Valley Zeeman splitting in semiconducting two-dimensional group-VI transition metal dichalcogenides

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**VALLEY ZEEMAN SPLITTING IN SEMICONDUCTING TWO-
DIMENSIONAL GROUP-VI TRANSITION METAL
DICHALCOGENIDES**

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June 2018

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Abbreviations

TMDs	transition metal dichalcogenides
2D	two-dimensional
PL	photoluminescence
MEF	magnetic exchange field
hBN	hexagonal boron nitride
VBM	valence band maximum
CBM	conduction band minimum
SOC	spin-orbital coupling
MOSFET	metal-oxide-semiconductor field-effect transistor
PMMA	poly (methyl methacrylate)
DI	deionized
PDMS	polydimethylsiloxane
CCD	charge coupled device
ML	monolayer
LEDs	light emission diodes
SEM	Scanning Electron Microscope
AFM	Atomic Force Microscope

Abstract

Atomically thin semiconducting group-VI transition metal dichalcogenides (TMDs) have attracted enormous interest because of their as-born bandgaps and other unique properties giving great potential in next-generation electronic devices, valleytronics, photodetectors and flexible optoelectronics applications. Electrons at K and K' valleys in 2D group-VI TMDs can be selectively excited by the circularly polarized light but energy degenerated due to the time-reversal symmetry, which is known as the valley degree of freedom. In the presence of an external out-of-plane magnetic field, the energy degeneracy is lifted thus there is an energy difference between the two emissions from the two valleys, known as the valley Zeeman splitting energy due to the breaking of time-reversal symmetry. Such unique features originating from the strong spin-orbital and spin-valley couplings make 2D group-VI TMDs highly competitive over the traditional semiconductors and even promising for the emerging valleytronics.

In this thesis, circularly-polarized photoluminescence (PL) spectroscopy has been exploited to investigate valley Zeeman splitting behavior of emerging 2D group-VI TMDs under various circumstances.

On the way towards the large-scale integration of potential valley Zeeman splitting based devices, one of the critical issues is whether the valley Zeeman splitting behavior changes with the strength of many body interactions induced by the different doping levels across the sample. Here, spatial variations of valley splitting evolution in exfoliated monolayer WSe_2 are investigated through magneto-PL mapping

measurements. It is found that for the neutral exciton emission, the valley Zeeman splitting behavior almost stays unchanged across the sample though the PL mapping measurements show the nonuniformity of the PL emission energy, which is caused by the unintentional doping during the sample preparation process. While for trion emission, the valley Zeeman splitting behavior changes a lot with the doping level from the sample center to the edge regions.

In order to realize two stable binary states in potential valley Zeeman splitting based devices, a large valley Zeeman splitting energy is on demand even under a small magnetic field. Here, exfoliated monolayer WSe₂ samples are transferred onto a ferromagnetic substrate of EuS. The net magnetization of EuS substrate results in a short-range magnetic exchange field (MEF) on the interface between the WSe₂ and EuS. And this MEF further leads to enhanced valley Zeeman splitting energies for both trion and exciton emissions of WSe₂ on the EuS substrate. The short-range MEF originating from proximity effect can be exploited to tune the valley Zeeman splitting behavior in future valleytronics.

Hexagonal boron nitride (hBN) with a layered crystal structure has less lattice mismatch with the group-VI TMDs and is often used as a platform to improve the optical quality of the 2D group-VI TMDs by suppressing the unintentional doping from the oxide substrate. Here, a modified method is developed to directly grow WS₂ and MoS₂ monolayers on hBN with a high yield and high optical quality. Benefiting from the well-resolved and super sharp exciton and trion PL peaks, the intrinsic valley Zeeman

splitting behavior in CVD-grown WS₂ and MoS₂ monolayers on hBN have been clearly revealed through in-situ magnetic-field-dependent PL imaging and spectroscopy at cryogenic temperature for the first time.

This thesis manifests that, valley Zeeman splitting behavior in 2D group-VI TMDs can be tuned not only by the different substrates, but also by the doping levels in such 2D group-VI TMDs. These fundamental studies enable us to step further towards the future valleytronics.

Publications

1. **C. Zou**, C. Cong, J. Shang, C. Zhao, M. Eginligil, L. Wu, Y. Chen, H. Zhang, S. Feng, J. Zhang, H. Zeng, W. Huang, and T. Yu. Probing magnetic-proximity-effect enlarged valley splitting in monolayer WSe₂ by photoluminescence. (online, *Nano Res.*).
2. C. Cong*, **C. Zou***, B. Cao*, L. Wu, J. Shang, H. Wang, Z. Qiu, L. Hu, P. Tian, R. Liu, and T. Yu. Intrinsic excitonic emission and valley Zeeman splitting in epitaxial MS₂ (M=Mo, W) monolayers on hexagonal boron nitride. (online, *Nano Res.*).
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Chapter 1 Introduction

In 2004, graphene was discovered experimentally by professor Andre Geim and professor Konstantin Novoselov [1]. It was the first time to demonstrate that graphene, as one of 2D materials exists in real life and this discover opened a new era for 2D materials. However, the gapless property of graphene greatly limits the potential applications in electronics since the absence of bandgap cannot achieve an “off” state in logic circuit. Although great efforts have been made to open the bandgap of graphene, including uniaxial strain engineering [2], an electric field perpendicularly applied to bilayer graphene [3] and so on, researchers try to find other 2D materials which can naturally overcome the gapless limitation of graphene. Group-VI TMDs, a kind of layered materials with universal form MX_2 , where M represents a transition metal atom, X stands for chalcogen atoms are among top lists. Since group-VI TMDs consist of many layers stacked by weak van der Waals interaction, it is easy to obtain monolayers by mechanical exfoliation method [4-6], liquid exfoliation method [7, 8] and later the directly chemical growth method [9, 10]. These semiconducting group-VI TMDs become to direct bandgap materials when they are thinned to monolayers [4, 11, 12]. Moreover, the light emitting from the 2D group-VI TMDs almost covers the whole visible optical spectrum due to the diversities of TMDs [13]. These unique properties of TMDs make them extremely promising in optoelectronics, sensors, valleytronics, and energy storages [14-21].

1.1 Introduction to Layered Semiconducting Group-VI TMDs

1.1.1 Crystal Structure of 2D Group-VI TMDs

Group-VI TMDs in a form of MX_2 are layered materials, where $\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{S}, \text{Se}$. As for the layers stacking, they are associated with each layer by the weak van der Waals interaction, hence monolayer group-VI TMDs can be simply obtained by mechanical exfoliation. According to the different stacking sequences and the metal atom coordination, the polytypes of group-VI TMDs can be divided into 2H, 3R, and 1T, as shown in Fig. 1.1 [5]. The most common stacking order is 2H stacking, in which the metal atoms have trigonal prismatic coordination and overall the crystal exhibits the hexagonal symmetry with a repeat unit of two layers. 3R stacking order exhibits the rhombohedral symmetry with a repeat unit of three layers, in which the metal atoms have trigonal prismatic coordination. While for 1T stacking order, the crystal overall possesses the tetragonal symmetry with a repeat unit of one layer, and the metal atoms have octahedral coordination. 1T stacking order usually exhibits a metallic phase and it can be converted from 2H stacking order upon Li interactions [22]. Moreover, the 3R-polytype can be transformed into the 2H-polytype upon heating [23].

Figure 1.1 Schematics of different stacking order: 2H (hexagonal symmetry, two layers per repeat unit, trigonal prismatic coordination), 3R (rhombohedral symmetry, three layers per repeat unit, trigonal prismatic coordination) and 1T (tetragonal symmetry, one layer per repeat unit, octahedral coordination). (Adapted from Ref. [5], Copyright 2012, Nature Publishing Group)

Considering the 2H-polytype (marked as 1H for a monolayer) is the most stable configuration and many semiconducting TMDs are found to be 2H-polytype, samples exploited in this thesis are with 2H stacking order. The repeat unit of 2H stacking order contains two single layers, as shown in Fig. 1.1. Each layer has a thickness of 6~7 Å and the transition metal atoms are sandwiched by two layers of chalcogen atoms, as shown in Fig. 1.2. As for the lattice structure, the metal atoms sits in the center of a trigonal prismatic coordination and are bound to six chalcogen atoms with strong covalent bonds. The symmetry of monolayer MX_2 is D_{3h}^1 space group [24].

Figure 1.2 Top view of monolayer MX₂ (left) and the unit cell of MX₂ (right). (Adapted from Ref. [24], Copyright 2015, Royal Society of Chemistry)

1.1.2 Electronic Band Structure of 2D Group-VI TMDs

Bulk group-VI TMDs materials such as MoS₂, WS₂, MoSe₂, WSe₂ are indirect bandgap semiconductors. Because of the similarity of crystal structure, the semiconducting MX₂ materials have a similar thickness dependent band structure evolution, that is, the band structure is converted from indirect bandgap to direct bandgap when these MX₂ are thinned to monolayers. Take MoS₂ for example, the band structures of different thicknesses are given by first-principle calculations (see Fig. 1.3).

Figure 1.3 Band structures of MoS₂ with different thicknesses using first-principle calculations. With the thickness decreasing, the band structure is converted from indirect to direct one. (Adapted from Ref. [25], Copyright 2011, American Physical Society)

Bulk MoS₂ has an indirect band structure with a bandgap of 1.2 eV, in which the valence band maximum (VBM) lies at Γ point and the conduction band minimum (CBM) locates between K and Γ points. With the decreasing thickness, the fundamental indirect bandgap increases while the optical direct gap (situated at K point) remains nearly unchanged, which further results in a indirect to direct bangap transition in monolayer MoS₂.

Theoretically, the thickness-dependent band strcuture evolution of group-VI TMDs are results of both states near K and Γ points. For the K point, the conduction band states mostly consist of strongly localized d orbitals at metal atoms. Since metal atoms are sandwiched by the chalcogen atoms, they have a minimal interlayer coupling and stays nearly unchanged with different layers [11]. These states form the nearly unchanged optical direct gap. However, states near Γ point result from a linear combination of d orbitals on metal atoms and antibonding p_z orbitals on chalcogen atoms. This combined effect has a strong interlayer coupling and highly dependent on the layers [11]. Hence, these states vary with the thickness of TMDs and mainly contribute to the indirect to direct bangap transition in monolayer group-VI TMDs. Table 1.1 summarizes the calculated electronic bandgaps of group-VI TMDs studied in this thesis.

Table 1.1 Summary of calculated electronic bandgaps of group-VI TMDs

Bandgap (eV)	Bulk (indirect)	Monolayer (direct)	References
MoS ₂	1.23	1.88	Ref. [26]
MoSe ₂	1.09	1.57	Ref. [26]
WS ₂	1.32	2.03	Ref. [26]
WSe ₂	1.21	1.67	Ref. [26]

1.1.3 Excitonic Structure of 2D Group-VI TMDs

With the excitation photon energy higher than the band gap, electrons in the direct-bandgap semiconductors can be optically excited to the conduction band and later accumulated at the bottom of the conduction band, creating same amount of holes in the top of the valence band. In 2D TMDs, these negatively charged electrons and positively charged holes are bound with each other by the Coulomb attraction. The neutral bound quasi-particle is called exciton, which is labeled as X_0 in this thesis. The formation of a neutral exciton results in a binding energy of the exciton. Thus the energy state of a neutral exciton is below the bandgap with the binding energy, as shown in Fig. 1.4.

Figure 1.4 Schematics of neutral (X_0), negatively (X_T , also known as X^-) and positively (X^+) charged excitons. E_g is the electronic bandgap energy, E_b is the exciton binding energy, E_b^T is the trion binding energy, and E_F is the Fermi level.

The typical exciton binding energies of monolayer group-VI TMDs are summarized in Table 1.2. Since the formation of excitons in the 2D TMDs are ultrafast [27], the optical transitions in neutral 2D TMDs are governed by excitons.

Table 1.2 Summary of exciton binding energies of monolayer group-VI TMDs

(eV)	Theoretical values	Experimental values
MoS ₂	1.1 in Ref. [28], 1.03 in Ref. [29]	0.57 in Ref. [30]
MoSe ₂	0.78 in Ref. [28], 0.91 in Ref. [29]	0.55 in Ref. [31]
WS ₂	1.04 in Ref. [29]	0.7 in Ref. [32], 0.32 in Ref. [33]
WSe ₂	0.90 in Ref. [29]	0.6 in Ref. [34], 0.37 in Ref. [35]

Moreover, if there are free electrons interacting with the neutral excitons in 2D TMDs, a neutral exciton is likely to bind an extra electron, forming a negatively charged exciton [36-38], which is labeled as X_T in this thesis. In analogy to the negatively charged exciton, an extra hole also can be captured by a neutral exciton, forming a positively charged trion [38].

Since there is also a binding energy to form a charged exciton, both the energy states of negatively and positively charged excitons are lower than that of the neutral exciton, the binding energy of a trion is given by the following equation [39], where E_F is the Fermi level at a given carrier density.

$$E_b^T = E_{X_0} - E_{X_T} - E_F \quad (1 - 1)$$

In nearly non-doping regime, the binding energy of a trion is the energy difference between an exciton and a trion, which is the energy required to excite an electron in a trion to the bottom of conduction band. While at a finite doping level, an exciton can be considered as the dissociation of a trion, transferring the extra electron to the Fermi level, thus the energy difference between an exciton and a trion is larger than the trion binding energy [39]. The typical trion binding energies of monolayer group-VI TMDs can be found in Table 1.3.

Table 1.3 Summary of trion binding energies of monolayer group-VI TMDs

(meV)	Theoretical values	Experimental values
MoS ₂	26 in Ref. [40]	18 in Ref. [39]
MoSe ₂	21 in Ref. [40]	30 in Ref. [41]
WS ₂	26 in Ref. [40]	30 in Ref. [42]
WSe ₂	22 in Ref. [40]	30 in Ref. [43]

In addition to the exciton and trion emissions in 2D TMDs, biexciton emission is also founded in 2D TMDs by researchers [42, 44-47]. The ground state biexciton is a four spatially symmetric quasiparticle, which can be understood as a bound two-exciton state, and it is formed when the system is at intermediate exciton densities [47, 48]. The ground state biexciton binding energy is given by the following equation, where E_{X_0} is the exciton energy, E_{XX} is the biexciton energy.

$$E_b^{XX} = 2E_{X_0} - E_{XX} \quad (1 - 2)$$

The theoretical calculations of ground state biexciton binding energies and the experimentally observed biexciton binding energies of monolayer group-VI TMDs are given in Table 1.4.

Table 1.4 *Summary of calculated ground state biexciton binding energies and observed biexciton binding energies of monolayer group-VI TMDs*

(meV)	Theoretical values	Experimental values
MoS ₂	22 in Ref. [49]	60 in Ref. [45]
MoSe ₂	18 in Ref. [49]	60 in Ref. [47]
WS ₂	21 in Ref. [50]	45 in Ref. [44], 65 in Ref. [42]
WSe ₂	37 in Ref. [46]	52 in Ref. [46]

From Table 1.4, we can see that there are large differences between the theoretical and experimental values. It implies that in 2D TMDs, the biexciton cannot be simply interpreted by the combination of two excitons. In 2015, Varga's group came up a model in which the biexciton in 2D TMDs consists of a charge attached to a trion (excited-state biexciton), and by using this model they recalculated the theoretical values for the biexciton binding energies of monolayer group-VI TMDs, which fit well with the experimental data, as shown in Table 1.5.

