of -5 V, and returns gradually to the initial high-resistance state. In addition, the PT gate voltage can be tuned separately by the drain voltage and vice versa (Fig. 5.11f-g). Our demonstration of gate tunable PT may have potential applications in memory devices.

Figure 5.11 Phase transition in hybrid 1T-TaS₂/graphene FET device. (a) Schematic of the hybrid FET device. (b) Optical image of fabricated device. Scale bar is 50 μm . (c) I_d - V_g plot of graphene FET. (d) Electrically driven PT in 8.8 nm thick 1T-TaS₂ flake. (e) I_d - V_g plot of the hybrid 1T-TaS₂/graphene FET showing the occurrence of an abrupt increase of current at a gate voltage V_g that depends on the drain voltage V_d (f). (g) Resistance switching under different gate voltages.

5.6 Summary

In conclusion, we have studied the electrically driven PT of 2D 1T-TaS₂ flakes with different thicknesses. At room temperature, we observed single PT in thin flake (≤ 8.8 nm) but both double and multiple transitions in thicker ones. The multiple PTs may be attributed to a surface electric screening effect. In addition, electric field thresholds, beyond which the PT becomes irreversible, have been observed. Finally, gate-tunable PT has also been demonstrated at room temperature in a hybrid 1T-TaS₂/graphene FET device. Our results may stimulate new understandings and more investigations on the CDW PTs towards potential applications in memristors and integrated circuits.

Chapter 6 Conclusions and future work

6.1 Conclusions of this thesis

In this thesis, I mainly introduced four works finished in the past four years about 2D materials and their heterostructures. Firstly, I introduced the successful fabrication of $\text{Mo}_x\text{W}_{1-x}\text{S}_2/\text{MoS}_2$ lateral monolayer heterojunction with in-plane tunable photoluminescence grown by CVD method. By the characterization of SNOM and Raman mappings, this alloy is proved to be composed of MoS_2 , WS_2 and their alloy with different compositions. MoS_2 is first grown at the center, then $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ grows following the edge of MoS_2 . PL mapping verified that this monolayer alloy had position dependent band gaps. We also calculated the composition of the alloy according to the corresponding band gaps.

In chapter 3, I introduced the growth of WS_2 bilayers with twist angles of 0° , 13° , 30° , 41° , 60° , 83° by CVD method. Compared to 0° stacked WS_2 bilayer with an indirect band gap, random twisted WS_2 bilayers such as 13° , 30° , 41° , *et al.*, present much more intensive photoluminescence (20 times stronger at 30°) and absence of the indirect transition peak. Also, another small peak A_I near to A excitonic transition peak was observed which is attributed to the interlayer exciton between the twisted layers. Calculation results show that the interlayer distance of random twisted WS_2 bilayer is larger than the one of AA or AB stacked WS_2 bilayer. The interlayer coupling evolution due to the larger interlayer distance makes the random twisted WS_2 bilayer to be a quasi-direct band gap materials which may have potential applications in optoelectronics and valleytronics. Furthermore, the WS_2

trilayers with the twisted top layer were shown and the excitonic peak shift and interlayer exciton were revealed by photoluminescence spectroscopy.

In chapter 4, I introduced the evident observation of efficient CL emission from monolayer TMDCs, including WSe₂, MoS₂ and WS₂, by employing an hBN/TMDC/hBN (vdW) heterostructure. In this configuration, a large number of e-beam induced carriers are generated mainly in the hBN layers, and subsequently diffuse to and recombine at the interface via the middle TMDC layer. The CL intensity exhibits a strong dependence on the thicknesses of the top and bottom hBN layers. With this method, we studied the strain-induced exciton peak shift from the suspended vdW sample by CL spectroscopy. The hBN/TMDC/hBN vdW heterostructure may open a door to the study of spatial, time and frequency-resolved optical properties of 2D materials by CL technique in the nanometer scale.

In chapter 5, I introduced thickness-dependent phase transition in 1-T TaS₂ by applying an electrical field. Electrically driven phase transition occurs at temperature of 60-300 K from high resistance state to low resistance state. The low resistance state is proved to be temperature independent. For a thinner 1-T TaS₂, a higher electrical field is needed to realize phase transition at room temperature. Also, thick film (>17.5 nm) experience multiple phase transitions until reaching to final low resistance state, which implies that there are several hidden NCCDW states. At last, we fabricate a TaS₂-graphene hybrid structure to achieve a steep slope in this hybrid FET.

6.2 Perspectives and future work

In the past decade, researchers have achieved enormous progress on 2D materials, such as graphene and TMDCs. While undoubtedly there is still much room for 2D materials, future research can be focused on two major directions: new materials and applications. Since graphene, a wide range of other 2-D materials were reported in the ever-growing literature, such as large band gap insulators (e.g., hBN), semiconductors (e.g., MoS₂), semimetals (e.g., WTe₂), CDW metals (e.g., 1T-TaS₂), and superconductors, and more recent organic-inorganic hybrid perovskites [133] and metal-organic framework materials [134]. These new 2D materials can be intrinsically layered or non-layered. 2D materials have shown their potential applications from microelectronic to biomedical imaging [69]. Moreover, graphene is currently being studied as transparent contact in optoelectronic devices and electrode materials in energy storage devices [135].

In the next step, I would like to propose two follow up work: (1) Tunneling FET based on van der Waals heterostructures; (2) Nanoscale luminescence study of 2D materials by CL spectroscopy.

1. In traditional MOSFETs, subthreshold swing (SS) at room temperature is theoretically limited to ~60 mV/dec. However, a tunneling FET does not have such a limitation because the carriers are transported by quantum tunneling rather than thermionic emission. It has been theoretically predicted that negative differential resistance and high peak-to-valley current ratio exist in the TMD/hBN/TMD heterostructure (see Fig.6.1) [58].

This resonant tunneling FET based on 2D TMDCs can provide a high switch speed and low energy cost.

Figure 6.1 Negative differential resistance are shown in the simulated J - V_{DS} curves for (a) graphene, (b) MoS_2 . The peak-to-valley ratio of MoS_2 is much higher than the one of graphene. [58]

Due to the unexpected doping in the 2D TMDCs source, they can be naturally n-type or p-type. So it is impossible to dramatically tune the Fermi level just by a gate voltage. One effective approach of Fermi level tuning is to select the different type of TMDCs as the top and bottom layers in a heterostructure. For example, we can select the p-type WSe_2 and n-type MoS_2 as the TMD layers and a 2 nm thick hBN layer as the middle tunneling barrier (Fig. 6.2). The I - V curve shows a rectifying property of this device similar to a diode. However, the expected negative difference ratio is not present in the device. In order to verify quantum tunneling, in the next stage, we need improve the device in several aspects: (1) Improve the interface contact during the transfer process; (2) Add both top and bottom gates to tune the Fermi level; (3) Vary the hBN layer thickness.

Figure 6.2 comparison of I-V curve of WSe₂/MoS₂ p-n diode and WSe₂/hBN/MoS₂ tunneling diode.

2. CL technique not only provides a high spatial resolution (nanoscale) but also a wide range of excitation energy, which make it a perfect tool to study wide band gap materials such as diamond and hBN. We have recently studied CL emission of twisted hBN/hBN heterostructure. Surprisingly, a strong emission peak at around 350 nm emerges at the junction parts (Fig. 6.3). As this emission peak is absent in the single hBN flake, it is possible to originate from the interlayer recombination. It is still preliminary and more evidence is needed to verify this emission peak. Furthermore, it will be also interesting to investigate this UV emission as a function of the twist angle of the hBN/hBN structure and interlayer coupling. CL spectroscopy can be applied also to investigate various monolayer TMDCs and heterostructures to study the interlayer coupling, defect-induced luminescence, and single photon emission.

Figure 6.3 Interlayer emission of hBN/hBN structure. (a) CL mapping of hBN/hBN sample. Green and purple lines show the shapes of top and bottom hBN layers. (b) CL spectra of four point selected from (a).

In short, 2D materials have become truly a multidisciplinary topic and still attract increasing attentions from various aspects. Exploring and discovery of new 2D materials are enriching the family of 2D materials and generating new phenomena and physics. Therefore, the future is bright for 2D materials

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