Synthesis and optical properties of atomically thin transition metal dichalcogenides

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**SYNTHESIS AND OPTICAL PROPERTIES OF ATOMICALLY
THIN TRANSITION METAL DICHALCOGENIDES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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**SYNTHESIS AND OPTICAL PROPERTIES OF ATOMICALLY
THIN TRANSITION METAL DICHALCOGENIDES**

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Abstract

Atomically thin layered transition metal dichalcogenide (TMD), as a very strong candidate for two-dimensional (2D) materials beyond graphene, has been in the research highlight for the past five years approximately. Unlike graphene, TMD materials have band gap, and the gap is a direct one in monolayer, enabling potential electronic application. Photoluminescence (PL) from monolayer TMDs exhibits strong intensity with the band edge emission within the visible and near-infrared range. The coupling of valley and spin in TMDs is another, and probably the most attracting point in this field. So far, the optical valley polarization and valley Hall effect have been reported in monolayer. Electrical control has also been realized in bilayer.

Mechanical exfoliation is a conventional way to obtain mono- and few-layer samples, but the size of a flake is limited from this method. Sulfurization and selenization inside a chemical vapor deposition (CVD) chamber has been demonstrated to be a very promising and popular way to get large-area thin films. Still, it is not trivial to get CVD-grown monolayer sample of high quality, especially when this field just started, back in 2012-2014. In this thesis, I will present how I optimized the CVD-synthesis of MoSe_2 thin films (low pressure) and isolated flakes (high pressure), as well as discussing about the corresponding studies on optical properties and electrical performance. The related content in Chapter 4 will include detailed elaboration on structural characterization from scanning transmission electron microscopy (STEM), PL, phonon properties, the influence of catalyst in growth on electrical performance and so forth. In addition, I will show my work on top-down methods in Chapter 3, which contains mechanical exfoliation and preparation of heterostructures, as well as layer-by-layer thermal annealing thinning.

Besides PL and valleytronics, research on phonon properties in TMDs have intrigued lots of people, not only in the high-frequency intralayer vibrational modes but also in the low-frequency interlayer shear and breathing modes. In Chapter 5,

relation between stacking sequences and the evolutionary trend of interlayer shear modes with increasing thickness has been shown. As layer number increases, AB-stacked layered materials (such as 2H-stacked MoSe₂) exhibit blue-shifted interlayer shear mode, while the trend is opposite in ABC-stacked samples (*e.g.* 3R-stacked MoSe₂). Experimental evidence was shown on CVD-grown few-layer MoSe₂ with multiple kinds of stacking types. With the help of bond polarizability model, stacking fault, such as ABCB stacking in 4 L MoSe₂, was further identified. Comparison of STEM and Raman spectroscopy on identification of stacking is given, revealing the advantage of Raman scattering, especially when layer number is larger than three.

Afterwards, I will present my recent studies on Raman scattering measurements of electric field effect on top-gated MoS₂. Focus is given on the fingerprint peaks, E_{2g}^1 and A_{1g} modes. Gate-tunable PL measurements and Raman study with a non-resonant laser excitation have been performed, confirming that the electron doping is successful. Raman spectra excited by the resonant 633 nm laser have demonstrated something new, which includes: (1) Electron-phonon coupling is stronger during resonance, mainly evidenced by the behavior of E_{2g}^1 mode. (2) Significant gate-tunable Raman intensity is observed. Absorption bleaching may play an important role in affecting the intensity. (3) Anomalous blue-shift of A_{1g} mode with increasing electron concentration. Detailed investigation has been done on exploring the blue-shift of A_{1g} mode with increasing electron concentration, which is actually the combined effect from antibonding electrons and resonance-related decoupling effect.

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Citations to Published Work

Majority of Chapter 3 appears in:

“Layer-by-layer thinning of MoS₂ by thermal annealing.” **X. Lu**, M. I. B. Utama, J. Zhang, Y. Zhao, and Q. H. Xiong. *Nanoscale* 5, 8904-8908, 2013.

Majority of Chapter 4 appears in:

“Large-Area Synthesis of Monolayer and Few-Layer MoSe₂ Films on SiO₂ Substrates.” **X. Lu**[#], M. I. B. Utama[#], J. Lin, X. Gong, J. Zhang, Y. Zhao, S. T. Pantelides, J. Wang, Z. Dong, Z. Liu, W. Zhou, and Q. H. Xiong. *Nano Lett.* 14 (5), 2419-2425, 2014.

“Etching-free patterning method for electrical characterization of atomically thin MoSe₂ films grown by chemical vapor deposition.” M. I. B. Utama[#], **X. Lu**[#], D. Zhan, S. T. Ha, Y. Yuan, Z. X. Shen, and Q. H. Xiong. *Nanoscale* 6, 12376-12382, 2014.

“Detrimental influence of catalyst seeding on the device properties of CVD-grown 2D layered materials: A case study on MoSe₂.” M. I. B. Utama, **X. Lu**, Y. Yuan, and Q. H. Xiong. *Appl. Phys. Lett.* 105 (25), 253102, 2014.

Majority of Chapter 5 appears in:

“Rapid and Nondestructive Identification of Polytypism and Stacking Sequences in Few-layer Molybdenum Diselenide by Raman Spectroscopy.” **X. Lu**, M. I. B. Utama, J. Lin, X. Luo, Y. Zhao, J. Zhang, S. T. Pantelides, W. Zhou, S. Y. Quek, and Q. H. Xiong. *Adv. Mater.* 27 (30), 4502-4508, 2015.

“Stacking sequence and group symmetries determine Raman intensities of interlayer modes in 2D layered materials – A simple bond polarizability model.” X. Luo, **X. Lu**, C. Cong, T. Yu, Q. H. Xiong, and S. Y. Quek. *Sci. Rep.* 5, 14565, 2015.

[#]Equally contributed.

Chapter 1 Introduction

1.1 Organization of This Thesis

In Chapter 1, I will give an introduction on atomically thin two-dimensional group IV TMD materials, in terms of synthesis and optical properties. Both top-down and bottom-up methods will be reviewed, with a particular focus on the research work done within the last five years. The introduction on optical properties was divided into three sections: (1) Band structure and photoluminescence. (2) Symmetry-related properties: valley polarization and second harmonic generation. (3) Intralayer and interlayer vibrational modes in mono- and few-layer TMDs.

In Chapter 2, I will describe the equipment for synthesis (chemical vapor deposition system, CVD), as well as the spectrometer used for the study of lattice vibrational modes (Horiba-JY T64000 micro-Raman spectroscopy). Comparison on the current two methods on reaching low-frequency region will be given.

In Chapter 3, I will introduce my PhD work on the preparation of thin film samples by using top-down method, which includes scotch tape-based mechanical exfoliation, preparation of heterostructures, and thermal annealing thinning.

In Chapter 4, I will present my PhD study on CVD synthesis of atomically thin MoSe₂ and WSe₂, together with optical properties and characterization of device performance. In this section, I will elaborate on the details of growth, such as the pressure-dependent morphology and the influence of using catalyst during growth on device performance. Some other aspects, including the SU8 patterning of CVD-grown MoSe₂ film and disappearance of interlayer breathing modes in CVD-grown WSe₂

nanoflakes will also be discussed.

In Chapter 5, I will focus on the correlation between stacking sequence and the evolutionary trend of interlayer shear modes with increasing thickness. Theoretical prediction based on bond polarization will be presented first. Afterwards, a case study by using CVD-grown few-layer MoSe₂ flakes will be demonstrated. Frequencies of the emerging new modes can be fitted within the linear chain model, indicating the origin of the vibrations. Combining structural characterization on scanning transmission electron microscopy (STEM), we are capable of showing that low-frequency Raman scattering is a rapid and nondestructive method for stacking identification.

In Chapter 6, I will discuss the gate-tunable resonant Raman scattering measurements on mono- and few-layer MoS₂. Gate voltage is applied through an ionic gel top-gated device. Dependence on gate voltage of photoluminescence spectroscopy has been conducted as well. Different excitation lasers are obtained by using a solid state 532 nm laser, a He-Ne 633 nm laser, and a tunable dye laser (from ~565 nm to ~610 nm).

Finally, I will conclude my thesis and provide some perspectives of future work in Chapter 7.

1.2 Two-dimensional Layered Nanomaterials

Nanomaterial refers to a structure with at least one dimension in the scale of 1-100 nm, which is also known as the nanoscopic scale (nanoscale). Structures with three dimensions within the nanoscale are called as zero-dimensional (0D) nanomaterial, with quantum dot as a typical example. Similarly, one-dimensional (1D) and two-dimensional (2D) nanomaterials have two and one dimension in the scale of 1-100 nm, respectively.

Nanowire, nanorod, and nanobelt can be categorized into the family of 1D nanomaterials. Graphene, as the most well-known 2D nanomaterial in the past decade, is a layered material. However, 2D nanomaterial does not necessarily have to be a layered material, such as the Au thin film used as contact material in device fabrication.

Besides graphene, group IV transition metal dichalcogenides MX_2 ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}, \text{Te}$), topologically insulating bismuth chalcogenides Bi_2X_3 ($\text{X} = \text{Se}, \text{Te}$), and black phosphorus are all layered materials. Note that the thickness of a single layer (1 L) graphene, MoS_2 , and black phosphorus is ~ 0.35 nm, ~ 0.70 nm, and ~ 0.50 nm, respectively. They are all 2D nanomaterials, although not in the range of 1-100 nm.

Experimental and theory theoretical studies on ultra-thin 2D layered materials are motivated with the discovery of fascinating properties and novel phenomena in mono- and few-layers, as well as 2D-based heterostructures [1-10]. For instance, quantum Hall effect has been observed in graphene at room temperature [11]. In single-layer MoS_2 and WS_2 , strong photoluminescence (PL) in the visible wavelength has been reported [12-14]. Compared to TMDs, the high carrier mobility of black phosphorus has made it popular in the recent development of 2D field effect transistor (FET) [15, 16]. Besides, the anisotropic behavior resulting from the crystal structure has made black phosphorus very attractive towards applications in optoelectronics [17, 18].

It is intuitive to ask why researchers want to go to thin layers. Can the interesting phenomena mentioned above be observed in relatively thicker samples, or even bulk materials? Generally speaking, in atomically thin 2D nanomaterials, the small size in the out-of-plane direction results in the quantum confinement effect. The confinement effect is a type of quantum size effect that occurs when physical size is comparable or smaller

than the characteristic length scale, such as the phonon mean free path and exciton Bohr radius. Quantum confinement effect on lattice vibrations in 2D materials has been observed by Raman spectroscopy: With the decreasing layer number, A_{1g}^1 , A_{1g}^2 , and E_g^1 modes in Bi_2Se_3 red-shift, while there is almost no difference for E_g^2 mode. This is in agreement with the phonon dispersion curve along the Γ -Z direction, as only E_g^2 mode exhibits a dispersionless trend [19]. What's more, in 2D nanomaterials, some of the unique properties are closely related to the thickness-dependent band structure and crystal symmetry. For example, as thickness decreases from bulk to thin layers in MoS_2 , the valence band maximum (VBM) at Γ point is going down and the conduction band minimum (CBM) gradually shifts to K point. Eventually in monolayer, it is a direct bandgap semiconductor. In contrast, the bandgap in MoS_2 from bilayer to bulk, is an indirect one [12, 13]. More details will be discussed in section 1.3.1.

Research in 2D nanomaterials is still very active and covers different aspects from fundamental studies to device application. Thus the importance on sample preparation, *i.e.*, how to obtain the suitable materials for experiments, has become self-evident.

1.3 Synthesis of Atomically Thin Layered Transition Metal Dichalcogenides

An ideal preparation method for 2D materials should produce sample with: (i) high crystalline quality; (ii) potentially scalable to wafer scale; (iii) spatial uniformity; and (iv) controllable layer numbers. The high crystalline quality criterion is especially required for proof-of-concept demonstration and fundamental research, such as for the emergence of

quantum transport phenomena (*e.g.*, Shubnikov de Haas oscillation) [20] and for reducing inter-valley scattering [21] in TMDs. Meanwhile, technological applications also demand high throughput and reproducibility, regardless of the sensitivity of the atomically thin materials to minute changes in synthesis environment. The preparation methods of 2D materials consist of “top-down” subtraction of layers from bulkier crystal, and “bottom-up” paradigm with crystal growth *via* synthesis. Here I will highlight the methods which are currently employed in producing mono- and few-layer TMD materials.

1.3.1 Top-down methods

Layered 2D materials are unique relative to other low-dimensional nanostructures since there is a top-down method, *i.e.*, mechanical exfoliation, which can consistently produce higher quality samples than most synthesis approaches in terms of structural perfection and carrier mobility. Mechanical exfoliation of TMDs, reported since as early as 1966, relies on the strong adhesion between substrate and the contacting layer [22]. Cleaving 2D layers mechanically with adhesive “scotch tape” (Figure 1-1 (a)) causes only minimal damage that the sample quality translates from the parent crystal to the substrate environment. However, the low throughput, absence of thickness control, and limited sample size (mostly $< 50\ \mu\text{m}$ in width) made exfoliation only practical for research purposes. It is important to note that not all layered materials can be exfoliated into thermodynamically air stable monolayer [7].

Wet exfoliation, which is applicable to a variety of 2D materials, has much higher throughput and scalability [3, 23-26]. Liquid phase exfoliation uses sonication in organic

solvent with surface energy similar to that of the layered materials to promote detachment of the layers from the bulk crystal, creating suspension which can then be spray-coated into a film (Figure 1-1 (b)) [24]. Unfortunately, the isolation yield of monolayer flakes is low. Other wet exfoliation involves intercalation of metal ions such as lithium, either *via* a long immersion or electrochemistry, to aid the layer separation (Figure 1-1 (c)) [27-29]. However, intercalation may create surface contamination, structural distortion (*e.g.*, 2H to 1T phase change in MoS₂), and damages that affect the material properties [30].

Figure 1-1. A selection of top-down methods for 2D TMDs: (a) mechanical exfoliation, (b) liquid phase exfoliation [24], (c) intercalation-assisted exfoliation [23].

There is another well-known top-down method in 2D TMDs, thinning. Laser thinning of MoS₂ (prepared by mechanical exfoliation) was reported in 2012 [31]. A green laser with energy of ~2.41 eV has been used to thin down the multilayer MoS₂ flake into monolayer. With laser-induced heat, sublimation of the upper layers occurs when the laser power is larger than 10 mW. Meanwhile, the bottom layer would stay intact until the power reaches ~17 mW [31]. However, laser-thinning can only produce monolayers. Bilayers and trilayers cannot be obtained in this way. Later, layer-by-layer thinning of MoS₂ down to monolayer was achieved by Ar⁺ plasma [32]. By adjusting the exposure time to plasma, one can control the thickness of the plasma-thinned MoS₂. Besides atomic force microscopy and high-resolution transmission electron microscopy, Liu *et al.* has further utilized Raman and PL spectroscopy to examine the thinning results, which shows

that the top layer is completely removed by plasma while the bottom layer remains almost unaffected [32]. Afterwards, thermal annealing method is developed [33, 34], which will be introduced in Chapter 3.

1.3.2 Bottom-up methods

Save for a few [35], nearly all bottom-up approaches for 2D TMDs follow non-catalytic, vapor-based synthesis. The growth of 2D TMDs was accomplished in the 1980s using molecular beam epitaxy (MBE) on another layered materials as the substrate, in a growth strategy called “van der Waals (vdW) epitaxy” [36]. The hetero-interface without dangling bonds between the two layered materials causes the interface to be bound by vdW interaction, which does not strain the lattices of the epitaxial material. vdW epitaxy allows defect-free interface even with large lattice mismatch reaching 50% [37], which has been achieved in nano-/micro-wire arrays [38-41]. Although it is slow and requires ultrahigh vacuum, MBE is powerful since *in-situ* characterizations of crystalline and electronic band properties are readily available [42, 43].

Figure 1-2. A selection of bottom-up methods for 2D TMDs: (a) sulfurization of pre-deposited film [44], (b) CVD from solid precursors, (c) metal-organic CVD [45].

Recent synthesis involves sulfurization/selenization of a Mo- or W-based precursor at temperature $\sim 500\text{-}1000\text{ }^{\circ}\text{C}$. One way is to use a substrate with pre-deposited Mo-/W-based precursor, such as Mo [44], MoO_3 [46], or WO_x thin film [47] (Figure 1-2

(a)), or $(\text{NH}_4)_2\text{MoS}_4$ (thiosalt) [48]. The layer number of the resulting sample is adjustable from the thickness of the pre-deposited precursor. However, difficulty to achieving uniformity of the pre-deposited precursor in sub-5 nm regime from thermal evaporation/dipcoating, prevents the synthesis of large area monolayer with large grain sizes. The use of atomic layer deposition (ALD) may control the thickness of the Mo-/W-based film with atomic precision [49]; however, the precursor is also very toxic and not widely available. To get larger grain size, one may use MoO_2 micron-sized flakes as the growth template, followed by peeling and sample transfer [50]. Unfortunately, the transfer process may inevitably degrade the properties of the resulting MoS_2 .

There is another approach performing sulfurization/selenization in vapor phase followed by deposition onto a substrate, the chemical vapor deposition (CVD). In CVD growth, substrates such as SiO_2 are commonly placed upside down atop the crucible of the precursor and the reaction chamber is stabilized at atmospheric pressure (Figure 1-2 (b)) [51]. The typical precursors are S or Se powder and MoO_3 or WO_3 powder, although nanoribbons [52] can also be used. High temperature vaporizes the precursors and carrier gas transports the vapors onto the substrate. Taking MoS_2 for instance, MoO_3 is reduced by sulphur into MoO_{3-x} during annealing to aid evaporation, and further reacted with sulphur to form MoS_2 [46, 51]. The CVD method is effective in synthesizing mono- and few-layered MoS_2 [51-53], MoSe_2 [54-58], WS_2 [47, 59-61], and WSe_2 [62, 63], in the form of either film or flakes. In such growth, clean substrate and precursors are crucial to obtain large area samples [53]. vdW epitaxy, which is common for 2D materials, can also be realized in CVD growth of TMDs [64, 65]. Recent progress has shown that CVD synthesis can achieve more: Monolayer alloy with tunable band gap [66-71] and

heterostructure with sharp interface [72-76] can be obtained in CVD.

To improve the crystallinity, grain size, and uniformity of the CVD-grown samples, previous studies have shown that aromatic organic molecules, such as perylene-3,4,9,10-tetracarboxylic acid tetrapotassium (PTAS), can help during growth. The molecule works as the seeding promoter (catalyst) [77]. At cases when the sample was produced with and without seeds appears visually comparable, PTAS seeding may also improve the nucleation density and repeatability of synthesis; however, the seed promoter may act as impurity and degrade electrical properties [78], which will be discussed in Chapter 4.

Control of layer number uniformly is generally difficult in CVD synthesis, requiring careful adjustments in growth parameters. Recently, thickness control is correlated with the length of oxygen plasma treatment of the underlying SiO₂ substrate [79]. Other precursor such as MoCl₅ also allows better controllability in uniformly controlling the layer number *via* a self-limiting mechanism in the vapor-solid phase change of MoS₂ [80]. Nevertheless, the spatial uniformity and electrical performance over a wide area is relatively poor for synthesis with solid precursors. One solution is to adopt the synthesis with metal-organic gaseous precursors (Figure 1-2 (c)) which produces high uniformity, 99% yield, and mobility reaching 30 cm²V⁻¹s⁻¹ at room temperature [45].

Besides sulfurization and selenization, direct vapor transport and vapor-solid crystallization can be conducted with precursor of the same stoichiometry as the desired material in CVD growth. The direct growth usually needs lower pressure or higher temperature since the melting point of MX₂ (M=Mo, W; X=S, Se, Te) is much higher than that of MoO₃ (WO₃) or S (Se, Te). Synthesis of monolayer MoS₂ from MoS₂ powder has

shown excellent crystalline and optical properties with ~100% valley polarization at 30 K [21].

1.4 Optical Properties of Mono- and Few-layer Transition Metal Dichalcogenides

The most pronounced difference between TMD materials and graphene, if we can only select one, is supposed to be the band gap. The direct benefit of having a band gap is on potential device application, such as FET. In terms of optical properties, a direct gap in the visible-wavelength range enables studies on PL. Information on exciton (lifetime, energy, binding energy, neutral/charged...) and defect states can be interrogated from PL spectroscopy.

1.4.1 Band Structure and Photoluminescence

Here I will take MoS₂ as an example of the group IV TMDs to illustrate the layer-dependent band structure and physical origin of valence band minimum (VBM) and conduction band maximum (CBM). Calculated band structure of bulk, four-layer (4 L), 2 L, and 1 L MoS₂ by using the PWscf package [81] is shown in Figure 1-3. The energy of direct-gap transition at K point of Brillouin zone hardly changes with different thickness, but the indirect bandgap increases monotonically as the number of layer decreases (from Figure 1-3 (a) to Figure 1-3 (d)). Remarkably, the indirect-gap transition energy becomes so high in monolayer MoS₂ that the material turns into a 2D direct bandgap semiconductor. To understand the layer-dependent band structure, it is very important to know the band character of states in valence band and conduction band. Theoretical

calculations show that the conduction band minimum at K point is primarily consisted of the strongly localized d orbitals from Mo atoms. Negligible interlayer coupling is expected to be from Mo atoms because they are located in the middle of the S-Mo-S unit cell. In contrast, states near the Γ point at the valence band and states near the Λ point (midpoint between K and Γ) at the conduction band are combined of d orbitals on Mo atoms and antibonding p_z orbitals on S atoms. They have strong interlayer coupling and their energies depend sensitively on thickness [12].

Figure 1-3. Calculated band structures of (a) bulk, (b) 4 L, (c) 2 L, and (d) 1 L MoS₂ [12].

In principle, the above analysis on thickness-dependent band structure alignment is supposed to be applicable to all the group IV TMDs, although there is some subtle difference. For example, for bilayer 2H-TMDs, the CBM locates at different points among MX₂ (M = Mo, W; X = S, Se, Te). Experimental results confirm that the CBM is located at the Λ point for bilayer MoS₂ and WS₂, while it is at the K point for bilayer WSe₂ [82]. A recent paper on gate-tunable PL measurements at room temperature and 77 K further confirms that the Λ point is lower than the K point in the conduction band of 2

L MoS₂ [83]. In contrast, there is an agreement on monolayer (CBM at K point) and multilayers with layer number ≥ 3 (CBM at Λ point).

Table 1-1. Optical band gap energy (Λ exciton) of monolayer and bulk MX₂ (M = Mo, W; X = S, Se, Te).

	-S ₂	-Se ₂	-Te ₂
Mo	1 L: ~1.9 eV Bulk: ~1.2 eV	1 L: ~1.56 eV Bulk: ~1.1 eV	1 L: ~1.1 eV Bulk: ~1.0 eV
W	1 L: ~2.0 eV Bulk: ~1.4 eV	1 L: ~1.65 eV Bulk: ~1.2 eV	1 L: ~1.1 eV Bulk: ~0.7 eV

Further comparison among MX₂ (M = Mo, W; X = S, Se, Te) shows that as anion goes from S to Te, the band gap increases, and the Mo-based compounds, in general, have smaller band gap energy compared to the W-based compounds. Table 1-1 has summarized the optical band gap energy (Λ exciton) of monolayer and bulk MX₂ (M = Mo, W; X = S, Se, Te).

Figure 1-4. Band alignment of monolayer MX₂ from calculations. Solid and dashed lines are obtained by PBE and HSE06, respectively. The water reduction (H^+/H_2) and oxidation (H_2O/O_2) potentials is indicated by dotted lines in the figure as reference. The vacuum level is considered as zero reference [84].

It is intuitive to ask what determines the band gap, which leads to the investigation of band alignment, as displayed in Figure 1-4. First of all, let's consider the common

cation system (MoX_2 or WX_2). The $d_{x^2-y^2}$ and d_{xy} orbitals of anion atom (Mo/W) are in the majority of the VBM of monolayer MX_2 , while the p_x and p_y orbitals of cation atom (S/Se/Te) are in the minority. At K point in the Brillouin zone, it is found that the VBM has the same character as the 5th band at the same point, which is approximately 4 eV lower than the VBM. Therefore, there is repulsion between the d orbitals of cation and p orbitals of anion. The d orbitals of Mo/W are pushed up forming the VBM. Magnitude of the repulsion is related to the overlap integral of p and d orbitals and their difference in terms of energy. Overall, a smaller energy difference or a larger overlap integral leads to larger separation between the VBM and the 5th band mentioned above. For increasing atomic number of anion, the p orbitals become shallower. Consequently, the anion with shallower p orbitals pushes the cation d orbitals upwards more than the anion with deeper p orbitals. In the meantime, the energy of CBM also increases with increasing atomic number from S to Te (one exception: from WSe_2 to WTe_2), but the magnitude is smaller. Therefore, the band gap becomes larger [84].

Next, it is the common anion system (MS_2 , MSe_2 , MTe_2 ; $\text{M} = \text{Mo/W}$), which can be understood through the position of the d orbitals of cation. The energy of the 5 d orbital in W atom is higher than that of the 4 d orbital of Mo atom. Thus, CBM and VBM of WX_2 are higher than those of MoX_2 , with one exception of WSe_2 & WTe_2 . Compare with WSe_2 and WTe_2 , WTe_2 has longer bond length, leading to a smaller overlap integral. The influence of decreasing overlap integral overrides the influence of increasing p orbital energy ($\text{Te} > \text{Se}$), and it causes the CBM in WTe_2 in lower state [84].

It is worth noting that the group IV TMDs MX_2 ($\text{M} = \text{Mo, W}$; $\text{X} = \text{S, Se, Te}$) have strong spin-orbit coupling originated from the d orbitals of the heavy metal atoms (Mo, W)

[85, 86]. The strong spin-orbit interaction causes a significant splitting in the valence band at K point, resulting in the so-called A and B excitons. The splitting energy is ~150 meV in MoS₂, and ~450 meV in WSe₂ [85]. The spin-orbit coupling also induces splitting in the conduction band, but the magnitude is much smaller. According to calculations, the splitting energy is only 38 meV in the conduction band of monolayer WSe₂ [87].

Figure 1-5. Thickness-dependent photoluminescence from MoS₂. (a) PL spectra of 1 L and 2 L MoS₂ with photon energy ranging from 1.3 to 2.2 eV. Inset: PL quantum yield of 1-6 L MoS₂. (b) Normalized PL spectra by the intensity of A exciton peak in 1-6 L MoS₂. Feature *I* in 4-6 L MoS₂ is magnified and the spectra are displaced for clarity. (c) Band-gap energy of mono and few-layer MoS₂, inferred from the energy of feature *I* for 2-6 L MoS₂ and from the energy of A peak of monolayer MoS₂. The dashed line refers to the band-gap energy of bulk MoS₂ [13].

The A exciton and B exciton can be resolved from PL spectroscopy [12, 13]. Figure 1-5 displays the PL spectra from MoS₂ with various thicknesses. Compared to bilayer, the PL from monolayer is much stronger. The quantum yield from direct excitonic state (*e.g.* A exciton) is related to the ratio $k_{\text{rad}} / (k_{\text{defect}} + k_{\text{rad}} + k_{\text{relax}})$. Intraband relaxation (k_{relax}) to band minimum is in extremely high rate from the indirect bilayer and thicker layers, while k_{relax} is much lower in monolayer [12]. Still, the major reason for enhanced PL intensity in monolayer is attributed to the nature of a direct gap semiconductor.

1.4.2 Symmetry: valley polarization and second harmonic generation

Besides band structure, which is directly related to excitonic energy and PL quantum

yield, symmetry is also associated with the optical properties in group IV TMDs, such as on valley polarization and second harmonic generation (SHG). Hereafter, I will mainly take 2H-MoS₂ as an example on further discussion in this section. The 2H stacked MoS₂ bulk crystal is abundant in nature. In contrast, other bulk compounds (as well as MoS₂ crystal with other phases) used for mechanical exfoliation are mostly synthesized in crystal growth lab. This causes the research studies in 2H-MoS₂ much more active than those in other TMDs.

Figure 1-6. Electronic and atomic structures at the K' and K valleys of 1 L (a–c) and 2 L (d–f) MoS₂. (a) Lattice structure of 1 L MoS₂. Inversion symmetry is spatially broken. (b) Conduction band minimum (CBM) and the valence band maximum (VBM) labelled by the z-component of their total angular momentum. Due to spin-orbit coupling, spin degeneracy at the VBM is lifted, leading to the coupled spin and valley index. (c) Optical selection rules on circularly-polarized light for the A and B exciton states at two valleys. (d) 2 L MoS₂ with Bernal AB stacking. (e) Spin degeneracy of the valence bands is restored by time-reversal and spatial inversion symmetries. Spin and valley are decoupled. (f) Optical absorption in 2 L MoS₂. Both valleys are equally populated with circularly polarized light [88].

The monolayer counterpart of 2H-stacked MoS₂ crystal is an ideal candidate for the study of coupled spin and valley, as a result of the spatially broken inversion symmetry

(shown in Figure 1-6 (a)) and the strong spin-orbit coupling. The spin-orbit interaction causes a large splitting of valence band at K and -K (K') points (shown in Figure 1-6 (b)) in MoS₂, which occurs for all the layer number from monolayer to bulk. K and -K points locate at the corners in the Brillouin zone, but they are not equivalent. Yet these two points are related due to the time reversal symmetry $E^\uparrow(K) = E^\downarrow(-K)$, and this symmetry is preserved in all the thicknesses. Interestingly, inversion symmetry is only broken in atomically thin odd layer number (*i.e.*, 1 L, 3 L, ...), resulting in $E^\uparrow(K) \neq E^\uparrow(-K)$. Therefore, the spin degeneracy is lifted $E^\uparrow(K) \neq E^\downarrow(-K)$ in monolayer as well. Spin is locked in each valley and the large splitting energy forbids the flip of spin index. The contrasting valley is accompanied by a valley-dependent selection rule for optical excitation with circularly polarized light: the interband transition at K (-K) couples only to σ^+ (σ^-) circularly polarized light [85, 89, 90]. It means that the K (-K) valley only absorbs and emits light with right-handed σ^+ (left-handed σ^-) circularly polarized light, which is displayed clearly in Figure 1-7 (a). By using photoluminescence spectroscopy, it is possible to probe the valley polarization.

Figure 1-7 (b) shows the PL spectra of monolayer MoS₂ at 83 K, with σ^+ circularly polarized 633 nm laser as excitation line. As we can see from the figure that the PL intensity from σ^+ polarization (in red) is approximately 3 times of that of the σ^- polarization (in blue). The net polarization is defined by $\left| \frac{I_{\sigma^+} - I_{\sigma^-}}{I_{\sigma^+} + I_{\sigma^-}} \right|$. Ideally and theoretically, the polarization value should be 100%, while it is only ~50% in Figure 1-7 (b). Experimentally, there are multiple factors which obstruct the observation of circular polarization.

Figure 1-7. Valley polarization in monolayer TMDs. (a) Valley and spin are coupled with optical selection rules in 1 L TMDs. λ_c (λ_v) refers to the splitting in conduction (valence) bands due to spin-orbit coupling [4]. (b) Circularly polarized PL of 1 L MoS₂ at 83 K, as well as the degree of polarization. The red and blue curves in the luminescence spectrum correspond to the intensities of σ^+ and σ^- polarizations, respectively. The black curve shows the net degree of polarization [91]. (c) Circular polarization of the A exciton as a function of the excitation energy. The solid line represents a fit to the experimental data (circles). Inset: Optical selection rules. [92]. (d) Degree of circular polarization as a function of temperature. The fitting curve in red assumes that the intervalley scattering rate is proportional to the phonon population, giving a phonon energy of 240 cm⁻¹ [93].

Excitation energy and temperature are two of the most important factors. Figure 1-7 (c) demonstrates that as the excitation energy is farther away from the excitonic energy of A exciton (~1.9 eV), the circular polarization decreases dramatically. In Si and Ge, spin and valley scattering is known to have a power-law dependence on wave vector because of scattering with long wavelength acoustic phonons [94]. The fitting result in Figure 1-7 (c) also indicates a power-law dependence on the decay, which suggests that the spin relaxation time in MoS₂ is dominated by the intervalley scattering of electrons and holes. Besides excitation energy, intervalley scattering is also related to temperature, as

displayed in Figure 1-7 (d). When the temperature is higher than 90 K, the circular polarization decreases rapidly, indicating the intervalley scattering is dominated by phonons. The steady-state photoluminescence polarization is inversely proportional to the valley scattering rate γ_v . Phonons near the K points can supply momentum change for the intervalley scattering. In such case, the valley scattering rate γ_v is proportional to the population of these phonons $\exp(-E_K / K_B T)$, where E_K is the phonon energy near the K points. The solid curve in Figure 1-7 (d) is a fit by assuming an $\exp(-E_K / K_B T)$ dependence, from which E_K is extracted to be 240 cm^{-1} , in agreement with the acoustic phonon energy near the K point reported in the bulk and monolayer MoS₂ [95, 96].

In fact, to fully confirm the observation of circular polarization is due to the coupled spin and valley, a controlled experiment has to be done to rule out the possibility of Hanle effect. In some semiconductor systems, there is circular polarization of luminescence originating from electron (hole) spin polarization, due to the spin-dependent optical selection rule [97]. When an in-plane magnetic field is applied to the sample, spin will be rotated and the circular polarization diminishes. That is the Hanle effect. Zeng *et al.* has applied an in-plane magnetic field $B = 0.65 \text{ T}$ on the monolayer MoS₂, and they observed no change in terms of valley polarization [93], further confirming the physical origin of the observed circular polarization. Apart from that, valley polarization, as a result of inversion symmetry breaking, is not supposed to be observed in bilayer TMDs. Several groups have found that in bilayer MoS₂ with 2H stacking, a small value of circular polarization was observed. Mak *et al.* and Zeng *et al.* attributed the phenomenon to substrate-induced broken inversion symmetry [88], and heating-induced structural anisotropy and consequently breaking inversion symmetry [93], respectively. The

intrinsic inversion symmetry in 2H-stacked bilayer TMDs, however, can be broken by applying a perpendicular electrical field. Wu *et al.* and Jones *et al.* have done some related work on 2 L MoS₂ [98] and 2 L WSe₂ [99], respectively. They have shown that the circularly polarized PL from bilayer TMDs can be effectively controlled by gate voltage. It is worth mentioning that in 3R-stacked MoS₂, inversion symmetry is broken in all thickness, such that the valley polarization can be observed in even layer number and bulk [100].

Unlike valley polarization, which is relatively complicated and unique in TMDs, second harmonic generation (SHG) is more straightforward. As long as there is no spatially inversion symmetry, SHG can occur. In 2H-stacked group IV TMDs (*i.e.*, Bernal stacking, AB stacking), SHG signal is supposed to emerge in odd layer number.

Figure 1-8. SHG effect in atomically thin MoS₂ and WSe₂. (a) The thickness dependence of surface nonlinear susceptibility and SHG intensity in 1-5 L MoS₂. The histogram represents the experimental results with uncertainties described by error bars. The results of model is shown in red squares (the model will be introduced in the main text) [101]. (b) Reversible SHG induced by back gate can be seen from the pristine bilayer WSe₂ sample. The spectra have been shifted vertically for clarity [102].

As expected from Figure 1-8 (a), there is no SHG intensity from 2 L and 4 L MoS₂ samples. However, the intensity difference among 1 L, 3 L, and 5 L needs further investigation to understand. By comparison, in Bernal stacked h-BN, SHG responses from 1 L, 3 L, and 5 L show negligible variation [101]. Li *et al.* introduced a simple model based on electrically decoupled layers. Also, they included the influence of the

reflection of both the fundamental and SHG fields from the underlying substrate into the model. Because the band gap of MoS₂ (< 3 eV for both direct and indirect gaps) is smaller than the SHG photon energy (~3 eV), light absorption was expected to play a significant role as well. The model was shown to well describe the trend (red square in Figure 1-8 (a)), but underestimates the magnitude of decreased SHG intensity as thickness increases. The additional reduction can be attributed to interlayer coupling. These effects modify the electronic structure of few-layer MoS₂ and results in further changes in the linear and nonlinear susceptibilities [101].

Similar to the valley polarization, electric control of SHG has been realized on a monolayer WSe₂ transistor by Seyler *et al.* [103]. Almost at the same time, Yu *et al.* have performed similar experiments on a back-gated bilayer WSe₂ device, and shown that hole accumulation can induce SHG signal in the p-type WSe₂ device [102]. A bond charge model [104] was shown to explain the results. It is found that the SHG signal is a result of Direct Current (DC) field nonuniformity caused by the localized accumulation charge. On a few ambipolar devices, SHG is even detected with electron accumulation, further confirming the analysis [102]. This result is fundamentally different from electric field control of SHG in monolayer WSe₂, which did not show threshold characteristics versus gate voltage [103].

1.4.3 Lattice Vibration: Intralayer and Interlayer Modes

The phonon properties of bulk TMDs have been studied for a long time [105-116]. Through infrared (IR) and Raman studies, most lattice modes can be observed and assigned. The conjugate pairs of A_{1g} and B_{1u} modes (~409 cm⁻¹), E_{1u}^2 and E_{2g}^1 modes

($\sim 384 \text{ cm}^{-1}$) have very similar frequency; the difference between conjugate pair is interpreted to be related to the layer-layer (*i.e.*, interlayer) interaction, which is also called as Davydov splitting/pairs [106, 107, 109]. Later, the second-order and resonant Raman spectra of MoS₂ and WS₂ were revealed, providing in-depth understanding of the lattice vibration modes [113-116]. Sugai *et al.* have studied the high-pressure Raman spectroscopy in 2H-MoS₂, 2H-MoSe₂, and 2H-MoTe₂ [111]. The pressure-dependent shifts were explained using the pressure dependent interlayer and intralayer force constants derived from a simple linear chain model proposed by Wieting [108]. The intensive studies on phonons in thin layers have only begun within the last decade. It is actually only after the resurgence of interest in graphene that confinement effect along the vdW gap (*i.e.*, out-of-plane direction) has been of the concern to the 2D community, especially in mono- to few-layer region ($< 10 \text{ L}$). Note that each layer of MX₂ (M = Mo, W; X = S, Se, Te) consists of X-M-X tri-atomic planes, such that a monolayer can also be called as one “tri-layer” (TL) [3].

There are basically two sets of Raman active modes in 2D layered materials. One set is the intralayer vibration modes, which appear in both atomically thin and bulk samples, usually at higher frequency side [117]. The other set is the interlayer vibration modes, such as the shear modes and breathing modes, where all the atoms within each layer displace collectively in the same direction with the same magnitude [117-119]. The interaction within a single layer is of covalent nature, such as M-X bonding in MX₂ layer, while the interaction between layers is mainly of the much weaker vdW type [105-108]. Lattice vibrational modes, including interlayer and intralayer modes, exhibit negligible frequency shift as thickness decreases from bulk to multilayer, but the layer-dependent

shifts become pronounced when the thickness is further reduced from few-layer to monolayer. An example has been shown in Figure 1-9 (a), with the fingerprint peaks of MoS₂, A_{1g} and E_{2g}^1 modes.

Figure 1-9. Intralayer vibrational modes in atomically thin MoS₂ and WSe₂. (a) Raman spectra of 1-6 L and bulk MoS₂. The solid line in the spectrum of 2 L is a double Voigt fit of experimental data (circles for 2 L, solid lines for the rest) [120]. (b) Raman spectra of 1-7 L and bulk WSe₂ in the range of 290- 330 cm⁻¹ under 488 nm excitation [121]. (c) Side view of atomic displacements for the A_{1g} , E_{2g}^1 , B_{2g}^1 , E_{2g}^2 , and E_{1g} vibrational modes in 2 L WSe₂ [121].

As thickness increases, A_{1g} mode upshifts by ~ 4.0 cm⁻¹ from 1 L to 6 L, and E_{2g}^1 mode downshifts by ~ 2.5 cm⁻¹ from 1 L to 4 L. The stiffened A_{1g} mode in thicker layers is expected. As more layers are added to form the bulk material from individual layers, the interlayer interactions due to vdW force increase the effective restoring forces acting

on the atoms, thus causing the blue-shift [120]. The redshift of E_{2g}^1 mode with increasing thickness is explained by surface effect [122]. This surface effect is due to the absence of interaction between neighbouring atoms in a few nanometers above the surface [123]. The surface effect will cause significant enhancement on the force constants in thin layers, resulting in the anomalously redshift frequency trend of E_{2g}^1 mode with increasing thickness [122]. Thus, the opposite shifts of E_{2g}^1 and A_{1g} modes in frequencies are combined results of thickness effect and surface effect.

Besides, with reduced dimensionality and lower symmetry in thinner layers, some Raman-inactive modes in bulk and multilayer can evolve to be Raman-active modes in few-layers, such as the B_{2g}^1 in few-layer WSe₂ (shown in Figure 1-9 (b)). According to group theory analysis, the counterpart of B_{2g}^1 mode will evolve into the Raman-active A_{1g} mode in even layer number (311.3 and 310.1 cm⁻¹ in 2 L and 4 L, respectively), and Raman-active A_1' mode in odd few-layer (311.0 cm⁻¹ in 3 L). This mode has A_2'' symmetry in 1 L, which is not Raman-active. Similar to E_{2g}^1 and A_{1g} modes, B_{2g}^1 mode also experiences both thickness effect and surface effect, causing the mode softened with increasing thickness [121].

Compared with the intralayer mode, the frequency of the interlayer mode is of lower frequency (mostly < 50 cm⁻¹), much closer to the detection limit of traditional Raman spectroscopy with a single monochromator and a notch filter, which makes the observation of low-frequency mode in few layer 2D materials challenging. The interlayer shear mode of bulk graphite located at 42 cm⁻¹ was first measured by Nemanich *et al.* in 1970's through triple grating Raman spectrometer [124]. Also through the triple grating setup, the low frequency interlayer shear mode E_{2g}^2 (33.7±1 cm⁻¹) of MoS₂ was first

detected by Verble *et al.* in 1972, and the interlayer force was found to be 100 times weaker than the intralayer force [125]. Later, interlayer shear mode in bulk MoSe₂ [111, 126], MoTe₂ [111], WS₂ [112], and WSe₂ [127] were measured.

Figure 1-10. Interlayer shear (S) and breathing (B) modes in few-layer 2H-stacked MoS₂. (a) Low-frequency Raman spectra of 1-12 TL MoS₂ measured by using the $\bar{z}(xx)z$ polarization configuration. (b) Plot of frequencies for interlayer breathing and shear modes as a function of thickness. Calculation results (open squares) and experimental data (solid dots) match very well. Lines are fitting results based on linear chain model. (c) Schematic of the linear chain model for N TL of MoS₂. One blue sphere stands for one trilayer. The force constant K is between the nearest neighbor TLs only [118].

Figure 1-10 displays the interlayer shear (S) and breathing (B) mode in few-layer 2H-stacked MoS₂. S1 (S2) stands for the interlayer shear mode with the highest (the 3rd highest) frequency. The 2nd highest frequency branch cannot be observed in even layer number because it is Raman-inactive; while in even layer number, the mode is Raman-active, but it is not allowed under the commonly used backscattering configuration. B1 (B2) stands for the interlayer breathing mode with the lowest (the 3rd lowest) frequency. The reason for the disappearance of the 2nd lowest branch is similar to that in the interlayer shear mode. Plot of shear and breathing mode frequencies as a function of layer number is shown in Figure 1-10 (b). Linear chain model was found to well describe the thickness evolutional Raman shift of interlayer vibrational modes. Linear chain model is a simple model in which the lattice vibrations are related to the

interlayer interaction within the layered material. This model only takes the interlayer coupling between the nearest-neighbor layers into consideration. Within the N -layer sample as shown in Figure 1-10 (c), $K = K_z$ and $K = K_x$ refer to the out-of-plane and in-plane force constant, respectively. With this model, the corresponding phonon frequencies (in the unit of cm^{-1}) can be represented as:

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

with N being layer number and K being the force constant per unit area. Without considering the substrate effect (*i.e.*, $K_i = 0 \text{ N/m}^3$) [128], K corresponds to K_z and K_x for breathing modes and interlayer modes, respectively. μ is the mass per unit area, and c is the speed of light. When $\alpha = 1$, it corresponds to the acoustic mode. In 2H-MoS₂, when $\alpha = N, N-2, 2, 4$, it leads to the frequency of S1, S2, B1, and B2, respectively [118].

1.5 Motivation and Objectives of this Thesis

Research studies on atomically thin group IV TMDs MX₂ ($M = \text{Mo, W}$; $X = \text{S, Se, Te}$) started with the 2H-stacked MoS₂ crystal, as it is abundant in nature. The limitation on 2H-MoS₂ at the early stage has motivated lots of scientists to develop various ways to obtain other compounds and phases. Although these materials belong to the same family, there are still considerable differences which have intrigued researchers. For instance, MoS₂ is an n-type semiconductor, while WSe₂ is p-type. Later, the research scope has even extended to other stacking configurations, such as 1T and 3R phases. Regardless of the limitation on samples, theoretical calculations can still proceed. The progress on fundamental studies in experiments and potential massive application is subjected to the

availability of samples. Thus, the first objective of this thesis is to solve the problem on sample preparation; precisely, on Se-based TMDs and samples with non-2H stacking.

Secondly, the emerging focus on stacking-related properties have raised the curiosity among the 2D community. Recently, there are papers published on how to engineer the phase to improve electrical performance [129] and stacking-related valley polarization [100]. Still, the fundamental understanding on stacking-related phonon properties is lacking. The second objective of this thesis is to study the correlation between stacking sequence and the low-frequency interlayer shear modes. Meanwhile, a rapid and nondestructive method on stacking identification is developed.

Finally, I will delve deeper to the fundamental properties of phonons. Dependence on thickness [118, 120], folding/twisting [130-132], stacking order [133, 134], polarization [135, 136], strain [137], carrier concentration [138], and excitation energy [139, 140] of phonon properties has been well studied in previous literatures. The combined effect of the above factors, however, is less investigated, except measurements related to anisotropy (*e.g.*, angle-resolved Raman scattering excited by several laser lines [141], thickness-dependent interlayer vibrational modes under parallel- and cross-polarized configurations [118]). For the last part of this thesis, I will present my recent research on gate-tunable resonant Raman scattering measurements on mono- and few-layer MoS₂. The experiments and the discovered phenomena may be complicated, but it will help to understand the intrinsic properties in group IV TMDs.

The study on gate-dependent phonon properties is interesting. Previous study on gate-tunable Raman spectroscopy of atomically thin group IV TMDs is only limited on 1 L MoS₂ [138], which makes me wonder on the cases of 2 L and 3 L. Besides smaller

quantum capacitance which causes less effective doping in thicker layers, the distribution of gate-induced electrons/holes will be different from that in monolayer. This is because of the band structure evolution as a function of layer number, which also causes the indirect-to-direct gap transition in MX_2 ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}, \text{Te}$). Investigation in different thickness will possibly uncover some gate-tunable effect which is related to the band structure. Moreover, dependence on excitation laser energy is something I would like to explore. Previous literature has reported that Raman study of doping effect in carbon nanotube shows dependence on excitation laser, due to the resonance to van Hove singularity [142]. There is van Hove singularity in MoS_2 as well, regardless of thickness [143, 144]. Apart from that, the existence of A and B excitons within the visible range also makes it meaningful to check the resonance effect.

Chapter 2 Instrumentation

2.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) refers to a chemical process used to produce high quality solid materials. In semiconductor industry, CVD is often used to produce thin film. With the growing interests in nanostructures, especially the mono- and few-layer 2D materials, CVD is widely seen in research labs for synthesizing atomically thin films. The main difference between physical vapor deposition (PVD) and CVD is that PVD only utilizes physical process. In a typical PVD process, a purified single solid source is gasified *via* evaporation in the high temperature zone. The vapor will then condense on the substrate to create the thin film or nanostructures in the low temperature regime. Note that there is no chemical reaction at all during the whole process. In CVD system, although the single source might be high purity solid as well, the process is quite different. For example, the growth of ZnO nanoflakes/nanowires adopts 99.99% ZnO powder as source. During the growth, there is reaction between ZnO (s) and the carrying gas H_2 , producing Zn vapor and H_2O vapor in the high temperature region. In the downstream where temperature lower, Zn vapor reacts with H_2O vapor, and returns to ZnO solid, either in the form of nanoflakes or nanowires [145]. The hydrogen in the transport gas actually works as catalyst, yet there is no denying that there is chemical reaction.

The basic elements of a CVD system include gas (upstream), furnace with quartz tube, and pump/exhaust (downstream). Depending on the number of independent power supplies and thermocouples which control each individual zone, there are single-zone and three-zone furnaces. As Figure 2-1 shows, a single-zone furnace only has one power

supply and one thermocouple. In the upstream region (between thermocouple and the gas cylinder which is not shown in the figure), there are copper rods and gas inlet which is the entrance for gas from gas-line to quartz tube. The copper rods can be replaced by transferring quartz tube, which is used when it is necessary to switch sources during synthesis. As to the type of gas, there is various selections: H₂, N₂, O₂, and Ar in our lab. Flow rate can be tuned through controller.

Figure 2-1. Setup of a CVD system with single-zone furnace. Notes with arrows were displayed in the figure for further clarification. Normally, at least one source will be put in the center of the quartz tube, where it is the closest to the thermocouple (also referred to the high temperature region). Heating wires, as indicated in the figure, are used to distribute heat from the center. Substrate, in most cases, is placed on the downstream region of the quartz tube: region between thermocouple and exhaust outlet. The copper rods on the upstream side can be replaced by transferring quartz tube, which is used to switch sources during synthesis.

On the downstream side, there is a mechanical pump. Between pump and the exhaust outlet of the quartz tube, there is a baratron gauge for monitoring pressure, control valve, filter, molecular sieve and etc. In general, these components are there either for the modulation and stabilization of pressure, or to protect pump from contamination and

moisture. When sulfur powder or selenium powder was used as a source, liquid nitrogen trap is indispensable. Sulfur and selenium are volatile with low melting point: ~ 388 K for sulfur and ~ 494 K for selenium. Liquid nitrogen trap is adopted to condensate sulfur or selenium vapor into solid, in order to stop sulfur / selenium from entering the pump, or even being discharged to the atmosphere.

To summarize, CVD system is a basic setup with gas, furnace, and pump. It is changeable depending on the need of samples. In fact, some labs even do not use pump or feedback system for stabilizing pressure. The transferring quartz rods, in recent years, have also been substituted by using magnets to move sources inside the quartz tube, which can help to improve the intactness of the atmosphere within the chamber.

2.2 Raman Spectroscopy

2.2.1 Basic Theory of Raman Scattering

Raman scattering is a process in which incident light is inelastically scattered by molecule vibrations or phonons, quanta of lattice vibrations in solids. The sample undergoes a light-induced transition between vibrational states. Raman scattering can be divided into Stokes and anti-stokes scattering. If the final vibrational state has higher energy than the initial state, which means that the scattered photon has lower energy than the incident photon, it is called Stokes scattering. The energy difference between incident and scattered photon is usually called as Raman shift in Raman spectroscopy literature, generally in the unit of wavenumbers (cm^{-1}). Similarly, for anti-Stokes scattering, the scattered photon has higher energy, leading to a negative Raman shift. Generally, the incident photon excites the system to a virtual state before relaxation into the final state. This is called non-resonant Raman scattering. At times, when the energy of excitation

laser or the scattered light is in proximity to the band gap or a real state with high density of states, resonant Raman scattering is likely to occur.

Experimentally, lasers used in Raman spectroscopy are usually in the range of 1 to 4 eV, with a wave vector on the order of 10^5 cm^{-1} in the sample. As the scattered light has minimal energy difference between the incident light, the phonons involved in the Raman scattering must be in the order of 10^5 cm^{-1} as well due to the conservation law of energy and momentum. However, the size of Brillouin zone, is on the order of 10^8 cm^{-1} typically. Therefore, phonons near the Brillouin zone center (the Γ point), also known as the long-wavelength phonons, actually participate in the Raman scattering process.

The observation of a given phonon mode on Raman spectroscopy experimentally relies on the symmetry selection rules and the scattering geometry. A phonon mode can be observed on Raman spectrometer only when $|e_i \cdot \tilde{R} \cdot e_s|^2$ has a nonzero value, where e_i is the polarization vector of the incident light, e_s is that of the scattered light, and $\tilde{R}$ is the second rank polarizability tensor, commonly called the Raman tensor. The Raman tensor $\tilde{R}$ is related to crystal symmetry, and the Raman-active vibrational modes can be predicted by group theory analysis, using the irreducible representation of the zone-center phonons, which are derived from knowing the space group of the material [146]. The $e_i \cdot \tilde{R} \cdot e_s$ is given by:

$$e_i \cdot \tilde{R} \cdot e_s = \begin{pmatrix} x & y & z \end{pmatrix} \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} \quad (2-1)$$

There are two widely used polarization configuration setups for 2D layered nano materials on Raman spectroscopy. That is, the parallel-polarized $\bar{z}(xx)z$ configuration and the cross-polarized $\bar{z}(xy)z$ configuration where the z axis is the out-of-plane direction of the nanosheet samples and corresponds to the direction of travel for the

incident and scattered light. The difference between both configurations lies in the polarization vector of the scattered light e_s : For $\bar{z}(xx)z$, $y = z = 0$, and x is non-zero; For $\bar{z}(xy)z$, the incident light is polarized along x direction with zero y and z components, while the outgoing scattering light is polarized along y direction with zero x and z components.

2.2.2 Conventional Setup of a Raman Spectroscopy

Figure 2-2. Schematic setup of a conventional backscattering Raman spectroscopy.

A conventional Raman spectrometer includes light source, sample stage, filter, and detector. Objective is only necessary for small size sample, or when high power density is needed to excite the sample. Figure 2-2 shows the schematic setup of a backscattering Raman spectroscopy. Incident light coming from a laser source is reflected by a beamsplitter, and goes to the sample *via* an objective. Under the backscattering configuration, scattered light is reflected from the surface of the sample, with the direction opposite to the incident light. The scattered light, which contains both Rayleigh signal, *i.e.*, elastic scattering of laser photons and the inelastic scattered signal (Raman

shift), passes through the beamsplitter and filter one after another. The filter can be either edge filter (long/short pass filter) or notch filter depending on usage. The cutting of an edge filter is usually closer to the laser line, enabling the detection of lower frequency; while the advantage of a notch filter is that Stokes and anti-Stokes signal can be collected simultaneously. Before reaching the CCD detector, there is a dispersive grating. 1800 grooves/mm grating is used commonly in Raman measurement, with the number referring to the number of grooves per millimetre. The more grooves there are (per unit length), the higher the resolution is. However, smaller number indicates higher collection efficiency, if not taking the blaze angle into account. Last but not the least, it is the CCD detector, which is supposed to operate at low temperature, because the dark current caused by thermal electrons increases with higher temperature. Either thermo-electric cooling or liquid nitrogen cooling works, while liquid nitrogen can reach lower temperature. In fact, the dark current is extremely low (less than 1 electron/ pixel/ hour) for liquid nitrogen cooled CCD detector, so this noise is practically negligible. Besides, there are two other types of noises: photon shot noise and readout noise. The photon noise is proportional to the square root of the signal intensity. The readout noise is quite the same for different electronics (between 6 to 10 electrons/ pixel). This readout noise is generally the most important noise with the liquid nitrogen cooled CCD detector. That is why longer acquisition time can improve signal to noise ratio under most circumstances.

2.2.3 Techniques towards Low Frequency Region

It is very difficult to detect phonon modes with a Raman shift $< 50 \text{ cm}^{-1}$, even with an edge filter. Thus, triple-grating Raman spectrometer was invented, and in fact the

interlayer shear mode of bulk graphite located at 42 cm^{-1} was first measured through this setup in the 1970's [124]. “Triple” means that there are three gratings on that path which scattered travels from sample to detector. In contrast, there is only one grating in the conventional Raman spectroscopy (Figure 2-2), thus also being referred to “single mode” setup.

Figure 2-3. Simplified schematics for reaching low frequency wavenumber on Raman spectroscopy. (a) Schematic diagram of a triple-grating Raman spectroscopy. (b) Schematic diagram of a Raman spectroscopy with single monochromator and three BraggGrate notch filters (BNF) [147].

Figure 2-3 (a) has demonstrated the simplified schematic diagram for a triple-grating Raman spectroscopy. Compared to the setup in Figure 2-2, the change is on the pathway of the scattered light: after the beamsplitter and before the Grating 3 (Grating 3 is also the grating in Figure 2-2). The polychromatic light enters the first stage (*i.e.*, Grating 1) through the entrance slit 0-1 and is dispersed by the Grating 1. Slit 1-2 works as a bandpass filter, which only allows light between wavelengths of λ_1 and λ_2 to pass. Grating 2 recombines all the dispersed light and focuses it into the middle of the slit 2-3, producing again a polychromatic light limited to the spectral range between wavelengths λ_1 and λ_2 . The function of Grating 3 is dispersive, the same with that in the single-grating

setup (monochromator). While the combination of Grating 1 and Grating 2 works as a tunable bandpass filter, cutting out a desirable portion of the spectrum (*i.e.*, rejection of stray light), and thus reaching low frequency. Recent development on BragGrate notch filters has enabled the detection of low frequency Raman spectra on single stage monochromator. Compared to the conventional triple-grating setup, the new technique has greatly enhanced the collection efficiency of the low frequency region. The interlayer shear and breathing modes in few-layer graphene flakes (unfolded, without twisting angle) have thus been observed [147-149]. It is also important to note that a single-mode laser with narrow linewidth is crucial to reach low frequency detection, as this will minimize the Rayleigh scattering background tremendously.

Chapter 3 Top-down fabrication of Mono- and Few-Layer TMD Materials

Top-down method is commonly used in the preparation of nanomaterials, as introduced in Chapter 1. The conventional top-down approaches on obtaining 2D nanoflakes include exfoliation and thinning. In this chapter, I will introduce Scotch-tape based mechanical exfoliation and thinning method by using thermal annealing.

3.1 Mechanical Exfoliation: Mono- and Hetero-structures

The tapes I have used in mechanical exfoliation haven been displayed in Figure 3-1 (a). The left one in blue is called UltaTape, and the right one in white color is MagicTM Tape from 3M company. Both can work for exfoliation of atomically thin 2D layered samples. The major difference is that the UltaTape is less sticky compared to the MagicTM Tape.

Mechanical exfoliation is widely used in preparing mono- and few-layer materials, as demonstrated in Figure 3-1 (b-h). The key factors for successfully producing thin layers rely on the crystalline quality of bulk crystal, as well as the surface condition of the substrate. If the crystallinity of the bulk crystal is poor, the material would tend to be broken into pieces, instead of being exfoliated along the out-of-plane direction. Substrate is another crucial element, and Si substrate capped with SiO₂ is a common choice. Selection on the thickness of SiO₂ mainly depends on optical contrast. As demonstrated in graphene, an unsuitable thickness of the oxide layer will cause graphene invisible (e.g. ~10 nm and ~150 nm SiO₂) due to interference effect [150-153]. Interference effect also affects light-related experiments, such as Raman spectrum and the observation of

luminescence [154]. Moreover, if a back-gate device is going to be fabricated on the exfoliated sample, a thick SiO_2 layer may not be as effective as a thin one in terms of gating effect. However, a thin oxide layer may give larger leakage current under most circumstances.

Figure 3-1. Mechanical exfoliation of 2D layered materials. (a) Tapes used in exfoliation. (b-h) Exfoliated atomically thin flakes of graphene (b), MoS_2 (c), WSe_2 (d), WS_2 (e), GaSe (f), SnS_2 with $P63mmc$ phase (g), and SnS_2 with $P-3m1$ phase (h). Scale bars correspond to $15\ \mu\text{m}$ in (b, c) and $10\ \mu\text{m}$ in (d-h). The substrates of (b-d, f-h) are $285\ \text{nm}\ \text{SiO}_2/\text{Si}$, while that of (e) is $100\ \text{nm}\ \text{SiO}_2/\text{Si}$. The thickness of (b) is estimated from optical contrast. The layer number from (c, d) are confirmed on Raman spectroscopy and photoluminescence spectrometer. Determination of thickness in (f-h) is conducted from atomic force microscopy. The different background color is due to automatic adjustment of the white light balance on the software. This function helps to better visualize thin layers, but it will cause variation on the contrast in optical images.

No matter what kind of substrate is chosen, a clean and smooth surface is essential for mechanical exfoliation. Pre-treatment of oxygen plasma or ozone is usually conducted as well after the substrate is cleaned with acetone, isopropyl alcohol (IPA), and deionized (DI) water in ultra-sonication. On one hand, it can help to decrease the concentration of chemical residual, making the substrate cleaner; On the other hand, it can make the surface of SiO_2 more hydrophilic [79]. My experience shows that the treatment of oxygen

plasma or ozone makes a difference on graphene, while almost no change when exfoliating MoS₂. The variation between graphene and MoS₂ is possibly related to the intrinsic hydrophobicity of the two materials. In fact, literature has shown that graphene is more hydrophilic than WS₂ [155, 156].

Figure 3-2. Protection of black phosphorus thin layers by coating PMMA. PMMA thin film was spin-coated on the sample, with spin rate of 4000 rpm. Two examples were shown on 9 L (a) and 6 L (b) exfoliated black phosphorus flakes. Scale bars correspond to 5 μm . There is no drop-like structure (commonly seen during the degradation of black phosphorus [157, 158]) even after 13 days. The different background color is due to automatic adjustment of the white light balance on the software. This function helps to better visualize thin layers, but it will cause variation on the contrast in optical images. Besides, the interference effect plays a role here due to the presence of PPMA layer.

Black phosphorus can be exfoliated, too. However, the degradation problem exists and people suffer from that. It is reported that the surface of black phosphorus is hydrophilic. Exposure to moisture and air with long time can completely etch away the material [157]. Later work from the same group found that absorption of water on surface is faster in thinner flakes than in thicker ones, and that the flakes can be etched layer-by-layer under ambient conditions [158]. In fact, droplet-like structures become to appear on the surface of the flakes even just 1 hour after the exfoliation [157]. What's worse, the structures kept growing when the samples were kept in air. My previous experience also shows that laser radiation during Raman scattering measurement can

accelerate the growth of droplet-like structures. A ~3 L black phosphorus flake was just gone within one hour after being radiated by a 633 nm laser (1.96 eV), with power under 50 μ W. In contrast, thicker samples are much tougher [159].

A thin layer of polymethyl methacrylate (PMMA) can help to protect the black phosphorus sample, which does not affect too much in terms of measurements on Raman and photoluminescence spectroscopies. The PMMA (Micro Chem) film was spin-coated on the sample, with spin rate of 4000 rpm. According to the datasheet, A4 PMMA (solids: 4% in anisole) with 4000 rpm corresponds to a thickness of ~200 nm. From our Raman scattering measurements, there is almost no difference between pristine and PMMA-coated black phosphorus on the phonon modes. Another group also used similar method to protect the black phosphorus and conducted measurements on Raman spectroscopy in 2015 [160]. Since black phosphorus is not the focus of this thesis, I will not elaborate the details here. The purpose of showing PMMA-coated black phosphorus thin flake is just to present an effective way (with negligible effect on the intrinsic properties) to protect air-sensitive exfoliated samples.

Figure 3-3. Mono- and few-layer MoS₂ flakes on different substrates, including 100 nm SiO₂/Si (a), 285 nm SiO₂/Si (b), and 285 nm SiO₂/Si substrate with holes (c). Sample regions that are on holes are suspended.

In this section, I have discussed a lot on color and optical contrast. Figure 3-3 has further demonstrated the influence of substrate on the optical contrast: Atomically thin

MoS₂ exhibits green color and blue color on 100 nm and 285 nm thick of SiO₂ layer, respectively. In Figure 3-3 (c), there are suspended samples (which means that there is air both above the upper surface and below the bottom surface) and supported samples (From bottom to bottom: air-sample-SiO₂-Si). The colors are quite different as well. All of these are closely related to the optical interference effect.

Figure 3-4. Optical contrast of atomically thin MoS₂. (a) Schematic diagram of setup on measuring the optical contrast of thin MoS₂ layers under a 36× objective (numerical aperture: 0.5) in a microspectrophotometer (Craic 20). n_0 , n_1 , n_2 , and n_3 refer to the complex refractive index ($n = n - ik$) from air, MoS₂, SiO₂, and Si, respectively, while d_1 and d_2 indicate the thickness. (b, c) Contrast spectra of single- to eight-layer MoS₂ on 285 nm SiO₂/Si substrate from pristine exfoliated samples (b) and calculation (c). (d) Extinction coefficient (red circles) and refractive index (blue circles) for atomically thin MoS₂ crystals as a function of the incident wavelength from Ref. [161]. (e) Fitting results on refractive index n and extinction coefficient k used in calculation. (f, g) Comparison between experimental and calculational results. As there is a deep valley between 500 and 600 nm (b, c), C_{max} position refers to the wavelength where the largest (negative) contrast is reached in the visible range. C_{max} value indicates the largest contrast value within the same range (can be read from y-axis of b and c), which is also the relative optical contrast as compared to the substrate. Experimental data are shown in dots, and lines are from linear fitting.

To correlate the relation between optical contrast and thickness in MoS₂ thin layers, I have conducted experiments and calculations following what have been done in graphene [150-152]. Experiments were performed under a 36× objective with numerical aperture (NA) of 0.5, on a microspectrophotometer (Craic 20). The measurement of optical contrast is affected by the intensity of illumination, exposure time, and the size of area where signal is collected [162]. The smallest area on our microspectrophotometer can be

down to $1.7 \times 1.7 \mu\text{m}^2$, while the size I adopted was $3.6 \times 3.6 \mu\text{m}^2$, as larger size gives higher collection efficiency. With fixed light intensity, exposed time, and size of area, the measured results were plotted in Figure 3-4 (b). The vertical axis means optical contrast $C(\lambda)$, which is defined as:

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)} = 1 - \frac{R(\lambda)}{R_0(\lambda)} \quad (3-1)$$

where $R_0(\lambda)$ is the reflectance from the substrate, and $R(\lambda)$ is the reflectance from the MoS₂ sample. If $C(\lambda) > 0$, it means that the SiO₂/Si substrate reflects more intense light than the MoS₂ sample, such as the region between 600-700 nm in the spectra. In contrast, if $C(\lambda) < 0$, e.g. the region of 450-550 nm, it shows that MoS₂ reflects more light than SiO₂/Si. We can see from Figure 3-4 (b) that thicker MoS₂ flakes have deeper valleys in the negative contrast region, indicating that as layer number increases, the reflected light from samples is also increasing in the range of 450-550 nm. Calculated contrast spectrum by using the Fresnel's equations [151] is shown in Figure 3-4 (c). In our calculation, we consider Si as semi-infinite and its extinction coefficient κ is 0. Refractive index n from air is wavelength-independent, and $n = 1$. The thickness of MoS₂ sample is $0.65 * N$ (N being layer number), and the thickness of SiO₂ layer is 285 nm. The extinction coefficient and refractive index of MoS₂ in our simulation originated from fitting of results from Ref. [161]. The fitting from discrete points in Figure 3-4 (d) to the two curves in Figure 3-4 (e) is by using the method of spline interpolation. Spline interpolation can produce piecewise continuous curve, passing through every point in Figure 3-4 (d). Between these points, there is a separate polynomial for each interval, each with its own coefficients. Fitting results were shown in Figure 3-4 (e), whose values are slightly smaller (~5% smaller) than those from Ref. [161].

We remark that the trend of curves and thickness-dependent evolution are very similar between experimental and calculational results, indicating a good agreement. For further analysis, we also note that there is a deep valley between 490 and 550 nm. The deepest valley (with position denoted to C_{max}), in terms of wavelength (x axis) and contrast value (y axis), varies for different thickness. Comparison between calculation and experiment was shown in Figure 3-4 (f) and (g), by using C_{max} position and C_{max} value as indicators. In general, the simulation result matches with the experimental data. The discrepancy might be resulted from several factors: (1) The local thickness of SiO₂ might deviate from the desired thickness due to imperfection in production, while 285 nm was set as constant in calculation. (2) The fitted refractive index and extinction coefficient have not fully captured the experimental features, yet values plotted in Figure 3-4 (e) are already the best fitting I can reach so far. (3) The incident angle of light is set to be 0° (to the normal) during calculation, without considering non-normal incidence. However, NA of the objective is 0.5, which means that incident angle varies from 0° to 30°. (4) Collection efficiency. (5) Reflection from the substrate actually contributes a significant part when we measured $R(\lambda)$ from the sample. This means that the measured optical contrast is precisely $1 - \frac{R + (1-R)^2 R_0}{R_0}$, while the calculated value is $1 - \frac{R}{R_0}$, which explains the larger value in calculation. From Figure 3-4 (g), we can see that the change of contrast per layer is much larger in calculation (~0.41/layer) than in experiments (~0.14/layer). Although it is possible that calculation overestimates the value, results show that experiment underestimates the contrast. For a 4 L MoS₂ flake, the C_{max} value changes from ~ -0.5 to ~ -0.3 with decreasing aperture size from $3.6 \times 3.6 \mu\text{m}^2$ to $1.7 \times 1.7 \mu\text{m}^2$. Increasing the size of collection is one of the methods to improving efficiency,

thus obtaining a measured contrast closer to the actual value. Therefore, the size and shape of the samples with different thickness are very critical.

Recent interest in 2D materials has shifted more towards heterostructures, due to the fascinating physical properties and attractive electrical performance [7, 163-168]. For example, atomically thin heterostructure is a suitable candidate for the study of carrier transfer [166, 167]. Light-emitting diode based on multilayer vdW heterostructures has displayed a high extrinsic quantum efficiency of nearly 10% [164]. Though heterostructure is not the focus of this thesis, the preparation method based on mechanical exfoliation is still very related in this section.

Figure 3-5. Preparation of MoS₂-graphene heterostructures. (a) Schematics of making a heterostructure sample. Firstly, mechanically exfoliated MoS₂ flake was prepared on PDMS substrate which is attached on a transparent glass slide. