Alloy engineering of two-dimensional transition metal dichalcogenides

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**NANYANG
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UNIVERSITY**

SINGAPORE

**ALLOY ENGINEERING OF
TWO-DIMENSIONAL TRANSITION METAL
DICALCOGENIDES**

LIU SHENG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

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TWO-DIMENSIONAL TRANSITION METAL
DICHALCOGENIDES**

LIU SHENG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2019

Statement of Originality

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This thesis **does not** contain any materials from papers published in peer-reviewed journals or from papers accepted at conferences in which I am listed as an author.

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A handwritten signature in black ink, appearing to be '刘盛' (Liu Sheng) in Chinese characters, written in a cursive style.

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Date

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Liu Sheng

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Abstract

The two-dimensional (2D) transition metal dicalcogenides (TMDs) have taken over the tremendous research attention from graphene in the last decade. The MX_2 (M=Mo and W; X=S, Se and Te) honeycomb lattice down to monolayer limit has direct band gap and large excitonic effect due to the out-of-plane quantum confinement. The robust excitonic levels with binding energy up to ~ 200 meV make TMDs become increasingly important for a variety of applications including photo-detectors, high-power transistors and other optoelectronics. The translation momentum, spin angular momentum and orbital angular momentum together in this 2D system are linked by spin-valley coupling, which gives rise to valleytronics and valley-related physics.

To fulfill the potential of valleytronics applications, stable valley polarization via intravalley recombination of the excitons need to be revealed. Prominent valley polarization in TMDs exists only at liquid nitrogen temperature regime. For years researchers have been trying to solve the depolarization mechanism and to make the valley polarization last to higher temperatures, or even room temperature. However, there is still no convincing conclusions. Previous works report various valley behaviors case-by-case. For example, most high temperature valley effects are observed in WX_2 , while MoSe_2 seems to have no valley response even down to liquid helium temperature.

Here in this thesis, by making ternary alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$, the intra- and inter-valley dynamics of the excitons can be studied systematically, in the same lattice system with modulated energy band structure. From studying this exciton dynamics, we hope to uncover the mechanism of intervalley depolarization and the strategy to enhance the valley effects. Firstly, we studied the band gap and spin-orbit engineering among the alloyed monolayers based on temperature dependent reflectance and photoluminescence spectroscopy. By fitting the exciton peak with temperature, all the parameters related to the excitons including line

width, energy position and phonon coupling with the lattice can be obtained for all the alloys. The Raman spectroscopy of the alloys were also studied to obtain information about their lattice symmetry and phonon energies. Secondly, the exciton fine-structures with one bright and one dark states were probed by monitoring the temperature-dependence of the exciton PL intensity, combining with the time-resolved photoluminescence spectroscopy which can qualitatively measure the radiative lifetimes. Lastly, the inter-valley depolarization has been evaluated based on the modulated bright-dark split energy Δ_{BD} among the alloys.

At last, we also explored the heteroatomic doping of MoSe₂ crystal with magnetic dopant manganese. High quality Mo-doped single crystal is grown by chemical vapor transport reaction (CVT) method, and monolayer to fewlayer samples can be exfoliated. We then carefully studied the optical and electronic properties, interlayer and intralayer phonon modes of the samples by PL and Raman spectroscopy. The first-principles calculation were used to calculate the localized magnetic ordering of the Mn-doped crystal.

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1 Background and Motivation

Ever since the first field effect transistor (FET) device was invented in Bell Laboratory[1], semiconductors have entered human life to such a degree that a “silicon age” has been fully established. Semiconductor bulk crystals like Si single crystal can be conveniently cut into thin wafers, making the large-scale integrated circuit (IC) the most powerful tool of human civilization in the last half of the 20th century. Without the intensive research and studies on semiconductors since 1940s, all of the modern digital and information technologies would not have existed.

The fundamental discoveries in physics and materials sciences are always the most important driving force towards technology. On the other hand, technology-driven growth often encounter inevitable bottlenecks which demand further profound critical thinking in addressing fundamental scientific questions. As the IC technology has already advanced from 100 to 6 nm, nearly reaching the extreme to trigger quantum tunneling[2], it is expected that the Moore’s law will end soon[3, 4]. What is the next plan for our human beings? One of the solution emerges naturally at the time when the first two-dimensional (2D) material graphene arises[5, 6].

The atomically thin thickness can certainly reduce the scale of devices due to its angstrom level thickness. Although graphene is metallic, its insulator and semiconductor counterparts hexagonal boron nitride (Hex-BN) and transition metal dichalcogenide (TMD) (see Fig. 1-1) soon follow up and come to the

Figure 1.1: Versatile two-dimensional building blocks. Graphene, H-BN (hexagonal crystalline boron nitride) and MoS_2 (on behalf of transition metal dichalcogenides) represents the various metallic, insulating and semi-conducting 2D materials.

spotlight[7, 8]. Using those 2D materials, unprecedented miniaturization of functional devices has been achieved[9–12].

However, due to the limited synthesis methods in those atomically thin films, the road to application is still full of challenges as large-scale synthesis technologies of these 2D materials are still unavailable. Fortunately, a lot of interesting physical properties, besides its size advantage, have been revealed by researchers. Actually, what makes the 2D semiconductor extremely promising is not merely its atomically thin size, but relies on the fascinating physics regarding the special carrier behaviors and novel light-matter interactions. Some important traits of 2D semiconductors will be discussed in the following sections to illustrate the motivation and research direction for this work.

1.1 The Dimensional Effects of Two-dimensional Semiconductors

Modern technology provides all kinds of nano-fabrication and operation, making it possible to tailor the dimensions of semiconductor materials. Different dimensions directly lead to diverse electron behaviors, which are closely associ-

ated with the optical and electrical properties of the material. A free electron in infinite space has energy dispersion: $E = \frac{\hbar^2 k^2}{2m}$, which can be any value as the dispersion is continuous. If the movement of an electron is spatially confined in certain directions, its energy dispersion in momentum space (k -space) will be largely changed. Imagine free electrons are filled into a cubic box with a certain volume of $\Omega = L_x \times L_y \times L_z$, with the periodic boundary conditions. The energy dispersion of the electrons can be written as:

$$E(k_x, k_y, K_z) = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 K^2}{2m}, \quad (1.1)$$

where m is the mass of electron and $K_x = \frac{2\pi l}{L_x}$, $K_y = \frac{2\pi m}{L_y}$, $K_z = \frac{2\pi n}{L_z}$ with

Figure 1.2: Density of states of electron in different boundary conditions.(a) is 3D; (b) is 2D; (c) is 1D; (d) is 0D conditions.[13]

$l, m, n=0, \pm 1, \pm 2$, when the sizes of all directions are finitely large (3D case), the energy dispersion will be the same as free electron. The density of states (DOS) has the relationship: $n_{3D}(E) = \frac{m}{\pi^2 \hbar^3} \sqrt{2mE}$, as shown in Fig. 1.2(a). What makes differences is that, in the cases of 2D, 1D and 0D, some or all of the directions become finite and comparable to the de Broglie wavelength of electrons, strong confinement in certain directions will change the behaviors of electrons dramatically. In 2D, the DOS will be irrelevant to energy and divided into plateaus (Fig. 1.2(b)). In 1D, the DOS shows a $1/\sqrt{E}$ dependence, displaying

multiple von Hove singularities (Fig. 1.2(c)). When dimension comes to 0D, all the energy states becomes atomic like sharp lines, as shown Fig. 1.2(d).

Among those dimensions, 2D materials are ideal platforms for research on the condensed matter physics due to the combination of prominent (out-of-plane) quantum confinement and scalable (in-plane) space left for novel electron behaviors, such as fractional quantum-Hall and spin quantum-hall effects[14, 15]. More novel physics are expected to emerge from these ever growing two-dimensional family.

1.2 Excitons in Semiconductors

When a semiconductor absorbs photons with energy larger than its band gap, electrons will be excited to conduction band, leaving an equivalent positive charged sites, the “hole”, behind. In early days’ studies, this excitation of electrons was regarded as pure effects of electron which should have no relation to the left-behind hole, hence the minimum energy to excite the electrons in semiconductor should be exactly the energy of the electronic band gap: $E_g^{opt} = E_g^{elec} = E_{CBM} - E_{VBM}$. However, in the following years, more and more experimental results show absorption peaks with energy non-negligibly smaller than the electronic band gap: $E_g^{opt} < E_g^{elec}$ [16–18]. Those observations stimulated researchers to consider the configuration that the coulomb interaction will bound the electron and hole into a pair, which can be regarded as a new quasi-particle named exciton, therefore lowering the total energy[19], as shown in Fig. 1.3. As an imaginary particle, excitons energy levels are trapped states by coulomb interactions between electrons in conduction band minimum (CBM) and holes in valence band maximum (VBM). Therefore, the energy to excite an electron decreases from E_g^{elec} to the energy difference between the trapped states with the VBM. Then the value of this energy decrease (energy difference between CBM and the trapped states) can

Figure 1.3: The photo-induced excitation model in semiconductor. (a) is without considering electron-hole (exciton) effect; (b) is with considering electron-hole (exciton) effect.

be defined as the binding energy of excitons: E_b . Generally, there are two kinds of excitons in bulk semiconductors, Mott-Wannier excitons with lower binding energy and Frenkel excitons with larger binding energy[20]. The distance between electron and hole in Mott-Wannier excitons is usually much larger than lattice parameters, with binding energy around 1~10 meV, while the Frenkel excitons have much smaller electron-hole distance (on the order of lattice parameter) and larger binding energy. For weakly-bounded excitons, hydrogen like models with discrete energy levels can well describe their binding energy and behaviors :

$$E_b = \frac{(q^2/4\pi\epsilon\epsilon_0)^2}{2(\hbar^2/\mu^*)n^2}, \quad (1.2)$$

where μ^* is the reduced mass of the electron-hole pair: $1/\mu^* = 1/m_e^* + 1/m_h^*$, and n is a positive integer, thus the excitons presents Rydberg levels[21, 22], as shown in Fig. 1.4. From the equation, we can see that binding force between electron and hole decreases when the system has a smaller carrier effective mass and larger dielectric constant. The dispersion of the excitons can be expressed as:

$$E = \frac{\hbar^2 k^2}{2m_e^* + 2m_h^*} + E_b, \quad (1.3)$$

when the semiconductor absorb a photon to generate a exciton, both conservation

Figure 1.4: The energy levels of excitons. $n=1$, 2 and 3 represent the first, second and third exciton levels.

of energy and momentum must be satisfied. So $k = 0$ should always be applicable, so the total energy of exciton $E = E_b$, thus the minimum energy of the photons which can generate excitons is:

$$\hbar\omega = E_g - E_b, \quad (1.4)$$

because of the transition efficiency will be greatly enhanced when the electron and hole have the same momentum, excitonic absorption and emission are usually much stronger in direct band gap semiconductors such as III-V and II-VI semiconductors [23, 24].

1.3 Excitons in Two-dimensional Transition

Metal Dichalcogenides

When the periodical lattice is transferred from 3D to 2D, the exciton behavior will change dramatically as the background environment including quantum- and dielectric-confinement changes[22]. The most prominent change of the excitons

in 2D materials is that their binding energy will increase by 4 to 10 times, into the level of $0.1\sim 1$ eV. However, for the atomically thin materials, their dielectric screening effect is greatly reduced because the electric field lines joining the electron and hole begin to extend outside of the sample, as shown in Fig. 1.5(a). Therefore, the effective dielectric constant is reduced. Consider the relation (1.2), the binding energy will be dramatically increased. Large exciton binding energy is observed in the TMD family from ~ 0.2 to ~ 0.4 eV[25, 26], making them a great platform for studying exciton behaviors in pure two-dimensional systems.

Figure 1.5: The illustration of the quantum- and dielectric-confinement induced by dielectric screening in 2D materials. (a) is schematics of the confinement of charge carriers and the reduced dielectric screening due to the absence of adjacent layers in 2D materials, comparing to the exciton in 3D bulk materials. (b) is the consequent decrease of optical band gap from electronic band gap due to the large exciton binding energy.[22]

Moreover, the band structure evolution of TMDs (MoS_2 , MoSe_2 , WS_2 and WSe_2) are found to have stark transition from indirect to direct band gap[7, 8], when the layer number is decreased down to monolayer, leading to a strong direct-band gap like excitonic absorption and emission, as shown in Fig. 1.6. This effect remains prominent even at room temperature, due to the large binding energies of these robust excitons which exhibit pico-second long exciton lifetime.

These properties thus triggered tremendous interests in studying the excitons of monolayer TMDs.

Figure 1.6: Band structure transition of TMDs from indirect to direct band gap when the layer is down to monolayer.[7, 8]

1.4 Berry Phase and Valley Physics of Excitons in TMDs

The 2D hexagonal lattice and the absence of inversion symmetry brings more fantastic properties and behaviors to the excitons in TMD monolayers. Among them, the most interesting ones are the valley-related physics and the subsequent valleytronics applications, which are fundamentally related to the Berry phase of the lattice[27, 28]. The Berry phase describes a classical or quantum system whose geometric phase is equal to a phase difference acquired over the course of a cycle, when the system is subjected to cyclic adiabatic processes[29].

By applying Berry-phase to the TMD crystal lattice, the valley physics can be clearly explained. The Bloch Hamiltonian is dependent on the reciprocal lattice vector k . When k experiences a whole circle in the Brillouin zone, the Bloch Hamiltonian will also experience the circle, and thus gain a Berry-phase. If doing path integral to the whole circle, the Berry curvature can be obtained:

$$\Omega_n(k) = i \left\langle \frac{\partial}{\partial k} u_{n,k} \right| \times \left| \frac{\partial}{\partial k} u_{n,k} \right\rangle, \quad (1.5)$$

which is strongly associated with the symmetry of the system. If the system possesses both time and space inversion symmetry, then the Berry curvature will be zero. If the spatial inversion symmetry is absent, each circle will make Berry curvature change sign. So, in solid matter, Ω here act as a quasi-magnetic field, which is protected by time reversal symmetry, but will change sign when there is broken space inversion symmetry[30].

TMD possesses hexagonal lattice with broken inversion symmetry (in its monolayer counterpart or bulk of its 3R polytype), thus the K and K' points (valleys) at Brillouin zone corners will have reciprocal lattice vector k with opposite signs. This will lead to the opposite signs of Berry curvature as well. Thus the electrons at the two valleys will experience effective magnetic field pointing up and down, respectively. This Berry-phase induced quasi-magnetic field will lock the spin of carriers to the valley, leading to valley selection rule of the carriers responding to circular polarized light excitation, as shown in Fig. 1.7. The valley selection rules can create a lot of novel and important physical effects, including valley polarization dichroism, valley Hall, spin valley Hall effects[31–34]. It is noteworthy that the valence bands of the TMD monolayers have large split around ~ 0.2 meV for Mo and ~ 0.4 meV for W families, due to the strong spin-orbit coupling induced by the heavy mass group VI transition metal atoms. This split of valence band can create two excitonic levels (A and B as shown in Fig. 1.7(b)) which will be occupied by carriers with opposite spins, making the configuration of excitons' spin states identical in each valley (K and K'). In other words, the spin and valley are inter-locked, so the valley physics have been added degree of freedom of spins.

The TMD in 3R stacking has broken inversion symmetry at any layer number, which will always satisfy the valley selection rule. For the 2H-stacking TMD, theoretically even layer number will have inversion symmetry and thus invalidate the valley selection rule. However, multiple research groups have reported valley

(circular) polarization or even valley coherence in bilayer TMDs [35–38]. The possible reasons to observe circular polarization in centrosymmetric TMD system is to be expected on the basis of pure spin-orbit physics, which is beyond the scope of this dissertation. Herein, the discussions will be emphasized to monolayer which has no inversion symmetry and will be a clear system to study exciton (valley) dynamics.

Figure 1.7: This Berry-phase induced valley selection rule and lockin of spin and valley degree of freedoms. (a) is valley hall effect; (b) is valley polarization; (c) linear excitation induced valley and spin hall effect; (d) circular excitation induced valley and hall effect.[31, 32]

The valley physics is so rich that any of the above effect will possibly change the whole picture of modern electronics, leading to new electronic devices and computation theories. However, the two valley of the TMDs are somehow connected in many inter-valley scattering channels, making it only observable at low temperature[33, 34], as shown in Fig. 1.8.

It can be noticed from the recent literature that the different TMDs also have distinct valley polarization strength, and the onset of those polarizations can oc-

Figure 1.8: Temperature dependence of valley effects. (a) indicates valley polarization of MoS₂ at low temperature; (b) indicates the temperature dependent valley polarization of MoS₂[33, 34]

cur at different temperatures. In some cases like WS₂, researchers even reported room temperature valley polarization and coherence[39, 40]. Following this trend, the differences of band structures, spin-orbit coupling, valley dynamics (recombination rates of valley-related excitons) among the material family could all be the reasons for the distinct valley exction behaviors. Therefore, alloys among the MX₂ (M=Mo, W; X=S, Se, and Te) can be designed and built to study the above changes. The knowledge learned from the alloy engineering will help to understand more about the unique excitonic and valley physics in the two-dimensional systems, towards fabricating functional valleytronic devices. Moreover, elements other than the above ones which have different valence electrons can also be doped to the system to endow new properties such as magnetism to the TMD family.

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2 Growth and Characterization of TMD alloys

In Chapter one, some novel exciton behaviors in two-dimensional transition metal dichalcogenides and the valley-related physics of the excitons have been introduced. Based on the idea focusing on using alloy engineering to modify the band structures, spin-orbit coupling, and valley dynamics (recombination rates of valley-related excitons), and endow the TMD with additional physical properties like magnetism besides its semiconductor nature, high quality alloy TMD monolayers need to be synthesized.

Figure 2.1: Simulation of formation enthalpy (ΔH) per anion of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ and $\text{WS}_{2(1-x)}\text{Se}_{2x}$ synthesized from MoS_2 and MoSe_2 or WS_2 and WSe_2 . [1].

Firstly, for elements in the format MX_2 ($\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{S}, \text{Se}, \text{and Te}$) which have equal valence electrons, the formation enthalpy of such alloy TMD are around zero or even negative in some cases, according to some recent simulations [1,

2], as shown in Fig. 2.1. The formation enthalpy ΔH can be decomposed as: $\Delta H = \Delta H_{VD} + \Delta H_{CEX} + \Delta H_{SR}$. While ΔH_{VD} stands for compression or expansion of the equilibrium lattice constant and the bond length of the constituents to the corresponding concentration averaged values; ΔH_{CEX} is charge exchange when mixing two types of anions; and ΔH_{SR} is from fully relax the alloy supercell using quantum mechanical forces. As mismatch is big in doping, $\Delta H_{VD} + \Delta H_{SR}$ is positive. In the alloying process of most semiconductor, charge exchange also needs to jump over potential barrier because of electron orbits repulsion, So ΔH_{CEX} is also positive. Here the charge exchange between S and Se is easy that ΔH_{CEX} can be negative and so can the whole formation enthalpy. However, for cation doping of TMD, the process is more difficult since different metal sources normally have quite distinct sublimation temperatures, and so are the products deposition temperatures.

Previously, monolayers of those TMD ternary alloys were directly synthesized using chemical vapor deposition (CVD) methods[3–6]. The as-grown alloy monolayers can possess full chemical compositions and tunable band gap between the two components, by measuring preliminarily their photoluminescence and Raman spectra at room temperature. These pioneering research has proved the stable existence of the monolayers of the ternary alloys of group VIB dichalcogenides. However, in a typical CVD synthesis of atomically thin crystal on substrates, the heterogeneous nucleation and the growth process are highly kinetically driven. This rapid process will lead to plenty of defects including vacancies, dislocations, thermal strains and small angle grain boundaries to the monolayer crystal[7–10]. For ternary alloy monolayers, the population of defects can be further increased due to the more complicated reactions containing more participant chemical compounds. Those defects will affect the features at electronic band edge and act as scattering or trapping centers. Consequently it will change the exciton recombinations and propagations, and disturb both the intra- and inter-valley dynamics,

which is certainly against the goal in this thesis work aiming at modifying the band structure, spin-orbit coupling and valley dynamics by alloy engineering. In other words, this research need high quality single crystals of alloy TMDs, which should be grown in equilibrium conditions and avoid most of the defects effects. It is noteworthy that in some case (e.g. WSe₂), point defects can be regarded as quantum dots localized in the 2D structure and band structure, behaving as perfect single photon emissions[10], however, it is not relevant in this work.

2.1 Synthesis of the Alloy Samples

To grow high quality single crystals of TMD, we used chemical vapor transport (CVT) reactions in sealed quartz ampoules. The term CVT describes a classification of various reactions transfer the solid phase to gas phases with the assistance of a gaseous reactant (the transport agent), and deposits in the form of crystals. It is a classical method widely used to grow compound semiconductor crystals[11–14]. CVT growth was developed from artificially simulating the reactions happened in the mantle of earth. During the natural history of earth, those reactions created stones and minerals, in particular at high temperatures, sometimes even at high pressure. The natural CVT reactions take thousands to millions of years to create mineral resources for human beings, until the scientists studied the process and found the secret recipes.

Bunsen firstly observed that the formation of crystalline iron(III)-oxide is associated with the presence of volcanic gases that contain gaseous hydrogen chloride. Today, we know that the volatilization and separation of Fe₂O₃ is based on the equilibrium reaction 2.1:

with the assistance of HCl, Fe₂O₃ is transformed into the gas phase carrying

Fe sources. This process is called dissolution, and the HCl which enhances the volatilization is called transport agent. At this point, the gaseous metal sources can participate in the reactions with other anions to form the crystal. For example, if we seal the resources in equation (2.1) with sulfur as well, the reactions can be re-written into:

as shown by (2.2), the cubic phase crystal FeS_2 which is widely used in photocatalysis can be successfully synthesized. The trick here is that the reaction needs a proper temperature gradient to maintain in the right direction, usually generated by a two- or multiple-zone tube furnace. If the reaction is exothermic, one end of the sealed quartz tube of which the crystal nucleation and growth will take place should be put to lower temperature; if endothermic, then the tube should be placed in the other way around.

TMD layered crystal can be found in natural mineral resources as molybdenite, which is synthesized by natural CVT reactions. Since the rise of two-dimensional materials, high quality single crystals of TMD have been grown using CVT reactions inside sealed quartz tubes, as the typical temperature gradient to maintain the formation of MX_2 is around 1000 to 900 °C. Previously when the TMD crystals are grown, the sources are usually metal powder, chalcogen powder and the commonly used transport agent is iodine [15–17]. If we take MoS_2 as an example, the reaction equation can be written as:

the formation of TMD crystals are exothermic thus the product end should be set to lower temperature end during the week-long growth period. The growth of TMD was so successful now that commercial products of high-quality crystals are available. However, in the above reaction configuration, if ternary crystals are being synthesized, the mixture of powders of metal (for cation alloy) or mixture of chalcogens (for anion alloy) should be placed in the source end of the tube. And the syntheses normally take a few weeks of heating in a reversed temperature gradient (put source end to lower T but product end to higher T), to make the pre-reactions (2.3) get confined in the source end of the tube, generating gaseous metal sources and the small alloyed molecules for the later transport to product end. During the pre-reaction period, the complicated inter-reactions between different metal or chalcogen atoms into molecules will increase the disorder degree or the system, leading to low yield of crystals with inhomogeneous phases including large-scale clusters of one compound inside the crystal structure.

Figure 2.2: Schematic of nucleation and growth of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ by chemical vapor transport reactions in the sealed quartz tube. (a) illustrates the load of the tube and the temperature gradient; (b) indicates the directly re-arrangement of the MoS_2 and MoSe_2 molecules into $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ single crystal.

In this work, in order to avoid inhomogeneity of the as-grown crystal and increase the crystal yield (as exfoliation to monolayers consume quantities of crystals), a modified CVT reaction in which superfine MoS_2 and MoSe_2 powders

Figure 2.3: P-T phase diagrams of CVT reactions of MnIn_2Se_4 . (a) is the result of using Cl_2 as agent; (b) is the result of using AlCl_3 as agent[18].

with less than $2 \mu\text{m}$ diameter (purchased from Sigma-Aldrich) are used directly as reaction sources along with the iodine transport agent, as shown in Fig. 2.2.

The reaction equation is shown as following:

in this configuration of chemical vapor reaction, there are always certain concentration of (SSe) molecules in the gaseous circulation inside the sealed quartz tube,

leading to homogeneous distribution of S and Se atoms, free of clusters. There is no need to keep the long-term temperature inverse, since there is no mixture of elementary substances which need to form molecules. Therefore, high quality of anion alloy of MoS_2 and MoSe_2 with different concentration of Se anions can be obtained.

Alloyed MoSe_2 which contains manganese, a dopant with unequal valence electrons, has been synthesized to study the additional properties and functions by doping to TMD. As there is strong repulsion of charge exchange between $3d$ -orbitals of Mn and $4d$ -orbitals of Mo, deposition and growth of the doped crystal needs some kinetic drive to overcome the thermodynamics potential barrier[19]. In order to optimize the synthesis, the temperature gradient, the partial pressure of the gaseous phases and the sources need to be adjusted. From previous references, we find that different transport agent can tune the partial pressure of the gaseous phases dramatically. Fig. 2.3 shows the different P-T phase diagram when Cl_2 and AlCl_3 are used as agent to transport MnIn_2Se_4 , respectively[18]. When Cl_2 acts as agent, the partial pressures of the gaseous components are much higher, leading to multiple phases in products easily. If AlCl_3 is used as agent, firstly, the partial pressure is lower. Secondly the partial pressure of gaseous phases containing of Mn decreases monotonously with decreasing temperature. It will provide a relatively strong kinetic drive to deposit Mn-based matter. In this way, the Mn-doped MoSe_2 crystal were successfully synthesized. The details of the Mn-doped part will be presented in Chapter 6 of this thesis.

2.2 Characterization of the Crystals

The as-grown $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ single crystals are layered crystal which can be easily exfoliated using scotch tapes. To obtain the S to Se ratio, X-Ray Photoelectron Spectroscopy (XPS) was measured on the surface of the single crystals.

Fig. 2.4 shows a typical XPS spectrum of one of the alloy crystals.

Figure 2.4: XPS spectra measured on a as-grown $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ single crystal.

By fitting the XPS peaks, the 3p3/2 and 3p1/2 peaks of Se and 2p3/2 and 2p1/2 peaks of S can be identified. Through comparing the peak intensities, the concentration of Se and S inside the crystal can be evaluated. The crystal measured in Fig. 2.4 consists of 53.3% S and 46.7% Se, in which the Se to S ratio are roughly around 1:1, thus the crystal chemical expression can be written as MoSSe.

To further check the crystal quality of the as-grown monolayer, the above MoSSe crystal was exfoliated to monolayer and transferred to copper grid with lacey carbon film for scanning transmission electron microscopy (STEM) measurement. The STEM high-angle annular dark-field (HAADF) image of a typical MoSSe monolayer is shown in Fig. 2.5. The HAADF image has a Z^2 (where Z is the atomic number) contrast of among each atom column. If the Z of one atom is bigger, the contrast of the image pixels at this atom site should be stronger and brighter. For the monolayer TMD alloy MoSSe, each Mo column has only one Mo atom, so the contrast of all Mo atoms should be the same. The columns

Figure 2.5: STEM image of a MoSSe monolayer. The insert shows the Z^2 contrast spectrum of the atom columns inside corresponding to the red box. The Z^2 contrast intensity decreases from Se-Se, Se-S, Mo to S-S atom columns.

of anions have three configurations: S-S, Se-Se and S-Se, which will display with distinct contrast, as shown in the simulation in Fig. 2.6.

Using the simulated intensity mapping, the distribution of S-S, Se-Se and S-Se columns can be tracked in the HAADF image of the MoSSe monolayer. From the image, generally both brighter and darker points related to Se-Se and S-S can be observed almost everywhere, and no large MoSe_2 or MoS_2 domains can be seen. These observations indicate that there are no inhomogeneous aggregations or clusters in the MoSSe monolayer (or the as-grown single crystal). The S and Se anions are evenly distributed in the crystal lattice, making the alloy a uniform material with its own intrinsic physical and chemical properties.

For the optical spectroscopy study of the two-dimensional $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ layers, different alloy crystals with x tuning from 0 to 1 are exfoliated using scotch tape, and transferred to Si substrate with a 280 nm thickness SiO_2 dielectric buffer layer. The typical optical micrographs of the samples are shown in Fig. 2.7. Fig. 2.7(a) and (b) show the sample bright field morphology under white light illustration, using a $100\times$ objective lens. The substrate presents purple color

Figure 2.6: The Z^2 -contrast map STEM simulation of MoS_2 , MoSSe and MoSe_2 monolayers, and the contrast is qualitative.

because of the interference induced by SiO_2 film and the Si-SiO_2 interface, and the contrast of the color can be slightly adjusted by the 2D layers according to dielectric constant and thickness change, which can be used to distinguish the layer number preliminarily[20–22]. Similar contrast can be seen from both MoS_2 and MoSSe layers. The contrast closest to the substrate purple color is the monolayer, while the bilayer is slightly different from monolayer. The optical contrast here is defined as the Michelson contrast[23]:

$$\text{Optical contrast} = \frac{R_{\text{MoS}_2(1-x)\text{Se}_{2x}} - R_{\text{SiO}_2}}{R_{\text{MoS}_2(1-x)\text{Se}_{2x}} + R_{\text{SiO}_2}}, \quad (2.9)$$

where $R_{\text{MoS}_2(1-x)\text{Se}_{2x}}$ is the reflected light intensity from the $\text{MoS}_2(1-x)\text{Se}_{2x}$ layers and R_{SiO_2} is that from the bare SiO_2/Si substrates. As the layer number keeps increasing, the nano-sheet becomes bluer and brighter. The similar contrast of the above two suggests that the alloy changes little of the structure and dielectric environment of MoS_2 .

Figure 2.7: The typical optical micrographs of the samples. (a) and (b) are the bright field images of MoS_2 and MoSSe samples, respectively. The scale bars are $10\ \mu\text{m}$; (c) and (d) are the corresponding fluorescent micrographs excited by blue light.

Under the same objective, the fluorescence microscopy images were obtained by blue light excitation with the aid of switable filters to select the emission band, as shown in Fig. 2.7 (c) and (d). Both samples show clear red fluorescence only in the monolayer region, which is in good agreement with the contrast identification from Fig. 2.7(a) and (b). It is worth to note that the photoluminescence of MoSSe looks weaker because the camera is less sensitive in longer wavelength. The fluorescent images prove that the alloys have the same layer-dependent band structure evolution that the monolayer band gap transfers to direct band gap. This result is consistent with previous theoretical and experimental observations[1, 2, 6]. Atomic force microscopy also has been used to measure the thickness of the alloy samples, as shown in Fig. 2.8. From the AFM topography of both MoS_2 and MoSSe monolayers, similar thickness (~ 0.7 to $0.8\ \text{nm}$ for both cases) can be obtained by measuring the section profile along the sample to substrate steps. The AFM images also show ubiquitous micro and sub-micro sized bubbles and ripples. Those local features will create potential fluctuations along the monolayers and

broaden the photoluminescence peaks. In Chapter 3, the fitting of the PL peaks to exclude the impact of these local features will be discussed.

Figure 2.8: The AFM topography of MoS₂ (a) and MoSSe (b) monolayers. The section profiles have been shown for both cases as insets in the image. The scale bars in (a) and (b) are 2 and 5 μm , respectively

2.3 Methodology of the Optical Spectroscopy Study

2.3.1 Raman Spectroscopy

The Raman spectroscopy of transition metal dichalcogenides has been intensively studied during the past decade, to reveal the symmetry, interlayer interaction, phase transition and electron-phonon interactions of these unique two-dimensional layered structures[24–28]. Especially in the Raman shift range with ultralow frequencies ($< 50 \text{ cm}^{-1}$), those interesting interlayer phonon vibration modes which are unique for 2D layered materials have been used to identify the layer number, stacking sequence and twisting of the crystals or vertical heterostructures. In the Brillouin zone center (Γ), those interlayer phonon modes represent the relative motions of different van der Waals (vdW) layers, where all the atoms within one layer are displacing collectively in the same direction. Since in TMDs the weak vdW force is the only restoring force, the frequencies of the

interlayer vibration modes are normally in the ultralow frequency region. For the alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ layers, there exists several interesting questions such as: how will the hybrid features of the phonon vibration modes manifest? How are they going to affect the exciton behaviors? Therefore, Raman spectra of the alloy 2D layers need to be measured carefully, in order to address those questions.

In this thesis, Raman scattering measurement was performed in back-scattering geometry using a micro-Raman spectrometer (Horiba-JY T64000). The excitation laser was introduced using a $100\times$ lens with a numerical aperture of 0.9, and focus onto the substrate with beam diameter around $1\sim 2\ \mu\text{m}$. The volume Bragg grating was used for 532 nm to further suppress the laser side bands[29], for the ultralow frequency Raman spectroscopy measurements. The mechanism of the volume Bragg grating is shown in Fig. 2.9 (a) in comparison with a normal ruled grating in Fig. 2.9(b). Only a narrow spectral range of the light beam is reflected within a narrow acceptance angle when the Bragg conditions are satisfied.

Figure 2.9: Different filtering mechanism between a Bragg grating and a ruled grating for cutting off laser side-band. (a) shows schematics of the volume Bragg grating. (b) shows the ruled grating.

The Raman signals are collected through the same lens with a confocal configuration to make sure that the collecting efficiency is high. A forestage triple grating system with a 1800 lg/mm grating was used to disperse the Raman sig-

nal to achieve as low frequency as 5 cm^{-1} . The schematic and a typical Raman spectra taken on MoS₂ monolayer and bilayer are shown in Fig. 2.10.

Fig. 2.10(a) presents the schematic of the spectrometer. The two forestage grating G1 and G2, and two inter-grating slits S2 and S3 together are the fore-monochromators which act as a ultra-narrow notch filter to filter the laser excitation out. Careful alignment of optics and light path is necessary to reach low frequency and confocal measurements.

The alignment of optics should be achieved to optimal condition to make sure efficient detection of signals. The pinhole which is very critical to improve signal resolution is required to match the size of the laser spot on the sample to the greatest extend. Typically, they are set around $1\text{ }\mu\text{m}$. Fig. 2.10(b) illustrates an ideal condition with perfect alignment, therefore, only the signal collected from the laser spot area will go through the pinhole to the liquid nitrogen cooled CCD. The size of the slits, S1 and S3, are usually identical (with a typical number $100\text{ }\mu\text{m}$). However, an enlarged slit S2 is necessary, usually much larger than $100\text{ }\mu\text{m}$, in order to let through the spatially dispersed signal light and block the laser line (Rayleigh signal). The block of laser and Rayleigh signal can not be perfect, as one can see from the orange-shaded area in the spectra shown in Fig. 2.10(c). However, the interlayer phonon vibration modes (not applicable to monolayer as no adjacent layers existed) are clear with a slight laser and Rayleigh tail.

2.3.2 Photoluminescence Spectroscopy and Polarized PL

Photoluminescence spectra of semiconductors can directly measure the band edge transition emissions and thus provide informations about the material, including optical band gap, exciton oscillator strength, transition efficiency (direct or indirect) and so on. Recently, the exciton and trion evolutions of TMD with respect to layer-dependence and temperature dependence have been studied using PL spectroscopy[30–33]. By adding a half-lambda ($\lambda/2$) or quarter-lambda

Figure 2.10: The schematic and a typical Raman spectra taken on MoS₂ monolayer and bilayer. (a) is the schematic of the Horiba-JY T64000 spectrometer setup. (b) is the schematic of the confocal setup of the microscope and the pinhole to control the confocal planes. (c) are typical Raman spectra of MoS₂ monolayer (black) and bilayer (red), respectively

($\lambda/4$) wave-plates to the laser excitation and in front of the detector, circular- and linear-polarized PL can be measured on TMDs, which are closely related to the Valley physics[34–37]. Therefore, PL and polarized PL need to measure on the alloy monolayers, to reveal the exciton behavior and valley physics upon alloy engineering of TMDs.

Figure 2.11: The schematic of the PL setup (a) and a typical PL spectrum (b) taken on MoSe₂ monolayer at 30 K.

All the steady-state PL measurement including polarized and temperature-

dependent PL were measured in backscattering geometry using a spectrometer (Horiba HR800) in the configuration shown in Fig. 2.11(a). 532 nm, 633 nm (He-Ne), 671 nm and 785 nm lasers were introduced using $100\times$ short focus lens or $50\times$ long focus lens (for low temperature measurement), and emission signals are collected through the same lens, resolved by a 300 lg/mm grating and finally go to a liquid nitrogen cooled CCD detector. Long wavelength pass filters corresponding to the laser line were selectively mounted in front of the CCD detector to filter out the excitation line. For temperature-dependent PL, the sample was mounted in a cryostation with circulating liquid nitrogen or helium. Laser excitation and signal were going through a quartz window using the $50\times$ long focus lens. A typical PL spectrum of MoSe₂ at 30 K is shown in Fig. 2.11(b). By tuning the excitation angle Φ and detection angle φ , circular polarization (when the $\lambda/4$ wave-plates are placed) and linear polarization (when the $\lambda/2$ wave-plates are placed).

The same setup in Fig. 2.11(a) is also applicable to measure the reflectance spectra. Using a white light source to replace the laser excitation, and remove the long pass filter in front of the detector to let the whole wavelength go to the CCD detector. When measuring the reflectance, firstly a reflected spectrum was taken on the sample, secondly another spectrum was taken on the substrate without sample on cover. Then the reflectance of the sample can be calculated as:

$$R = \frac{I_{Sam} - I_{Sub}}{I_{Sub}}, \quad (2.10)$$

I_{Sam} and I_{Sub} are the reflected light intensity from sample and blank substrate, respectively. R is the reflectance of the sample. As the excitons of TMD monolayer are strong oscillators which can absorb a lot of photons in a narrow energy range, there will be dips in the reflectance spectra, as shown in a typical reflectance spectrum of MoSSe under 30 K (Fig. 2.12). The B-exciton, A-exciton and the

trion which contains A-exciton and an additional charge are all in the reflectance, showing decent dips.

Figure 2.12: A typical reflectance spectrum taken on a MoSSe monolayer at 30 K.

2.3.3 Time-resolved Photoluminescence Spectroscopy

As a (2D) quantum system, the excitons in TMD monolayers have large binding energy up to 200~400 meV[38, 39] (as mentioned in Chapter 1, section 1.3). Due to the large binding energy, the giant oscillator strengths of the excitons (f_{ex}) have been reported for TMD monolayers in several literature[40–42]. The exciton recombination lifetime (σ_{ex}) has relationship with the oscillator strength: $f_{ex} \sim 1/\sigma_{ex}$. Therefore, the exciton recombination lifetime and thus the PL lifetime of the TMD monolayers can be as short as sub-nanosecond[33, 43–45]. The 2D system-induced shortening of lifetime can be also observed in earlier cases of quantum well structure of traditional direct band gap semiconductors like GaAs. For GaAs, the bulk system has smaller oscillator strength with lifetime as long as tens of nanoseconds[46, 47], while when the quantum well has been formed, the lifetime can be reduced to 1 ns or even sub-nanosecond level[48–51].

Although the direct measurement of exciton lifetime is very difficult, photoluminescence lifetime can be measured optically. The average PL lifetime has

relationship with exciton lifetime in the following:

$$\langle\tau\rangle^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}, \quad (2.11)$$

the $\langle\tau\rangle$ is the average PL lifetime, while τ_r and τ_{nr} are radiative and non-radiative recombination lifetime. Usually the non-radiative lifetime (τ_{nr}) is short[52, 53], so the exciton (radiative) lifetime (τ_r) is proportional to the measurable PL lifetime ($\langle\tau\rangle$). Since the PL lifetimes of TMD monolayers are in nanosecond or sub-nanosecond level, time-resolved photoluminescence using femto-second or pico-second pulsed lasers as excitation source is needed.

In this work, time-resolved Photoluminescence (trPL) via time-correlated single photon counting (TCSPC) is utilized to measure the PL lifetime of those alloy TMD monolayers. The setup is illustrated in Fig. 2.13(a). The fluorescence lifetime measurement was performed using a confocal microscopy with a $50\times$ long focus lens. 400~500 nm tunable pulse excitations (8 MHz, repetition rate 100 fs) were introduced to the sample, and the photoluminescence emission from sample was analyzed by the single photon avalanche diodes (SPAD) to resolve the time decay. A set of suitable long- and short-pass filters (corresponding to the excitonic emission spectral position) were used to select the photoluminescence. A typical trPL spectrum taken on MoSe₂ monolayer sample is shown in Fig. 2.13(b), and exponential decay function can be used to fit the lifetime τ .

In TCSPC, the time interval between the sample excitation by a pulse laser and the photon emission is measured. A “start” is initiated by the electronics steering the laser pulse. The sensitive single-photon detectors will later collect the signal and finalize the “stop”. The whole process will be repeated for numerous times to integrate the photon counts and to reveal the statistical nature of the fluorophores emission. Then the time delays are plotted into a histogram showing the occurrence of emission over time after the excitation pulse. In the setup, two

Figure 2.13: The setup of lifetime measurement and a typical time-resolved PL spectrum taken on a MoSe₂ monolayer at 295 K.

SPADs have been equipped with a correlation analyzer, thus the time-correlation of photons can be recorded as well.

2.4 Summary

In this chapter, the synthesis of transition metal dichalcogenide alloys by chemical vapor transport has been introduced. High-quality alloyed TMD single crystals exhibit flake appearance. XPS was used to check the concentration of S and Se of the crystal, showing a consistent result according to the loading sources. Alloyed TMD crystals can be exfoliated to monolayers. The MoSSe monolayer has been measured using HAADF-STEM, indicating that the alloyed crystals have homogeneous phase, free of S or Se clusters or aggregations. The characterizations of the crystals show that the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ crystals have high quality and provide suitable platform to study the intrinsic optical properties. At last, the spectroscopy techniques and setups have been introduced in detail, including Raman, PL, polarized and time-resolved PL spectroscopy. Typical data from real samples have been given to specify the measurement.

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3 Band Gap, Spin-orbit and phonon Engineering of the TMD Alloys

In semiconductor science and technology, the band gap is arguably the most critical parameter for almost all applications involving photon absorption and emission events, such as solar cells, solid-state lighting, detectors, displays, lasers and so on. In this chapter, the engineering of band gap and spin-orbit coupling through making ternary alloys $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($0 \leq x \leq 1$) has been systematically studied. The band gap engineering can largely tune the band gap range with negligible change to the crystalline structure. The spin-orbit engineering can modulate the energy difference between the A and B excitonic levels, thus changing the carrier dynamics. Therefore, the optical and optoelectronic properties of the TMD family can be effectively modulated and designed via alloy engineering.

Since decades ago alloy engineering has been utilized to tune and expand the energy band gap range of semiconductors[1–4]. Apparently early works mainly focused on bulk semiconductors such as single crystals of silicon, III-V and II-VI compounds. As an elementary substance, silicon crystal lattice has large size mismatch and unavoidably detrimental defects with introducing any dopant, which constrains the doping concentration to less than 4 % and limits the alloy engineering[3–6]. For the III-V and II-VI compounds, elaborate and costly syn-

theses are needed as the crystal growth is too difficult for classical monocrystal pulling and the formation temperature is too high for normal CVD process[7, 8].

Recently the complete chemical composition tunability of semiconductors have been achieved in several material systems. Peidong Yang *et al.* first grew single-crystalline $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires across the entire compositional range from $x=0$ to 1 at low-temperature using chemical vapor deposition assisted by halide[9, 10]. Later, complete composition of alloying between the halogens (Cl, Br and I) in organolead halide perovskites have been achieved, to reveal tunable emission and lasing covering the whole visible spectral range[11–14]. Most of those results are obtained in low-dimensional nanostructures including nanowire, nanoplate and quantum dot. It can be inferred that the low-dimensional system has more tolerance to lattice mismatches, and thus the band gap of those alloys can be widely tuned without the detrimental defects that are often unavoidable in bulk materials. In the TMD case, both the direct growth of alloy monolayer by CVD, and the layer-by-layer long-term growth of alloy single crystal by CVT are achievable[15–18]. Therefore the band gap, spin-orbit and phonon engineering for 2D TMDs can be studied.

3.1 Band gap tunability of the TMD alloys

Monolayer and bilayer samples are exfoliated from the as-grown bulk crystals of MoS_2 , MoSe_2 and $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ onto $\text{Si}/\text{SiO}_2(285\text{ nm})$ substrate. The photoluminescence spectra at room temperature (295 K) were measured and plotted in Fig. 3.1. The PL intensity of the monolayer and bilayer spectra in each sample are divided by the maximum intensity of the monolayer, in order to highlight the distinct PL intensity between the mono- and bilayer. As a result, the alloy crystals have the similar indirect-to-direct band gap transition when the layer number is down to one layer. The result is consistent with the fluorescence image

Figure 3.1: Room temperature ($T=295\text{K}$) PL spectra of monolayer (blue trace) and bilayer (red trace) exfoliated from MoS₂ (a), MoSSe (b) and MoSe₂ (c).

shown in Chapter 2, Section 2.2, indicating the alloy has similar band structure to the pristine TMD.

The (optical) band gap can be measured for all the alloy monolayers using both PL and reflectance spectra. Fig. 3.2 displays the PL spectra of 5 different alloy monolayer samples including the pristine MoS₂ and MoSe₂ at room temperature 295 K (Fig. 3.2(a)) and liquid nitrogen temperature 78 K (Fig. 3.2(b)). For the alloy MoSSe, the S and Se concentrations have been identified by XPS and STEM in Section 2.2 of Chapter 2, showing overall homogeneous distribution in the crystal lattice. The S and Se concentration of the other two alloys can be calculated using the band gap energy positions, which follow Anderson's rule[19, 20]:

$$E_g(\text{MoS}_{2(1-x)}\text{Se}_{2x}) = (1 - x)E_g(\text{MoS}_2) + xE_g(\text{MoSe}_2), \quad (3.1)$$

using the optical band gap values obtained from the photoluminescence spectra, as shown in Fig. 3.3. $x \approx 0.2$ and 0.8 are obtained for the two alloys, respectively. The band gap evolution trends with changing x are nearly parallel at 295 K and 78 K (Fig. 3.3), indicating the band gap engineering is homogeneous and makes intrinsic effects to the alloys. It can be concluded that complete chemical compositions can be achieved in tuning the Se concentration, making continu-

Figure 3.2: PL spectra for 5 different alloy monolayers at room temperature (a) and 78 K (b), the pristine MoS₂ and MoSe₂ monolayers are included as the starting and end points of Se doping.

Figure 3.3: Se concentration dependent optical band gap of the alloy monolayers at room temperature (orange trace) and 78 K (blue trace).

ous band gap tunability cover a 300 meV range, among the 5 alloy monolayers: MoS_2 , $\text{MoS}_{1.6}\text{SeS}_{0.4}$, MoSSe , $\text{MoS}_{0.4}\text{SeS}_{1.6}$ and MoSe_2 . This large tunability can provide numerous excitons at different energy positions, which may also vary the recombination dynamics of them. Therefore, the alloy monolayers may provide a golden platform to study exciton behaviors.

3.2 Spin-orbit coupling engineering of the TMD alloys

Figure 3.4: The schematic of the A exciton, B exciton and the energy difference ΔE_{BA} between them induced by spin-orbit coupling. (a) schematically shows the energy levels in excitonic representation from the ground state $|0\rangle$ to the excited excitonic A and B levels, assuming non-resonant excitation. The relevant occupation generate rates and the decay rates of both A and B excitonic energy levels are labeled. (b) indicates the size difference of the hexagonal prisms of MoS_2 and MoSe_2 . The S (decorated with yellow) and Se (decorated with green) atoms have different sizes and their outer electron orbitals also have different sizes.

Besides the band gap tunability in two-dimensional TMDs, the more interesting part is that the spin-orbit coupling (split) has been engineered as well. The typical exciton representation of TMD monolayer system is shown in the Fig. 3.4(a),

containing two excitonic levels with energy difference at hundreds of meV. The strong spin-orbit coupling splits the valence band of TMD into two sub-bands (A and B), thus the excited charges can be bound to holes in different sub-valence-bands due to the Coulomb interactions, forming two excitonic levels[21–25]. When photons with high energy encounter the TMD monolayers, both excitonic levels can efficiently absorb photons (G_B and G_A in Fig. 3.4(a), are the generation rate at B and A levels) and form excitons due to their giant oscillator strength. The excitons will emit photons consequently by the recombination (Γ_B and Γ_A in Fig. 3.4(a)) to the ground states $|0\rangle$, which are more efficient than free carrier recombination.

By measuring the absorption (reflectance) and PL of the alloy monolayers, the energy position of the two excitonic levels and the energy differences between them, namely the spin-orbit split ΔE_{BA} , can be obtained. Fig. 3.5(a) shows the reflectance spectra of all the 5 monolayer samples at 30 K. At this temperature, the exciton absorption bands are strong and clear dips in the reflectance spectra. For both A and B excitons, clear evolution of their energy positions can be seen with varying the temperature, indicating that the energy differences between them noticeably increase with increasing the Se atomic concentration. This means that the spin-orbit split ΔE_{BA} of the alloy monolayers is proportional to the Se atomic concentration inside the crystal lattice.

As shown in Fig. 3.4(b), the MoS_2 and MoSe_2 hexagonal prisms have different sizes, so that the $4p$ -orbital of Se will have stronger exchange interaction with the $4d$ -orbital of Mo than the $3p$ -orbital of S does, leading to lifted spin degeneracy. More effectively, the bigger proton number (heavier mass) of Se atoms can contribute more to the spin-orbit coupling of the valence electrons[26–28]. In general, a Se atom will generate stronger localized spin-orbit coupling around its neighborhood sites than a S atom can do because of the heavier mass and larger size comparing to S.

Figure 3.5: energy difference between A and B excitons) of different alloy monolayers revealed by reflectance at liquid helium temperature (30K). (a) indicates the reflectance spectra for all the 5 monolayers in stacking plot. (b) shows the Se concentration dependent spin-orbit split ΔE_{BA} .

We have shown in Section 2.2 of Chapter 2 that the Se and S atoms are homogeneously distributed in the lattice, so this spin-orbit split changes by Se doping can be integrated to the alloy lattice, resulting an intrinsic properties of the alloyed monolayer semiconductors other than non-intrinsic properties from clusters or any new third-party phases. As a result, the MoSe_2 crystal lattice has much stronger spin-orbit coupling than that of MoS_2 , and the spin-orbit split ΔE_{BA} must be larger. The alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($0 \leq x \leq 1$) will have spin-orbit split ΔE_{BA} in the middle of MoSe_2 and MoS_2 , also following the Anderson's rule:

$$\Delta E_{BA}(\text{MoS}_{2(1-x)}\text{Se}_{2x}) = (1 - x)\Delta E_{BA}(\text{MoS}_2) + x\Delta E_{BA}(\text{MoSe}_2), \quad (3.2)$$

the calculated x is in good agreement with the values obtained from band gap as shown in Fig. 3.3. Similarly the Se concentration dependence of the ΔE_{BA} (shown in Fig. 3.5(b)) exhibits linear dependence as the band gap, with great consistence to the Anderson's rule. The optical band gap and spin-orbit split

energy values are collected into Table. 3.1 (the band gap values are from room temperature, while the spin-orbit split is temperature independent). While Se concentration increases, the alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ has narrowing band gap and broadening spin-orbit split. The combination of the two will change the exciton behaviors prominently, including the exciton recombination dynamics and efficiency, the line width and emission intensity (regarding to both absorption and emission), the carrier relaxation from high energy B to low energy A exciton, the intervalley scattering and spin-flip efficiencies, and so on. The B to A exciton relaxation and the intervalley scattering will be discussed later in Chapter 4 and 5, respectively.

Table 3.1: Table of Se concentration dependent band gap and spin-orbit split.

Se concentration (x)	0.0	0.2	0.5	0.8	1.0
Band gap (eV)	1.866	1.791	1.711	1.616	1.562
Spin-orbit split (meV)	137	153	179	201	229

3.3 Temperature dependent reflectance and PL of the alloyed monolayers

Temperature, as thermal energy, plays a key rule to the exciton behaviors of direct band gap semiconductors. For example, Room temperature (~ 295 K) has thermal energy around 25.4 meV, which is comparable or larger than the typical energy range of Coulomb interaction and exchange interaction induced split. This is one of the reasons why those spectral fine structures of semiconductor and nanostructures normally can only be observable at low temperature[29]. Prominently changing temperature of a semiconductor crystal (in 10~100 K scale) can change the lattice constant (in some cases phase transitions can take place) and phonon population (distribution) of the lattice, which will lead to change of band

structure and carrier (electron and hole) dynamics[30–32].

The population of phonon is not a fixed value. The phonon oscillators with a fixed frequency ω is temperature dependent. The average number of phonons $\langle n \rangle$ and energy $\langle E \rangle$ carried by phonons have relationship following Bose-Einstein distribution:

$$\langle n \rangle = \frac{1}{\exp(\frac{\hbar\omega}{k_B T}) - 1}, \quad (3.3)$$

$$\langle E \rangle = \hbar\omega \langle n \rangle = \frac{\hbar\omega}{\exp(\frac{\hbar\omega}{k_B T}) - 1}, \quad (3.4)$$

where k_B and ω are Boltzmann constant and average phonon frequency. The phonon effects are more and more active with increasing temperature until Debye temperature[33, 34].

Excitons are bound electron-hole pairs, thus can be strongly influenced by the interaction with phonons. Phonon-induced scattering can disturb the momentum and angular momentum of carriers, killing the coherence which is inherited from the polarized (linear or circular) optical excitation[30]. Therefore, the properties of excitons which are related to momentum of carriers will be strongly dependent on temperature. For TMD monolayers, the berry phase endows valley-related angular momentum to the carriers at band edge, so the valley-related behaviors of the excitons including valley polarization and valley Hall effect have strong temperature dependence[22, 35–37]. To study the behaviors of excitons through temperature dependent reflectance and PL spectra, elementary informations of exciton recombination dynamics can be obtained.

3.3.1 Temperature dependent behaviors of excitons in alloyed monolayers

Temperature dependent reflectance and PL spectra of the 5 alloyed monolayers are measured to study the different exciton behaviors among TMD alloys. A

Figure 3.6: The temperature dependent reflectance and PL spectra of the alloyed monolayer MoSSe. (a) is the temperature-dependent reflectance spectra. (b) is the temperature-dependent PL spectra.

2.33 eV excitation (532 nm solid state laser) was used to pump the carriers to above the B excitonic level, by cooling and relaxation, the carriers will occupy the A and B excitonic levels and emit photons via excitonic recombination. The analyses in this subsection are mainly focused on A exciton, because 1) the A excitonic energy level is close to the band gap and thus can be used to track the band gap value; 2) the spectral line of A is much more prominent as it is the lowest excited state. Fig. 3.6(a) shows the temperature-dependent reflectance spectra of a typical MoSSe monolayer, while the other $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ samples have the similar spectra (the 30 K spectra have been shown in Fig. 3.5(a)). The A exciton and trion absorption lines are strong and sharp at low temperature. As temperature increases, the line widths become broad and the exciton and trion merge into one asymmetric peak. However, the resonance oscillator is still clear to observe when it reaches room temperature. Because of the large exciton binding energy up to ~ 200 meV, the room temperature thermal energy 25.4 meV can hardly dissociate the excitons.

As the excitons are robust along all the temperatures, the PL emission via excitonic recombination is prominent at both low and high temperatures. Fig. 3.6(b) shows the temperature-dependent PL spectra of the MoSSe monolayer. The PL peaks also broaden significantly with increasing the thermal energy, indicating strong interactions between carriers and phonons. It is worthwhile to note that both reflectance and PL spectra show clear blue shift with decreasing temperature, which is due to the band gap broadening induced by lattice constant decreasing. The continuous shift of band gap, free of interruptions, also proves that there is no phase transition during the temperature evolution.

In order to systematically study the band gap evolution and the line width change of exciton peaks, a voigt profile has been used to fit the spectral line shape of the PL peaks:

$$I = I_0 + A \frac{2\omega_L \ln 2}{\pi^{3/2} \omega_G^2} \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{(\sqrt{\ln 2} \frac{\omega_L}{\omega_G})^2 + (\sqrt{4 \ln 2} \frac{x - x_c}{\omega_G} - t)^2} dt \quad (3.5)$$

where I and I_0 are the PL intensity and baseline of spectra, respectively. A and x_c are the integral peak area and position. ω_G and ω_L are the widths of Gaussian and Lorentzian components of the peak profile. Fig. 3.7 shows a typical fitting process

Figure 3.7: The typical fitting of PL peak of MoSSe monolayer at liquid Helium temperature.

in the PL spectrum of a monolayer MoSSe at 30 K. At this temperature, the peaks are sharp and clear, which can be easily fitted into one exciton and one trion peak. Trion is another quasi-particle which has an exciton bound to an additional free electron and the total energy is further reduced, so the trion peak is located the lower energy side of exciton peak. Although the fitting is not challenging mathematically, the determination of Gaussian and Lorentzian widths (ω_G and ω_L) should follow the fundamental physical rules. By considering the excitons as electric dipoles and oscillators, the energy dispersion of photons from excitonic emission in the lattice should follow Lorentzian distribution, the width ω_L is due to the interaction with the lattice vibration (phonon) and thus can be regarded as homogeneous broadening of the system[38–40]. In the meanwhile, the monolayer crystal has randomly distributed potential fluctuations due to crystalline defects and nano ripples of the 2D sheet[41, 42], which slightly offset (in meV range) the energy of the exciton oscillators. These offsets generate Gaussian distributions of the oscillators, leading to inhomogeneous broadening. Here “inhomogeneous” means that it does not stem from the intrinsic lattice properties.

All the temperature dependent PL spectra of the alloyed monolayers, including the pristine MoS₂ and MoSe₂ can be fitted with the above voigt profile in similar procedure. We first fit the spectra at bottom temperature (10 K). The full width at half maximum (FWHM) of the neutral exciton transition at the optical band gap is typically of the order of 10 meV (50 meV) at $T \approx 5$ K (300 K) when exfoliated onto Si/SiO₂ substrates[43–45]. The limitation of the homogeneous width can reach ~ 5 meV when encapsulated with two-side h-BN coverage [38–40].

In our fitting, the homogeneous width (ω_L) at bottom temperature ranges from 6.0 to 7.3 meV, corresponding to the alloyed TMD monolayers from MoSe₂ to MoS₂. The high-quality spectral line of MoSe₂ which we observed is consistent with previous research works[38–40, 43]. The inhomogeneous width (ω_G) can be

Figure 3.8: Temperature dependence of the energy position of A exciton peaks among $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloyed monolayers. The raw data points of MoS_2 , $\text{MoS}_{1.6}\text{Se}_{0.4}$, MoSSe , $\text{MoS}_{0.4}\text{Se}_{1.6}$ and MoSe_2 are denoted as black square, circle, up triangle, down triangle and diamond, and the fitting of them are shown in dash lines with blue, cyan, orange, wine and red colors.

obtained also from the fitting at bottom temperature. For the fitting of spectra at higher temperatures, the ω_G must be fixed to let the ω_L which coupled with intrinsic lattice properties change with temperature. In fact, as long as the PL spectra are taken at fixed position on the alloyed monolayers, the ω_G related to non-intrinsic and environmental factors should be identical.

From the fitting results of the temperature dependent PL of all alloyed monolayers, we first focus on the PL peak position of A exciton transition, as its value is close to the direct energy band gap of the lattice ($E_g = E_A + E_{\text{Bind}}$). Fig. 3.8 shows the temperature dependence of the A exciton peak position among all the alloyed monolayers. The raw data points of MoS_2 , $\text{MoS}_{1.6}\text{Se}_{0.4}$, MoSSe , $\text{MoS}_{0.4}\text{Se}_{1.6}$ and MoSe_2 are denoted as open black square, circle, up triangle, down triangle and diamond. The temperature dependence of the PL peak position follows a standard hyperbolic cotangent relation[34, 40, 46]:

$$E_G(T) = E_G(0) - S\langle\hbar\omega\rangle \left[\coth\left(\frac{\langle\hbar\omega\rangle}{2k_B T}\right) - 1 \right], \quad (3.6)$$

where the $E_G(0)$ and $E_G(T)$ is the band gap at zero temperature and a certain temperature (here we use the fitted A exciton peak position data from bottom temperature to 295 K), S is a dimensionless coupling constant, and $\langle \hbar\omega \rangle$ is an average phonon energy of all relative phonons. This notation is adopted from the vibration model of Huang and Rhys[47]. The fitting curves match well with the raw data points of MoS₂, MoS_{1.6}Se_{0.4}, MoSSe, MoS_{0.4}Se_{1.6} and MoSe₂, which are shown in blue, cyan, orange, wine and red dashed lines in Fig. 3.8, respectively. The fitting parameters are collected to Table 3.2 as shown following.

Table 3.2: Table of fit parameters for temperature dependence of optical band gaps of alloyed TMD monolayers.

Sample	$E_G(0)$ (eV)	S	$\langle \hbar\omega \rangle$ (meV)
MoS ₂	1.954	2.68	36.2
MoS _{1.6} Se _{0.4}	1.844	2.82	33.6
MoSSe	1.793	2.93	32.3
MoS _{0.4} Se _{1.6}	1.696	3.03	30.7
MoSe ₂	1.659	3.11	28.3

The fitted dimensionless coupling constant S for all the alloyed monolayers are around 2.68~3.11. The values are close because all the monolayers share the identical hexagonal lattice with D_{3h} symmetry and similar lattice vibration modes. The high symmetry and isotropy of the lattice makes the E and A phonon modes highly degenerated[48–50]. The S values of those alloyed TMD monolayers are prominently larger than those of typical bulk semiconductors like Si and GaAs which have S values around 1~2[51–53]. The possible reason could be that the purely two-dimensional lattice has larger Grüneisen parameter γ as the volume change of 2D lattice receives no contribution from its Angstrom-level thickness[54, 55], so the in-plane lattice constants of the 2D lattice are more preferred to change when the crystal is subject to temperature change.

The pristine TMD monolayers, including MoS₂, MoSe₂ and the tungsten counterparts, show prominent in-plane (E_{2g}) and out-of-plane (A_{1g}) vibration modes

in their Raman spectra[48, 56]. In general, the average optical phonon energy (vibration frequency) of MoS₂ is larger than that of MoSe₂ due to the heavier atomic mass of Se atoms, as the vibration frequency of the oscillator has relationship: $\omega \propto \sqrt{K/m}$ (K is force constant, m is atomic mass). Apparently, the phonon energy of MoS₂(1- x)Se_{2 x} will be smaller than MoS₂ and larger than MoSe₂, which depends on the Se concentration x . From the fitting results, the average phonon energy of the alloyed TMD monolayers are consistent with the theoretical prediction. The Raman spectroscopic study of those alloyed monolayers will be detailedly discussed in the next subsection.

Figure 3.9: Temperature dependence of the homogeneous broadening of A exciton peaks among MoS₂(1- x)Se_{2 x} alloyed monolayers. The raw data points of the homogeneous line width ω_L in MoS₂, MoSSe and MoSe₂ are denoted as black circle (a), diamond (b) and square (c), and the fitting of them are shown in dash lines with blue, orange and red colors.

The temperature dependence of band gap (PL position) can provide critical information on how strong the lattice change affects the band gap. Besides that,

monitoring the homogeneous broadening of exciton peak is more meaningful, since it can reveal how phonons affect the exciton coherence, oscillator strength and recombination rate, and so on[38–40, 57]. Fig. 3.9 shows the temperature dependence of the homogeneous line width ω_L of MoS₂, MoSSe and MoSe₂ monolayers. All the exciton ω_L broadens significantly with increasing temperature. The overall line width of MoS₂ is noticeably wider than that of MoSe₂, and the MoSSe line width sits between the two pristine ones. The shaper line width and higher optical quality (refer to quantum efficiency) have been reported in previous research works[38–40, 57]. From the fitting results of Equation (3.6), MoSe₂ exhibits the lowest average phonon energy among all the alloyed monolayers. A smaller coupling with optical phonons in MoSe₂ may explain its relatively narrower line width among the material family.

The homogeneous width ω_L increases more than one order of magnitude with increasing temperature, showing signature of an efficient coupling with phonons. Therefore, the evolution of the line width (denoted as γ here to distinguish with phonon frequency ω) can be phenomenologically approximated by a phonon-induced broadening[40, 57]:

$$\gamma = \gamma_0 + c_1 T + \frac{c_2}{e^{\langle \hbar \omega \rangle / k_B T} - 1}, \quad (3.7)$$

where γ_0 and c_1 describe the linear increase due to acoustic phonons at liquid helium temperature range. The parameter c_2 is a measure of the strength of the phonon coupling. $\hbar \omega$ is the averaged energy of relevant optical phonons, which will be obtained by fitting the optical band gap energy evolution with Eq. (3.6) for consistency.

The fit parameters for all the alloyed monolayers are shown in Table. 3.3. It can be seen that from MoSe₂ to MoS₂, all the parameters increase monotonously. MoS₂ has the largest line width (γ), stronger coupling with acoustic and optical

phonons (c_1 and c_2), and larger average phonon energy ($\langle \hbar\omega \rangle$). Due to the stronger coupling with larger average phonon energy, the homogeneous broadening of MoS₂ is more significant among the MoS_{2(1-x)}Se_{2x} alloyed monolayers. It is worthwhile that besides the band gap and spin-orbit engineering, the interaction between carrier (exciton) and phonon can also be tailored by making ternary alloy of TMD. This tunability of exciton-phonon interaction will open opportunities to precisely design and control carrier and exciton behaviors including effective mass, energy dispersion, relaxation dynamics, coherence and so on.

Table 3.3: Table of fit parameters for temperature dependence of homogeneous broadening ω_L of alloyed TMD monolayers.

Sample	γ_0 (meV)	c_1 ($\mu\text{eV}/\text{K}^{-1}$)	c_2 (meV)	$\langle \hbar\omega \rangle$ (meV)
MoS ₂	7.3	31	144.1	36.2
MoS _{1.6} Se _{0.4}	7.1	29	116.5	33.6
MoSSe	6.8	25	92.4	32.3
MoS _{0.4} Se _{1.6}	6.2	22	61.6	30.7
MoSe ₂	6.0	19	54.8	28.3

3.3.2 Analysis of the trion behaviors

During the fitting of temperature dependent PL spectra in the above sections, besides the A exciton peak there is a prominent trion peak, which is commonly observed in TMD monolayers[43, 58, 59]. As shown in Fig. 3.10, there are two types of trions: 2 electrons with 1 hole or 2 holes with 1 electron. Upon optical excitation, great amounts of free carriers are created. Those electrons and holes rapidly pair to each other, forming excitons due to the greatly enhanced Coulomb interaction (Keldysh type of Coulomb interaction) [60]. In any semiconductor crystal, there should be plenty of surplus carriers, which can be captured by excitons to form a new quasi-particle with three particle components, trion. Whether the trion is negatively or positively charged depends on the doping type of the crystal.

Figure 3.10: The formation schematic of Trion in two-dimensional TMD crystal. The red ball and blue dashed circle denote free electrons and holes in the 2D lattice. The exciton is shown as electron-hole pair in blue shade, and the trion is shown as three particles (2 electrons with 1 hole or 2 holes with 1 electron) in red shade.

Figure 3.11: The dependence of Trion binding energy on Se atomic concentration of the alloyed TMD monolayers. (a), (b) and (c) are the typical PL and reflectance spectra combo at 10 K for MoS₂, MoSSe and MoSe₂ monolayers, respectively. (d) is the dependence of Trion binding energy on Se atomic concentration, calculated from the reflectance and PL spectra.

To observe decent trion absorption or PL line, the binding energy between an exciton and electron (hole) should be big enough. The trion binding energy which describes the stability of a trion can be written as the following:

$$E_b(Trion) = E_{Exciton} - E_{Trion}, \quad (3.8)$$

where $E_{Exciton}$ and E_{Trion} can be obtained from reflectance and PL spectra, as shown in Fig. 3.11. The figure shows the typical PL and reflectance spectra combo at 10 K for MoS₂, MoSSe and MoSe₂ monolayers (the other two alloyed monolayers have similar spectra to the three), and results of trion binding energy are calculated using the data and equation (3.8).

Table 3.4: Table of trion binding energy $E_b(Trion)$ of the alloyed TMD monolayers.

Samples	MoS ₂	MoS _{1.6} Se _{0.4}	MoSSe	MoS _{0.4} Se _{1.6}	MoSe ₂
$E_{bind}(Trion)$ (meV)	44.1	40.3	36.2	33.8	32.3

Apparently the trion binding energy can be modulated by tuning the Se and S fraction of the alloys. From MoS₂ to MoSe₂, the trion binding energy linearly decreases from 44.1 to 32.3 meV (shown in Fig. 3.11(d) and Table. 3.4). Previous results have shown that dielectric environment can affect the trion binding energy[61]. In the alloyed monolayers, as the atoms and chemical bonding (S and $\langle\text{Mo-S}\rangle$ to Se and $\langle\text{Mo-Se}\rangle$) vary significantly, the dielectric constant will change a lot[62]. In the meanwhile, the Bloch function also changes a lot, making the crystal field distinct from case to case. Those changes will affect the effective mass of the carriers, therefore changing the trion binding energy.

It is notable that the trion binding energy of all the alloyed TMD monolayers are beyond the thermal energy at room temperature. So the trion population and the trion peak in PL spectra ideally should be prominent at room temperature. However, in actual experiments, one can see more pronounced trion peaks at

cryogenic temperature, which usually leads to narrower line width of exciton and trion features. From previous voigt profile fitting of the temperature dependent PL spectra of all the alloyed monolayers, the trion peak integral intensity can be obtained. We then normalized the intensities by dividing to the minimum intensity at room temperature. The intensity ratio I_T/I_0 (I_0 and I_T are the trion intensity at room temperature and T) shows significant temperature dependence, as shown in Fig. 3.12. The trion intensity evolution of MoS_2 to MoSe_2 are labeled with blue, cyan, orange, wine and red traces.

Figure 3.12: The temperature dependence of Trion peak intensity among the alloyed TMD monolayers.

From the trends, although the trion binding energy of MoS_2 is known to be the highest (44.1 meV) among the 5 alloyed specimens, its trion population increases the least with decreasing temperature. Comparing to room temperature, the trion intensity of MoSe_2 at 10 K increases by ~ 114.4 times, while MoS_2 only increases by ~ 2.3 times. The results suggest that the trion binding energy is not the major factor of trion formation and trion population. Since the excitons and trions for all the alloyed TMD monolayers are robust at room temperature, so the more significant factor that affects trion density should be the carrier (mainly electron) density. As we know the exciton population of TMD monolayer is enormous due to the giant oscillator strength, which can be seen from the strong resonance in

reflectance spectra. When the density of free electrons is high, the chance for an exciton to capture an additional electron will also be high, as shown in Fig. 3.10. It can be concluded from the temperature dependent trion intensity that the MoSe₂ lattice contains much greater free electron density than MoS₂, and the electron density of the alloyed lattices are in between.

Figure 3.13: The temperature dependence of contribution from electron doping to the trion formation among the alloyed TMD monolayers.

Follow the above discussion, by monitoring the trion population we can determine the n -doping level of the MoS₂(1- x)Se_{2 x} alloys. It is noted that most MoS₂ and MoSe₂ are reported as n -doped semiconductor by investigating the FETs[63–65]. In order to examine the doping level of the alloyed monolayers with excluding the factors from exciton density, we define a parameter to evaluate the contribution of electron density to the trion formation: $(I_T/I_0)/(I_T/I_E)$. I_T/I_0 is the normalized trion intensity which has been shown in Fig. 3.12. I_T and I_E are the PL intensity of trion and exciton at same temperature, which can be obtained from the voigt profile fitting in Subsection 3.3.1. The I_T/I_E ratio can measure the relative trion population. By dividing the normalized trion intensity I_T/I_0 by I_T/I_E , the temperature dependence of trion population can be evaluated. With fixed exciton population, more free carriers can directly increases the transition from an exciton to trion. In other words, the parameter $(I_T/I_0)/(I_T/I_E)$ can

measure the n -doping level of the lattice.

The temperature dependent $(I_T/I_0)/(I_T/I_E)$ for all the alloyed monolayers are shown in Fig. 3.13. It can be seen from the curves that the n -doping level of MoS₂ and slightly Se-doped MoS_{1.6}MoSe_{0.4} are relatively low. The further Se-doping apparently can increase the n -doping level, as MoSe₂ and MoS_{0.4}MoSe_{1.6} have spectacular $(I_T/I_0)/(I_T/I_E)$ values around 25 and 15 as temperature decreases. The large n -doping level creates great amount of free electrons, which can transfer excitons to trions efficiently. As a result, the n -doping level can be largely tailored by making ternary alloy of TMD, which will be very helpful in their optical and optoelectronic applications, for example, the doping-level can largely affect the Fermi-level, and change the transport and photo-induced transport properties of TMDs.

3.4 Raman spectroscopy of the TMD alloys

In previous sections, the temperature dependent PL spectra and the voigt profile fitting provided great information about phonons and interactions between exciton and phonon. In this section, by Raman spectroscopic study including layer-dependent, ultra-low frequency and polarization-resolved Raman, more details about the phonon properties of the MoS_{2(1-x)}Se_{2x} alloys will be discussed. 2.33 eV excitation (532 nm solid state laser) is used to avoid in resonance with exciton and exclude exciton-phonon effects. The off-resonance Raman spectroscopy can detect the pure vibration modes from atoms, containing lattice symmetry information.

3.4.1 Layer-dependent and polarization-resolved Raman spectra of the alloyed TMDs

Fig. 3.14 shows the Raman spectra of all the alloyed monolayers and layer-dependent evolution of the Raman modes among alloyed fewlayers. For the TMDs, the monolayer and fewlayer counterparts have simplified and degenerate Raman modes as compared to the bulk crystals. In Fig. 3.14(a), the monolayer spectra among the alloys are plotted in stacking for comparison. The MoS_2 and MoSe_2 have very simple Raman pattern at Raman shift ranging from 200 to 400 cm^{-1} , which have been studied thoroughly[48–50, 56, 66–70]. There are only two prominent peaks in the range: A_{1g} and E_{2g} modes, which denotes the out-of-plane and in-plane vibrations, respectively. For monolayer and odd-number-layer TMD, since the inversion symmetry is absent, the precise Mulliken notation of the symmetry specie for out-of-plane and in-plane vibrations should be A_1' and E' (E''). Here A_{1g} and E_{2g} notations are used for consistency with the bulk and even-number-layer TMDs. Although the Raman fingerprints for the pristine monolayers are simplified, the alloyed monolayers show complicated Raman patterns, which contains not only Raman features similar to the A_{1g} and E_{2g} modes from MoS_2 and MoSe_2 , but also conjugated new features.

In subsection 3.3.1 the average phonon energy have been fitted from temperature dependent PL for all the alloyed monolayers, which indicates that the MoS_2 has the largest phonon energy. Apparently this result is consistent with the Raman peaks of MoS_2 , showing much higher frequency than MoSe_2 . The Raman frequencies of MoS_2 are greater than that of MoSe_2 , which to some extent matches the fitting results from last section that the MoS_2 monolayer has larger average phonon energy (~ 49 meV) than that of MoSe_2 (~ 34 meV). From the simple evaluation of phonon energy based on Raman, the values are very close to the fitting results from the temperature dependent PL. The alloys have the intermediate

phonon energies, with more complicated vibration configurations, as shown in Fig. 3.15. The alloyed phase largely lifts the degeneracy of phonon modes.

Figure 3.14: The Raman spectra of all the alloyed monolayers and layer-dependent evolution of the Raman modes among alloyed fewlayers. (a) shows the off-resonance Raman spectra of all the alloyed monolayers at room temperature (295 K). (b) shows the layer-dependent Raman spectra of the MoS₂ mono- to quadra-layer samples. (c) shows the layer-dependent Raman spectra of the MoSe₂ mono- to quadra-layer samples. (d) shows the layer-dependent Raman spectra of the MoSSe mono- to quadra-layer samples.

By investigating the Raman evolution from MoS₂ to MoSe₂, it can be found that the Raman spectra of the alloyed monolayers are not simply showing two sets of Raman modes, but possess largely broadened Raman bands around the original positions of the A_{1g} and E_{2g} modes of MoS₂ and MoSe₂. This phenomenon agrees well with the HRTEM characterization in Chapter 2, the alloyed lattice contains homogeneous phase without noticeable aggregation or domains. Therefore, the alloyed samples generally contains mixed chalcogenides (S and Se) in its molecular configuration. This makes the vibrational motion asymmetric (as shown in Fig. 3.15(b)), which is in stark contrast to the symmetric vibrational motion of A_{1g}

Figure 3.15: The schematic diagram of the vibrational normal modes the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloys. (a) shows the pure phase MoS_2 and MoSe_2 . (b) indicates the conjugated vibrational modes in alloyed phase.

and E_{2g} modes in pure phase (as shown in Fig. 3.15(a)). Those new vibrational modes will have vibration frequencies in between A_{1g} and E_{2g} modes of MoS_2 and MoSe_2 , and the anharmonic vibration will also affect the surrounding normal vibrations. As a result, the complexity of the system is largely increased and several broadened Raman bands appear in the wave number range from about 220 to 320 cm^{-1} . For the alloy MoSSe with half S half Se, the lattice contains maximum concentration of S-Se in the same atom column of chalcogenides, so the population of the anharmonic vibrational modes reaches maximum. With increasing Se atomic concentration further, the Se becomes the major anions in the lattice, so the pure MoSe_2 vibrational modes pop-up in the spectrum of $\text{MoS}_{0.4}\text{Se}_{1.6}$.

The Fig. 3.14(b), (c) and (d) shows the layer-dependent Raman spectra for MoS_2 , MoSe_2 and MoSSe , respectively. The Raman modes of MoS_2 crystal are expected to stiffen as additional layers are added to form thicker layers. The interlayer Van der Waals interactions increase the effective restoring forces acting on the atoms. From the experimental results, the out-of-plane A_{1g} mode is stiffen as predicted, however, the in-plane E_{2g} is “soften” (wavenumber decreases), which are attributed to additional interlayer interactions[66, 67]. The Raman modes of

MoSe₂ has almost the same layer-dependence of its A_{1g} and E_{2g} modes, while the only difference is that the A_{1g} frequency is smaller than E_{2g}. In MoSSe case (Fig. 3.14(d)), the Raman peaks are broader, and no significant shift of Raman modes can be observed for the layer-dependent spectra. On the microscopic level, the broad modes around 220 to 320 cm⁻¹ could contain both A- and E-related modes, as we know that the frequencies of those anharmonic vibrations (shown in Fig. 3.15(b)) are in the relevant range. The frequency red- (from E mode) and blue-shift (from A mode) of the peaks can cancel each other, resulting in no shift of peaks. On the other hand, the two modes around 370 to 410 cm⁻¹, which are related to the E_{2g} and A_{1g} modes of MoS₂, should present red and blue shifts. However, the strong phonon-phonon interactions enhanced by the anharmonic vibrations largely broaden the line width of the Raman bands, making the shift of them insignificant.

Figure 3.16: The polarization-resolved Raman spectra of the MoS_{2(1-x)}Se_{2x} alloys. (a), (b) and (c) are the polarization-resolved Raman spectra of the MoS₂, MoSe₂ and MoSSe monolayers.

To reveal the symmetry and vibration details of the mixed Raman modes in alloyed TMD monolayers, polarization-resolved Raman spectra are measured. As illustrated in Fig. 2.9 of Chapter 2, we fix the detection analyzer and set the excitation polarization (the laser) 0 and 90 degree to measure parallel ($\bar{z}(xx)z$) and perpendicular ($\bar{z}(yx)z$) polarized Raman spectra, respectively. Fig. 3.16 (a) and (b) show the polarization-resolved Raman for the pristine TMD MoS₂ and MoSe₂. Fig. 3.15 shows that atom motions of A_{1g} mode are in the out-of-plane direction (along z direction), therefore the vibration and polarizability changes are in the laser propagating direction. When referring to the laser electric field which are perpendicular to its propagation, A_{1g} vibration presents holohedral symmetry, leading to no polarization change of the scattering light from the excitation. So for the A_{1g} parallel ($\bar{z}(xx)z$) configuration will yield the maximum intensity, while the perpendicular ($\bar{z}(yx)z$) will yield minimum. In stark contrast to A_{1g}, the E_{2g} is depolarized, and thus can be selected out by the perpendicular ($\bar{z}(yx)z$) polarized Raman.

Using the above standard, the Raman bands at around 220 to 320 cm⁻¹ are mainly A-like modes since the intensity is only prominent at parallel ($\bar{z}(xx)z$) configuration. This result is reasonable because the E_{2g} intensity of the pristine MoSe₂ is very weak, and the anharmonic vibrations can further eliminate the E-like modes.

3.4.2 Interlayer Raman modes of the alloyed TMDs

With Van der Waals force acting as restoring force, the layered crystals (including graphene, TMD, and so on) with layer number $N \geq 2$ have lattice vibrations with ultralow frequencies (< 50 cm⁻¹), which are defined as interlayer phonon modes and receive intense attentions during the last decade [56, 71–73]. By making MoS_{2(1-x)}Se_{2x} single crystals, we are able to obtain two-dimensional alloy samples with different layers by exfoliation. Based on the previous charac-

terizations (HRTEM, PL and Raman spectroscopies), Each layer of the alloyed samples will have homogeneously distributed S and Se atoms corresponding to the stoichiometry, creating novel interlayer interactions between alloyed monolayers. Therefore, these samples are naturally interesting for interlayer Raman spectroscopic study.

Figure 3.17: The schematic of the interlayer shear (E_{2g}^2) mode. (a) indicates the schematic among a trilayer configuration. (d) shows the simplified model with interlayer Van der Waals force as the only restoring force.

Previous research works have well studied the interlayer shear modes (as shown in Fig. 3.17) in graphene and TMDs[56, 71, 72], which are intense Raman peaks around 20 to 40 cm^{-1} frequency range. Using the triple mode (section 2.3.1), the interlayer phonon modes of alloyed TMDs can be revealed in this low frequency region. The Brillouin zone center (Γ) interlayer phonon modes represent the vibrations of different vdW layers, where all the atoms within each layer are displacing collectively in the same direction, as shown in Fig. 3.17(a). Fig. 3.17(b) shows the simplified model, a linearly chain model, considering the interlayer Van der Waals force as the only restoring force of the multiple oscillator system. Using the shear mode frequency obtained from the Raman and the linear chain model with only the nearest neighbor interactions, the interlayer force constants can be derived.

Fig. 3.18 shows the low frequency Raman spectra of the alloyed TMDs. Among

Figure 3.18: The Raman spectra of low frequency shear modes of the alloyed TMDs. (a), (b), (c), (d) and (e) are spectra of samples from MoS_2 to MoSe_2 .

the alloys, the interlayer shear modes can be seen clearly and they all blue-shift with increasing layer number. The result is consistent with the previous observations in pristine TMDs[56, 71, 73]. Fig. 3.18(g) is the plot of Raman peak positions against layer number, where the peak frequencies keep decreasing as the Se atomic concentration increases. The linear chain with N spheres has $2N$ degree of freedom, and therefore has N transverse eigen modes, corresponding to the interlayer shear modes. The corresponding frequency of the α^{th} eigen mode of the N^{th} layer can be obtained as:

$$\omega = \sqrt{\frac{K}{2\mu\pi^2c^2} \left(1 - \cos \left(\frac{(N-1)\pi}{N} \right) \right)}, \quad (3.9)$$

where K is the force constant, μ is the mass per unit area of a $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ layer ($\mu=3.07 \times 10^{-6}$ kg/m² for MoS_2 , $\mu=4.47 \times 10^{-6}$ kg/m² for MoSe_2 , and the μ for alloys are in between). The mass per unit area of a $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ can

be calculated using the relationship: $\mu = (1 - x)\mu(\text{MoS}_2) + x\mu(\text{MoSe}_2)$. And c is the speed of light in cm/s. The layer dependent shear mode positions can be well fitted for all the alloys, as shown in Fig. 3.19. The fitting parameters

Figure 3.19: The fitting of the interlayer shear modes frequency with linearly chain model. The data and fitting for samples from MoS₂ to MoSe₂ are shown in blue, cyan, orange, wine and red.

are collected to Table. 3.5. The mass μ changes with the concentration of Se and S atoms, which apparently contribute a lot to the Raman frequency. In the meanwhile, MoS₂ has the largest force constant of the interlayer shear (E_{2g}^2) mode among the alloys, for all other alloys, the force constant decreases as increasing Se atomic concentration. The interlayer shear (E_{2g}^2) mode can be split into two acoustic phonons of the same energy and opposite momentum[71]. It means that the phonon energy obtained from the interlayer shear modes of alloyed TMDs can measure the energy of the acoustic phonons. The results is consistent with the fitting results in section 3.2.1 that the MoS₂ has both larger optical and acoustic phonon energies.

Table 3.5: Table of fitting parameters of linearly chain model.

Samples	MoS ₂	MoS _{1.6} Se _{0.4}	MoSSe	MoS _{0.4} Se _{1.6}	MoSe ₂
μ (10^{-6} kg/m ²)	3.074	3.354	3.773	4.193	4.473
K (10^{19} N/m ³)	3.115	2.836	2.747	2.818	2.816

3.5 Summary

In conclusion, we have synthesized MoS_{2(1-x)}Se_{2x} ($0 \leq x \leq 1$) alloyed single crystals. By exfoliating the layered crystals, monolayer to fewlayer alloyed sample can be obtained. The alloyed TMDs have the same indirect-to-direct band gap transition when their layer number is down to one. For the alloyed monolayers, the band gap and spin-orbit split can be fully modulated between MoS₂ and MoSe₂, which can largely expand the optical and optoelectronic applications of the TMDs. Besides, the tunability of spin-orbit split allows tailoring of the energy difference between A and B excitons, which will provide a good platform to study the exciton recombination and relaxation.

The temperature-dependent PL of all the alloyed monolayers provide detailed information of their optical qualities. The monolayer MoSe₂ has the most narrow line width among the alloys, due to the weaker coupling to phonons and the lower phonon energies. The homogeneous broadening of line width due to the interactions between exciton and phonon can be modulated among the alloys, which might open opportunities to manipulate the exciton behaviors. Besides the exciton, the trion binding energy can be tunned from 44 to 32 meV. Trion formation affects many optoelectronic properties related to Fermi level and doping. By calculating the temperature dependent Trion intensity, it can be concluded that the n -doping level of MoS_{2(1-x)}Se_{2x} monolayers increases as the Se atomic concentration increases.

The Raman spectra prove that the symmetry of the alloyed samples is identical to the binary samples. The mixture of S and Se introduces anharmonic vibrations

to the system, and changes the phonon energy and phonon dispersion. The Raman bands become broadened and the E-like modes at MoSe₂ frequencies are suppressed. By measuring and fitting the layer-dependent interlayer shear modes of the alloys, the mass per unit area and force constant are obtained. The results show that MoS₂ has the strongest interlayer interactions. The distinct interlayer modes between alloys set a good model to identify the interlayer modes between any TMD or two-dimensional layers, which will be helpful for characterization for new heterostructures of 2D materials in the future.

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4 Bright and dark excitons in alloyed TMD monolayers

In last chapter, the band gap and spin-orbit engineering of alloyed TMDs have been discussed. Despite the lattice size changes and energy tunability, it is worthwhile to notice that the two-dimensional lattices generally have exciton binding energy up to 200 meV[1–5]. This overall large binding energy ensures stable excitons in all the alloyed TMD monolayers. With varying the band gap and spin-orbit coupling, those very robust excitons can be used as advantageous indicators to study the carrier dynamics around the band edge. Studying the behavior difference of excitons at different 2D alloyed lattice can also benefit the understanding of their recombination dynamics and mechanism.

Luminescence from spontaneous radiative recombination of excitons in semiconductor and nanostructures are lying at the heart of their optical and optoelectronic applications[6, 7]. Nanostructures including quantum well (QW) and quantum dot (QD) can spatially confine electrons and give rise to quantum-size effects. Recently quantum systems of semiconductors become more important as the confined excitons (carriers) are promising candidate for quantum information technologies[8–10]. Other than in bulk semiconductors, the excitons in QW and QD usually contain multitude of energy scales that can be distinguished: 1) quantum confinement energy, 2) electron-hole interactions, including the direct (electrostatic) and the exchange (spin) Coulomb interactions, which will lead to energy

splittings in the exciton level structure, the so called exciton fine-structure[11–15]. Those fine-structures include spin-forbidden (the so-called dark states) and spin-allowed (bright states) transitions. The bright excitons are highly radiative with high-oscillator strength and short lifetime. The dark excitons need large external energies (electric or magnetic) to become optically active, and thus their recombination can be prevented by Pauli exclusion principle, resulting in longer lifetime up to even micro-second scale[15, 16].

Similar to quantum dots and quantum wells, enhanced exchange coulomb interactions can be observed in two-dimensional TMD monolayers due to the quantum and dielectric confinement from out-of-plane direction. Therefore, exciton fine structures can exist at both A and B excitonic levels of 2D TMD monolayers. The existence of bright and dark states will turn the excitonic absorption and recombination from a one-level system to two-level system (if we consider A-B spin-orbit split, it is actually a four-level system. The relaxation from higher energy level B to the lower one A will be discussed specifically in the last section of this chapter). As the energy difference between bright and dark excitons (Δ_{BD}) are theoretically predicted at merely several to dozens of meV scale[17, 18], the interactions between the bright (singlet-like) and dark (triplet-like) states will be strongly affected by external energy such as thermal, electric and magnetic energies[11, 15, 19]. It will also affect the recombination dynamics dramatically.

Therefore, the behaviors of bright and dark excitons and the interactions between them can be extremely important for the fundamental understanding of the exciton-related properties in 2D TMDs, which always has both fundamental and practical significance to the field. The experimental observation of the dark states in TMD monolayers are very difficult since large external magnetic and electric energies are needed to flip the spin and make dark states brightened[19–23]. The current experimental evidences of dark excitons are concentrated in WX_2 ($X=S$ and Se) TMDs, which are believed to have the largest Δ_{BD} among the four binary

TMDs, up to 30~40 meV[17, 20, 22]. However, the MoX_2 ($\text{X}=\text{S}$ and Se) TMDs should have smaller Δ_{BD} than WX_2 due to smaller spin-orbit coupling[17, 19]. The smaller Δ_{BD} is likely to cause stronger bright-dark interaction and more complicated exciton recombination dynamics, making MoX_2 monolayers interesting platform to provide critical insight about excitons in two-dimensional lattice.

In this chapter, we discuss a set of optical experiments that provide evidence of the dark excitons in TMD ternary alloys $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($0 \leq x \leq 1$). By varying the Se atomic concentration, the bright-dark energy split Δ_{BD} can be modulated, and the subsequent changes of excitonic emission are monitored by temperature dependent PL and time-resolved PL spectroscopy. The relatively small and alloy-dependent Δ_{BD} will generate subtle changes among the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayers, making the exciton dynamics very diverse.

4.1 The dark excitons in alloyed TMD monolayers

4.1.1 Spin splitting of conduction band in TMD monolayers

Spin-orbit coupling (SOC) and spin exchange are the two dominant spin-related interactions in TMD monolayers. The effects of spin-orbit interaction are particularly noticeable in materials without inversion symmetry, e.g., the TMD monolayers. We have shown in last chapter that the valence band of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayer split into two spin-related sub-bands with energy differences ΔE_{BA} from 137~229 meV (the SOC of WX_2 are even higher at ~ 400 meV). The reflectance spectra of MoX_2 and WX_2 at 10 K are shown in Fig. 4.1. In Fig. 4.1(b) all the spectra are horizontally offset to set each A exciton energy position as zero. The ΔE_{BA} of WX_2 is apparently much larger than MoX_2 , due to the much larger mass of W atoms.

Figure 4.1: Reflectance spectra of MoX_2 and WX_2 at 10 K. (a) shows the reflectance spectra in stacking plot. In (b) all the spectra are horizontally offset to set each A exciton energy position as zero.

The effects of SOC in the conduction band (CB), in contrast, are much weaker since the band is remote to the atom nucleus. Although it is small, the interband coupling to remote bands results in a finite CB splitting[24, 25]. The small CB split is very difficult to detect both electrically and optically. Using an extension of the $\vec{k} \cdot \vec{p}$ original model[26], the CB splitting has been theoretically revealed[17, 26]. Fig. 4.2 shows the calculated spin-orbit splitting of the conduction band around the K point for TMD monolayers including MoX_2 and WX_2 [17]. The black and yellow traces are from tight-binding model and DFT, suggesting good agreement among each other. From the calculation, the Mo, W, S and Se atoms generally give contributions to the CB split Δ_C in comparable energy scale, but the contribution from the transition metals has opposite sign to that from the chalcogen atoms. The metal contribution is positive (meaning the spin-up sub-band is higher than the spin-down sub-band), while the chalcogen atoms have negative contribution. Because of the mass difference, W and Se have larger absolute contribution values than Mo and S. Thus WS_2 combines the largest positive with the smallest negative contribution, resulting in a clearly positive

splitting ($\Delta_C > 0$). On the contrary, MoSe₂ combines the smallest metal SOC (positive) and the largest chalcogen SOC (negative), resulting in negative splitting ($\Delta_C < 0$), as shown in Fig. 4.2.

Figure 4.2: Calculated spin-orbit splitting of the conduction band around the K point for TMD monolayers. The black and yellow traces are from tight-binding model and DFT, respectively[17].

Among the four binary TMDs, MoS₂ is special as it contains the smallest positive (Mo) and negative (S) contributions. So the sign of its CB split Δ_C is not well understood. While its sign is still in debate[17–19], the split energy value should be very small. In general, the CB split, although small can split the spin-related sub-bands as well as the larger VB split do. The spin non-degenerate levels will create forbidden transitions according to spin selection rule, which are the dark states in TMDs.

4.1.2 Identification of dark excitons in alloyed TMD monolayers

Since both CB and VB splits exist in TMD monolayers, we are able to experimentally study the multiple transitions in the MoS₂(1- x)Se_{2 x} alloyed monolayers.

The typical band structure at K point of TMD monolayers is show in Fig. 4.3(a). It is noticeable that in this chapter, only the K valley (without the K' with opposite momentum and degenerate energy level) will be considered as we mainly focus on the intra-valley recombination dynamics of bright and dark excitons. The physical picture and properties will be the same for carriers in the two valleys unless one of the valley is activated, which will be discussed in the next chapter (chapter 5).

Figure 4.3: The typical band structure at K point of TMD monolayers and the exciton representation showing excitonic levels. (a) is the direct band gap at K point. (b) is the converted exciton representation from the band edge states. Solid and dash lines show bright and dark excitons, respectively.

The VB split is large and positive among all the TMDs (Fig. 4.1), resulting in a higher spin-up sub-band ($|\uparrow\rangle$) and a lower spin-down sub-band ($|\downarrow\rangle$). The CB split Δ_C will be varied. In Fig. 4.3(a) we show a case with clear positive CB split (WX_2 like). In total there will be four transitions around band edge, two are spin-allowed while the other two are spin-forbidden. When converted to exciton representation showing excitonic levels (Fig. 4.3(b)), fine structure containing bright ($|K_{e\uparrow}K_{e\uparrow}\rangle$ or $|K_{e\downarrow}K_{e\downarrow}\rangle$, shown in solid line) and dark ($|K_{e\downarrow}K_{e\uparrow}\rangle$ or $|K_{e\uparrow}K_{e\downarrow}\rangle$, shown in dash line) states can be found in both A and B levels. Due to the intercross transition between CB sub-bands and VB sub-bands, one can

see the bright-dark splits Δ_{BD} of A and B excitonic levels have the same scale (equal to Δ_C) but opposite order. The luminescence from B (bright) exciton can be regarded as hot luminescence as the carriers at B level with higher energy prefer relaxation to A level with lower energy. The B to A relaxation will be discussed specifically in the last section of this chapter, and thus we can separate the A and B levels and emphasize in a simplified two-level system at one time, while the properties of the A and B will be opposite and confirm the validity for each other.

Figure 4.4: The simplified two level system containing one bright and dark states. The bright and dark states are shown in green solid line and red dashed line, respectively. When the bright-dark split Δ_{BD} changes sign, the bright-dark levels will swap. The carriers (excitons) are shown in blue spheres, which change the occupation and population with changing temperature.

Fig. 4.4 shows a schematic diagram for the simplified two level system containing one bright (green solid line) and dark (red dashed line) states. When the bright-dark split Δ_{BD} changes sign, the bright-dark levels will be swapped. Besides the fact that the A and B levels have reversed Δ_{BD} , the Δ_{BD} itself (at A or B) which is inherited from CB split Δ_C also has possibilities to change sign when the SOC is modulated by varying alloy components.

The Δ_{BD} has small absolute value, which is generally smaller than 40 meV. So the occupation and population of the two levels will be strongly affected by temperature, as shown in Fig. 4.4. At low temperature, most of the carriers

(excitons) will occupy the lowest level. As temperature increases, the upper level will gradually be occupied via thermal energy induced energy fluctuation. At high temperature (e.g., room temperature, 295 K), the thermal energy 25 meV is comparable to or even larger than the energy split $|\Delta_{BD}|$, therefore the upper level will be more populated with carriers (excitons). As a result, temperature dependent PL spectra will reveal the thermal energy modulated population differences between the two levels.

Figure 4.5: The temperature dependent PL spectra of the alloyed monolayers. (a), (b), (c), (d) and (e) display the PL spectra for alloyed monolayers from MoS_2 to MoSe_2 .

Fig. 4.5 shows the temperature dependent PL spectra of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$

monolayers excited by a 2.33 eV excitation (532 nm solid state laser). The off-resonance excitation can pump carriers to high energy and occupy both A and B excitonic levels. In Section 3.3.1 the voigt profile fitting of the PL spectra has been introduced. Using the voigt function, we successfully obtain the exciton and trion peaks. In Fig. 4.5, the fittings of the RT (295 K) spectra are illustrated with shaded peaks. The spectra at lower temperatures, especially the liquid helium ones show clear profile of exciton and trion components. For the alloyed samples (except MoS₂), the *n*-doping level is high so that the trion emission is strong at low temperature, which has been discussed in Section 3.3.2. In order to emphasize the exciton intensity, the upper part of the trion peaks at 10 K are excluded from the plot (blue trace) to maintain a suitable vertical scale. All the exciton peaks have strong temperature dependences, and some are easy to distinguish. For example, the B exciton peak of MoS₂ at RT (green shaded in Fig. 4.5(a)) is less prominent than that at low temperature, and the A exciton peak of MoS_{1.6}Se_{0.4} at RT (red shaded in Fig. 4.5(b)) is much weaker than the low temperature ones. However, for some exciton peaks, it is not intuitive to obtain their profile and intensity. By fixing the Δ_{BA} and Δ_{TA} (energy differences between B and A excitons, Trion and A excitons) and gradually increasing the homogeneous broadening of the excitons according to the thermal energy increase and exciton-phonon interactions (see details in Section 3.3.1)[27–29], the profiles of all the exciton peaks can be reliably resolved at each temperature.

The temperature dependent PL intensity of A and B excitons (integrated peak area) for each alloy components are shown in Fig. 4.6. All the PL intensity data points are normalized by the PL intensity at room temperature (I/I_{RT}), in order to highlight the temperature dependence of the excitons. The MoS₂, MoS_{1.6}Se_{0.4} and MoSSe alloyed monolayers yield prominent PL emission via both A and B excitonic recombinations, and their exciton peak intensities (I/I_{RT}) display clearly opposite temperature dependencies, as shown in Fig. 4.6(a), (b)

and (c). The opposite temperature dependencies of A and B exciton intensity are in good consistence with the swapped bright-dark splits of A and B levels, suggesting that there exists two interacting states in both A and B excitonic levels. The bright states in TMD monolayers can always yield photons efficiently at all the temperatures due to the giant oscillator strength and exciton binding energy which is one order of magnitude larger than thermal energy. The strong temperature dependence indicates that one of the two split levels should be a dark exciton state.

Figure 4.6: The temperature dependent PL intensity of A and B excitons among the alloyed monolayers. (a), (b), (c), (d) and (e) denotes the alloyed monolayers from MoS₂ to MoSe₂.

In Fig. 4.6(a), the A and B exciton intensity of MoS₂ decreases and increases

with decreasing temperature, showing the bottom states in A and B levels are dark and bright states, respectively, which is identical to the energy diagram shown in Fig. 4.3(b). So the excitonic configuration of MoS_2 is WX_2 like, which is well accepted to have the lowest A excitonic sub-band as a dark state. As Se atomic concentration increases to $x = 0.2$ ($\text{MoS}_{1.6}\text{Se}_{0.4}$, Fig. 4.6(b)), both A and B exciton intensity display weak temperature dependence. When the Se further increases to $x = 0.5$ (MoSSe , Fig. 4.6(c)), the temperature dependence of A exciton intensity becomes inversely proportional to temperature, in the meanwhile the temperature dependence of B exciton intensity becomes proportional to temperature. The exciton behavior is opposite to MoS_2 , but consistent with $\text{MoS}_{0.4}\text{Se}_{1.6}$ and MoSe_2 (Fig. 4.6(d) and (e)). As the CB split energy Δ_C of MoSe_2 has reversed sign comparing to WX_2 , its bright-dark split energy is also swapped from WX_2 . As a result, for MoSSe , $\text{MoS}_{0.4}\text{Se}_{1.6}$ and MoSe_2 , the bottom sub-state of A excitonic level is bright ($\Delta_{BD} < 0$), and the bottom of B is dark ($\Delta_{BD} > 0$). It is also noticeable that for MoSe_2 and the more Se alloy $\text{MoS}_{0.4}\text{Se}_{1.6}$, the B emission is very weak and insufficient for comparison with varying temperature, which is another evidence that the bottom B sub-band is dark state.

Comparing the temperature dependent exciton behaviors of all the alloyed monolayers, it can be seen that the alloy engineering has strongly affected the interactions between the bright and dark excitons. Using A excitonic level as an example, MoS_2 has the bright-dark split $\Delta_{BD}(\text{MoS}_2) > 0$, while MoSe_2 has $\Delta_{BD}(\text{MoSe}_2) < 0$. By increasing the Se atomic concentration x of the alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$, the Δ_{BD} of A excitonic level will experience transition from positive to negative, and the transition is likely to happen at $\text{MoS}_{1.6}\text{Se}_{0.4}$. At the transition point, the bright and dark states are too close to be affected by thermal energy, leading to the temperature independent PL intensity via excitonic recombination. The B excitonic level will experience the similar transition, with Δ_{BD} from negative to positive.

4.1.3 The bright-dark split energy in alloyed TMD monolayers

The evolution of the excitonic peak intensity in alloyed TMD monolayers with varying temperature can probe the dark excitons and energy order between dark and bright states. Besides that, we also notice that the evolution curves among alloys are dramatically different: 1) some are placid and some are steep, 2) the sharp transition points from RT plateau to low temperature plateau are different, 3) the evolution curve of $\text{MoS}_{1.6}\text{Se}_{0.4}$ as a special case has nearly no temperature dependence.

We then analyze the bright state population in a simple two-level model with a bright and dark states. In thermal equilibrium, the bright state population follows the Boltzmann distribution[19, 22]:

$$N_B(T) = \frac{\exp(-\Delta_{BD}/k_B T)}{\exp(-\Delta_{BD}/k_B T) + 1} \text{const}, \quad (4.1)$$

where $N_B(T)$ is the temperature dependent bright state population, which can be monitored through the exciton peak intensity in steady state PL spectroscopy. k_B is the Boltzmann constant. And the sign of the bright-dark split energy Δ_{BD} determines whether the lower-lying state is bright ($\Delta_{BD} < 0$) or dark ($\Delta_{BD} > 0$).

It is noticeable that the dark (triplet-like) intravalley excitons and the singlet-like intervalley excitons are degenerate and occupy the lowest energy, so do the triplet-like intervalley excitons and the bright excitons. This means that the intervalley recombinations can affect the simple two-level model. However, on one hand, the intervalley recombination is a phonon assisted process which is less prominent comparing to intravalley recombination. On the other hand, in thermal equilibrium, the fraction of the total exciton population in bright states via both intra- and intervalley recombinations is given by $\exp(-\Delta/k_B T)/[2\exp(-\Delta/k_B T) + 2]$ [19]. This expression yields the same characteristic temperature variation as the

simple two-level model introduced above. From fitting Eq. (4.1) to the experimentally determined variation of $N_B(T)$ with temperature, we are able to obtain the Δ_{BD} of all the alloyed monolayers, as shown in Fig. 4.7.

Figure 4.7: The fitting of the A and B excitonic PL intensity among the alloyed monolayers. (a), (b), (c), (d) and (e) denotes the alloyed monolayers from MoS_2 to MoSe_2 .

The fittings of A and B excitons in MoS_2 , $\text{MoS}_{1.6}\text{Se}_{0.4}$ and MoSSe yield Δ_{BD} with opposite sign, which is consistent with the band diagram where the bright-dark fine-structures originate. The fittings of the A exciton in MoS_2 and MoSe_2 give positive and negative Δ_{BD} , respectively. All the Δ_{BD} values are collected and shown in Table. 4.1.

The $|\Delta_{BD}|$ values from fittings of A and B excitons in MoS_2 , $\text{MoS}_{1.6}\text{Se}_{0.4}$

Table 4.1: Table of fitted bright-dark split Δ_{BD} of A and B excitons among the alloyed TMD monolayers.

Samples	MoS ₂	MoS _{1.6} Se _{0.4}	MoSSe	MoS _{0.4} Se _{1.6}	MoSe ₂
$\Delta_{BD}(A)$ (meV)	11.2 ± 1.3	0.27 ± 0.14	-8.5 ± 1.4	-14.9 ± 1.1	-21.1 ± 1.3
$\Delta_{BD}(B)$ (meV)	-11.2 ± 1.7	-0.21 ± 0.11	8.2 ± 1.6		

and MoSSe are nearly the same, suggesting that the bright-dark split order are swapped from A excitonic level to B level. These results also prove that the fitting with the simplified two-level model is self-consistent and reliable. The A exciton bright-dark split changes from 11.2 ± 1.3 meV (MoS₂) to -21.1 ± 1.3 meV (MoSe₂), as illustrated in Fig. 4.8. MoS₂ has been proved to have dark exciton as the bottom energy level, which could also explain the relatively poor optical properties and quantum efficiency of MoS₂ among the MoX₂ family[4, 28, 30, 31].

Figure 4.8: The evolution of bright-dark split Δ_{BD} along the alloyed TMD monolayers by varying Se atomic concentration. The bright and dark states and transitions are denoted by green solid line and orange dashed line.

MoS_{1.6}Se_{0.4} could be the most special case among the MoS_{2(1-x)}Se_{2x} alloys, as the bright-dark split is as small as ~ 0.27 (-0.21) meV. In this minimized energy split, the interactions between bright and dark states are so strong that the two can form a superposition state. This superposition state will not be affected by thermal energy at all since there are no population competition between the

dark and bright states. It will also combines the properties of both bright and dark excitons, for examples, the large oscillator strength (from bright) and long-lived exciton lifetime (from dark). It will also affect the exciton recombination, especially the intervalley transitions significantly, which will be further discussed in the next chapter (Chapter 5).

As the Se atomic concentration increases after $\text{MoS}_{1.6}\text{Se}_{0.4}$, the Δ_{BD} becomes negative (-8.5 ± 1.4 , -14.9 ± 1.1 , and -21.1 ± 1.3 meV for MoSSe , $\text{MoS}_{0.4}\text{Se}_{1.6}$ and MoSe_2 , respectively). The lowest exciton level becomes bright, and the $|\Delta_{BD}|$ value increases with increasing Se atomic concentration, as shown in Fig. 4.8. The results can well explain the previous literatures showing great optical quality of MoSe_2 monolayers[28, 32–34].

It is worthy to notice that the PL spectra (A exciton related) of WX_2 are always more complicated than the MoX_2 , especially MoSe_2 [2, 28, 35]. Here we show the low temperature PL spectra of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ and WX_2 monolayers to compare their features, as shown in Fig. 4.9. Fig. 4.9(a) shows the PL spectra of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloyed monolayers and (b) shows the PL spectra of WX_2 monolayers. The spectra of both WS_2 and WSe_2 have peak complexes along the low energy side of the A exciton peaks. In stark contrast, MoSe_2 , $\text{MoS}_{0.4}\text{Se}_{1.6}$ and MoSSe (the red, wine and orange traces in Fig. 4.9(b)) have very “clean” spectra, which only contains two sharp exciton and trion peaks.

The bright-dark split model can well explain the distinct PL features among the TMD monolayers. As shown in Fig. 4.9(c), a WX_2 like A excitonic energy diagram has dark exciton as the lowest energy level. At low temperature, the carriers will mostly occupy the dark states, and thus the excitons will be prevented from recombination. In this way, large amount of carriers will have more chances to hop to the localized states in the energy band gap, or form bi-excitons. The long-lived dark exciton will enhance the emission from localized states, which is the reason that the recent observations of single photon emission from localized

Figure 4.9: The PL profile of TMD monolayers at 10 K and the effects of dark excitons. (a) shows the PL spectra of MoS₂(1-x)Se_{2x} alloyed monolayers at 10 K. (b) shows the PL spectra of WX₂ monolayers at 10 K. (c) illustrates the effects of dark excitons to the band edge transition.

states in two-dimensional TMDs are concentrated in WSe₂[5, 9, 36, 37]. Similarly, we find that the MoS₂ also has multiple band edge and localized states besides its exciton and trion, as shown in blue trace of Fig. 4.9(a), which is due to the low-lying dark states. The MoS_{1.6}Se_{0.4} has mixed features, the exciton and trion peaks are clean and prominent which is due to the bright nature of MoSe₂, while there is also indispensable localized emission band besides which is from the dark nature of MoS₂.

4.2 The time-resolved PL spectroscopy of alloyed TMD monolayers

The time-resolved photoluminescence (TRPL) spectroscopy can monitor the carrier dynamics by detecting the decay of the emitted photons from a material system. The decay lifetime detected in TRPL spectra combine the contributions

from both radiative and non-radiative recombination channels:

$$\frac{1}{\langle\tau\rangle} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}, \quad (4.2)$$

where $\langle\tau\rangle$ is the average photoluminescence lifetime, τ_r and τ_{nr} are the radiative and non-radiative lifetimes. For the TMD monolayers, the radiative channel is mainly from the bright exciton recombination, which will be very fast due to the large exciton binding energy and giant oscillator strength[29, 38]. The dark excitons can prevent the carriers (excitons) from recombination and serve as one of the non-radiative channels. If the dark state is populated, it can also serve as a reservoir of carriers. Its long-lived lifetime will force carriers to other channels including non-radiative ones, as shown in Fig. 4.9 of Section 4.1.3. Therefore, the occupation of dark exciton levels will result in longer average lifetime, which can be detected by TRPL.

In fact, previously TRPL has been used as important experimental evidences for identification of dark states in quantum well and quantum dot[11–15]. By varying temperature, the occupation of the dark states can be enhanced or reduced to realize the change of lifetime. The measurement methodology has been introduced thoroughly in Section 2.3.3. We used a 500 nm pulse excitation (8 MHz, 100 fs) to excite the sample, and the photoluminescence emission from sample was analyzed by a single photon avalanche diodes (SPADS) to resolve the time decay. A series of long-pass and short-pass filters were used to select the specific exciton peaks of interest.

Fig. 4.10 shows the TRPL spectra of A and B excitons of the alloyed monolayer at 295 K (room temperature). All the spectra contain one fast and one relatively slow relaxation component. The fast one and slow decay are likely to be from an initial nonthermalized hot relaxation and the following thermalized relaxation which contains radiative and non-radiative channels[39, 40]. Therefore,

Figure 4.10: The time-resolved PL spectra of the alloyed TMD monolayers at 295 K (room temperature). (a) and (b) indicate the A exciton and B exciton, respectively.

a biexponential decay function can be used to fit the TRPL spectra:

$$I = I_0 + A_1 \exp \left[\frac{-(t - t_0)}{\tau_1} \right] + A_2 \exp \left[\frac{-(t - t_0)}{\tau_2} \right], \quad (4.3)$$

where I_0 is the intensity offset generated by background signal. τ_1 , τ_2 and A_1 , A_2 are the lifetime and amplitude of the two exponential components.

For A excitons emission at 295 K (Fig. 4.10(a)), from MoS₂ to MoSe₂, the lifetime increases, which indicates that the dark states of MoSSe and MoSe₂ are more populated than MoS₂. At 295 K, the thermal energy will activate the upper sub-band of the A excitonic level, which is bright for MoS₂ and dark for MoSe₂ according to previous results. The TRPL results are in agreement with the bright-dark two level model. For B excitons emission at 295 K (Fig. 4.10(b)), the hot relaxation (the fast decay) is dominate for both MoS₂ and MoSSe, which matches the hot luminescence nature of B excitonic emission. The thermalized relaxation (the slower decay) shows comparable lifetime for MoS₂ and MoSSe which is larger than that from the A exciton. This fact suggests that the emission from B level is strongly affected by the B to A relaxation, which will indispensably change the

dynamics and lifetime of B exciton emission, thus making the TRPL data of B not applicable to the identification of dark states. The B to A relaxation will be discussed specifically in next section of this chapter.

It is interesting to observe that the PL lifetime of A exciton PL emission among the alloyed monolayers at 78 K display the opposite trend, comparing to 295 K spectra. As shown in Fig. 4.11, at 78 K, the MoS₂ lifetime (blue trace) becomes the longest, while the lifetime of MoSSe and MoSe₂ (orange and red traces) are shorter. Like quantum dot, the bottom sub-band of MoS₂ is a dark state. So when the temperature is low, the transition from low-lying dark state to the higher bright state will be largely suppressed. For MoSSe and MoSe₂, the bottom exciton is bright, so the temperature decrease will constrain the electrons to the lower bright states, thus making the average PL lifetime shorter or comparable to the ones at room temperature.

Figure 4.11: The time-resolved PL spectra of A exciton among the alloyed TMD monolayers at 78 K.

Fig. 4.12 indicates the temperature dependent TRPL spectra of A excitons among the alloyed TMD monolayers. Fig. 4.12(a), (b) and (c) denote the spectra of MoS₂, MoSSe, and MoSe₂. As temperature decreases from 295 K to 78 K, the fast exponential channel (with lifetime τ_1) becomes faster and faster until

reaching the instrument response function (IRF), which is ~ 25 ps. This global decrease of the decay time τ_1 among all the alloyed monolayers indicates that the channel has no relationship with the excitonic recombination process including bright-dark interactions. Given its ultrafast time scale, it is likely due to the hot carrier relaxation in the non-thermalized regime. The low temperature will cool down the lattice vibration and carrier scattering, and thus accelerate the relaxation process, leading to the decrease of τ_1 .

Figure 4.12: The temperature dependent TRPL spectra of the alloyed TMD monolayers. (a), (b) and (c) denote the alloyed monolayers, MoS₂ MoSSe, and MoSe₂, respectively.

Besides the above ultrafast channel, the slower decay channel must be related to excitonic recombination which takes place after the non-thermalized regime terminates. The decay channel (with lifetime τ_2) experiences the bright-dark interactions and its temperature dependence follows the two-level model shown in Section 4.1.3. As shown in Fig. 4.12(a), the temperature dependent TRPL of A exciton in MoS₂ shows clear increase of the lifetime τ_2 . It can be inferred

that the low temperature constrains the carriers to the bottom dark states, thus the long-lived dark excitons dramatically change the lifetime τ_2 . Both MoSSe and MoSe₂ have bottom sub-bands as bright states, which will be more populated with decreasing temperature. The shortening of the lifetime τ_2 at lower temperature is consistent with the two-level model. It is also noticeable that the τ_2 decreases more prominently in MoSSe than in MoSe₂. This difference can be explained using the various bright-dark split Δ_{BD} obtained in Section 4.1.3. The A level of MoSSe and MoSe₂ have $\Delta_{BD}(\text{MoSSe}) \approx -8.5$ meV, and $\Delta_{BD}(\text{MoSe}_2) \approx -21.1$ meV. 98.6 K and 244.9 K are needed to provide enough thermal energy to overcome $\Delta_{BD}(\text{MoSSe})$ $\Delta_{BD}(\text{MoSe}_2)$, respectively. At temperature range from 295 to 98.6 K, the occupation of the bottom bright state of MoSSe will keep increasing due to the reduced thermal energy. While at temperature range from 295 to 244.9 K, the occupation of the bottom bright state of MoSe₂ will keep increasing due to the reduced thermal energy. At temperatures below the 98.6 and 244.9 K for MoSSe and MoSe₂, most of the carriers already occupy the bright states, therefore the lifetime is no longer temperature-dependent.

4.3 The relaxation from B to A excitonic states

Besides the prominent PL emission from A excitonic level, there is always an interesting phenomenon in the TMD monolayer system: given that the A exciton is at the lowest excited energy level, there is still observable emission from the B exciton recombination. This hot luminescence from B excitons points out that the relaxation from B to A excitonic states is different to the usual non-thermalized carrier relaxation in semiconductors. Previously we have shown that the alloy engineering of TMD can modulate the spin-orbit coupling and the exciton dynamics, from which we now address the issue of the relaxation from B to A excitonic states.

As A exciton is the lowest excited energy level which will be occupied by most of the carriers in the system during the non-thermalized process, it can be used as a reference to evaluate the population in B excitonic level. We use the ratio between PL intensity of the B and A excitons (I_B/I_A) to describe the degree of relaxation from B to A excitonic levels. Fig. 4.13(a) shows I_B/I_A of different alloys by varying the Se atomic concentration x . The red and blue traces are I_B/I_A data points at 295 and 10 K. At both temperatures, I_B/I_A decreases as the Se atomic concentration x increases. Especially, $\text{MoS}_{0.4}\text{Se}_{1.6}$ and MoSe_2 have very limited PL emission from B exciton as the I_B/I_A is nearly zero.

Figure 4.13: The ratio between PL intensity of the B and A excitons (I_B/I_A) in $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayers. (a) shows Se atomic concentration dependence of the I_B/I_A ratio. (b) shows the temperature-dependence of the I_B/I_A ratio. The wine dashed line indicates $I_B/I_A = 0$ which means very limited PL emission of B exciton.

From previous results, we know that the energy difference between B and A levels Δ_{BA} increases as x increases. In normal conditions, the smaller the energy difference between two levels is, the transition (relaxation) between the two levels will be more efficient. However, in $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ the situation is totally opposite. As Δ_{BA} is smaller (MoS_2), the B emission is more prominent, indicating less efficient relaxation from B to A. This result suggests that there are other factors

which have more impact on the B to A relaxation than Δ_{BA} .

Fig. 4.13(b) shows the temperature-dependence of the I_B/I_A ratio in the alloyed monolayers MoS_2 , $\text{MoS}_{1.6}\text{Se}_{0.4}$ and MoSSe . At room temperature, the I_B/I_A is more or less at the same level for the three alloys. With decreasing temperature, I_B/I_A of MoS_2 increases significantly, I_B/I_A of $\text{MoS}_{1.6}\text{Se}_{0.4}$ remains nearly unchanged, and I_B/I_A of MoSSe decreases. Those characteristic temperature variations indicate that the B to A relaxation is not a phonon-assisted process following simple Boltzmann distribution. By carefully investigating the excitonic levels and fine-structures, the dark states and the order of bright-dark split must play a key role in determining the relaxation from B to A excitonic levels. Fig.

Figure 4.14: The excitonic level energy diagram with fine-structures.

4.14(a) and (b) show the excitonic level energy diagram including fine-structures of MoS_2 and MoSe_2 , respectively. The system has three relaxation process with different rates: B to A relaxation (γ_{BA}), B bright excitonic recombination (γ_B) and B bright excitonic recombination (γ_A). The PL intensity of B exciton is related to the population in the bright state of B level, which follows the rela-

tionship:

$$N_B(T) = \frac{e^{1/\gamma_B}}{e^{1/\gamma_A} + e^{1/\gamma_{BA}}}, \quad (4.4)$$

since γ_B and γ_A are comparable according to the TRPL spectroscopic study in Section 4.2, the scale of γ_{BA} will largely change the PL intensity of B exciton. In MoSe₂, the bottom sub-states in B and A are dark and bright states. As the bottom sub-state of A is bright state (large oscillator strength), the carriers recombine with hole efficiently. It will release space for the carriers from higher energy levels efficiently. So the B to A relaxation which mainly takes place between those two bottom sub-states will also be efficient. However, in MoS₂, the bottom sub-state of A is dark. Large amount of carriers will occupy the sub-state for long time since they are prevented from recombination, especially at low temperature. So the B to A relaxation will be suppressed as there is no space at bottom sub-state of A. In the meanwhile, most of the hot carriers at B excitonic level occupy the bottom sub-state which is a bright state. In this manner the B excitonic level bright exciton of MoS₂ can have sufficient time to recombine and emit photons. As temperature decreases, the B excitonic level is getting brighter.

4.4 Summary

In conclusion, the TMD monolayers (MoX₂ and WX₂) have spin-orbit coupling (SOC) in both valence and conduction band. The inter-cross transitions between the conduction sub-bands and valence sub-bands result in spin-allowed and spin-forbidden states. Those are the bright (singlet-like) and dark (triplet-like) excitons in TMD. By making ternary alloyed MoS_{2(1-x)}Se_{2x} ($0 \leq x \leq 1$) monolayers, the conduction band split energy Δ_C can be modulated, leading to the tuning of bright-dark split Δ_{BD} . Using temperature-dependent PL and time-resolved PL spectroscopy, we obtain sufficient evidences to prove the existence of dark excitons and the energy position of them in the alloyed monolayers. The interac-

tions between the bright and dark excitons are found to be vital for the exciton dynamics and recombination.

By fitting the temperature-dependent PL peak intensity of both A and B excitons with a simplified two-level model, we are able to obtain the Δ_{BD} values among the alloyed $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayers. For each alloy, the Δ_{BD} has the same value with opposite sign for A and B exciton. The Δ_{BD} changes with varying the Se atomic concentration. Taking A exciton as a paradigm (the opposite is B then), the Δ_{BD} from 11.2 ± 1.3 meV for MoS_2 to -21.1 ± 1.3 meV MoSe_2 . During the evolution, the order of the bright-dark energy levels is swapped, due to the distinct SOC contributions from S and Se atoms. The transition point which has nearly zero Δ_{BD} has been identified to be $\text{MoS}_{1.6}\text{Se}_{0.4}$ among the alloys. The PL intensity from both A and B excitons of $\text{MoS}_{1.6}\text{Se}_{0.4}$ have no temperature-dependence, since the zero Δ_{BD} is not subject to thermal energy change. The zero Δ_{BD} also create a superposition state which combines the properties of bright and dark excitons.

The relaxation from B to A excitonic levels is determined by the bright-dark split order, as well as the excitonic recombinations. In MoS_2 , the B to A relaxation takes place between a bright (bottom B) and a dark (bottom A) states and is suppressed by the fulfilled dark state. Therefore, the carriers at B has sufficient time to recombine and emit photons. The situation is reversed for MoSe_2 , where the bottom sub-states are dark (B) and bright (A), the relaxation will be unobstructed as the bright excitons in A level recombine efficiently and leave plenty of spaces for the carriers from higher energy places.

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5 Tailoring Valley Polarization and Valley Coherence of TMDs via Alloy Engineering

The valley polarization and the relevant physical properties of TMD monolayers are very promising for future optoelectronic and electronic applications, as they provide an additional valley degree of freedom (DOF) to the carriers[1–3]. The spin-valley interlock at the K and K' valleys can link the translation momentum, spin angular momentum and orbital angular momentum of electrons, providing a higher dimensional system with multiple DOFs. These multiple DOFs are naturally suitable for encoding information, and promotes the concerning of the “valleytronics”.

The valley selection rules can create a lot of novel and important physical effects, including valley polarization dichroism, valley Hall, spin valley Hall effects[4–7]. By selectively activating and filling carriers (using circular polarized excitation) to the conduction band of one of the K and K' valleys, the valley polarization can be observed. These carriers which originate from the K and K' valleys will carry left- and right-handed angular momentums, respectively, and thus can be spatially separated without the presence of magnetic field. Moreover, the two sets of separated carriers will process oppositely polarized spin-states. In this way, the spin-polarized currents can be utilized together with other spintronics

including spin transistors and giant magnetoresistance (GMR) devices, to connect the optical pumping with spin-transport[3, 8, 9].

All the above physical and technological merits lying in valley physics will need effective mechanism to suppress the carrier intervalley scattering. However, there are depolarization channels between the K and K' valleys, such as the phonon-assisted intervalley scattering. Most of the literature report that the valley effects will be only valid at low temperature, typically close to liquid nitrogen range. With increasing temperature the valley polarization fades away rapidly, which is an evidence for the phonon-related effects according to a Boltzmann distribution[5–7]. Since 2012, researchers have been trying to solve the intervalley depolarization problems and improve the valley stability. It can be noticed from the recent literature that different TMDs might have case-by-case valley polarization stability, making valley polarization last to different temperatures. In some cases of WS_2 , some even reported room temperature valley polarization and coherence[10–12]. However, those demonstrations are mostly equivocal with missing solid mechanisms, and have not been well accepted so far.

In this chapter, systematical studies of valley polarization and valley stability versus temperature have been done on the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($0 \leq x \leq 1$) alloyed monolayers. In the previous chapter, we have shown that the alloy engineering can change the bright-dark split and the interactions between the two states, leading to distinct intravalley dynamics. Here, it can be found that the interactions between bright and dark states can modulate the intervalley dynamics as well. Since the dark excitons are stable with long lifetime up to μs level[13–17], the intervalley depolarization between the dark excitons are minimized. The alloy engineering can modulate the interactions between bright and dark states, and thus change the valley polarization degree of the bright states. By carefully designing the alloys, we are able to enhance the valley stability of TMDs.

5.1 Valley Polarization of A exciton in alloyed monolayers

5.1.1 Calibration of PL intensity of excitons

Figure 5.1: The power dependent PL spectra of the alloyed monolayers. (a), (b) and (c) display the power dependent PL spectra for alloyed monolayers from MoS₂ to MoSe₂.

To measure the valley polarization, we need to monitor the exciton peak intensity which stands for the intensity of intravalley radiative recombination, as shown in Fig. 1.7(b). We first calibrate the PL intensity of excitons by chang-

ing the pump fluence of the excitation. Fig. 5.1 shows the power-dependent PL spectra of the alloyed monolayers at 30 K excited by a 2.33 eV excitation (532 nm solid state laser). This off-resonance excitation can excite both A and B excitonic levels to show the fluence-dependence of all the excitons.

As shown in the figures, the PL intensity of the excitons (including trion peaks) are linearly dependent on the laser power: $I = \alpha P$, where α is the power coefficient which is related to absorption. High power has been used in the power-dependent PL measurement, which is up to 12 mW. However, the absorption and recombination still remains as one-photon process ($\alpha = 1$). The measurement indicates that the excitation power and accumulation time during the measurement have no observable effect to the PL intensity per unit excitation power, and the excitons and trion won't affect each other as the intensity ratio between them is fixed. Therefore we can fix the laser power to a suitable level to excite the system and collect the PL intensity for the calculation of the polarization. It is also noticeable that the full width at half maximum (FWHM) of the exciton peaks are stable under large pump fluence. As the valley polarization is commonly known as resonant effect[6, 18, 19], we will choose the laser which is near resonant the exciton peak center as the excitation source.

5.1.2 Enhanced valley polarization by bright-dark interaction

As we have shown in Section 2.3.2 and Fig. 2.11, we used a set of two quarter- λ wave-plates to generate and detect circular polarized light. One of the quarter- λ wave-plates is placed before incident on sample, to convert linearly polarized laser into circularly polarized excitation source. The other quarter- λ wave-plate will be placed before the detector to analyze the polarization of emission.

We first measured the PL spectra of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloyed monolayers with circularly polarized light at low temperature, the result are shown in Fig. 5.2. The

A excitons of each alloy are excited resonantly. At this temperature, apparently MoS₂ shows strong valley polarization, as the left-handed circular (notated as $\sigma+$) excitation yield major left-handed emissions via recombination within the Valley 1 to ground state $|0+\rangle$ (as shown in Fig. 5.3(a)). As the phonons are mostly squeezed by the low temperature, the intervalley scattering via phonons must be limited. However, the MoSe₂ sample shows no valley polarization unambiguously, as the $\sigma+$ (red trace, Fig. 5.2 (e)) and $\sigma-$ (blue trace, Fig. 5.2 (e)) peaks overlap each other perfectly. It is also noticeable that the alloy MoS_{0.4}Se_{1.6} also doesn't show any observable valley polarization.

The absence of valley polarization has been seen in several previous research works[20–22], but the reason is still not clear. At low temperature, it implies that the intervalley depolarization channel is very efficient, which should not be related to phonon assisted scattering. From Fig. 5.2(b) and (c), prominent valley polarization can be observed in MoS_{1.6}Se_{0.4} and MoSSe, which suggests that the band structure modulation of MoSe₂ with doping S atoms to the lattice could have activated its valley polarization.

In the last chapter, we have revealed the fine-structure at band-edge of the MoS_{2(1-x)}Se_{2x} alloys. It can strongly affect the intravalley excitonic recombinations. We now expand the one-valley system which we discussed previously in Fig. 4.14 to a full picture with two valleys, as shown in Fig. 5.3. The bottom states at A exciton level for MoS₂ and MoSe₂ are dark and bright states, respectively. As the two valleys are energy degenerated, they possess the same fine-structure. For MoSe₂, the intervalley transition will mainly happen between the two bright states which has degenerate energy. It is likely that the exchange Coulomb interaction ($\gamma_{exchange}$) between the two bright excitons are very efficient due to the out-of-plane quantum confinement, so they can flip spins through the strong exchange interaction. However, for MoS₂, the intervalley transition will mainly happen between the two dark states. As the dark exciton is very ro-

Figure 5.2: The circularly excited PL spectra of the alloyed monolayers showing valley polarization at low temperature. (a), (b), (c), (d) and (e) display the power dependent PL spectra for alloyed monolayers from MoS₂ to MoSe₂, respectively.

Figure 5.3: The excitonic level energy diagram showing intravalley recombination and intervalley scattering.

bust with long-lived (spin) lifetime, the exchange interaction ($\gamma_{exchange}$) could be minimized.

The strong valley polarization of MoS₂ and the absent valley polarization of MoSe₂ both can be well explained using this two-level model. For MoS₂, the dark excitons will keep their spin angular and orbital angular momenta since the intervalley $\gamma_{exchange}$ is limited. The circularly polarized excitation will initially pump carriers to the excitonic levels inside one valley, for instance Valley 1, and then the dark exciton will keep the carrier in Valley 1 and pass it to bright excitons via thermal energy assisted fluctuation. In this way, without scattering carriers to Valley 2, the emission will mainly originate from Valley 1 recombination, which will present the same polarization to the excitation due to the adiabatic circle of berry-phase. However, for MoSe₂, the situation is totally opposite. The initial carriers via circular excitation will form bright excitons, which hardly interact with the dark states within the same valley, as the Δ_{BD} is large (~ 22 meV from previous fitting result). The bright excitons in Valley 1 will be very populated and exchange with the bright excitonic states of Valley 2, the two bright states will reach equilibrium rapidly and recombine equivalently, so that there is no circular polarization can be observed.

This model can also be applied to the other alloys. With slightly S doping, the

Figure 5.4: Temperature dependent valley polarization of the alloyed TMD monolayers.

lowest states are still bright, so there is no circular polarization for MoS_{0.4}Se_{1.6}. When the S atomic concentration keeps increasing, the MoSSe has considerable valley polarization. The reason could be that the small Δ_{BD} (~ 8 meV for MoSSe from previous fitting result) opens the interaction between bright and dark excitons. It is worthwhile to notice that the valley polarization of MoS_{1.6}Se_{0.4} is very strong, even stronger than the MoS₂. To gain more information, temperature dependent circular-resolved PL spectra are taken from the alloys, and the valley polarization degrees are calculated using:

$$CP = \frac{I(\sigma+) - I(\sigma-)}{I(\sigma+) + I(\sigma-)}, \quad (5.1)$$

where CP is the valley polarization degree, $I(\sigma+)$ and $I(\sigma-)$ are PL intensity of the two circular luminescence. The calculated results as function of temperature are shown in Fig. 5.4.

The MoSe₂ samples shows strictly no valley polarization at any temperature, which is in agreement with its bright-dark split energy. It is surprising that the MoS_{0.4}Se_{1.6} presents valley polarization around $\sim 14\%$. As the $|\Delta_{BD}|$ value

Figure 5.5: The circularly excited PL spectra of the alloyed monolayers showing valley polarization at room temperature (295 K). (a), (b), (c), (d) and (e) display the power dependent PL spectra for alloyed monolayers from MoS_2 to MoSe_2 , respectively.

is smaller for $\text{MoS}_{0.4}\text{Se}_{1.6}$, the thermal energy opens the bright-dark interaction slightly, but this slightly polarized carriers can be easily scattered at high temperature end (e.g., 150~295 K), so in this temperature range no polarization exists. At suitable temperatures (60 to 150 K), the thermal energy is still enough for bright-dark interaction, meanwhile the phonon is suppressed, thus the polarization has been preserved. When the temperature is extremely low (e.g., < 60 K), the bright-dark interaction has been blocked, so the circular polarization totally disappear. As a result, the intervalley depolarization processes complicated factors. At high temperature regime, the phonon scattering and exchange between intervalley bright excitons both act as depolarization factors. At low temperature regime, the exchange interaction dominates the depolarization process.

Figure 5.6: The intervalley exchange between the superposition states in $\text{MoS}_{1.6}\text{Se}_{0.4}$.

Among the alloys, the most special case is the $\text{MoS}_{1.6}\text{Se}_{0.4}$. From the cyan trace in Fig. 5.4, we can see that its valley polarization is very strong and can sustain at even room temperature. Fig. 5.5 shows the circular-resolved PL spectra of the alloys at 295 K. $\text{MoS}_{1.6}\text{Se}_{0.4}$ shows clear polarization up to $\sim 35\%$ (Fig. 5.5(b)). The reason for this special case should be attributed to its special band structure. Back to Section 4.1.3, we know the Δ_{BD} of $\text{MoS}_{1.6}\text{Se}_{0.4}$ is only 0.21~0.27 meV. In such small energy split, a superposition state ($|BD\rangle$) could be formed, which inherits properties of both dark and bright states. This superposition states can

both effectively block intervalley exchange and efficiently emit photons via recombination. Its intravalley recombination is so efficient that the phonon scattering can never counteract the polarization even at room temperature.

5.2 Valley Polarization of B exciton in alloyed monolayers

Figure 5.7: The A and B valley polarization in $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloys at 30 K and the corresponding excitonic fine-structure. (a) and (b) are the valley polarization of A and B excitons of the alloys at 30 K. (c) and (d) are the corresponding exciton fine-structure schematics.

In Section 4.3 the hot luminescence of B excitons in the alloys have been discussed. The alloys, especially the ones with more S atoms have prominent PL emission from B excitonic level. So it is natural to think whether there will be robust valley polarization from the B excitons, as the berry curvature is identical for B and A excitons within the same valley. Fig. 5.7(a) and (b) have shown the valley polarization of A and B excitons at 30 K. As the Δ_{BD} of A and B

levels are swapped (see Section 4.1.2), the A and B should have opposite valley polarization, meaning when one is strong, the other is weak. As shown in Fig. 5.7(c) and (d), when the bottom of A is dark (valley polarization is strong), the bottom of B is bright (valley polarization is weak).

Figure 5.8: The valley polarization of B exciton in alloyed MoSSe at room temperature. (a) shows the spectra. (d) shows the valley polarization as a function of photon energy.

Here the valley polarization of B exciton among the alloys has roughly opposite trend comparing to the valley polarization of A excitons, and MoSSe turns out to have the strongest valley polarization of B exciton (Fig. 5.7(b)). As we discussed previously, because the Δ_{BD} in B exciton level is too negative, the total PL intensity from B level of MoSe₂ is too weak to display any prominent valley polarization. However, the B exciton of MoSSe has both prominent PL intensity and valley polarization degree, because of that the B fine-structure of MoSSe have suitable Δ_{BD} value combining with a dark bottom state. We measured the temperature dependent valley polarization of all the B excitons in TMD, and surprisingly we find that MoSSe has prominent room temperature valley polarization, as shown in Fig. 5.8.

In fact, the valley polarization of B exciton levels in MoS_{2(1-x)}Se_{2x} alloys are overall more prominent than their A excitons, as shown in the Fig. 5.9. Especially the MoSSe presents enhanced valley polarization from low temperature to

Figure 5.9: The temperature dependent valley polarization of B exciton in the alloyed TMDs.

high, comparing to its A exciton valley polarization shown as the orange trace of Fig. 5.4. As the valley polarization of A and B excitons possess different temperature dependence within the same lattice and phonon scattering background, the dynamics differences between the A and B excitons should be addressed for this valley polarization issue, using MoSSe as a model system.

Figure 5.10: The PL lifetime mapping of a MoSSe monolayer sample at room temperature. (a) and (b) show the lifetime mapping of A and B excitons. The inserts are the optical micrographs of the monolayer sample.

We measured the fluorescence lifetime image on the MoSSe sample, by scanning the pulsed laser using scanning mirrors, to obtain the xy spatial mapping of TRPL spectra. With different long and short wavelength pass filters in front of the single

photon detector (SPD), the lifetime mapping of the A and B excitons are obtained individually, as shown in Fig. 5.10(a) and (b).

Figure 5.11: The comparison between TRPL spectra of A and B excitons in MoSSe monolayer sample. (a) and (b) show spectra at 295 and 78 K, respectively.

The lifetime mappings of both A and B profile the outline of the sample (the insert images in Fig. 5.10) exactly with fidelity, showing the homogeneousness of the sample. It also guarantees the validity of the decay data integrated from the mapping. With varying temperature, we integrate the TRPL spectra for A and B excitons at different temperatures, which are shown as red and blue curve in Fig. 5.11. Fig. 5.11(a) and (b) show spectra at 295 and 78 K, respectively. As we addressed in Section 4.2, the lifetime shortening of the non-thermalized decay components saturates at about 78 K due to the 25 ps resolution limitation of the instrument response function (IRF). However, the the non-thermalized decay components in MoSSe B exciton reaches the IRF initially at room temperature (blue trace in Fig. 5.11(a)), comparing to the relatively slow decay in A exciton (red trace in Fig. 5.11(a)). Until 78 K (Fig. 5.11(b)), the A and B decay curves overlap. The ultrafast initial decay of B exciton exposes the hot luminescence essence of B excitons.

Fig. 5.12 shows the temperature dependent TRPL spectra of A and B excitons in MoSSe. For the A exciton, both the two decay components become shorter

Figure 5.12: The temperature dependent TRPL spectra of A and B excitons in the MoSSe monolayer sample. (a) and (b) show A and B excitons, respectively.

with decreasing temperature. There are two possible reasons, one could be the cooling of lattice vibration, and the other one is that the carrier population at the lowest bright state increases. The two factors will enhance and suppress valley polarization simultaneously, resulting in no evident valley polarization at most temperatures. However, for the B exciton, its hot luminescence essence makes the decay equivalently fast from room temperature to low temperatures, as shown in Fig. 5.12(b). In the meanwhile, the lowest dark state block the intervalley exchange, which is more dominant than the phonon scattering. Therefore, the enhanced valley polarization of B excitons can be detected.

5.3 Summary

In conclusion, the bright-dark interaction can be modulated via anion alloy engineering of MoX_2 ($\text{X}=\text{S}$ and Se), and therefore changes the intervalley dynamics significantly. Our results indicate that the bright excitons at the K and K' valleys can efficiently transit between each other via exchange coulomb interaction. The exchange between the dark excitons are effectively blocked. Therefore the bright-dark split order Δ_{BD} is vital to the valley polarization in the TMD mono-

layer system. With dark excitons as the lowest states (WX_2 and MoS_2), the dark excitons will preserve the carriers intravalley since the intervalley exchange ($\gamma_{exchange}$) is limited. The carriers in the dark states which have long lifetime can be gradually passed to the bright excitons via thermal fluctuations and other vertical processes (in k -space). In this way, the emission will be mainly from intravalley recombination, which will enhance the valley polarization. With bright excitons as the lowest state (MoSe_2), the intervalley exchange is so efficient, that two degenerated bright states at the K and K' valleys will reach equilibrium and eliminate the valley polarization.

The valley depolarization process is composed of the bright-dark split order, and the phonon scattering effects. The bright-dark split order determines the existence or absence of valley polarization, while the phonon effects provide an additional temperature dependence. By making $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ alloys, Δ_{BD} can be modulated to enhance the valley polarization. For instances, the A exciton of $\text{MoS}_{1.6}\text{Se}_{0.4}$ and the B exciton of MoSSe both present enhanced valley polarization which can even last to room temperature. Especially in $\text{MoS}_{1.6}\text{Se}_{0.4}$, the bright and dark states are so close with Δ_{BD} at about $0.21\sim 0.27$ meV. The two states can form a superposition state, which combines the properties of both dark (stability) and bright (radiative), leading to a robust valley polarization.

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6 Growth and Optical Properties of Mn-Doped MoSe₂ Crystal

In the previous chapters, transition metal dichalcogenides (TMDs) alloys based on elements with equal valence electrons within the group *VIB* (Mo and W) and group *VIA* (S, Se and Te) have been investigated and discussed. The alloy in this similar-element configuration can lead to large concentration tunability, thus achieving engineering of band gap, spin-orbit split, exciton relaxation and valley dynamics. However, those tunabilities are mostly modification and combinations of the intrinsic properties within the TMD family. In this chapter, based on our synthesis and measurements of manganese (Mn) doped molybdenum diselenide (MoSe₂), more insights and perspectives will be provided on building new alloy system of TMDs by doping with metal atoms consisting unequal valence electrons.

As we know, most modern electronic technologies are based on electrical control of the electrons' motions. Using devices like field effect transistor (FET), the on/off of an electron flow can be delicately harnessed, and coded into "0" or "1", respectively. That is the very foundation of all the logic functions of modern electronics, and where all digital techniques come from. Ever since last century, researchers have been working hard to reduce the scale of FET to make IC smaller and more compact. Until now, the endeavor is likely to reach the summit, as IC technique has already advanced from 100 to 6 nm, nearly reaching extreme to trigger quantum tunneling. Moore's law will draw to a close[1].

Fortunately, besides reducing size, there are other strategies to improve the devices from a fundamental view of material and physic sciences. One way is to reduce the dimensions from 3D down to 2D. From the arising of graphene, BN and 2D TMDs, people see a promising future world of vertical assembled 2D devices. We already have metal (graphene), insulator (BN) and semiconductor 2D building blocks[2–4]. And recently anti-ferromagnetic and ferromagnetic layers step into the spotlight[5, 6]. Heterostructures consisting of those 2D bricks will dramatically reduce the sizes of devices and improve performances. Another way is to add one extra spin degree of freedom (DOF) to a semiconductor, to form spintronics. This approach will completely change the working way of electronics and computations. In this way, on/off switches of electron flow and spin up/down can be integrated into one system. To achieve the goal, magnetic atoms need to be doped into semiconductor without destroying the crystal lattice or the properties of semi-conductivity. Such a platform for harnessing enlarged DOF electrons is called diluted magnetic semiconductor (DMS). For examples, Mn doped ZnO and GaAs[7–9]. Unfortunately, those DMSs can only present ferromagnetism at low temperature less than 150 K[9]. So far the experimental devices based on those DMSs still need to apply large external magnetic field at low temperature when processing. A very recent report on a WS₂/GaMnAs heterostructure spintronic device from Prof. Zhang Xiang’s group have proved it again that low temperature is compulsory for magnetism of DMS[10]. Simulations have predicted that as the concentration of magnetic dopants increases, the ferromagnetic transition curie temperature (T_C) of the DMS will increase as well and finally reach room temperature[11–13]. However, in experiment it is still difficult to achieve that because the unequal valence environment will prevent the dopants from entering the lattice. There are several advantages for 2D TMD to be a good host for magnetic dopants. First, the two-dimensional materials with large specific surface area will increase surface energy, making it easier for the dopant to get inside the

lattice. Secondly, the exchange of magnetic dopants with surrounding ions will be enhanced due to the 2D quantum confinement. Moreover, there will be no disordered spins because of the 2D nature, and also no vertical (out-of-plane direction) anti-ferromagnetic pairs.

6.1 The synthesis of Mn-doped MoSe₂ crystal

A long-term CVT reaction in sealed quartz tube was performed to obtain Mn-doped MoSe₂ crystal, as shown in Fig. 6.1(a). The sources including high quality molybdenum (Mo), manganese (Mn) and selenium (Se) powders in stoichiometric proportions ($\text{Mn}_{(0.05\sim 0.1)}\text{Mo}_{(0.95\sim 0.9)}\text{Se}_2$), and small amounts of AlCl_3 as transport agent, were loaded in one side of the tube. The tube was then put into a tube furnace, aligning to the middle of two heating zones which can be set to different temperatures. By setting the temperature of the zone containing chemical sources higher than the other side, a temperature gradient will be built to drive the transport and reaction of chemical vapors. After two weeks, millimeter size crystals with flake looking yield in the low temperature end of the tube (shown in Fig. 6.1(b)), which presents layered features. The as-grown crystals can be exfoliated by using scotch tape, as same as the commercial pristine MoSe₂ or other two-dimensional crystals.

We then transfer the exfoliated thin layers to TEM grid for characterization. Fig. 6.1(c) are the HRTEM images and the related diffraction pattern. Both of them show clear hexagonal shape, indicating that the atoms are in hexagonal lattice structure. The diameters of the hexatomic ring along zig-zag and armchair directions are 0.314 and 0.363 nm, respectively, which are in good agreement with previous experimental and theoretical results. The diffraction pattern is bright and sharp without any distortion or multi-fold, and the spots match the Miller indices of the main crystal planes (labeled with yellow numbers). Energy dispersive

Figure 6.1: Synthesis and characterization of the pristine and Mn-doped MoSe₂ crystals. (a) is the schematic of the chemical vapor transport reaction in a sealed quartz tube, the chemical sources are loaded in the high temperature end and the products will nucleate and grow in the low temperature end. (b) shows the appearance and typical size of the grown Mn-doped MoSe₂ single crystal. (c) is a HRTEM image of an exfoliated few-layer Mn-doped MoSe₂ sample. (d) is the EDX intensity mapping of Mn-doped MoSe₂ crystal. The left top panel is the HRTEM image of the region of interest on the sample, while the rests are EDX intensity mapping of all the elements of Mn-doped MoSe₂ crystal.

X-ray (EDX) intensity mapping has been taken on the sample during the HRTEM measurement. The region of interest on the sample, EDX intensity mapping of Mo, Se and Mn are shown in Fig. 6.1(d). The characteristic X-rays of Mo and Se show very strong intensity, and the atomic number ratio between Mo and Se calculated from the signal intensity is approximately around 1 : 2. The characteristic signal of Mn is much weaker than Mo and Se, showing about 2.9% of the total cations. However, its intensity is observable and the homogeneous distribution of the signal counts profiles the sample appearance accordingly. These facts suggest that the as-grown crystal samples have high-quality hexagonal lattice, which is consistent with the pristine MoSe₂, and Mn atoms have been successfully doped during the growth.

6.2 The static, time-resolved and temperature dependent PL spectroscopy of Mn-doped MoSe₂

Mono- and few-layer samples on Si/SiO₂ (285 nm) substrates are prepared by mechanical exfoliation using the pristine and Mn-doped MoSe₂ crystals. Fig. 6.2(a) shows the room temperature photoluminescence mapping of two exfoliated samples by scanning in a two-dimensional matrix. The insets are the corresponding optical micrographs, indicating the lateral scale and the color contrast of the mono- (light purple) and bi-layers (dark purple). In the PL mapping, we can see that monolayer regions of both samples present strong PL emissions while the bilayers have nearly no emission. The spectral peak positions of the PL emissions are denoted by the color contrast (see the scale bar besides). The pristine (red) and Mn-doped MoSe₂ (blue) monolayers have different PL peak positions. In Fig. 6.2(b), two typical PL spectra subtracted from the mapping are shown. The PL

peak position of the Mn-doped MoSe₂ monolayer blue-shifts 10 nm (~ 20 meV) from the pristine one. The time-resolved photoluminescence of the two samples have been measured, as shown in Fig. 6.2(c). The TRPL spectra of both samples display one decay, thus can be fitted with a single exponential decay function. The PL lifetime of the Mn-doped MoSe₂ monolayer is around 5.83 ns, which is more than twice the lifetime in pristine monolayer (2.24 ns).

Figure 6.2: The photoluminescence, time-resolved and temperature-dependent PL of the pristine and Mn-doped MoSe₂ monolayers. (a) shows the PL peak position mapping of the pristine (red) and Mn-doped (blue) MoSe₂ monolayers at room temperature; the insets are optical micrographs of the samples. (b) indicates the typical spectra extracted from the mapping, showing the peak positions. (c) shows the time-resolved PL spectra of the pristine (green) and Mn-doped (orange) MoSe₂ monolayers at room temperature. (d) Temperature-dependent PL of the pristine (green) and Mn-doped (orange) MoSe₂ monolayers down to liquid nitrogen temperature.

The blue-shift of the PL emission and the prolonged PL lifetime demonstrate that the band edge energy and the excitonic recombination of monolayer MoSe₂ has been changed by Mn-doping. To resolve the exciton behaviors, we measured

the temperature-dependent PL of the monolayer samples. The PL spectra of the Mn-doped (orange trace in Fig. 6.2(d) left panel) and pristine samples (green trace in Fig. 6.2(d) right panel) are plotted as stacked lines regarding different temperatures. The 20 meV difference between the exciton peaks of the pristine and Mn-doped MoSe₂ is always there at all the temperatures, and the peak positions and line-widths of the two sample has similar temperature-dependence (see the fitting in supporting information). By carefully examining the PL peak evolution, one can see distinct excitonic features between the Mn-doped and pristine MoSe₂ monolayers. The trion peak of the pristine sample is more prominent than exciton at liquid nitrogen temperature, and stays robust until the temperature exceeds 240 K. In stark contrast to the pristine MoSe₂ sample, the Mn-doped sample hardly shows any trion emission even at 78 K. From those results, it can be concluded that the Mn-doping can suppress the formation of trion and reduce its population in MoSe₂ monolayer.

6.3 The Raman spectra of Mn-doped MoSe₂ and DFT simulation of vibration modes

To further investigate the doping effects to the crystal lattice structure of MoSe₂, We measured the layer-dependent Raman spectra of the pristine and Mn-doped MoSe₂ monolayers. Fig. 6.3(a) and (b) show the Raman spectra in the ranges of A_{1g} and interlayer shear (E_{2g}²) modes, respectively. In each layer number, the A_{1g} peak of Mn-doped MoSe₂ blue-shifts $\sim 1.8 \text{ cm}^{-1}$ comparing to the pristine counterpart. On the contrary, the interlayer shear mode of doped MoSe₂ slightly red-shifts $\sim 0.7 \text{ cm}^{-1}$. Fig. 6.3(c) displays the layer dependent peak positions for A_{1g} and shear mode of the doped and pristine samples. Although the peak position values differ, the layer-dependent evolutions of the peak positions are similar and parallel for the doped and pristine MoSe₂. This sug-

gests that the doping and doping-induced structure effects are equivalent in all the layers. It is a reasonable result since the crystals are grown in a sealed tube within thermodynamics equilibrium environment.

Figure 6.3: The Mn-doping effects on the vibration modes of MoSe₂ revealed by Raman spectra and DFT calculation. (a) contains the Raman spectra in the range of A_{1g} mode of the pristine (green) and Mn-doped (orange) MoSe₂ of 1 to 4 layers. (b) contains the Raman spectra in the range of the interlayer shear mode (E_{2g}^2) of the pristine (green) and Mn-doped (orange) MoSe₂ from mono- to quadru-layer. (c) shows the layer-dependent Raman peak positions of the pristine (green) and Mn-doped (orange) MoSe₂. The A_{1g} mode of Mn-dope MoSe₂ (orange circle) shows red-shift from the pristine MoSe₂ (green circle), while the shear mode of Mn-dope MoSe₂ (orange diamond) shows blue-shift from the pristine MoSe₂ (green diamond). (d) is the schematic description of the constructive model of DFT calculation and the force constant k_{MSe-1} and k_{SeSe-3} associated with the pair of Se ions in an A_{1g} vibration; M indicates Mo and Mn. In the model, Mn dopant is placed to Position 0, and then the atoms labeled with bigger numbers are at farther position to the dopant. (e) indicates the compressive force constants of each ions at different positions in the doped system, as mapped in (d). At each atomic sites, two force constants are shown in red and blue bars for $U=3$ and 4 eV, respectively.

DFT calculation is performed to understand the Mn-doping induced change of Raman modes. Supercell of size $4 \times 4 \times 1$, with one Mo ion replaced by Mn ion, is equal to a monolayer systems with 6.25% doping concentrations. Although the concentration is larger than the experimental result, there is only one Mn dopant in the supercell, so the localized doping effect will be accurate and the global doping effects can be comparable to the experimental data. As shown in

Fig. 6.4, the Mn dopant is at Position 0 (labeled with bold red font), and then the surrounding atom labeled with larger number will be at position farther to the dopant. The most relevant atoms are the nearest neighbor (NN) Se labeled with 1 and the next nearest neighbor (NNN) Mo labeled with 2. The localization of Mn *d*-orbital electrons is modeled using the Hubbard model, with $U = 3$ and 4 eV considered to reduce the uncertainty of the simulation. To rationalize the red-shift of A_{1g} peak frequency, force constants among the ions in the pristine and doped systems are analyzed in similar fashion as reported in the study of Luo *et al.*[14]. The frequency of A_{1g} mode can be derived from the equation containing motion of the ions:

$$\omega^2(A_{1g}) = \frac{k_{MSe-1C} + k_{SeSe-3C}}{m_{Se}}, \quad (6.1)$$

where ω is the frequency of the A_{1g} mode; k_{MSe-1C} and $k_{SeSe-3C}$ are the generalized compressive force constants as illustrated in Fig. 6.4 (in the superscripts 1C and 3C, 1 and 3 means the ion label, C means compressive); m_{Se} is the ionic mass of one Se ion. In Fig. 6.5(a) we track the compressive force constants from all the Se sites around the Mn dopant. The x -axis indicates the numerical label of the atoms; the green solid lines denote the force constants in pristine system. At each Se site, two force constants in red and blue bars are shown for $U=3$ and 4 eV, respectively. Global decrease of the compressive force constants can be seen across the Mn-doped system, with k_{MSe-1C} and $k_{SeSe-3C}$ each weakened by about 7% and 13%. Particularly, there is a significant reduction of k_{MSe-1C} by more than 20% within the NN sites around the Mn dopant.

Therefore, the red-shift of the A_{1g} frequency can be attributed to the softening of the force constant which is generalized Mn-doping induced, as depicted in Equation (1). Besides this, non-neglected vibrations from Mo ions surrounding the Mn dopants (Position 2, 5 and 6) are observed, in contrary to those Mo ions in the pristine system which normally remain stationary in an A_{1g} configuration. This additional Mo vibrations can penetrate into the A_{1g} vibrating bodies and in-

Figure 6.4: The schematic description of the constructive model of DFT calculation and the force constant k_{MSe-1} and k_{SeSe-3} associated with the pair of Se ions in an A_{1g} vibration; M indicates Mo and Mn. In the model, Mn dopant is placed to Position 0, and then the atoms labeled with bigger numbers are at farther position to the dopant.

Figure 6.5: The force constants of different atoms surrounding the dopants. (a) indicates the compressive force constants of each ions at different positions in the doped system, as mapped in Fig. 6.4. At each atomic sites, two force constants are shown in red and blue bars for $U=3$ and 4 eV, respectively. (b) shows the additional vibration of Mo atoms in the lattice, which will assist the red-shift of the A_{1g} frequency.

crease the mass of them, which must cause further red-shift of the A_{1g} vibrational frequencies. The simulated red-shift and the experimental results are consistent with each other, as shown in Fig. 6.6. For the interlayer shear mode, its vibration frequency has the following relationship: $\omega^2(E_{1g}^2) \propto K/m$ [15]. K is the force constant and m is the average mass of the monolayer. Since the interaction between adjacent MoSe_2 monolayers is governed by very weak London Dispersion type of vdW force, the Mn dopant sitting in the inner atomic layer of the MoSe_2 monolayer should have limited effects on the interlayer interaction. However, the total mass will decrease significantly as Mn is nearly half the mass of Mo. If K remains unchanged but m decreases, the frequency of interlayer shear mode will blue-shift.

Figure 6.6: The red-shift of A_{1g} frequency revealed by experimental data and DFT simulation.

6.4 The charge density distribution and localized ferromagnetism induced by Mn-doping

Besides tracking the vibration modes, the charge density and the contribution per ion in the system can be obtained from the DFT calculation. Spin polarized

density functional theory calculations are performed on super-cell configurations using the Vienna *Ab-initio* Simulation Package (VASP) code[16, 17] working in a Plane Augmented Wave (PAW) basis set with Local Density Approximation (LDA) of the exchange correlation functional. Super-cell of size $4 \times 4 \times 1$, with one Mo ion replaced by a Mn ion, is used to simulate 6.25 % doping concentration in monolayer system.

Figure 6.7: The charge distribution on each ion and the density of states (DOS) in the Mn-doped and pristine MoSe₂ monolayers. (a) indicates the average charge contributed by each ion (averaged among the ions sharing the same ion label in Fig. 6.4). Ions with positive charges are donating electrons while those with negative charges are accepting electrons. Solid lines with green and red colors represent the amount of charge donated by Mo and accepted by Se in the pristine MoSe₂ monolayer, respectively. (b) is the electronic DOS of the pristine MoSe₂ monolayer and doped MoSe₂ monolayers with $U = 3$ and 4 eV. The energy scales of the systems are aligned at the Mo 1s core level, with the pristine system's valence band maximum normalized to 0 eV, marked with the red dotted line. Fermi energy levels of the doped systems are marked with the red solid lines.

We use an energy cut-off of 450 eV for the planewave basis set and a Monkhorst-Pack k point mesh[18] centered about the Γ point with a density of $6 \times 6 \times 1$. A sufficient vacuum separation of 11 Å is used to prevent interactions between adjacent layers due to periodic boundary conditions. Higher energy cut-offs and larger vacuum separations are also tested, with no significantly different results obtained. The atomic coordinates are fully relaxed using the blocked Davidson iteration scheme until the maximum energy difference between iterations is less

than 10^{-5} eV and the residual force is less than 0.003 eV/Å. Self-consistent calculations use a more stringent energy convergence criterion of 10^{-9} eV. Localization of Mn d electrons is modeled using the Hubbard model, with $U = 3$ and 4 eV considered. Due to the lack of experimental data on the magnitude of U , we choose our U in the range of commonly used electronic structure calculations[19, 20]. The results show no qualitative difference in terms of the conclusions made from them; nevertheless results from systems of both U values are presented for completeness sake. Phonon calculations are performed using density functional perturbation theory (DFPT) as executed by Phonopy[21]. Charge distribution of the systems is performed using Bader analysis[22].

Fig. 6.7(a) shows average charge from each ion in the above $4 \times 4 \times 1$ Supercell. Solid lines with green and red colors represent the amount of charge donated by Mo and accepted by Se in the pristine MoSe₂ monolayer, respectively. Red and blue bars are results for $U=3$ and 4 eV. Compared to the pristine system, exchange of electrons among the positive and negative ions in the doped system are overall less. Interestingly, it can be seen that the charge of Mn is less positive than those of Mo, namely Mn ions are donating less electrons. Since Mn is in group VIIB which has one more valence electron than Mo and W which are group VIB elements, the Mn-doped TMDs, especially Mn-doped MoS₂ are expected to be N-type doped previously[12, 13]. In this case, Mn behaves more like an acceptor than the previously anticipated donor. As the Mn dopant donates less, the NN Se ions (with ion label 1) are also not accepting as much electrons as those further away from Mn are. This acceptor-like behavior of Mn dopant will make the doped MoSe₂ more neutral and decrease the carrier density, which is in good agreement with the low population of trions observed in the temperature-dependent PL spectra shown in Fig. 6.2(d). It is also noteworthy that the charge distribution closely resembles that of the distribution of k_{MSe-1C} force constant shown in Fig. 6.5(a), suggesting that the charge exchange and force constants between Mn

dopant and NN Se are correlated. The weaker charge exchange indicates that the binding force between the ions are also weaker, which may contribute to the decrease of force constants as well.

Figure 6.8: The FET devices fabricated on both the pristine and Mn-doped MoSe₂ monolayers with back gate configuration, and the measurement of the devices' performance. (a) and (b) are the micrographs of the devices, to measure the gate tuning effects, a series parallel bar electrodes made of Cr/Au (5 and 80 nm) are deposited on the sample. (c) and (d) are the source-drain current measured by sweeping the gate voltage from -80 to 80 V. The source-drain voltage was fixed at 2 V during the measurement.

Field effect transistor (FET) devices have been made on both the pristine and Mn-doped MoSe₂ monolayers with back gate configuration (using the silicon substrate beneath the SiO₂ dielectric layer) , as shown in Fig. 6.8(a) and (b), respectively. The gating effect of the devices were measured by sweeping the gate voltage from -80 to 80 V at a source drain voltage $V_{ds} = 2V$. From the gate sweep, we can see that the Mn-doped MoSe₂ monolayer has much better transistor performance regarding to mobility and on/off ratio qualitatively. From the linear scale plot (Fig. 6.8(c)), the doped device shows a better switching performance, i.e. at positive gate voltage, $V_{bd} = 80V$, the on-state current is much higher; at negative gate voltage, the device can be switched to an off-state with much

lower off-current. The result is in contrary to the previous measurement in Mn-doped MoS₂ which shows the Mn-doping makes the device performance largely degraded[23]. The difference here could be that the hexagonal prism in MoSe₂ is much bigger than that of MoS₂, leaving a bigger space for the cation (Mn or Mo). Therefore the Mn-dopant can induce less mismatch and scattering in MoSe₂ than MoS₂.

To evaluate the effects of Mn doping on both electronic and magnetism properties of MoSe₂, spin-resolved density of states (DOS) of the doped system is studied in comparison with that of the pristine system, as shown in Fig. 6.7(b). Spin-polarized gap states have been observed for the Mn doped systems, in good agreement with previous reports[12, 13]. Projected DOS of the gap states (Fig. 6.9(a)) indicates that the gap states receive contributions from exclusively the Mn 3*d*-orbitals, NN Se 4*p*-orbitals and NNN Mo 4*d*-orbitals, while the contribution from ions further away from the dopant is negligible. The projected DOS on individual orbitals from those relevant ions are shown in Fig. 6.9(a). For the Mn 3*d* states, d_{z^2} , d_{xz} and d_{yz} , and d_{xy} and $d_{x^2-y^2}$ have lowest, intermediate and highest overlap with the Se 4*p* states, according to how much the orbital geometries match with the trigonal prismatic environment of the Se atoms. Therefore, the three groups of orbitals form the lowest (a_1), intermediate (e_1) and highest (e_2) anti-bonding states, respectively, due to crystal field splitting (Fig. 6.9(b)). As the d_{z^2} states has the smallest overlap with the Se 4*p* states, the NN Se states prefer more to occupy high energy e_1 and e_2 states. This occupation configuration can be also seen clearly in the isosurface plots taken at corresponding energy ranges of the three different anti-bonding states (Fig. 6.10), in which the shapes of charge density resemble those of the corresponding d-orbitals. On the other hand, the NNN Mo 4*d* orbitals are divided into two levels only (a_1 and e_1), and the d_{z^2} , d_{xy} and $d_{x^2-y^2}$ states all mix together. We attribute this difference between Mn and NNN Mo to the spatial size difference between the 3*d*-orbitals of

Mn and the 4d-orbitals of Mo. The smaller size of Mn 3d-orbital makes it easier for d_{z^2} to evade the NN Se's electron than the $4d_{z^2}$ of Mo, causing the $3d_{z^2}$ of Mn occupy the lowest a_1 state alone. Besides crystal field splitting (ΔE_{cf}), the Mn 3d states also undergo an intratomic (Hund's) exchange splitting (ΔE_{ex}), making up-spin and down-spin states have different energies.

Figure 6.9: The projected density of state onto individual orbitals of respective ions and the average magnetization per atom. (a) is the projected DOS onto the Mn d-orbitals, the nearest neighbor Se p-orbitals and the next nearest neighbor Mo d-orbitals. (b) illustrates the gap states originated from crystal field split ΔE_{cf} and intratomic Hund's exchange ΔE_{ex} . (c) indicates the average magnetization of the n th nearest neighboring ions whose ion labels are mapped in Fig. 6.4. Ions 2, 5 and 6 are Mo and 1, 3, 4, 7 are Se.

Previous studies have reported that the Mn d_{z^2} states dominate the a_1 level, giving rise to the localized (up-spin) magnetic moment[12, 13]. In our results, although from Mn part its d_{z^2} orbital contributes to a_1 alone, the NNN Mo 4d-orbitals (d_{z^2} , d_{xy} and $d_{x^2-y^2}$) as a whole has more contribution to the a_1 . The electron sharing is significant within the NNN Mo around the dopant Mn. Upon further scrutiny, we also find that the a_1 state is a single flat band below the Fermi level.

Those results collectively demonstrate that the up-spin gap states are arising from a global effect following the interactions between Mn dopant and the neigh-

borhood atoms within range of NNN Mo, and the NNN Mo 4d-orbitals states dominantly contribute to a_1 and e_1 states, which are in contrary to previous studies on Mn-doped TMD systems.

Figure 6.10: Isosurface plots of spin charge density around Mn in the $4 \times 4 \times 1$ supercell system with Hubbard $U = 3$ eV. Energy ranges of the plots are from -0.07 to 0 eV (a1 and a2), 0.06 to 0.16 eV (b1 and b2), 0.46 to 0.56 eV (c1 and c2), -0.9 to -0.6 eV (d1 and d2). The isosurface values are taken at $0.001 \text{ e}\text{\AA}^{-3}$ for a b and c, $0.002 \text{ e}\text{\AA}^{-3}$ for d. The supercells are merged and cropped to facilitate easier visualization; for column 1, Mn is the rightmost metal ion; for column 2, Mn is the second leftmost ion of the third row.

The average localized magnetization of the doped system is found to be $1.304 \mu_B$ for $U = 3$ eV and $1.427 \mu_B$ for $U = 4$ eV and is dominated by magnetization of Mn, with $2.445 \mu_B$ and $2.998 \mu_B$ for $U = 3$ and 4 eV. For the surrounding Mo and Se atoms, significant magnetization is only observed in the NN Se and NNN Mo. This neighborhood magnetizations are anti-ferromagnetically (AFM) coupled with the dopant Mn, as shown in Fig. 6.9(c).

6.5 Summary

In conclusion, Mn-doped MoSe₂ single crystal has been successfully grown using chemical vapor transport reaction in sealed ampule. The as-grown crystal has high crystalline quality, nearly identical lattice structure as the pristine MoSe₂ crystal, and contains about 2.9% Mn concentration. By exfoliating the as-grown layered crystal, monolayer to fewlayer Mn-doped MoSe₂ samples on substrate have been obtained. Using those samples, we have measured layer-dependent Raman spectra on both Mn-doped and pristine MoSe₂. PL, time-resolved and temperature-dependent PL have been studied on the Mn-doped and pristine MoSe₂ monolayers. DFT calculations have been done to understand the doping effect on the Raman and PL spectra, also to provide more insights to the spin-polarized gap states and localized magnetization induced by Mn dopants and its interaction with neighborhood atoms.

The Raman spectra show noticeable red-shift of A_{1g} vibration frequency in mono- to quadru-layers. The DFT simulation of the vibrations indicates that the weakened force constants and additional vibration of nearest neighbor Mo atoms contribute most to the red-shift. In the meanwhile, the interlayer shear mode shows non-negligible blue-shift, which can be attributed to the decrease of the total molecular mass induced by doping of lighter Mn atoms. The PL spectral line position of Mn-doped monolayer shows obvious blue shift about 20 meV due to the doping effect. The PL lifetime of the doped monolayer has increased by twice the lifetime of the pristine monolayer. The possible reason for the increase of lifetime could be that the trion population is strongly suppressed, as trion generally has quicker recombination rate than exciton. From the charge distribution extracted from DFT simulation, the Mn dopant behaves more like an acceptor than previously expected donor due to its small size and small 3d electron cloud. This result suggests the Mn-doping will reduce charge density and

make the crystal more neutral, which is in good agreement with our observation of suppressed trion in low temperature PL.

The Raman and PL have both been proved to be very sensitive to the low concentration Mn-doping level. The layer-dependent Raman can evaluate the homogeneity of the Mn-doping in overall crystal. For instance, in our case the doping of Mn is homogeneously distributed in the MoSe₂ single crystal, ensuring us to fabricate monolayer and fewlayer Mn-doped samples. These results will be useful reference for future study on alloy TMDs with low concentration doping of unequal valence elements. The fact that Mn-doping is p-type other than n-type also provides new knowledges on the doping of TMDs, meaning that the size-effect of the dopant is considerable and as important as the valence electronic configuration.

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7 Conclusions and Future Perspectives

7.1 Conclusions

In conclusion, we have synthesized high quality $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ($0 \leq x \leq 1$) alloyed single crystals using chemical vapor transport (CVT) reactions in sealed ampules. By exfoliating the layered crystals, monolayer to fewlayer alloyed samples can be obtained. For those alloyed monolayers, the (optical) band gap can be fully modulated between MoS_2 (1.87 eV) and MoSe_2 (1.56 eV). Besides, the tunability of spin-orbit coupling allows tailoring of the energy difference between A and B excitons (Δ_{BA}) from 137 to 229 meV. MoSe_2 has the most narrow line width among the alloyed monolayers, pointing to the weaker coupling of excitons to phonons with lower phonon energies. The homogeneous broadening of line width due to the exciton-phonon interactions can be modulated among the alloys. Besides the exciton, the trion binding energy can be tunned from 44 to 32 meV. Trion formation affects many optoelectronic properties related to Fermi level and doping. By calculating the temperature dependent Trion intensity, it can be concluded that the n -doping level of $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ monolayers increase as the Se atomic concentration increases.

The Raman spectra prove that the symmetry of the alloyed samples is identical to the pristine ones. The mixture of S and Se introduces anharmonic vibrations

to the system, and changes the phonon energy and phonon dispersion. The Raman bands become broadening and the E-like modes at MoSe₂ frequencies are suppressed. By measuring and fitting the layer-dependent interlayer shear modes of the alloys, the mass per unit area and force constant are obtained, and MoS₂ has the strongest interlayer interactions. The distinct interlayer modes between alloys set an ideal model to identify the interlayer modes between any TMD or two-dimensional layers, which will be helpful for characterization for new heterostructures of 2D materials in the future.

Therefore, the alloy engineering of MoS_{2(1-x)}Se_{2x} ($0 \leq x \leq 1$) makes the 2D system with versatile properties in energy band gap, spin-orbit coupling, phonon modes, excitonic effects and electron doping level. These engineered alloys can be designed for specific electronics and optoelectronic applications.

Besides the spin-orbit split change in valence band (VB), the conduction band (CB) split energy Δ_C can also be changed by spin-orbit engineering, leading to modulated exciton fine-structure and bright-dark energy split Δ_{BD} . Sufficient evidences have been obtained to prove the existence of dark excitons and the energy position of them in the alloyed monolayers. By fitting with the temperature-dependent PL peak intensity of both A and B excitons with a simplified two-level model, we are able to obtain the Δ_{BD} values among the alloyed MoS_{2(1-x)}Se_{2x} monolayers. For each alloy, the Δ_{BD} has the same value with opposite sign for A and B exciton. The Δ_{BD} changes with varying the Se atomic concentration. Taking the A exciton as a paradigm (the opposite is B then), the Δ_{BD} from 11.2 ± 1.3 meV for MoS₂ to -21.1 ± 1.3 meV MoSe₂. During the evolution, the order of the bright-dark energy levels is swapped, due to the distinct SOC contributions from S and Se atoms. The transition point which has nearly zero Δ_{BD} has been identified to be MoS_{1.6}Se_{0.4} among the alloys. The PL intensity from both A and B excitons of MoS_{1.6}Se_{0.4} have no temperature-dependence, since the zero Δ_{BD} is not subject to thermal energy change. The zero Δ_{BD} also create a superposition

state which combines the properties of bright and dark excitons.

The relaxation from B to A excitonic levels is determined by the bright-dark split order, as well as the excitonic recombinations. In MoS₂, the B to A relaxation takes place between a bright (bottom B) and a dark (bottom A) states and is suppressed by the fulfilled dark state. Therefore, the carriers at B has sufficient time to recombine and emit photons. The situation is reversed for MoSe₂, where the bottom sub-states are dark (B) and bright (A), the relaxation will be unobstructed as the bright excitons in A level recombine efficiently and leave plenty of spaces for the carriers from higher energy places.

Other than the intra-valley dynamics mentioned in the above paragraphs, the modulated bright-dark interaction can also affect the inter-valley dynamics significantly. Our results indicate that the bright excitons at the K and K' valleys can efficiently transit between each other via exchange coulomb interaction. On the other hand, the exchange between dark excitons are effectively blocked. Therefore, the bright-dark split order Δ_{BD} is vital to the valley effects of the TMD monolayers. If dark excitons is the lowest states (e.g. WX₂ and MoS₂), carriers will be preserved intravalley by the dark states since the intervalley exchange ($\gamma_{exchange}$) is limited. The long-lived dark states can gradually pass the carriers which carrying valley memories to the bright excitons via thermal energy and other vertically processes. In this way, the emission will be mainly from intravalley recombination, which will enhance the valley polarization. In stark contrast, if bright exciton is at the lowest state (e.g., MoSe₂), the intervalley exchange is so efficient, that two degenerated bright states at the K and K' valleys will reach equilibrium rapidly and cancel the valley polarization.

The valley depolarization process is composed of the bright-dark split order, and the phonon scattering effects. The bright-dark split order determines the existence or absence of valley polarization, while the phonon effects provide an additional temperature dependence. By making MoS_{2(1-x)}Se_{2x} alloys, Δ_{BD} can

be modulated to enhance the valley polarization. For instances, the A exciton of $\text{MoS}_{1.6}\text{Se}_{0.4}$ and the B exciton of MoSSe both present enhanced valley polarization which can even last to room temperature. Especially in $\text{MoS}_{1.6}\text{Se}_{0.4}$, the bright and dark states are so close with Δ_{BD} at about $0.21\sim 0.27$ meV. The two states can form a superposition state, which combines the properties of both dark (stability) and bright (radiative), leading to robust valley polarization.

Finally, Mn-doped MoSe_2 single crystal was grown using CVT to investigate the doping of TMD with magnetic dopants. The as-grown crystal has high crystalline quality and contains about 2.9% Mn atomic concentration. We have measured the layer-dependent Raman spectra on monolayer to few-layer samples of both Mn-doped and pristine MoSe_2 . The Raman spectra show pronounced red-shift of A_{1g} vibration frequency in mono- to quadru-layers. The DFT simulation of the vibrations indicates that the weakened force constants and additional vibration of the nearest neighbor Mo atoms contribute most to the red-shift. In the meanwhile, the interlayer shear mode shows non-negligible blue-shift, which can be attributed to the decrease of the total molecular mass induced by doping of lighter Mn atoms.

The PL spectral line position of Mn-doped monolayer shows obvious blue shift about 20 meV due to the doping effect. The PL lifetime of the doped monolayer has increased as twice as the lifetime of the pristine monolayer. Taking into account the strongly suppressed trion peak at liquid nitrogen temperature, the population decrease of trion possibly causes the observed lifetime elongation. From the charge distribution extracted from DFT simulation, the Mn dopant behaves more like an acceptor than previously expected donor due to its small size and small $3d$ electron cloud. This result suggests the Mn-doping will reduce charge density and make the crystal more neutral, which is in good agreement with our observation of suppressed trion in low temperature PL.

The Raman and PL have both been proved to be very sensitive to the low concentration Mn-doping level. The layer-dependent Raman can evaluate the

homogeneity of the Mn-doping in overall crystal. For instance, in our case the doping of Mn is homogeneously distributed in the MoSe₂ single crystal, ensuring us to fabricate monolayer and fewlayer Mn-doped samples. These results will be useful reference for future study on alloy TMDs with low concentration doping of unequal valence elements. The fact that Mn-doping is p-type other than n-type also provides new knowledges on the doping of TMDs, meaning that the size-effect of the dopant is considerable and as important as the valence electronic configuration.

7.2 Future perspectives

7.2.1 Ultrafast spectroscopy study of the valley coherence

In Section 5.2, we have revealed the enhanced valley polarization of B exciton in MoSSe, which is able to last to room temperature. A interesting following question is: how is the valley coherence? Does the K and K' valleys emit photons coherently? How long is the coherent regime?

To address these questions, we measured the linear polarization of the MoSSe monolayer sample. Using a set of half- λ wave-plates, we are able to resolve the parallel and perpendicular polarization configuration. The strong linear polarized luminescence in an isotropic lattice (e.g., the TMD hexagonal lattice) semiconductor is likely to originate from the coherence of the excitons. In normal semiconductors, the coherence depends on how stable the alignment of the dipoles is. For monolayer TMDs, its atomically thin thickness ensures that there are no alignment issues from z -axis. And the linear excitation will excite the K and K' valleys simultaneously and equivalently:

$$I_{\parallel} = I_{\sigma+} \sin(\omega t) + I_{\sigma-} \cos(\omega t), \quad (7.1)$$

if the phase of the two valleys $\langle\omega\rangle$ keep unchanged and coherent, the two circular emissions will compose to the linear emission under the original polarization.

Figure 7.1: Valley polarization and valley coherence of the B exciton of MoSSe at room temperature. (a) and (b) are the circular polarization resolved PL spectra and valley polarization degree of MoSSe at 293 K. (c) and (d) are the linear polarization resolved PL spectra and valley coherence degree of MoSSe at 293 K.

Fig. 7.1 shows the valley polarization and valley coherence measurement of the B exciton of MoSSe at room temperature. The linear polarization degree is calculated by $LP = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, and the circular polarization degree is $CP = (I_{\sigma+} - I_{\sigma-}) / (I_{\sigma+} + I_{\sigma-})$. It can be seen that the linear polarization almost reaches the circular polarization degree. The result indicates that the valley coherence is very robust that the two valleys can absorb and emit photons simultaneously and keep the phase unchanged.

To further study the valley coherence and obtain more information including coherence lifetime, we plan to use transient absorption (TA) with circularly po-

larized pump and probe sources, to study the non-thermalized and thermalized regime. Therefore, we could know the full dynamics information of the two valleys and understand why they are coherent. Understanding the valley coherence will be fundamentally meaningful, and also helpful to the understanding of coherence in other low-dimensional systems.

7.2.2 The magnetic response of Mn-doped MoSe₂

Figure 7.2: The magnetic response of the pristine and Mn-doped MoSe₂ monolayers revealed by photoluminescence and polarized photoluminescence. (a) and (b) are the valley polarization degree of the pristine and Mn-doped MoSe₂ monolayers when applied magnetic field up to 6.5 Tesla. (c) and (d) are the valley splitting degree of the pristine and Mn-doped MoSe₂ monolayers when applied magnetic field up to 6.5 T.

Although we haven't observed decent magnetic response from the Mn-doped MoSe₂ single crystal by direct magnetic susceptibility measurement in the magnetic properties measurement station (MPMS), the monolayer still have some

magnetic responses (valley Zeeman splitting, as shown in Fig. 7.2). Which we could further measure in higher magnetic field up to 30 T. We also plan to measure the magneto-resistance of the Mn-doped monolayer with comparing to the pristine ones, with or without B-field.

Moreover, our DFT shows that the net magnetization induced by Mn dopant is not from the $3d$ -orbital of Mn alone, but from a global effect of all the surrounding atoms including $3p$ -orbitals of the nearest neighbor Se and $4d$ -orbitals of the next nearest neighbor Mo atoms. This result provides views on the mechanism of the magnetization of DMS from a new angle, and also gives hints for the further design of alloy to improve the magnetic properties. For example, changing the host materials to have stronger electron sharing with the magnetic dopants, or tuning the charge density using gate to enhance the exchange between electrons from the dopants and the lattice environment.

List of Publications

- (1) Sheng Liu, Shishuai Sun, Chee Kwan Gan, et al. Manipulating efficient light emission in two-dimensional perovskite crystals by pressure-induced anisotropic deformation. *Science Advances*, 2019, 5(7): eaav9445.
- (2) Huanqing Ye, Guangfeng Liu, Sheng Liu, David Casanova,* Xin Ye, Xutang Tao, Qichun Zhang,* and Qihua Xiong*. Molecular-Barrier-Enhanced Aromatic Fluorophores in Cocrystals with Unity Quantum Efficiency. *Angewandte Chemie International Edition*, 2018, 57(7): 1928-1932.
- (3) Huanqing Ye, Viktor Bogdanov, Sheng Liu, Saumitra Vajandar, Thomas Osipowicz, Ignacio Hernandez, and Qihua Xiong*. Bright Photon Upconversion on Composite Organic Lanthanide Molecules through Localized Thermal Radiation. *The Journal of Physical Chemistry Letters*, 2017, 8(23): 5695-5699.
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