Table 1.5 *Summary of biexciton binding energies of monolayer group-VI TMDs*

(meV)	MoS ₂	MoSe ₂	WS ₂	WSe ₂
Varga's model [49]	69	58	67	59

Besides the exciton, trion, and biexciton emissions in 2D TMDs, localized-state emissions are also observed at low temperatures. These localized-state emissions are often caused by the defect-related bound excitons.

Figure 1.5 Electrical and optical control of light emission from monolayer WS₂ at 4.2 K. (a) PL spectra at various gate voltages with the excitation power of 65 μW. (b-d) PL intensity mapping as a function of gate voltages with the excitation power of 65, 1570, 6000 μW. (Adapted from Ref. [44], Copyright 2015, American Chemical Society)

From Fig. 1.5(b), by applying different gate voltages, the carrier density in the 2D TMDs is changed, which further tunes the intensity and peak positions of the exciton, charged exciton, biexciton, and localized-state emissions. The gate and excitation tunable capacities of these emissions provide great opportunities to study the fundamental physics behind them.

1.2 Valley Zeeman Splitting in Semiconducting Group-VI TMDs

1.2.1 Overview of Zeeman Effect

The Normal Zeeman Effect was first discovered by Pieter Zeeman [51] and later was interpreted by Hendrik Lorentz. It describes that the interaction between the applied magnetic field and magnetic moment of the subject. In a simpler way, spectral lines split into several components under a static magnetic field because of Zeeman effect. Considering a hydrogen atom model, where an electron is circulating around the nucleus. In quantum mechanics, the energy states of the electron are quantized namely that the electron can only have certain values of energy. And these energy eigenstates can be described by the principal quantum number n . In addition to the principal quantum number n , there are other three quantum numbers to describe the motion of the electron which are orbital quantum number (l), magnetic quantum number (m_l), and spin quantum number (s). The orbital quantum number l describes the magnitude of the orbital angular momentum through the equation, where l ranges from 0 to $n-1$.

$$L^2 = \hbar^2 l(l + 1) \quad (1 - 3)$$

The magnetic quantum number m_l describes the projection of the orbital angular momentum along z axis:

$$L_z = m_l \hbar \quad (1 - 4)$$

And m_l ranges from $-l$ to $+l$ in integral step. For instance, if $l=1$, then m_l can be 0, ± 1 . Which means, for a given value of l , there are $(2l+1)$ -fold degeneracies for the possible values of m_l . The spin quantum number s describes the spin angular momentum of a given particle, here for an electron, $s = \frac{1}{2}$. For the projection of spin angular momentum of an electron along z axis (m_s), it can take either $\frac{1}{2}$ or $-\frac{1}{2}$ [52].

Consider a simple singlet states' system with energy level of $l = 2$ and $l = 1$, where all electrons are paired, and the spin is zero, the total angular momentum $\mathbf{J}$ is equal to the orbital angular momentum $\mathbf{L}$. When an external magnetic field is applied along the z axis, degeneracies of energy spectra are lift due to the energy of its magnetic moment in the field, which is given by:

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B \quad (1 - 5)$$

Since $\mathbf{B}$ is along the z axis and the magnetic dipole moment μ_z is given by:

$$\mu_z = \frac{-e}{2m_e} L_z = m_l \frac{-e\hbar}{2m_e} \quad (1 - 6)$$

Thus,

$$\Delta E = -\mu_z B = m_l \frac{e\hbar}{2m_e} B = m_l \mu_B B \quad (1 - 7)$$

And $\mu_B = \frac{e\hbar}{2m_e}$ is named as the Bohr magneton.

Figure 1.6 Singlet energy level splitting upon an external magnetic field, since all electrons are paired, spin is not considered. The red lines indicate the transitions with selection rule $\Delta m_l = 0, \pm 1$.

As shown in Fig. 1.6, the $l = 2$ energy level splits into 5 levels ($2l + 1 = 5$). While the $l = 1$ energy level splits into 3 levels ($2l + 1 = 3$). According to the selection rule, transitions can only happen with $\Delta m = 0, \pm 1$, as indicated by 9 red lines in Fig. 1.6. Due to the uniform splitting of the energy levels, there are only 3 different transition energies: $E_0 - \frac{e\hbar B}{2m_e}$, E_0 and $E_0 + \frac{e\hbar B}{2m_e}$.

Discussion above does not involve the unpaired electrons (spin contribution) and it is called the normal Zeeman effect. Another situation is the spin of either initial or the final states or both is non-zero, in this case, it is called the anomalous Zeeman effect and was first discovered by Thomas Preston.

Since the spin contribution is considered in the anomalous Zeeman effect. The total angular momentum is:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (1 - 8)$$

Hence, the total magnetic moment is:

$$\boldsymbol{\mu} = -g_l\mu_B \frac{\mathbf{L}}{\hbar} - g_s\mu_B \frac{\mathbf{S}}{\hbar} \quad (1-9)$$

Take $g_l = 1$ and $g_s = 2$ for approximation, equation (1-9) can be written as:

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S}) \quad (1-10)$$

So, the energy shift compared with the zero-field energy level, can be written as:

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} = gm_j\mu_B B \quad (1-11)$$

And the Landé g-factor, is given by:

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad (1-12)$$

m_j ranges from $-j$ to $+j$ in integral step [53].

From equation (1-11), we can see that Zeeman splitting of the energy levels depends on j , l , and s when taking spin-orbit effect into consideration.

If the external magnetic field is large enough, which can overpower the spin-orbit effect and decouple $\mathbf{L}$ and $\mathbf{S}$; thus the projection of $\mathbf{L}$ behaves as if $S = 0$. In this case, it is called Paschen-Back effect and was first explained by F. Paschen and E. Back, and the splitting shift is given by:

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} = (m_l + 2m_s)\mu_B B \quad (1-13)$$

The Zeeman splitting is greater than the fine-structure splitting, thus 3 closely spaced doublets can be observed upon an external magnetic field.

For the normal Zeeman effect. The spectral line splits into 3 components. The unsplit component, which is called π component, remains unchanged in energy and originates from the transition where $\Delta m_l = 0$. The other two split lines are both shifted

by the same magnitude but in opposite directions, originating from the transitions where $\Delta m_l = \pm 1$. These two components are called $\sigma^\pm$ components. As shown in Fig. 1.7, when viewed in longitudinal configuration, which means the line-of-sight is in the direction of magnetic field, the $\sigma^\pm$ components become oppositely circularly polarized and are shifted to the zero-field level by the energy given in equation (1 – 7), while the unshifted π component is absent. When viewed in transverse configuration, which means the line-of-sight is perpendicular to the magnetic field, all the components are present and linearly polarized, the polarization of $\sigma^\pm$ components is perpendicular to the field direction and the polarization of π component is parallel to the field direction.

Figure 1.7 Schematics of the polarization of the Zeeman components for normal Zeeman effect. (Adapted from Ref. [54], Copyright 2018, GmbH, Germany)

Because of the helicity of Zeeman components, the splitting energies between the components can be obtained by comparing the emission energies of σ^+ and σ^- signals.

1.2.2 Inversion Symmetry Breaking in 2D Group-VI TMDs

Bulk or even-layer 2H-MX₂ (M=Mo, W; X=S, Se) semiconducting materials have

the high symmetry with the space group D_{6h}^4 [24, 55], as shown in Fig. 1.8. The chalcogen atoms of a given layer are horizontally rotated 180 degrees compared to its adjacent layer, and the metal atoms are arranged precisely on top of the chalcogen atoms of its nearby layer. Hence, there is the inversion symmetry in the bulk or even-layer 2H-MX₂. However, when thinned to monolayer or odd-layer 2H-MX₂, the inversion symmetry vanishes, as discussed in Fig. 1.2.

Figure 1.8 Illustration of bulk or even-layer 2H-MX₂ (left) and the unit cell (right).

(Adapted from Ref. [24], Copyright 2015, Royal Society of Chemistry)

The breaking of inversion symmetry in monolayer 2H-MX₂ leads to a large spin-orbital coupling (SOC), which further results in the splitting of valence and conduction bands at K and K' points in the vector space [56, 57], as shown in Fig. 1.9, note that the splittings of conduction bands for MoX₂ and WX₂ have opposite signs [58].

Figure 1.9 Schematics of spin-orbital induced splitting of valence and conduction bands for MoX₂ and WX₂ ($X=S, Se$), the red dashed and blue solid lines represent the spin-up

and -down states, respectively. (Adapted from Ref. [58], Copyright 2013, American Physical Society)

Detailed spin-orbital coupling induced splittings of valence and conduction bands are given in Table 1.6.

Table 1.6 The SOC splittings of the valence band Δ_{SOC}^v (eV) and conduction band Δ_{SOC}^c (eV). (Adapted from Ref. [58], Copyright 2013, American Physical Society)

	Δ_{SOC}^v	λ	$\Delta_{\text{SOC}}^{c(\text{pt})}$	$\Delta_{\text{SOC}}^{c(\text{FP})}$	$E_{1,2}$	$E_{-1,0}$	$E_{1,0}$
MoS ₂	0.148	0.073	0.003	-0.003	4.840	1.395	3.176
WS ₂	0.430	0.211	0.026	0.029	5.473	1.526	3.667
MoSe ₂	0.184	0.091	0.007	-0.021	4.296	1.128	2.862
WSe ₂	0.466	0.228	0.038	0.036	4.815	1.267	3.275

However, due to the tiny value of the splitting energy for the conduction band [59-63], the splitting of conduction band is usually neglected. Thus, there are two optical transitions in the PL spectra, which are named as A and B excitons [24]. Table 1.7 presents the observed A and B exciton transitions in monolayer MX₂ (M=Mo, W; X=S, Se).

Table 1.7 Summary of A and B exciton transitions in monolayer MX₂ (M=Mo, W; X=S, Se).

	A exciton (eV)	B exciton (eV)
MoS ₂	1.88 @RT in Ref. [4]	2.03 @RT in Ref. [4]
MoSe ₂	1.57 @RT in Ref. [64]	1.87 @RT in Ref. [64]
WS ₂	1.94 @RT in Ref. [65]	2.33 @RT in Ref. [65]
WSe ₂	1.4~1.8 @RT in Ref. [66]	2.05 @RT in Ref. [65]

1.2.3 Time-reversal Symmetry Breaking in 2D Group-VI TMDs

In last section, we carefully discussed the spin-orbital induced splitting of valence band, which is a direct result of inversion symmetry breaking in monolayer group-VI TMDs. However, considering the time-reversal symmetry of the K and K' valleys in monolayer group-VI TMDs, the energies of particles from these two valleys are naturally degenerate. Upon an out-of-plane external magnetic field, the time-reversal symmetry no longer exists, thus the valley degeneracy can be lifted, resulting in an energy difference between the emissions from the K and K' valleys.

1.2.4 Valley Zeeman Splitting in 2D Group-VI TMDs

For conventional Zeeman effect, the applied magnetic field directly interacts with the magnetic moments of the atoms, giving energy shifts accordingly. While in monolayer group-VI TMDs, external magnetic field interacts with the magnetic moments of valley electrons, bringing about a valley Zeeman energy splitting. Note that valley Zeeman splitting is also known as valley splitting.

Figure 1.10 Schematics of the optical selection between the conduction and valence bands in K' and K valleys of MoX_2 ($X=\text{S, Se}$) for σ^+ and σ^- polarized light without the external magnetic field (left) and with the external magnetic field (right). Upon external magnetic field, band structures of K' and K valleys have opposite shifts with respect to their condition without the magnetic field. The magnetic moments in a given valley consist of three contributions: the spin (μ_s); atomic orbital (μ_l); valley (μ_k), also known as delocalized Bloch wave function. (Adapted from Ref. [67], Copyright 2016, American Chemical Society)

Because of the helicity of valley Zeeman components, the valley splitting energy can be determined by the energy difference between the σ^+ and σ^- emissions in the presence of magnetic field, labeled as orange and blue transitions in Fig. 1.10. The valley splitting energy ($B>0$) with respect to grand state ($B=0$) in a given valley is determined by [68]:

$$\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} = -(\mu^c - \mu^v)B \quad (1 - 14)$$

Considering the applied magnetic field is perpendicular to the monolayer samples.

In the K valley, the spin contribution to the total magnetic moments is:

$$\mu_s^c = \mu_s^v = -\mu_B \quad (1 - 15)$$

For the orbital contribution of valence band to the total magnetic moments mainly arises from hybridization of $d_{x^2-y^2} + \tau i d_{xy}$ orbitals with angular moment [68]:

$$l = 2\hbar \quad (1 - 16)$$

Thus, the orbital magnetic moment from the valence band is:

$$\mu_l^v = -2\mu_B \quad (1-17)$$

However, for the orbital contribution of conduction band, it arises from hybridization of d_{z^2} orbitals with zero angular momentum [17, 56, 69, 70].

For the valley contributions of valence and conduction bands, they are given by:

$$\mu_k^v = -\left(\frac{m_0}{m_*^v}\right)\mu_B \quad (1-18)$$

$$\mu_k^c = -\left(\frac{m_0}{m_*^c}\right)\mu_B \quad (1-19)$$

m_*^v and m_*^c are the effective masses of the conduction and valence bands, and $\mu_B = 0.05788 \text{ meV}/T$ is the Bohr's magneton [71]. In the approximation of $m_*^v = m_*^c$, we have $\mu_k^v = \mu_k^c$, and the valley splitting energy in K valley is:

$$\Delta E = -2\mu_B B \quad (1-20)$$

The identical situation exists in the K' valley with a splitting energy of $2\mu_B B$, then the total valley splitting for exciton emission between σ^+ and σ^- signals is:

$$\Delta E_{total} = -4\mu_B B \quad (1-21)$$

In the case of trion emission, the intervalley trion is more stable than the intravalley trion due to the exchange interactions [68, 72]. Hence the trion emission is mainly from the inter-valley trions. In the intrinsic or low doping regime, the extra electron contribution to the magnetic moments should be considered when calculating the total magnetic moments of a trion. However, the extra two electron contributions from σ^+ and σ^- signals cancel each other. As a result of cancelation, the valley splitting energy of trion emission between the σ^+ and σ^- signals is similar to the case of excitation, which is $-4\mu_B B$. Recent studies on the valley splitting of trion emission reveal that the valley

splitting behavior of trion emission is dependent on the doping level, as a result of enhanced many body interactions [73].

1.3 Motivation and Significance of the Thesis

Silicon-based microelectronic devices have ruled the semiconductor industry for several decades. These microelectronic devices are put together to form integrated circuits, which are the building blocks for modern electronics. According to the Moore's law, the number of transistors on integrated circuits doubles about every two years. Which means, with the development of silicon-based semiconductor technology, the dimension of a single metal-oxide-semiconductor field-effect transistor (MOSFET) has become smaller and smaller and the gate oxide will finally reach to the physical limit. When the gate oxide is thinned to the atomic level, the leakage current induced by the quantum tunnelling effect is not negligible, which deteriorates the performance of the MOSFET.

2D TMDs, as the most promising successor of traditional semiconductors, have many unique properties, such as flexibility, low power consuming, and various bandgaps covering all visible and infrared spectrum ranges. In traditional silicon-based devices, two binary states are realized by the current on/off states of the MOSFET. Differently, monolayer group-VI TMDs possess valley degree of freedom because of the spin-orbital coupling and inversion symmetry breaking. Upon an external out-of-plane magnetic field, the degeneracy of the two valleys can be lifted, thus there is an

energy difference between the σ^+ and σ^- emissions (known as valley splitting) from the two valleys with the excitation of σ^+ and σ^- polarized light, respectively. These σ^+ and σ^- emissions with an energy difference can be utilized as binary states for future information processing.

Despite the great potential of valley splitting in monolayer group-VI TMDs. There are a lot of fundamental understandings to be clarified. Considering the integration of valleytronic devices on a large monolayer TMD, a question is whether the sample's nonuniformity influences the valley splitting behavior. In addition to the well-resolved and intrinsic PL spectra of exfoliated monolayer WSe₂, the exfoliated WSe₂ monolayer is neutrally nonuniformed, possibly due to the moisture in atmosphere. Hence it is a good candidate to study the sample's nonuniformity influence on the valley splitting. It is also a good way to understand the physics between the valley splitting behavior and doping levels, since the nonuniformity is mainly caused by the different doping levels in local regions.

Valley splitting energies between σ^+ and σ^- emissions are very small even under a strong external magnetic field. For the purpose of stable binary states represented by the σ^+ and σ^- emissions from the two valleys, large valley splitting energies are required even under a small external magnetic field. An intuitive thought is whether a magnetic substrate can enlarge the valley splitting energies. Hence, EuS as a ferromagnetic material is used as the substrate and the valley splitting behavior of the exfoliated monolayer WSe₂ on EuS is carefully studied.

Another issue is that monolayer WS₂ and MoS₂ crystals on SiO₂/Si usually present a broad peak of highly merged exciton and trion emissions, which make it extremely difficult to fit the PL spectra and study the intrinsic valley splitting behavior of monolayer WS₂ and MoS₂. Hence, a new method is needed to grow monolayer WS₂ and MoS₂ on hBN. The clean, flat surface and hexagonal structure of hBN can help improve the optical properties of monolayer TMDs, and the intrinsic valley splitting behavior of monolayer WS₂ and MoS₂ can be revealed by studying the as-grown monolayer WS₂ and MoS₂ crystals on hBN.

To sum up, nonuniform exfoliated monolayer WSe₂ on SiO₂/Si is studied for the fundamental understanding between the doping levels and valley splitting behavior; EuS, as a ferromagnetic material is used as the substrate to study whether it can enlarge the valley splitting energies or not; high-quality monolayer WS₂ and MoS₂ grown on hBN are studied for the fundamental understanding of intrinsic valley splitting behavior of monolayer WS₂ and MoS₂. All the efforts have been devoted to a better understanding of the fundamental physics of valley splitting.

1.4 Organization of the Thesis

This thesis mainly focuses on the valley splitting of monolayer group-VI TMDs. Studies provided here are intended for a better understanding of fundamental physics of valley splitting and taking a small step towards the valleytronic devices.

The thesis is organized as follows:

Chapter 1 is an introduction and can be divided into two parts, the first part is a brief introduction to the group-VI TMDs including the crystal, electronic, and excitonic structures of group-VI TMDs. The second part is an introduction to the valley splitting, which includes the inversion and time-reversal symmetry breaking, Zeeman effect, and the theoretical interpretation of valley splitting in monolayer group-VI TMDs.

Chapter 2 is mainly about the sample preparation and the experimental techniques exploited in this thesis. The sample preparation includes the mechanical exfoliation of a bulk crystal, transfer methods, and the chemical vapor deposition (CVD) growth method. The experimental techniques include the Raman spectroscopy to determine the thickness of samples, circularly polarized PL spectroscopy to determine the valley splitting energies of samples and our customized magneto-Raman/PL system.

Chapter 3 presents the studies about the sample's nonuniformity influence on the valley splitting. The exfoliated monolayer WSe₂ is used, and the nonuniformity is studied by the evolution of PL spectra across the sample. Valley splitting behavior of both exciton and trion emissions are studied at the center and the edge regions, which correspond to the lower and the higher doping levels, since the edge area is directly exposed to atmosphere and easier to get doped by the moisture.

Chapter 4 explores the valley splitting enhancement of WSe₂. EuS, as a ferromagnetic insulator, is utilized as the substrate for the exfoliated monolayer WSe₂. Valley splitting behavior of both exciton and trion emissions of exfoliated monolayer

WSe₂ on EuS are studied. A controlled experiment is also studied by placing the exfoliated monolayer WSe₂ on SiO₂/Si substrate.

Chapter 5 focuses the intrinsic valley splitting behavior of monolayer WS₂ and MoS₂. A modified CVD growth method is developed to obtain high-quality WS₂ and MoS₂ monolayers on hBN. Valley splitting behavior of monolayer WS₂ (exciton and trion emissions) and monolayer MoS₂ (exciton emission) are studied at selected magnetic fields.

Chapter 6 is the conclusions and prospects of the thesis.

Chapter 2 Experimental Techniques

In this chapter, experimental techniques in this thesis are discussed, which can be roughly divided into two parts.

The first part focuses on the sample preparation, which includes the mechanical exfoliation and CVD growth method. Moreover, transfer technique during the preparation of heterostructures is also discussed.

The second part is the major technique exploited to study the optical properties of monolayer group-VI TMDs, which includes Raman spectroscopy, PL spectroscopy and customized magneto-Raman/PL system.

2.1 Preparation of Atomically Thin 2D Group-VI TMDs

2.1.1 Mechanical Exfoliation of the Bulk Crystals

In 2004, graphene (a single-layer of carbon atoms) was obtained by professor Andre Geim and professor Konstantin Novoselov *via* mechanical exfoliation of the bulk graphite [1]. Since then, it has been an effective method to acquire varieties of monolayer 2D crystals including 2D TMDs, phosphorene, 2D boron nitride [5, 74]. There are two major advantages of mechanical exfoliation method. (1) It is the cheapest and most facile method to obtain mono- and few- layer 2D crystals. (2) Due to the intrinsic properties of bulk materials, the exfoliated mono- and few- layer 2D crystals usually maintain the intrinsic properties which is great for the fundamental studies of a given material.

Figure 2.1 Schematic of exfoliation process. (Adapted from Ref. [74], Copyright 2018, Elsevier B.V.)

The exfoliation process is shown in Fig. 2.1. Plenty of theoretical and experimental studies have been conducted to optimize the geometry control and the yield of 2D crystals [75-78]. The peeling angle and adhesive strength are the key factors during the exfoliation process [74]. In particular, the exfoliated sample size increases when the peeling angle between the scotch tape and substrate increases. Moreover, the sample size increases with the increasing adhesive strength between the 2D crystal and substrate.

To obtain exfoliated monolayer crystals, following steps are needed. Firstly, place the bulk crystal on a piece of scotch tape then some tiny thick flakes are left on the tape due to the adhesive force. After that, use another piece of scotch tape to cover the first one, gently press and peel it off. After repeating the above actions several times, gently press the last piece of tape on the pre-cleaned substrate. A couple of minutes later, remove the tape and some monolayer samples can be found under the microscope. Note that the Si substrate capped with 300nm SiO₂ can provide a good optical contrast during the searching of monolayer samples under an optical microscope [79, 80].

2.1.2 Directly Growth via Chemical Vapor Deposition

Although mechanical exfoliation of the bulk crystals can provide optically high-quality monolayer TMDs, the potential application is greatly limited due to its low yield. To overcome the shortage of exfoliation method, CVD growth method is developed to produce large-scale monolayer TMDs in previous reports [81-84]. The most common method to grow TMDs is the direct sulfurization of transition metal oxides. However, this method is inefficient when hBN is used as substrate. More details can be found in chapter 5. In order to overcome this problem, a modified CVD growth method is developed.

Figure 2.2 Schematic of the CVD system for the growth of MS_2 ($M=Mo, W$) on $hBN/SiO_2/Si$

The experimental setup of the modified CVD growth method is shown in Fig. 2.2. In order to synthesize the MS_2 ($M=Mo, W$) onto the pre-exfoliated hBN on the SiO_2/Si substrate, electron beam evaporation system is used to deposit a MO_x ($M=Mo, W$) film (1 nm in thickness) on the hBN. Then, the coated substrate is placed at a face-down position in the heating range of the furnace. Pure Ar gas with a flow rate of 100 sccm is used as the carrying gas during the whole process. The temperature of the heating range

is increased to 750 °C and maintained for 10 mins during the growth process. After that, the heater is turned off and the furnace is naturally cooled down to the room temperature.

The CVD grown WS₂ and MoS₂ on hBN in chapter 5 are obtained by using this method.

2.2 Preparation of Heterostructures

Transfer methods are extremely crucial during the preparation of heterostructures.

In general, there are two transfer methods, which are wet and dry transfer methods.

The simplified wet transfer process of CVD grown TMDs is shown in Fig. 2.3.

Figure 2.3 Schematic of wet transfer process

Usually, the wet transfer method for CVD grown samples includes the following steps. Firstly, the substrate with as-grown samples is spin coated with a thin film of poly (methyl methacrylate) (PMMA) and heated at 170 °C for 1min to solidify the PMMA layer. After that, the substrate is immersed into the KOH solution, and due to the strong corrosion of KOH solution, the substrate is etched and sinks to the bottom of the solution. In the meanwhile, the PMMA film, as a supporting layer, holds the samples and floats on the surface of KOH solution since PMMA film is hydrophobic. Then, the PMMA

film with the samples underneath is repeatedly transferred to deionized water (DI water) in order to remove the residual KOH. Next, the PMMA film with the samples underneath is gently scooped up to avoid any bubble formation by using the target substrate. After the transferred layer is fully dried, the residual PMMA is removed by using acetone.

Wet transfer method is the most commonly used technique to transfer large-scale CVD grown 2D materials and the operation steps are relatively effortless. However, the wet transfer method cannot provide a site-to-site stacking precisely and it is involved with water and chemicals which may degrade the optical and physical quality of the transferred sample.

On the contrary, dry transfer method is much more challenging and time consuming which offers site-to-site stacking with a micron class accuracy. Moreover, dry transfer discussed here only involves with viscoelastic stamps, avoiding use of any wet chemicals, which is perfect for protecting the fragile 2D materials and transferring these materials onto a suspend substrate as there are no capillary forces involved in the process. The dry transfer method is more suitable for transferring small exfoliated samples rather than large-scale CVD grown samples. Figure 2.4 shows the schematics of dry transfer setup and process.

Figure 2.4 Schematics of dry transfer setup and process. (Adapted from Ref. [85], IOP Publishing Group)

The experimental setup for the dry transfer process consists of an optical microscope with a long-working-distance objective lens to monitor the transferring process and a micro-manipulator with three degrees of freedom to precisely target the desired site on the substrate. The stamp used here is commercially available polydimethylsiloxane (PDMS) from Gelpak company and the model is PF-20-X4. One side of the PDMS is adhered to a glass slide for handling and the 2D materials are deposited on the other side of the PDMS through mechanical exfoliation of bulk crystals by using scotch tape. Then the glass slide is inversely fixed on the micro-manipulator and with the help of optical microscope, the desired 2D materials can be located. The thickness of a selected sample can be determined by Raman and contrast spectroscopy

[86, 87]. After that, the target substrate is fixed on the microscope stage and by tuning the micro-manipulator under the microscope, it is easy to align the desired flakes on the target portion of the substrate. Next, the stamp is evenly pressed against the substrate and peeled off with extra care. The peeling speed directly influence the interfacial surface between the sample and substrate.

The heterostructure of WSe₂/EuS in chapter 4 is obtained by the dry transfer method mentioned above.

2.3 Raman Spectroscopy

2.3.1 Basic Principles of Raman Scattering

In 1928, C. V. Raman and his Ph. D. student K. S. Krishan firstly discovered a new kind of radiation from atoms and molecules [88] and later was named as Raman scattering. Unlike the elastic Rayleigh scattering, Raman scattering is an inelastic scattering process. However, such scattering can be observed only under a strong illumination, which greatly limits the application of Raman scattering at that time. Nowadays, Raman spectroscopy has been widely used for crystal structure and molecule vibration studies in condensed matter physics thanks to the strong illumination of laser.

Consider the particle model of light in the case of light-matter interactions, some photons pass through the molecules while others are scattered. Nearly all the scattering is an elastic process without any energy change in photons, which is called Rayleigh scattering. Only a very small part of scattering is an inelastic process with energy loss

(Stokes Raman scattering) or gain (Anti-Stokes Raman scattering) in photons.

Schematics of different scattering processes is shown in Fig. 2.5.

Figure 2.5 Schematics of different scattering processes

When incident photons interact with molecules, molecules are excited from the ground state to a virtual state, which is different from an energy eigenstate and not stable. Thus, the excited molecules will decay very quickly to the ground state with different vibrational energy levels, emitting the scattered photon. For the Stokes Raman scattering, molecules are initially at the ground state with the lowest vibrational energy level, while for anti-Stokes Raman scattering, molecules are initially at the ground state with a higher vibrational energy level due to thermal fluctuation. The population of molecules at ground state with the lowest vibrational energy level is much greater than that of with a higher vibrational energy level, according to the Boltzmann distribution. Thus, the

intensity of Stokes Raman scattering is stronger than that of anti-Stokes Raman scattering [89]. The Stokes and anti-Stokes scattering processes can be described by the following equation:

$$h\nu_s = h\nu_i \pm h\nu_m \quad (2 - 1)$$

And h is the Planck constant, ν_i , ν_m and ν_s are frequencies of incident photon, molecular vibration and scattered photon, respectively. The $+$ and $-$ are signs for anti-Stokes and Stokes Raman scattering, respectively. And the Raman scattering intensity is given by [90]:

$$I_R = \nu^4 I_0 N \left(\frac{\partial \alpha}{\partial Q} \right)^2 \quad (2 - 2)$$

ν and I_0 are frequency and intensity of incident laser, N is the number of scattering molecules in a given state, α is the polarizability of the molecules, and Q is the vibrational amplitude. The $\left(\frac{\partial \alpha}{\partial Q} \right)$ is a Raman active indicator, which means only molecular vibrations that cause a change in polarizability can lead to the Raman scattering.

When the incident photon energy is approximate to the electronic transition energy between the excited and ground states, the population of molecules excited by the incident photons will be greatly increased, which leads to an enhanced Raman scattering intensity. Therefore, it is called Resonance Raman scattering.

2.3.2 Raman Fingerprint of 2D Group-VI TMDs

The lattice vibrations of 2H stacking bulk group-VI TMDs in class of MX_2 ($\text{M}=\text{Mo}$, W ; $\text{X}=\text{S}$, Se) consist of 18 phonon modes (3 acoustic and 15 optical modes). Since the bulk MX_2 has the D_{6h} point group symmetry, the irreducible representations of the lattice vibrations at Γ point are expressed as the following equation [91, 92], where one set of A_{2u} and E_{1u} are acoustic modes, the other set of A_{2u} and E_{1u} are infrared (IR) active modes, A_{1g} , E_{1g} and E_{2g} are Raman (R) active modes, and the rest are inactive modes.

$$\Gamma = 2A_{2u} + 2E_{1u} + A_{1g} + E_{1g} + 2E_{2g} + 2B_{2g} + B_{1u} + E_{2u} \quad (2-3)$$

For few-layer MX_2 , due to the reduction in symmetry, the lattice vibrations can be discussed with the odd and even number of layers since the odd-layer MX_2 is lack of inversion symmetry, while for even-layer MX_2 , the inversion symmetry is restored.

For odd number of layers, the point group symmetry is D_{3h} , hence the lattice vibrations at Γ point are expressed as the following equation [92, 93], where one A_2'' and one E' are acoustic modes, the other A_2'' is IR active mode, the other E' is both R and IR active, A_1' and E'' are R active modes.

$$\Gamma = 2A_2'' + 2E' + A_1' + E'' \quad (2-4)$$

For even number of layers, the point group symmetry is D_{3d} , hence the lattice vibrations at Γ point are expressed as the following equation [94, 95], where one set of A_{2u} and E_u are acoustic modes, the rest of the A_{2u} and E_u are IR active modes, A_{1g} and E_g are R active modes.

$$\Gamma = 3A_{2u} + 3E_u + 3A_{1g} + 3E_g \quad (2-5)$$

The detailed schematics of lattice vibrations for 1L-MX₂, 2L-MX₂ and bulk MX₂ are shown in Fig. 2.6.

Figure 2.6 Symmetry and normal displacements of each optical vibrations of 1L-MX₂, 2L-MX₂ and bulk MX₂. (Adapted from Ref. [96], Copyright 2015, Royal Society of Chemistry)

Raman spectroscopy is a non-destructive method to determine the thickness of 2D TMDs, Fig. 2.7 shows the Raman spectra evolution of MoS₂ sample with the increasing thickness.

Figure 2.7 (a) Raman spectra of exfoliated monolayer, few-layer, and bulk MoS₂. (b) Frequencies of E_{2g}^1 and A_{1g} modes, and their differences as a function of layer number. (Adapted from Ref. [87], Copyright 2010, American Chemical Society)

The Raman peak at $\sim 385 \text{ cm}^{-1}$ is attributed to E_{2g}^1 mode, originating from the in-plane vibrations of atoms, while the Raman peak at $\sim 403 \text{ cm}^{-1}$ is attributed to A_{1g} mode, originating from the out-of-plane vibrations of atoms. The frequency difference between the A_{1g} and E_{2g}^1 is a fingerprint to determine the layer thickness of MoS₂ samples. Note that this method is less credible when the layer number is greater than five [96]. The thickness of CVD grown MoS₂ on hBN in chapter 5 is determined by this method. Note that the frequency difference between E_{2g}^1 and A_{1g} modes of monolayer CVD grown MoS₂ is $\sim 2 \text{ cm}^{-1}$ greater than that of exfoliated monolayer MoS₂.

The Raman spectra of CVD grown MoSe₂ with different thickness are shown in Fig.

2.8.

Figure 2.8 Raman spectra of CVD grown monolayer, few-layer and bulk MoSe₂. (Adapted from Ref. [97], Copyright 2013, The Optical Society)

The weak Raman peak at $\sim 290 \text{ cm}^{-1}$ is attributed to E_{2g}^1 , while the Raman peak at $\sim 242 \text{ cm}^{-1}$ is attributed to A_{1g} . With the decreasing thickness of MoSe_2 , the frequency of A_{1g} mode shifts to the lower wavenumbers. This Raman feature of MoSe_2 is used to roughly determine the thickness of the sample.

While for the WS_2 sample, the Raman spectra of WS_2 with different thickness are shown in Fig. 2.9.

Figure 2.9 (a) Polarized Raman spectra of exfoliated monolayer, few-layer and bulk WS_2 . (b) Frequencies of E_{2g}^1 and A_{1g} modes as a function of layer number. (c) Intensity ratio and FWHM of A_{1g} and E_{2g}^1 modes. (Adapted from Ref. [98], Copyright 2013, Royal Society of Chemistry)

With the increasing thickness of WS_2 sample, the E_{2g}^1 mode softens, while the A_{1g} mode stiffens. The frequency of E_{2g}^1 mode slightly decreases with the increasing thickness, while the frequency of A_{1g} mode slightly increases. Overall, the frequency difference of A_{1g} and E_{2g}^1 modes increases with the increasing thickness. In addition,

the intensity ratio between A_{1g} and E_{2g}^1 modes also increases with the increasing thickness. This method is utilized to determine the thickness of CVD grown WS_2 on hBN in chapter 5.

The Raman spectra of exfoliated WSe_2 as a function of layer number are shown in Fig. 2.10.

Figure 2.10 Raman spectra of exfoliated monolayer and few-layer WSe_2 in the range of (a) $100\text{--}160\text{ cm}^{-1}$, (b) $210\text{--}290\text{ cm}^{-1}$, (c) $295\text{--}415\text{ cm}^{-1}$, respectively. Frequencies of (d) A_{1g} mode and (e) Raman peak at $\sim 308\text{ cm}^{-1}$ as a function of layer number. (Adapted from Ref. [99], Copyright 2013, John Wiley & Sons, Inc.)

The Raman peaks at $\sim 250\text{ cm}^{-1}$ and $\sim 260\text{ cm}^{-1}$ are attributed to E_{2g}^1 and A_{1g} modes, respectively. Moreover, the Raman peak at $\sim 308\text{ cm}^{-1}$ vanishes when the sample is thinned to monolayer. Both A_{1g} and the Raman peak at $\sim 308\text{ cm}^{-1}$ have blue shifts with the decreasing sample thickness. By verifying the Raman peak at $\sim 308\text{ cm}^{-1}$ and comparing the intensity ratio between E_{2g}^1 and A_{1g} modes, one can determine the

thickness of WSe₂. This method is used to determine the thickness of exfoliated WSe₂ flakes in the thesis.

2.4 Photoluminescence Spectroscopy

Photoluminescence spectroscopy is a non-destructive probing method to study the optical and electronic properties of materials. The spectral, spatial and temporal contents of photoluminescence provide rich information of a certain material. Generally, photoluminescence is one kind of the luminescence which describes the emission of light from a substance after being excited by a light source. For conventional III-V semiconductor compounds, photoluminescence generally describes the following processes: when the incident photon's energy is appropriate, an electron at the valence band will be excited to the conduction band and recombine with the hole after a short period of time, emitting a photon. For an ideal pure semiconductor, the excited electron and its linked hole together form an exciton by Coulomb forces, representing the minimum excitation in this material. The excitons can be roughly divided into three categories [100].

(1) Frenkel exciton: it has a small radius and the movement of the exciton through the crystal is restricted to a hopping mechanism, Frenkel exciton usually exists in molecular crystals.

(2) A charge transfer exciton: the radius of this kind is larger than the Frenkel exciton. It usually exists in ionic crystals and the formation of a charge transfer exciton

can be understood as: an electron is transferred from a lattice anion to a nearest neighbour cation.

(3) Wannier exciton: it has the largest radius compared to the other two excitons. Since it can move freely in the crystal, it is also called free exciton. Wannier exciton usually exists in semiconductors.

The Wannier excitons are quite common in 2D semiconducting TMDs and the annihilation of the Wannier excitons results in the exciton emission in the PL spectrum. In addition, there are also bound exciton and charged exciton emissions in 2D semiconducting TMDs, which have already been discussed in chapter 1.

2.5 Customized Magneto-Raman/PL System

As mentioned in chapter 1, in order to visualize the valley splitting in monolayer group-VI TMDs, an external out-of-plane magnetic field is required to break the time-reversal symmetry. Thus, a customized magneto-Raman/PL system together with a cryostat is needed. Illustration of our customized magneto-Raman/PL system and optical head are shown in Fig. 2.11.

Figure 2.11 (a) Schematic of customized magneto-Raman/PL system. (b) The optical head.

For a better illustration, our customized magneto-Raman/PL system can be divided into four parts.

(1) Cryostat with a huge electromagnet inside: during the experiment, the cryostat is filled with liquid helium to provide a cryogenic environment to cool down the electromagnet. By controlling the current inside the superconducting coil, the magnetic field in our system can be tuned from -7 T to 7 T.

(2) Piezo positioning stage: our piezo positioning stage have three degrees of freedom, which are x-axis, y-axis and z-axis. The z-axis positioner is used to focus our sample, while x-axis and y-axis positioners are used to locate our interested area. With the x-axis and y-axis positioners, a rectangular range of $5000 \mu m^2$ can be reached. An additional scanner is utilized for mapping functionality with a maximum area of $30 \mu m^2$.

(3) The optical head: there are four signals emerging in the optical head. The incident laser (532nm) to excite the mounted sample, the white light and corresponding signal to the charge coupled device (CCD) to visualize the sample and the output signal to the spectral meter. Polarizers and quarter wave plate are used in order to acquire circularly polarized PL spectra.

(4) Spectral meter: our advanced spectral meter is equipped with gratings of 600 and 1800 lines/mm, which are appropriate for PL and Raman measurements, respectively. One of our featured functionalities is the oscilloscope mode, which enables us to see the response of selected spectral range almost instantly. This functionality is extremely user-friendly when tuning the output signal response.

Chapter 3 Spatial Variations of Valley Zeeman Splitting in Monolayer WSe₂

3.1 Introduction

Monolayer (ML) transition metal dichalcogenides (TMDs) in the class MX_2 ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{Se}$) are one branch of two-dimensional (2D) materials which attract numerous attention due to their direct-bandgap structures which overcome shortages of the gapless graphene [101-103]. Moreover, the broad families of TMDs even cover the whole visible frequency range and become promising candidates for the next generation electronics [13, 104-106]. Besides the direct-bandgap nature of ML MX_2 , inversion symmetry breaking of ML MX_2 leads to a large spin-orbit coupling (SOC) [107-109], which further results in the splitting of valance bands at K/K' valleys. This splitting of valance bands can be probed as A and B excitons through optical methods. In addition to the strong SOC in ML TMDs, K and K' valleys are energy-degenerated but inequivalent due to the time-reversal symmetry [110, 111]. This energy degeneracy can be lifted upon an out-of-plane external magnetic field due to time-reversal symmetry breaking. Among these MX_2 , ML WSe₂ provides a good platform to study the valley splitting phenomena due to its strong intrinsic and well-resolved photoluminescence (PL) spectra at low temperatures. Although there are some works studying the doping influence on the valley splitting by applying electric field [43, 73, 112], studies of valley splitting evolution crossing the ML TMDs are still rare. In this work, the valley splitting

evolution crossing the exfoliated WSe₂ is well studied by circularly polarized magneto-PL mapping at a low temperature. With the spatial evolution across the samples, there is a gradually doping effect which can be manifested by the blue shifts of trion (X_T) and A exciton (X_0) emissions. The different doping regions indicate the different electron-electron interaction strength, which further influences the valley splitting behaviors on the ML WSe₂. Particularly, the valley splitting behavior of X_0 emission is almost independent on the doping level. While doping level plays a critical role for the valley splitting behavior of X_T emission. When considering more electrons in the TMDs, despite the inter-valley trions have lower energy level and are more stable, intra-valley trions also exist. These intra-valley trions induced by higher doping level possess different excitonic fine structure and might be responsible for the variation of valley splitting behavior.

3.2 Experimental Details

3.2.1 Sample Preparation

Monolayer WSe₂ flakes were mechanically exfoliated from a purchased bulk WSe₂ crystal (2D semiconductors Inc.) onto a Si substrate capping with a 300 nm SiO₂.

3.2.2 Photoluminescence Spectroscopy and Imaging Study of Monolayer WSe₂

Monolayer WSe₂ flakes were firstly characterized at 77 K. The monolayer WSe₂ samples were mounted on a customized confocal micro-PL spectroscopy/image system which is described in chapter 2. By filling the liquid nitrogen into the tank, the system can work properly at 77 K. After the characterization at 77 K, the liquid nitrogen was purged out by the helium gas, then the liquid helium was filled into the tank to cool our system to 4.2 K. A continuous-wave laser of 532 nm with a power of $\sim 100 \mu\text{W}$ was used during the experiment. The laser spot size is estimated to be $\sim 1 \mu\text{m}$ in diameter.

3.3 Results and Discussion

3.3.1 Spatial Variations of Valley Zeeman Splitting in the Relatively High-doping Regime

Figure 3.1 (a) Optical images of exfoliated WSe₂, the white dash arrow indicates the direction of spatial evolution from the center to the edge. (b) Raman spectrum of presented WSe₂ flake @RT. (c) Contour plot of peak position on the exfoliated WSe₂ as

a function of spatial distribution (define the center as 0 μm) @ 77 K. (d) Contour plot of peak position on the exfoliated WSe₂ as a function of spatial distribution (define the center as 0 μm) @ 4.2 K. (e) PL spectra @77 K acquired from the center and edge regions indicated by green and red spots in the PL mapping inset. (f) PL spectra @4.2 K acquired from the center and edge regions indicated by green and red spots in the PL mapping inset.

By using all-dry-transfer method, the WSe₂ flake was transferred onto 300 nm SiO₂/Si substrate. Figure 3.1(a) shows the optical image of the exfoliated WSe₂ flake and the white arrow represents the spatial evolution path in our later study. The absence of Raman peak around 308 cm⁻¹ and the frequency of A_{1g} mode suggest that our sample is monolayer WSe₂ (see Fig. 3.1(b)) [99, 113]. In order to trace the spatial evolution of PL spectra, a contour plot of peak position on the exfoliated WSe₂ as a function of spatial distribution is given at both 77 K and 4.2 K (see Figs. 3.1(c)-(d)), note that we define the center position as 0 μm . As shown in the contour mapping, both X_T and X₀ emissions have blue shifts as the spatial location changing from the center to the edge (indicated by white dash line in Fig. 3.1(a)). Single spectra are extracted from center and edge regions at both 77 K and 4.2 K (see Figs. 3.1(e)-(f)). At 77K, well-resolved trion and exciton emissions are present, while emissions from the localized states are not observed due to the thermal fluctuation. At 4.2 K, there are X₀ and X_T emissions located at ~1.74 eV and ~1.71 eV respectively, which are consistent with previous reports [46, 114-116]. The spots of the inset are where the spectra come from. Besides the X₀ and X_T emissions,

there are two localized-state emissions labeled as L_1 and L_2 , respectively. At the edge region of the ML WSe₂, the PL spectrum is shown in Fig. 3.1(f) lower panel. In addition to the peaks seen in Fig. 3.1(f) upper panel, there is one more localized-state emission labeled as L_3 . Moreover, the increasing of intensity ratio between the X_T and X_0 emissions at the edge region suggests that more electrons are localized at the edge region which facilitate the formation of more trions. These localized emissions at 4.2 K are due to the greater suppression of thermal fluctuation compared to that of at 77 K. To visualize the peak evolution quantitatively, single spectra are extracted from PL mapping data with a scanning step of 400 nm. Then the peak positions of X_T and X_0 emissions are plotted along the spatial locations (see Fig. 3.2). From Fig. 3.2(c), a blue shift of ~ 5 meV can be obtained for X_T emission between the center and the edge regions at 4.2 K. While for X_0 emission (see Fig. 3.2(d)), this blue shift is ~ 8 meV.

Figure 3.2 (a) Peak evolution of X_T emission as a function of spatial distribution @77 K. (b) Peak evolution of X_0 emission as a function of spatial distribution @77 K. (c) Peak evolution of X_T emission as a function of spatial distribution @4.2 K. (d) Peak evolution of X_0 emission as a function of spatial distribution @4.2 K.

The blue shifts of X_T and X_0 emissions can be understood as follows. Quantitatively, the X_0 energy can be determined by the equation $E_{exc} = E_g - E_b$, where E_g is the electronic bandgap which is defined by the total energies needed to separately tunnel an electron and a hole into the 2D material; E_b is the X_0 binding energy, note that X_0 energy E_{exc} is also known as the optical bandgap, which is usually probed by PL spectra compared with the electronic bandgap E_g [117]. The many-body interactions due to quantum confinement in 2D materials are enhanced compared with 3D systems since it is compensated almost exactly by the attractive long-range correlations [118]. When scaling down to 2D materials, the long-range Coulomb correlation is less efficient and the short-range exchange (eg: electron-electron interaction) having its origin in the Pauli exclusion-principle becomes dominant [119].

Figure 3.3 Schematics of band structure for intrinsic and doped case.

This short-range exchange of electron gas further affects the X_0 energy as shown in Fig. 3.3: there is a reduction of electronic bandgap E_g due to Pauli blocking. Meanwhile, the screening induced by short-range exchange effects decreases the binding energy of the X_0 [120]. The total changing of X_0 energy is a result of these two factors.

In addition to the evolution of PL peaks along spatial locations, valley splitting behaviors of X_T and X_0 emissions are also studied at the center and the edge of the exfoliated WSe_2 sample. A detailed schematic of circularly polarized PL measurement setup is illustrated in Fig. 3.4(a).

Figure 3.4 (a) A detailed schematic of circularly polarized PL measurement setup. (b) PL images of X_T emission energies under the magnetic fields of 7 T, 0 T and -7 T with σ^+ and σ^- polarizations. (c) PL images of the X_0 emission energies under the magnetic fields of 7 T, 0 T and -7 T with σ^+ and σ^- polarizations.

A polarizer and a quarter wave plate are used to generate either right (σ^+) or left (σ^-) circularly polarized excitation. At top of the optical head, another polarizer is used to selectively acquire σ^+ or σ^- signals. The excitation wavelength is 532nm (2.33 eV). As clearly shown in Figs. 3.4(b)-(c), the sample nonuniformity is visualized across all the magnetic fields. At edge area, there is clear blue shifts for both X_T and X_0 emissions compared with that from the center area. Without the magnetic field ($B = 0T$), there are no differences between σ^+ / σ^+ and σ^- / σ^- for both X_T and X_0 emissions. From Fig. 3.4(b), upon an external magnetic field, X_T peak position under σ^+ / σ^+ and σ^- / σ^- shifts oppositely with each other compared with that at zero field. Similar phenomenon can also be observed for X_0 emission in Fig. 3.4(c). More detailed PL images of the X_T and X_0 emission energies under different magnetic fields with σ^+ / σ^+ and σ^- / σ^- configurations are provided in Fig. 3.5.

Figure 3.5 (a) PL images of the X_T emission energies under selected magnetic fields with σ^+ and σ^- polarizations. (b) PL images of the X_0 emission energies under selected magnetic fields with σ^+ and σ^- polarizations.

To more intuitively present valley splitting behavior of X_T and X_0 emissions, typical polarization-resolved PL spectra extracted from the center and edge regions with σ^+ / σ^+ and σ^- / σ^- configuration at selected magnetic fields are given in Fig. 3.6.

Figure 3.6 (a) PL spectra of monolayer WSe_2 extracted from the center area under different magnetic fields with σ^+ and σ^- polarizations. (b) PL spectra of monolayer WSe_2 extracted from the edge area under different magnetic fields with σ^+ and σ^- polarizations.

The fitted splitting energies, which are the statistical average values of both X_T and X_0 emissions at selected center and edge area as marked in Fig. 3.4(c) are given in Fig. 3.7.

Figure 3.7 (a) Valley splitting energies of X_T emission as a function of magnetic field, the green data points are collected from center area and the red data points are collected from edge area. (b) Valley splitting energies of X_0 emission as a function of magnetic field, the green data points are collected from center area and the red data points are collected from edge area.

At the center area, the valley splitting energies of X_T emission show a linear relationship with the external magnetic field and the slope is -0.231 ± 0.011 meV/T (see green fitting in Fig. 3.7(a)). While for X_0 emission, the valley splitting energies also show a linear dependence with the external magnetic field and the slope is -0.237 ± 0.005 meV/T (see green fitting in Fig. 3.7(b)). The slope for the X_T emission corresponds closely to that of the X_0 emission, which is a typically neutral state and can be found in literatures [68, 112, 121]. At the edge area, the valley splitting dependence of X_T emission on the magnetic field becomes sub-linear which is different from the linear case at the center region (see red curve in Fig. 3.7(a)). The sub-linear dependence is probably due to the enhanced many-body interactions since more electrons

accumulate at the edge region. This sub-linear dependence may be related to two factors: r_S , which describes the strength of coulomb repulsion; r_X , which describes the strength of exchange interaction. The edge area of the ML WSe₂ is doped due to the moisture in atmosphere, the shifts of X_T and X_0 emissions manifest that the doping process happens gradually from the center to the edge. Upon doping effect, r_S is nearly unchanged when doping density is near the neutral point, while for r_X , there is a sudden increase when doping into the upper conduction band. In this case, there is a critical magnetic field, at which the electrons in the upper conduction band are fully spin and valley polarized. When the magnetic field is larger than the critical value, the exchange interaction vanishes, and the magnetic response becomes sublinear (see red curve in Fig. 3.7(a)) [73]. While for the X_0 emission, the valley splitting energies still show a linear dependence with the external magnetic field (see green fitting in Fig. 3.7(b)) and the slope is -0.239 ± 0.003 meV/T. Moreover, the slope for the X_0 emission at the edge region corresponds closely to that of at the center region. This reveals that the valley splitting behavior of X_0 emission is nearly independent on the doping density.

3.3.2 Spatial Variations of Valley Zeeman Splitting in the Relative Low-doping Regime

Similar experiments were conducted on a smaller monolayer WSe₂ flake. A contour plot of peak position on the smaller exfoliated WSe₂ as a function of spatial distribution is given at 77 K (see Fig. 3.8(a)).

Figure 3.8 (a) Contour plot of peak position on a smaller exfoliated WSe_2 as a function of spatial distribution (define the center as $0 \mu\text{m}$) @ 77 K . (b) PL spectra @ 77 K acquired from the center and edge regions indicated by green and red spots in the PL mapping inset.

Unlike the large shifts of X_T and X_0 emissions on larger monolayer WSe_2 , there are much smaller shifts of X_T and X_0 emissions on the smaller flake. The smaller energy

shifts of X_T and X_0 emissions imply there is less doping effect at the edge compared to that of the larger flake. The smaller energy shifts can be more intuitively observed from the Fig. 3.8(b). The valley splitting between σ^+/σ^+ and σ^-/σ^- at selected magnetic fields for center and edge area are given in Fig. 3.9.

Figure 3.9 (a) PL spectra of the smaller monolayer WSe₂ extracted from the center area under different magnetic fields with σ^+ and σ^- polarizations. (b) PL spectra of monolayer WSe₂ extracted from the edge area under different magnetic fields with σ^+ and σ^- polarizations.

For the X_0 emission, the valley splitting energies extracted from center and edge area are nearly identical, which is consistent with the previous discussion. A more detailed valley splitting energies of X_T and X_0 emissions as a function of external magnetic field from center and edge area are given in Fig. 3.10.

Figure 3.10 (a) Valley splitting energies of X_T emission as a function of magnetic field, the green data points are collected from center area and the red data points are collected from edge area. (b) Valley splitting energies of X_0 emission as a function of magnetic field, the green data points are collected from center area and the red data points are collected from edge area.

At the center area, the valley splitting energies of X_T emission show a linear relationship with the external magnetic field and the slope is -0.230 ± 0.005 meV/T (see green fitting in Fig. 3.10(a)). While for X_0 emission, the valley splitting energies also show a linear dependence with the external magnetic field and the slope is -0.232 ± 0.001 meV/T (see green fitting in Fig. 3.10(b)). Both slopes of X_T and X_0 emissions give a g-factor around 4, which implies the nearly neutral states at the center.

At the edge area, the valley splitting energies of X_T emission still exhibit a linear relationship with the magnetic field and the slope is -0.200 ± 0.006 meV/T (see red fitting in Fig. 3.10(a)), which is smaller compared to that extracted from center area. Because this edge area is in a lower doping region, r_s decreases with the increasing doping level, hence the interaction effects weaken and the slope of magnetic response decreases [73, 122-124]. The slope for the X_0 emission at the edge region is -0.231 ± 0.004 meV/T (see red fitting in Fig. 3.10(b)) corresponds closely to that of at the center region, which again manifests that the valley splitting behavior of X_0 emission is nearly independent on the doping density.

3.4 Conclusions

To sum up, the valley splittings of X_T and X_0 emissions crossing the exfoliated monolayer WSe₂ flakes are well studied by circularly polarized magneto-PL spectroscopy at a low temperature. Blue shifts of both X_T and X_0 emissions are due to gradually doping and the possible dopants are the moisture in atmosphere thus the edge area is more easily to be affected. In the range of relatively higher doping region, the valley splitting behavior of X_T emission changes from the linear dependence on the external magnetic field to the sub-linear dependence. While in the range of lower doping region, the valley splitting behavior of X_T emission maintains a linear relationship with the external magnetic field and the slope of the magnetic response decreases with the increasing doping level. The variation of valley splitting behavior of X_T emission might

be explained as follows. There are inter-valley and intra-valley trions in the system, as shown in Fig. 3.11.

Figure 3.11 Illustration of inter-valley and intra-valley trions (Adapted from Ref. [114], Copyright 2015, Nature Publishing Group)

A trion can be treated as an exciton plus an excess electron. When the excess electron is from the same valley of the exciton, as shown in the second and fourth conditions, this kind of trion is called the intra-valley trion. If the excess electron is from the other valley, as shown in first and third conditions, this kind of trion is called the inter-valley trion. Usually, the inter-valley trion has a lower energy level and is more stable. When the system is in low-doping regime, most of the trions are inter-valley trions. However, when the system is in higher-doping regime, intra-valley trions are not negligible and these intra-valley trions induced by higher doping level possess different excitonic fine structure and might be responsible for the variation of valley splitting behavior [114]. On the other hand, the valley splitting behavior of X_0 emission is nearly independent on the doping density. This work not only enriches the fundamental study of doping effect on valley splitting but also is beneficial for future valleytronics.

Chapter 4 Probing Magnetic-proximity-effect Enlarged Valley Splitting in Monolayer WSe₂ by Photoluminescence

4.1 Introduction

ML TMDs with the chemical formula MX₂ (e.g. M = Mo, W; X = S, Se) have attracted enormous attention in nanoelectronics and optoelectronics due to their novel properties for both fundamental studies and potential applications [108, 125-129]. Compared with gapless graphene [130], ML MX₂ are semiconductors with a direct band gap in the visible range of spectrum. There are two energy-degenerate valleys K and K' located at the corners of the Brillouin zone in ML MX₂ [131, 132]. Due to breaking of inversion symmetry in ML TMDs [110, 111], the two valleys are inequivalent with different orbital magnetic moments and have valley-selective circular dichroism behavior [24, 111, 133]. Thus, it is possible to manipulate the valley degree of freedom, which can be utilized in future valleytronic devices [134, 135].

Valley physics in ML TMDs can be studied by circular-polarization-resolved PL spectroscopy under an external magnetic field [112, 114]. In addition to the valley polarization, the valley degeneracy can be lifted by applying an out-of-plane external magnetic field, since the external magnetic field breaks the time-reversal symmetry [68, 112]. Previously, valley splitting was observed by applying large magnetic fields in MoSe₂ (10 T) [68], MoTe₂ (29 T) [67], WSe₂ (30 T) [136], MoS₂ and WS₂ (~65 T) [137]

on SiO₂/Si substrates. Although these works are very important and pioneering, these large magnetic fields are not practical for valleytronic device applications. Intuitively, a well-prepared heterostructure consisting of ML TMD on a magnetic substrate can lead to the enhanced valley splitting due to an interfacial MEF. For two-dimensional materials, this MEF was firstly revealed in a EuS/Graphene heterostructure [138] and later has been realized for CVD grown ML WSe₂ on a ferromagnetic EuS substrate, in which a valley splitting of 2.5 meV for A excitons was obtained at only 1 T by magneto-reflectance measurements [139]. This remarkable valley splitting is induced by the MEF at the heterostructure interface due to the magnetic proximity effect.

Here, considering the unique advantage of strong light emission from such 2D semiconductors, we conduct systematic circular-polarization-resolved magneto-PL measurements in exfoliated ML WSe₂ on the ferromagnetic substrate of EuS and on the nonmagnetic substrate of SiO₂/Si. For ML WSe₂ on the nonmagnetic SiO₂/Si, the valley splittings as a function of the applied magnetic field of both A excitons and trions are linear and show no saturation in the applied magnetic field range. In contrast, for ML WSe₂ on EuS the valley splittings of both A excitons and trions dramatically increase with the increasing magnetic field when $|B| < 1$ T, which is completely different from the case of ML WSe₂ on SiO₂/Si. For larger magnetic fields, $|B| > 1$ T, the valley splittings of A excitons and trions continue increasing but with a much smaller rate and the increasing rate is very similar to the case of ML WSe₂ on SiO₂/Si. The enhanced valley splittings of both A excitons and trions in ML WSe₂ on the ferromagnetic

substrate EuS are due to an interfacial MEF, resulting from the magnetic proximity effect. These results demonstrate that the valley splitting of ML WSe₂ can be controlled by the magnetic properties of the substrate which is beneficial for future valleytronic devices.

4.2 Experimental Details

4.2.1 Sample Preparation

The atomically thin flakes of WSe₂ were exfoliated from bulk crystals (purchased from 2D semiconductors Inc.) and transferred onto typical SiO₂/Si substrate. For the WSe₂ sample on EuS substrate, precisely dry transfer method was utilized to transfer exfoliated WSe₂ onto the preselected area of EuS. The EuS substrate was from Prof. Zeng's group and it was obtained by electron beam evaporation. The thickness of EuS substrate is 10 nm.

4.2.2 Photoluminescence Spectroscopy and Imaging Study of As-prepared Samples at Cryogenic Temperature

The optical images were recorded by an optical microscope (Olympus BX51) equipped with a coordinate stage. Thus, the WSe₂ samples were roughly located before they were mounted on the cryogenic holder. Photoluminescence and Raman spectra were acquired at cryogenic temperature (4.2K) by using a customized magneto-Raman/photoluminescence system with a precisely controlled sample stage consisting

of x-y-z axes positioners and x-y axes scanners. A 532 nm continuous-wave laser with a power of 700 μ w was used as the excitation. The laser spot is around 1 μ m. 600 and 1800 lines/mm gratings were used for the Raman and photoluminescence measurements, respectively. External magnetic fields in the range from -7 T to 7 T were applied perpendicularly to the WSe₂ samples (Faraday geometry). A homemade optical head is exploited to generate and detect circularly polarized signals.

4.3 Results and Discussion

4.3.1 Theoretical Analysis of Valley Zeeman Splitting on SiO₂/Si and EuS Substrates

Valley physics of ML TMDs has become one of the hottest topics in condensed matter physics recently. The breaking of inversion symmetry creates two degenerated but inequivalent K and K' valleys in ML TMDs. Figure 4.1(a) presents the valley selection rule for an A exciton.

Figure 4.1 (a) Valley selection rules of σ^+ and σ^- excitation for an A exciton are presented. The blue (red) vertical lines show transitions of spin-up (-down) electrons in K (K') valleys by σ^+ (σ^-) excitation. (b) Valley splitting of A excitons in WSe₂ on a nonmagnetic substrate has only contribution from the atomic orbital magnetic moment in the valence band represented by the black arrow. (c) Valley splitting of trions in WSe₂ on a nonmagnetic substrate, which consists of an A exciton in the K valley and an electron in the K' valley. (d) Valley splitting of A excitons in WSe₂ on a magnetic substrate has an additional contribution due to magnetic exchange field ΔE_{MEF} , represented by the thick orange arrow. (e) Similarly, valley splitting of trions in WSe₂

on a magnetic substrate also has the additional element (ΔE_{MEF}) due to the magnetic exchange field.

For the K valley, only electrons with spin-up can be excited from the upper valence band to the upper conduction band, while electrons with spin-down can be excited from the lower valence band to the lower conduction band, due to the giant spin-orbit coupling [56]. The situation is just the opposite in the K' valley, where spin-up and -down are exchanged, due to spin-valley locking. In the absence of an external magnetic field, the two valleys are degenerate. However, when an external magnetic field B is applied, the degeneracy of these two valleys is lifted, which can be understood as follows. The A exciton energy is given by:

$$E_{X0} = E_C - E_V - E_B \quad (4 - 1)$$

E_C and E_V are conduction band edge and valence band edge respectively, and E_B is the binding energy of the A exciton. As is known, σ^+ polarized light can excite electrons in the K valley, while σ^- polarized light can excite electrons in the K' valley. So, the A exciton energy excited by σ^+ polarized light can be written as:

$$E_{X0}^+ = E_C^+ - E_V^+ - E_B \quad (4 - 2)$$

While A exciton energy excited by σ^- polarized light can be written as:

$$E_{X0}^- = E_C^- - E_V^- - E_B \quad (4 - 3)$$

Note that E_B remains the same in the two cases. Hence the valley splitting is

$$\Delta E = E_{X0}^+ - E_{X0}^- = E_C^+ - E_C^- - (E_V^+ - E_V^-) \quad (4 - 4)$$

Since the valence band edge and the conduction band edge possess different magnetic moments, there will be a different energy shift when an out-of-plane magnetic field is applied. Thus, the valley splitting energy is [68],

$$\Delta E = E_C^+ - E_C^- - (E_V^+ - E_V^-) = -(\mu^C - \mu^V)B \quad (4 - 5)$$

Here, μ^C and μ^V are the total magnetic moments of the conduction and valence bands, respectively. The total magnetic moments consist of the magnetic moments due to orbital, carrier spin, and delocalized Bloch wave-function in the valence band and the conduction band.

In the case of A excitons on a nonmagnetic substrate (NMS) such as SiO₂/Si, the only non-zero contribution comes from the orbital magnetic moment in the valence band, which is $-2 \mu_B$ in the K valley (indicated by black arrow in Fig. 4.1(b)). Meanwhile, there is another $+2 \mu_B$ in the K' valley, so the total valley splitting of A excitons on a nonmagnetic substrate (NMSE) is [67, 68, 112, 121, 136, 137],

$$\Delta E_{NMSE} = -4 \mu_B B \quad (4 - 6)$$

In the case of a σ^+ polarized trion, which consists of an A exciton in K valley and an electron in the K' valley – intervalley trion (see Fig. 4.1(c)), the extra electron contribution in the K' valley should be considered in addition to $-2 \mu_B$ of the A exciton case. However, when calculating the total valley splitting of σ^+ and σ^- polarized trion, the contributions of the extra electrons under σ^+ and σ^- configuration cancel each other. As a result of the cancellation, the valley splitting of trions on a nonmagnetic substrate (NMST) is also [112],

$$\Delta E_{NMST} = -4 \mu_B B \quad (4 - 7)$$

The case for A excitons in a ML TMD on a magnetic substrate is described in Fig. 4.1(d). The valley splitting of A excitons has now an additional element (ΔE_{MEF}) due to the MEF induced by the magnetic proximity effect. The contribution due to the externally applied magnetic field ΔE_{MSE} is expected to be the same as for the nonmagnetic case ΔE_{NMSE} . Thus, the total valley splitting of A excitons (TE) is

$$\Delta E_{TE} = \Delta E_{MSE} + \Delta E_{MEF} \quad (4 - 8)$$

As shown in Fig. 4.1(e), for an intervalley trion consisting of an A exciton in the K valley and an electron in the K' valley, the contribution to the valley splitting by an external magnetic field, ΔE_{MST} , is the same as ΔE_{NMST} . Then, considering the contribution of MEF, the total valley splitting of trions (TT) on a magnetic substrate is

$$\Delta E_{TT} = \Delta E_{MST} + \Delta E_{MEF} \quad (4 - 9)$$

4.3.2 Optical Characterization of WSe₂ on SiO₂/Si and EuS Substrates

The flakes of WSe₂ were mechanically exfoliated from WSe₂ crystals onto a SiO₂/Si substrate and a EuS substrate grown by e-beam evaporation. Optical microscope images of the samples are shown in Figs. 4.2(a)-(b). The encircled area shows the monolayer WSe₂ and the corresponding PL mapping images are shown in Figs. 4.2(c)-(d). A detailed experimental setup for magneto-PL measurements is illustrated in Fig. 4.2(e), a polarizer and a quarter wave plate are used to generate either σ^+ or σ^- excitation. At

top of the optical head, another polarizer is used in order to detect σ^+ or σ^- emission signal. Throughout the measurements, a laser beam of 2.33 eV photon energy is focused on $\sim 1 \mu\text{m}$ spot, with a power of 700 μW .

Figure 4.2 Optical microscope images of ML WSe_2 on (a) SiO_2/Si , (b) EuS substrate and corresponding PL mapping images at zero field on (c) SiO_2/Si and (d) EuS . (e) Schematic setup of the circular-polarization-resolved magneto-PL measurement. A

polarizer and a quarter wave plate are used to generate either σ^+ or σ^- excitation. At top of optical head, another polarizer is used in order to detect σ^+ or σ^- emission signal. (f) Raman spectra of ML WSe₂ on SiO₂/Si and EuS substrates. There are two peaks around 251 cm⁻¹ and 265 cm⁻¹, which correspond to E_{2g}¹ and A_{1g} modes, respectively. (g) PL spectra of ML WSe₂ on SiO₂/Si and EuS substrates excited by a 532 nm laser show A exciton (X₀) and trion (X_T) emission peaks.

The sample is placed on a cryogenic sample holder at 4.2 K so that the magnetic field can be applied perpendicularly to the sample (Faraday geometry). Raman spectra are acquired at 4.2 K, which are shown in Fig. 4.2(f). There are two peaks in the range of 251 cm⁻¹ - 265 cm⁻¹ for WSe₂ on both SiO₂/Si and EuS, which correspond to E_{2g}¹ and A_{1g} modes, respectively. Based on the previous reports, our WSe₂ samples are confirmed to be monolayer ones [99, 113]. For ML WSe₂ on the EuS substrate, E_{2g}¹ has a blue shift compared with that on SiO₂/Si which is probably due to the compressive strain of the interfacial surface [140, 141] since E_{2g}¹ is sensitive to strain. For WSe₂ on EuS, the thermal expansion coefficient of EuS is larger than that of WSe₂ [142, 143], which results in a compressive strain between the surface when cooling the heterostructure to cryogenic temperature. However, for WSe₂ on SiO₂/Si, such strain can be neglected since the thermal expansion coefficient of SiO₂ is very close to that of WSe₂ [144]. Besides, the charge transfer process between EuS and WSe₂ which increases electron doping level in WSe₂ broadens the width of A_{1g} mode due to the strong electron-phonon coupling of the A_{1g} mode [145]. Figure 4.2(g) shows PL spectra

of WSe₂ on both substrates at 4.2 K at zero magnetic field. For WSe₂ on SiO₂/Si, the peaks around 1.74 eV and 1.71 eV are due to A excitons (X₀) and trions (X_T), respectively. Here the A exciton peak is more pronounced than the trion peak, while for WSe₂ on EuS, the trion peak is dominant. This can be explained by having a closer look at the heterostructure formed by WSe₂ and EuS. EuS is a ferromagnetic material with a work function of 3.3 eV [146], while the work function of ML WSe₂ is 4.3 eV [147]. Therefore, in the heterostructure, a charge transfer process takes place, that is, electrons transfer from EuS to WSe₂ due to the higher work function of WSe₂ [148]. These electrons facilitate the formation of more trions in WSe₂, hence the trion emission peak is dominant in the spectra due to higher doping level compared to the SiO₂/Si substrate case.

4.3.3 Enhanced Valley Zeeman Splitting with the EuS Substrate

To investigate the valley splitting of ML WSe₂ on nonmagnetic SiO₂/Si and ferromagnetic EuS substrates, circular-polarization-resolved magneto-PL measurements were conducted.

For WSe₂ on SiO₂/Si, in the absence of an external magnetic field, there is no valley splitting between σ^+ and σ^- emission as shown in Fig. 4.3(a). Note that the peak near 1.71 eV is due to trion emission, while the one near 1.74 eV is from A excitons [43, 46, 116, 149]. When the magnetic field is increased to 7 T, there is an energy splitting between σ^+ and σ^- emission. The magnetic field suppresses the trion peak intensity

under σ^+ configuration (blue curve) while for the A exciton peak, the intensity of σ^+ emission is slightly stronger than that of σ^- emission. When applying -7 T, the results are reversed, namely the trion peak intensity under σ^- configuration (red curve) is suppressed and the A exciton peak intensity of σ^- emission is slightly stronger than that of σ^+ emission. A previous report showed, that the valley polarization of A exciton emission is mainly dependent on the initially, optically created valley polarization rather than influenced by the magnetic field [121].

Figure 4.3 Circularly polarized magneto-PL spectra of WSe_2 on (a) nonmagnetic SiO_2/Si and (b) ferromagnetic EuS under magnetic fields of -7 T, 0 T, and 7 T are

presented. The blue (red) curves are defined as emission collected of σ^+ (σ^-) polarized light where the sample is excited by σ^+ (σ^-) polarized light. Open circles are original collected data, all spectra are presented by subtracting the background spectrum.

Our results show that the valley polarization of A exciton emission is slightly sensitive to the magnetic field, which is also found in literature [114]. For the valley polarization of trion emission, it is also dependent on the magnetic field in addition to the initially, optically created valley polarization. The different valley polarization behavior between A exciton and trion emission from ML WSe₂ is probably due to the fact that the PL emission time of the trion is much longer than that of the A exciton [121].

The same measurements were also conducted for WSe₂ on the magnetic EuS and can be seen in Fig. 4.3(b). At zero field, the peak near 1.72 eV arises from trion emission, while the peak near 1.75 eV is due to A excitons. There is a blue shift for both A exciton and trion emission compared to that of ML WSe₂ on SiO₂/Si at zero field. This is probably due to the compressive strain between ML WSe₂ and EuS [150, 151], which is also in agreement with our Raman results. Another interesting feature is that the trion emission intensity is stronger than that of the A exciton emission at zero field, which is due to the charge transfer process and a detailed discussion has been given in the previous paragraph. The PL spectra acquired at 7 T and -7 T show an energy splitting between σ^+ and σ^- emission, which are similar to that of ML WSe₂ on the SiO₂/Si substrate, albeit with larger magnitude.

Figure 4.4 (a) Experimentally determined valley splittings of *A* excitons versus magnetic field in *WSe*₂ on nonmagnetic *SiO*₂/*Si* (red squares) and ferromagnetic *EuS* (black squares) are presented. (b) Experimentally determined valley splittings of trions versus magnetic field in *WSe*₂ on nonmagnetic *SiO*₂/*Si* (red dots) and ferromagnetic *EuS* (black dots). Valley splittings are extracted from the PL spectra at selected magnetic fields as the difference between the peak energies of σ^+ and σ^- polarized emissions for *A* excitons and trions.

In order to elaborate the valley splitting enhancement of ML *WSe*₂ on *EuS*, valley splittings of *A* excitons in ML *WSe*₂ on *SiO*₂/*Si* and *EuS* are plotted as a function of the magnetic field in Fig. 4.4(a). The red squares are collected from ML *WSe*₂ on *SiO*₂/*Si*. They show a linear relationship with the magnetic field with a slope of -0.23 meV/T for *A* excitons, concomitantly the effective *g*-factor can be extracted as 3.97, which is in agreement with the previous reports (see Table 4.1) [114, 116, 121, 139].

Table 4.1 Summary of the effective g -factors of ML WSe₂ on SiO₂/Si

Substrates	A exciton g -factor	Trion g -factor
SiO ₂ /Si (reference)	-3.7 ± 0.2 [121]	-4.4 ± 0.2 [121]
	-4.37 ± 0.15 [116]	-6.28 ± 0.32 [116]
	3.14 to 5.72 [114]	-
	~ 3.46 [139]	-
SiO ₂ /Si (in this work)	3.97 ± 0.02	4.15 ± 0.03

For valley splitting data collected from ML WSe₂ on EuS (black squares in Fig. 4.4(a)) we observe for small magnetic fields, $|B| < 1$ T, that the absolute value of the valley splitting increases dramatically for a non-zero magnetic field and it reaches up to 2.4 meV at -1 T. This valley splitting originates from two parts, one is induced by the external magnetic field (ΔE_{MSE}), and the other is induced by the MEF (ΔE_{MEF}). So, the total valley splitting can be expressed as $-g\mu_B(B + B')$. Here, B' is the MEF and B is the external applied field. We assume that the effective g -factor of the A excitons in ML WSe₂ on EuS is the same with that on the SiO₂/Si substrate, which is theoretically 4. In this case, the MEF can be roughly estimated as

$$B' = -\frac{\Delta E}{g\mu_B} - B \quad (4 - 10)$$

Hence, the value of MEF in our case is around 9 T. Note that the MEF is a short-range field induced by the magnetic proximity effect, which means it is highly influenced by the interface between WSe₂ and EuS. Our estimated MEF is slightly smaller than that in the previous report [139]. Such a difference can be caused by both sample preparation and post-annealing process.

In order to explore the influence of MEF on trion emission, valley splittings of trions in ML WSe₂ on SiO₂/Si and EuS are plotted as a function of the magnetic field, as shown in Fig. 4.4(b). The red dots are collected from ML WSe₂ on SiO₂/Si. Similarly to the A exciton case, it shows a linear relationship with the external magnetic field, with a slope of -0.24 meV/T, consequently, the effective g -factor can be extracted as 4.15, which is comparable with the effective g -factor of A excitons. The similar valley splitting behavior of A excitons and trions in ML WSe₂ on SiO₂/Si matches well with theoretical calculations [112]. In contrast, the valley splitting of trions in ML WSe₂ on EuS (black dots in Fig. 4.4(b)) shows considerable enhancement compared to the trions case on SiO₂/Si. The orange guideline of trions shows a similar large enhancement within $|B| < 1$ T compared with the guideline of A excitons in WSe₂ on EuS and increases slowly with the external magnetic field when $|B| > 1$ T. By comparing the valley splittings of A excitons and trions in ML WSe₂ on EuS, we find that the MEF enhances the valley splitting energies of both A excitons and trions.

The nonlinear behavior of the valley splittings of A excitons and trions in ML WSe₂ on EuS suggests that the MEF between the WSe₂ and EuS substrate is highly dependent on the magnetization of the EuS substrate [139]. Within $|B| < 1$ T, the magnetization of the EuS substrate is highly sensitive to the magnetic field, resulting in greatly enhanced valley splitting energies. When $|B| > 1$ T, the magnetization slowly becomes saturated thus the valley splitting behavior is similar to the case of ML WSe₂ on SiO₂/Si.

4.4 Conclusions

We have performed circular-polarization-resolved magneto-PL measurements on ML WSe₂ with SiO₂/Si and EuS substrates. Valley splittings of both A excitons and trions are enhanced due to the MEF resulting from the magnetic proximity effect when EuS is used as the substrate. More specifically, within $|B| < 1$ T, the valley splitting energies are greatly enhanced, while for $|B| > 1$ T, the valley splitting behavior is similar to the case of ML WSe₂ on SiO₂/Si. The nonlinear valley splitting enhancement of both A excitons and trions is due to the field-dependent magnetization of EuS. Based on our estimation, the value of MEF between the WSe₂ and EuS is around 9 T. Our results demonstrate that the valley splittings of A excitons and trions in ML WSe₂ can be controlled by the magnetic properties of the substrate which can be utilized in future valleytronic devices.

Chapter 5 Valley Zeeman Splitting in Epitaxial MS₂ (M=Mo, W) Monolayers on Hexagonal Boron Nitride

5.1 Introduction

2D TMDs of 2H structure such as WS₂, MoS₂, WSe₂ and MoSe₂ become emerging semiconductors not only because of possessing a direct energy band gap, but also owning an extra valley degree of freedom. The direct energy band gap of visible light range, the strong spin-orbit/spin-valley coupling, and the newly discovered ferromagnetism in 2D materials offer rich new physics and promise plenty of applications, such as 2D light emission diodes (LEDs), 2D lasers, 2D valleytronics, and so on [24, 105, 107, 152-162].

CVD process is believed to be the most suitable method to produce 2D materials for intensive fundamental study and especially for practical applications. Currently, the most common method of growing atomically thin layers of TMDs through CVD process is to make metal oxide powders reacted with sulfur or selenium vapor. This method works fairly well for the substrates of SiO₂/Si, quartz, sapphire, mica, and Au foils, which have been extensively investigated [163-171]. Meanwhile, it is known that hBN is the most desirable substrate for growing or transferring 2D materials onto it as hBN could provide a clean, flat and neutral surface/interface to 2D materials, which guarantees high crystal or optical quality of 2D TMDs and promotes 2D TMDs to

exhibit their intrinsic properties [172-180]. Unfortunately, until now, there are very few reports on growing TMDs monolayers on hBN substrate by using this strategy [173, 181-183] or using WCl_6 and sulfur [172]. Though the CVD grown WS_2 and MoS_2 monolayers on hBN show much better optical quality compared with the CVD grown or mechanical exfoliated WS_2 and MoS_2 monolayers on SiO_2/Si substrates [172, 173, 182, 183], the detailed and systematic studies of their properties such as optical and spin-valley properties are lacking, which may be due to the limitation of the small size and low production [172, 182].

Typically, monolayers of TMDs prepared by mechanical exfoliation of natural crystals are used when research interests are focused on exploiting intrinsic properties and fundamental sciences of 2D TMDs. Indeed, exfoliated WSe_2 and MoSe_2 monolayers on SiO_2/Si exhibit excellent optical quality, such as well-resolved and sharp exciton (X_0) and trion (X_T) emission peaks [68, 112, 116, 184-186]. This is the main reason that Se-based 2D TMDs are chosen for the studies of valley physics in 2D semiconductors, such as valley splitting, one of the most interesting valley physics belonging to 2D TMDs [68, 112, 116, 184]. However, for S-based TMDs, like WS_2 and MoS_2 , the exfoliated monolayers on SiO_2/Si , though show certain improvement in optical quality compared to CVD grown monolayer WS_2 and MoS_2 on SiO_2/Si , present a broad peak of highly merged exciton and trion emissions at room temperature, or very weak and broad separated exciton and trion emissions with strong emission of localized states even at cryogenic temperature [44, 174, 187, 188]. Such poor optical quality greatly limits

investigations of intrinsic light emission properties and physics usually reflected by the emissions. Very recently, Cadiz et al. observed very narrow optical transition linewidths in MoS₂ and WS₂ monolayers encapsulated in hBN [174]. But the encapsulation process is complicated and not suitable for large-area and high-yield production.

Here, we developed a method of directly growing atomically thin WS₂ and MoS₂ layers on hBN through CVD process. The as-grown triangular WS₂ and MoS₂ monolayer flakes cover almost the entire hBN surface and well align themselves into certain orientation, indicating a high production yield of the epitaxial growth process. Compared to the exfoliated monolayers from natural crystals on SiO₂/Si, our CVD grown samples on hBN exhibit significantly improved optical quality with the neutral exciton linewidths of ~5.6 meV and ~7.2 meV at cryogenic temperature for MoS₂ and WS₂ monolayers on hBN, respectively. Intrinsic excitonic emissions such as well-resolved and super sharp exciton and trion PL peaks are observed. The intrinsic valley Zeeman splitting in CVD grown WS₂ and MoS₂ monolayers on hBN have been clearly revealed by in-situ magnetic-field-dependent PL imaging and spectroscopy at cryogenic temperature for the first time.

5.2 Experimental Details

5.2.1 Sample Preparation

The atomically thin WS₂ and MoS₂ flakes were grown through a chemical vapor deposition process in our previously developed tube furnace system [165]. Instead of

metal oxide powders, metal oxide (WO_x and MoO_x) thin films of 1 nm in thick were deposited onto the pre-exfoliated hBN flakes on SiO_2/Si substrate by e-beam evaporation. The substrate was fixed on a rotating sample holder in order to improve the film uniformity. After that, the chamber was pumped to 5×10^{-7} Torr. Then, the e-beam power was maintained at 3.9% to provide a stable depositing rate of 0.1 Å/s. Pure Ar gas with a flow rate of 100 sccm was used as carrying gas. The growth temperature is controlled to be 750 °C and growth duration is 10 minutes. The referential samples, mechanical exfoliated WS_2 and MoS_2 monolayers were made from natural crystals (purchased from 2D semiconductors Inc.) and transferred onto typical SiO_2/Si substrate.

5.2.2 Characterization of As-grown Samples at Room Temperature

The as-grown samples were firstly characterized at room temperature. The optical and fluorescence images were recorded by an optical microscope (Olympus BX51) equipped with a Mercury lamp. Scanning Electron Microscope (JEOL JSM-6700F) and Atomic Force Microscope (WITec alpha 300 RA with AFM function) were employed for morphological studies of atomically thin WS_2 and MoS_2 flakes on hBN. Raman and photoluminescence spectroscopies were conducted by WITec alpha 300 RAS Raman/PL system with excitation laser of 532 nm and a 100X objective lens of 0.95 numerical aperture (NA). To avoid heating effect, the laser power was controlled below

0.1 mW. The laser spot size is around 500 nm in diameter. A 2400 lines/mm grating and a 600 lines/mm grating were used for Raman and PL measurements, respectively.

5.2.3 Photoluminescence Spectroscopy and Imaging Study of Monolayer Flakes at Cryogenic Temperature

The as-grown WS₂ and MoS₂ monolayer flakes on hBN were also investigated at cryogenic temperature (4.2 K) by using a customer designed confocal micro-PL spectroscopy/image system with a non-magnetic piezo-crystal controlled sample stage consisting of x-, y-, and z- axis positioners and x-, y- axis scanners. The excitation source is a continuous-wave laser of 532 nm with a power of ~0.3 mW. The laser spot size is estimated to be ~1 μ m in diameter. A 600 lines/mm grating was used for PL measurements. Magnetic fields in the range of ± 8 T were applied perpendicular to the plane of as-grown WS₂ and MoS₂ monolayer. The light emission from either K' or K valley was selectively probed by controlling the circular polarization states of the incident and scattering lights.

5.3 Results and Discussion

5.3.1 Characterization of CVD Grown Monolayer WS₂ on hBN

Though our previously developed method demonstrates the success of growing large-area WS₂ monolayer on SiO₂/Si [165], it is not so successful for growing WS₂ monolayer flakes directly on hBN. As shown in Fig. 5.1, when WO₃ powders are used

as the precursor, WS_2 layers prefer to nucleate at the edges of hBN flakes and grow laterally like the extension of the hBN, instead of growing on top of the basal plane of hBN.

Figure 5.1 (a, b) SEM images of CVD grown atomically thin WS_2 layers on hBN by using WO_3 powders as precursors.

The strategy designed in this work is to provide transition metal sources by precoating the hBN flakes and the exposed area of SiO_2/Si with a uniform thin film of WO_x . The following sulfurization process promotes the growth of atomically thin WS_2 flakes directly on top of hBN (Fig. 5.2(a)). While the refractive index and thickness of hBN flake do not offer an acceptable optical contrast of WS_2 monolayers on hBN (Fig. 5.2(b)), scanning electron microscope (SEM) image does display what we expected, the population of atomically thin WS_2 flakes on the entire surface of hBN, indicating a high yield of this new method (Fig. 5.2(c)). The bright fluorescence emission further reveals the majority of the products are monolayer flakes (Fig. 5.2(d) and Fig. 5.3), which possess a direct band gap. The triangular shape of the as-grown WS_2 flakes is pictured out by atomic force microscope (AFM) image and the height profile confirms the formation of the monolayers (Fig. 5.2(e)).

Figure 5.2 (a) Schematic diagram of growing WS₂ monolayer flakes on hBN. (b-d) Optical, SEM and fluorescence images of atomically thin WS₂ layers grown on hBN. (e) AFM image of WS₂ monolayers. Inset shows the height profile crossing the selected flake. (f) Raman spectrum of the monolayer WS₂ grown on hBN. (g) PL spectra of the monolayer WS₂ grown on hBN and mechanically exfoliated monolayer WS₂ on SiO₂/Si. The measurements were conducted at room temperature.

Figure 5.3 (a-c) Optical images of CVD grown atomically thin WS_2 layers on hBN. (d-f) the corresponding fluorescence images showing the high yield of producing WS_2 monolayer flakes.

A perfect alignment of crystal orientations among the as-grown flakes is also observed in the AFM image, implying the epitaxial growth of WS_2 monolayers on hBN by this method. The high yield and epitaxial growth occur in almost all pieces of hBN (Fig. 5.4) and the statistic size distribution histogram of as-grown WS_2 can be found in Fig. 5.5.

Figure 5.4 (a-c) SEM images of CVD grown atomically thin WS_2 layers on hBN. (d-f) The zoom-in SEM images show that the triangular-shaped atomically thin WS_2 flakes are well aligned with underlying hBN.

Figure 5.5 (a) Selected SEM images of as-grown WS_2 on hBN. (b) Statistic size distribution histogram of samples in (a).

The typical Raman spectrum of monolayer WS₂ grown on hBN is displayed in Fig. 5.2(f). The E_{2g}¹(Γ) peak at 355 cm⁻¹ originates from the in-plane vibrations of atoms while A_{1g}(Γ) mode at 417 cm⁻¹ originates from the out-of-plane vibration of atoms. In addition to the E_{2g}¹(Γ) and A_{1g}(Γ) modes, the peak at ~300 cm⁻¹ is attributed to 2LA(M) – 2E_{2g}²(Γ), the peak at ~320 cm⁻¹ is attributed to 2LA(M) – E_{2g}²(Γ), and the peak at ~350 cm⁻¹ is attributed to 2LA(M), where LA(M) is a longitudinal acoustic mode, caused by the in-plane collective movements of the atoms [165, 189]. PL spectra of the monolayer WS₂ grown on hBN and mechanically exfoliated monolayer WS₂ on SiO₂/Si are shown in Fig. 5.2(g). Very interestingly, the WS₂ monolayer directly grown on hBN by CVD process exhibits a much sharper PL peak (linewidth of 29 meV), compared to that (linewidth of 80 meV) of monolayer WS₂ on SiO₂/Si through mechanical exfoliation of natural crystal. An obvious blue shift of PL peak is also noticed compared to monolayer WS₂ exfoliated on SiO₂/Si, which is probably due to the Coulomb screening difference, strain, and the less electrically perturbation for the monolayer WS₂ grown on hBN [150, 175, 182, 190]. Such remarkable sharpening and hardening of PL peak of the CVD grown monolayer WS₂ on hBN result from the significant improvement of sample's crystal and optical quality by suppressing the unintentional doping from the oxide substrate. This is a known and widely adapted advantage of using hBN as a substrate. It is also noticed that the monolayers prepared by this method are chemically robust. The good PL features maintained even after the samples being stored

in ambient for more than a year. The observation of such narrow intrinsic exciton emission peak promises more opportunities of further investigating WS₂ monolayer.

To further probe the intrinsic excitonic emission from the epitaxial WS₂ monolayer flakes on hBN, PL microscopy and mapping are conducted at cryogenic temperature. As comparison, light emission of WS₂ monolayer exfoliated from natural crystals is also measured. For the exfoliated sample, though the neutral exciton and charged trion emissions are able to be resolved, for example by careful curve fitting, the two emission features are heavily merged and together with a bunch of localized emissions (Fig. 5.6(a) top). In obvious contrast, the exciton and trion emissions of the CVD grown monolayer WS₂ on hBN are well separated and their linewidths are only ~7 meV and ~10 meV, respectively (Fig. 5.6(a) bottom). Figs. 5.6(b) and 5.6(c) show the PL mapping of the CVD grown monolayer WS₂ on hBN, extracted from the integrated intensity and energy of neutral exciton emission.

Figure 5.6 (a) PL spectrum of mechanically exfoliated WS_2 monolayer on SiO_2/Si substrate (top) and PL spectrum of CVD grown WS_2 monolayer on hBN (bottom). (b) PL mapping extracted from the integrated intensity of neutral exciton emission. (c) PL mapping extracted from the energy of the neutral exciton emission. The measurements were conducted at 4.2 K.

The intrinsic exciton, trion emission energies and the trion associate energy are 2.083 eV, 2.046 eV and 37 meV, respectively, which agree well with the reported theoretical and experimental values [33, 49, 191-193]. Usually, the exfoliated samples from a natural crystal are believed to be of high quality and uniformity. In fact, we notice that the nonuniformity of, such as the exciton emission energy, does exist in the exfoliated WS_2 monolayer on SiO_2/Si (Fig. 5.7).

Figure 5.7 (a, b) Optical and fluorescence images of mechanically exfoliated monolayer WS_2 on SiO_2/Si . (c) PL image extracted from the energy of exciton (X_0) emission. The nonuniformity is presented.

Taking the advantage of the well-resolved intrinsic excitonic emissions of our CVD grown WS_2 monolayer flakes on hBN, and to visualize such intrinsic emissions from different flakes, we perform the PL mapping in a selected area (Fig. 5.8) at cryogenic temperature. As the dimension of the flakes is beyond the resolution of our system, the individual triangular flakes are hardly resolved. The nonuniformity of both exciton emission strength and energy are observed in the scanning area.

Figure 5.8 Fluorescence image of the CVD grown atomically thin WS_2 flakes on hBN.

5.3.2 Valley Zeeman Splitting of CVD Grown WS_2 on hBN

Since the exciton and trion emissions from our CVD grown WS_2 monolayer flakes on hBN are well-resolved and intrinsic, we are able to probe physical phenomenon carried in such light emissions from the excitonic states. Here, our focus is to visualize

the magnetic field tuned valley splitting. Figure. 5.9 presents the PL images of the exciton (X_0) and trion (X_T) emission energies under selected magnetic fields. At zero field, though both the exciton and trion emissions exhibit different energies cross the mapping area, a good correspondence between the two PL images of the exciton (X_0) (Figs. 5.9(a1) and 5.9(b1)) and trion (X_T) (Figs. 5.9(a2) and 5.9(b2)) emission energies at K' and K valleys, indicating the degeneracy of the exciton and trion states. A remarkable contrast appears in both exciton and trion emission energy mappings under a high magnetic field, *i.e.* ± 8 T. In details, at magnetic field of $+8$ T, both the exciton and trion emission energies at K' valley are higher than those at K valley. Such contrast is totally opposite for the magnetic field of -8 T. The energy difference in the light emissions from the exciton and trion excitonic states at two valleys under a magnetic field evidences the breaking of valley degeneracy, alternatively the occurrence of valley Zeeman splitting, which is induced by the net magnetic moment of W orbital angular momentum in the valence band under an out-of-plane external magnetic field [68, 112, 116, 184].

Figure 5.9 (a1-f1) PL images of the exciton (X_0) emission energies under the magnetic fields of 0 T, +8 T and -8 T with σ^+ and σ^- polarizations. (a2-f2) PL images of the trion (X_T) emission energies under the magnetic fields of 0 T, +8 T and -8 T with σ^+ and σ^- polarizations. The measurements were conducted at 4.2 K.

Similar observation has been reported in MoSe_2 and WSe_2 , which show well-resolved and intrinsic PL peaks, through magnetic-field-dependent PL measurement [68, 112, 116, 184], but rarely in WS_2 nor MoS_2 due to the poor light emission features such as over broad and merged PL peaks. To deeply understand this magnetic field tuned evolution of excitonic states in two valleys, more importantly to visualize such valley splitting in many pieces of the as-grown WS_2 monolayer flakes on hBN, we carry out

in-situ magnetic-field-dependent PL mapping by swiping the magnetic field strength from +8 T to -8 T (Figs. 5.10 and 5.11).

Figure 5.10 PL images of exciton (X_0) and trion (X_T) emission energies of CVD grown WS_2 monolayer flakes on hBN from both K' and K valleys under positive magnetic fields.

Scale bar: 4 μm .

Figure 5.11 PL images of exciton (X_0) and trion (X_T) emission energies of CVD grown WS_2 monolayer flakes on hBN from both K' and K valleys under negative magnetic fields.

Scale bar: $4 \mu m$.

With the increase of the field strength positively, the exciton and trion emissions from K' valley are gradually increasing while the energies of the exciton and trion

emission from K valley decrease. The opposite trend is perceived under a negatively increasing field.

Though variety of light emission energies exists cross the scanning area, the evolution of valley splitting seems keeping consistent locally. To further exploit this hypothesis and reveal the intrinsic magnetic field dependency of valley Zeeman splitting in CVD grown WS_2 monolayers on hBN, we select three individual areas showing uniform light emission energies in the PL images to do the statistical analysis (Fig. 5.12) and extract the averaged PL spectra from the selected three individual regions as typical spectra.

Figure 5.12 Selected areas of different exciton (X_0) emission energies from K' valley at zero magnetic field.

The relative shifts of exciton and trion emission peaks under a strong magnetic field obviously display and represent the difference in energy gaps of corresponding excitonic

states at two valleys (Fig. 5.13(a)). The valley Zeeman splitting energy as a function of magnetic field strength fits into a perfect straight-line shape (Fig. 5.13(b)).

Figure 5.13 (a) Typical PL spectra (X_0 and X_T emissions after removing the background) of CVD grown monolayer WS₂ on hBN under different magnetic fields from the selected area 1 (see Fig. 5.12). (b) The measured valley Zeeman splitting as a function of the magnetic field for exciton (X_0) and trion (X_T). The measurements were conducted at 4.2 K.

The extracted slopes are -0.22 meV/T and -0.29 meV/T for exciton and trion, respectively. The intrinsic g-factors of the CVD grown WS₂ monolayer flakes on hBN are obtained to be 3.85 for exciton and 5.04 for trion, which agree well with the theoretical prediction and are very close to the experimental observation for WSe₂ and MoSe₂ [68, 112, 116, 184]. The slopes and g-factors of both exciton and trion for the other areas indeed consist with each other (Fig. 5.14).

Figure 5.14 The plots of valley Zeeman splitting energy as a function of magnetic field strength for the selected area 2 (a) and 3 (b) shown in Fig. 5.12.

5.3.3 Characterization of CVD Grown Monolayer MoS₂ on hBN

We extend our strategy to grow MoS₂ monolayers on hBN. MoS₂ monolayer is one of the most widely studied 2D TMDs. Unfortunately, the optical quality of CVD grown MoS₂ monolayers, even the exfoliated ones are not as good as that of MoSe₂ or WSe₂. A broad peak consisting of unresolvable exciton and trion is typically observed in the PL spectra of monolayer MoS₂ even at low temperature [188], which hinders study of intrinsic emission properties and new physics associated with such promising 2D system. It is obvious that the newly developed method works well for high yield growth of atomically thin MoS₂ flakes on hBN (Figs. 5.15(a) and 5.15(b)).

Figure 5.15 (a, b) Optical and SEM images of atomically thin MoS₂ flakes grown on hBN. (c) PL spectra of CVD grown MoS₂ monolayer flakes on hBN and exfoliated MoS₂ monolayer on SiO₂/Si. (d) PL image of the MoS₂ flakes on hBN by extracting the integrated intensity of the intensive peak at 1.88 eV. The frame in (b) shows the PL mapping area. The measurements were conducted at room temperature.

The triangular shape, epitaxial growth and monolayer products are clearly featured in the zoom-in SEM image, AFM image and Raman spectroscopy (Fig. 5.16) and the statistic size distribution histogram of as-grown MoS₂ can be found in Fig. 5.17.

Figure 5.16 (a) Zoom-in SEM image. (b) AFM image with the height profile. (c) Raman spectrum of CVD grown monolayer MoS₂ flakes on hBN. The height profile and separation between Raman E_{2g}¹ and A_{1g} mode confirm the monolayer nature of the as grown MoS₂ flakes.

Figure 5.17 (a) Selected SEM images of as-grown MoS₂ on hBN. (b) Statistic size distribution histogram of samples in (a).

5.3.4 Valley Zeeman Splitting of CVD Grown MoS₂ on hBN

Similar to WS₂, the excitonic light emissions from CVD grown monolayer MoS₂ flakes on hBN exhibit a blue shift. The narrowing of excitonic emission (as shown in Fig. 5.15(c)) implies the improvement of optical quality of the CVD grown MoS₂ monolayers on hBN. The PL image extracted from the integrated intensity of the dominant peak at 1.88 eV for the CVD grown MoS₂ flakes on hBN further demonstrates the high yield of this method (Fig. 5.15(d)).

Figure 5.18 (a) PL spectrum of mechanically exfoliated MoS₂ monolayer on SiO₂/Si substrate (top) and PL spectrum of CVD grown MoS₂ monolayer flakes on hBN (bottom). (b) PL images of the exciton (X_0) emission energies under different magnetic fields with σ^+ and σ^- polarizations. Scale bar: 5 μm . (c) Typical PL spectra (X_0) of monolayer MoS₂ under different magnetic fields with σ^+ and σ^- polarizations. (d) The measured valley Zeeman splitting as a function of the magnetic field for exciton (X_0). The measurements were conducted at 4.2 K.

Cooling a semiconductor to a cryogenic temperature is commonly used to suppress thermal fluctuation influence and uncover its natural properties. Here, we perform the in-situ low temperature (4.2 K) PL spectroscopy and imaging studies of the as-grown MoS₂ monolayer flakes on hBN. A dramatically sharp peak appears at 1.96 eV with a linewidth of 5.6 meV, which is much narrower than that of the exfoliated sample on SiO₂/Si (Fig. 5.18(a)). And to the best of our knowledge, it is the narrowest PL peak reported from CVD grown MoS₂ monolayers. Such sharp PL peak is believed to represent the intrinsic light emission from the neutral exciton of MoS₂ monolayers. The well-resolved and super narrow exciton emission peak presented in our CVD grown MoS₂ monolayer flakes on hBN offer great possibility of uncovering valley physics in such 2D direct-bandgap semiconductors, such as the valley splitting. By mapping up the selected area (Fig. 5.15(b)) at cryogenic temperature and extracting the exciton emission energies from both K' and K valley at different magnetic fields (Fig. 5.18(b) and Fig. 5.19), we clearly demonstrate the degeneracy of the excitonic states between two valleys at zero field and the lifting of such degeneracy under a strong magnetic field in CVD grown monolayer MoS₂ flakes on hBN. Such magnetic field induced valley splitting is also reflected by the shifts of the exciton emission peaks shown in Fig. 5.18(c). The valley Zeeman splitting energy of the neutral exciton as a function of magnetic field strength is shown in Fig. 5.18(d). The extracted slope is -0.079 meV/T. The g-factor of the CVD grown MoS₂ monolayer flakes on hBN is determined to be 1.36, which is

smaller than that of WS₂ and Se-based 2D TMDs [68, 112, 116, 184] and might be due to the intrinsic properties of MoS₂ [174]. Further studies are ongoing.

Figure 5.19 PL images of exciton (X_0) emission energies of CVD grown MoS₂ monolayer flakes on hBN from both K' and K valleys under positive and negative magnetic fields. Scale bar: 10 μm .

5.4 Conclusions

In summary, a method of directly growing WS₂ and MoS₂ monolayer flakes on hBN with a high yield has been successfully developed. High optical quality of the as-grown monolayer flakes is obtained. With further optimized recipe based on this growth method, not only high optical quality and high yield, but also large-size monolayer MS₂ (M=Mo, W) can be obtained, which is beneficial for future electronic or valleytronic applications without additional sample transfer process. The intrinsic exciton and trion emissions have been studied by probing the well-resolved and sharp PL peaks. The magnetic-field-dependent PL mapping visualizes the valley Zeeman splitting in WS₂ and MoS₂ monolayer flakes grown on hBN. The intrinsic g-factors of these two promising 2D semiconductors are determined. This work paves a new way to produce WS₂ and MoS₂ monolayers of high optical quality and further exploit new physics and applications of such interesting 2D systems.

Chapter 6 Conclusions and Prospects

6.1 Conclusions

In this thesis, valley Zeeman splitting of monolayer group-VI TMDs under different circumstances have been studied by magneto-PL spectroscopy. Essentially, this thesis consists of three parts. In the first part, spatial variations of valley Zeeman splitting in exfoliated monolayer WSe₂ has been studied *via* circularly polarized magneto-PL spectroscopy. In the second part, we have transferred the exfoliated monolayer WSe₂ onto EuS substrate, and the substrate influence on the valley Zeeman splitting has been studied by comparing the results with that on bare SiO₂/Si substrate. In the last part, we have synthesized the atomically thin WS₂ and MoS₂ on hBN substrate *via* improved chemical vapor deposition method, and the intrinsic valley Zeeman splitting of WS₂ and MoS₂ has been studied *via* circularly polarized magneto-PL spectroscopy.

Part I: spatial variations of valley splitting in monolayer WSe₂

Monolayer WSe₂ on SiO₂/Si was prepared by mechanical exfoliation method. The nonuniformity of the exfoliated WSe₂ has been visualized by PL mapping at zero field and this nonuniformity is probably due to the unintentional doping by the moisture. Center and edge regions have been selected to study spatial variations of valley splitting. The major difference between the two regions are the unintentional doping levels. The valley Zeeman splitting behavior of exciton emission stay unchanged with the increasing doping level. In the range of relatively higher doping region, the valley

splitting behavior of trion emission changes from the linear dependence on the external magnetic field to the sub-linear dependence. While in the range of lower doping region, the valley splitting behavior of trion emission maintains a linear relationship with the external magnetic field and the slope of the magnetic response decreases with the increasing doping level. The varying valley Zeeman splitting of trion emission is probably due to the changing of many-body interaction strength under different doping levels.

Part II: enlarged valley Zeeman splitting of monolayer WSe₂ on EuS

Monolayer WSe₂ was prepared by exfoliation method and transferred to EuS by using all-dry transfer method. The valley Zeeman splitting of exciton and trion emissions of monolayer WSe₂ on EuS has been studied by circularly polarized magneto-PL measurements. SiO₂/Si substrate has been selected to conduct a controlled experiment. For the WSe₂ on EuS substrate, the valley splitting energies of both exciton and trion emissions have been enhanced due to the magnetic exchange field, which originates from the proximity effect.

Part III: intrinsic valley Zeeman splitting of monolayer WS₂ and MoS₂ on hBN

Monolayer WS₂ and MoS₂ flakes on hBN have been successfully synthesized *via* improved chemical vapor deposition method. Metal oxide (WO_x and MoO_x) thin films of 1 nm in thick were deposited onto the pre-exfoliated hBN flakes instead of placing the metal oxide powder in the furnace. High optical quality of our as-grown samples has been confirmed by observing the well-resolved intrinsic emissions. The intrinsic valley

Zeeman splitting of monolayer WS₂ and MoS₂ on hBN has been studied by circularly polarized magneto-PL measurements. For the monolayer WS₂ samples, the intrinsic valley Zeeman splitting behavior agrees well the theoretical calculations. While for the monolayer MoS₂ samples, the magnetic response of valley Zeeman splitting is much smaller than the theoretical calculations and further studies are needed.

6.2 Prospects

(1) hBN/WSe₂/hBN sandwich structures

As discussed in chapter 3, the unintentional doping in monolayer exfoliated WSe₂ is probably due to the moisture in atmosphere. To verify the hypothesis, the exfoliated WSe₂ should be completely isolated from the moisture. It is known that hBN has a layered structure similar to TMDs. The small lattice mismatch between hBN and TMDs makes hBN an ideal substrate for improving the optical quality of the TMDs. Previous reports have confirmed that hBN substrate can not only suppress the unintentional doping from the oxide substrate, but also provides a less perturbed electrical environment [182]. Actually, Viti *et al.* used the similar sandwich structure to protect black phosphorus from degradation [194]. By building the hBN/WSe₂/hBN heterostructure, spatial variations of valley Zeeman splitting can be further studied by eliminating the influence of moisture.

(2) Strain influence on the valley Zeeman splitting

The strain influence on the valley Zeeman splitting is rarely studied since it is hard to apply tensile or compressive strain at a cryogenic stage. Conventionally, one can transfer the target sample on a flexible polyethylene terephthalate (PET) substrate, then the tensile strain can be easily applied by stretching the PET substrate in atmosphere [141]. However, it is not suitable for a low temperature and vacuum environment. In order to apply tensile strain to our WSe₂ at a cryogenic temperature, a nonluminous substrate with a negative coefficient of thermal expansion is needed. Graphene is a good candidate with a negative coefficient of thermal expansion and can be easily obtained by mechanical exfoliation method [195]. The exfoliated WSe₂ can be transferred precisely onto graphene by all-dry transfer method. When cooling the WSe₂ and graphene together, the WSe₂ will shrink, while the graphene will expand. Thus, the tensile strain can be applied on the WSe₂ sample and the WSe₂ lattice will be distorted under the tensile strain which will further influence the electronic structure of WSe₂, it is likely that the strain will influence the valley Zeeman splitting behavior.

(3) Zeeman splitting in bilayer WSe₂

Monolayer group-VI TMDs possesses valley degree of freedom. The strong spin-orbit coupling as a result of inversion symmetry breaking makes the chirality locked to identical valleys. In the presence of an out-of-plane magnetic field, the degeneracy can be lifted. For bilayer 2H-stacking TMDs, the inversion symmetry is restored. Thus, the valley Zeeman splitting literally should no longer exist. However, Jiang *et al* have reported that Zeeman splitting still persists in 2H-MoTe₂ bilayer, which is a result of

spin-valley-layer coupling [196]. It is interesting to study the Zeeman splitting in bilayer WSe_2 . Moreover, by using all-dry transfer method, the twisted angle between the two monolayer WSe_2 can be controlled. Whether the twisted angle influences the Zeeman splitting in bilayer system needs further studies.

References

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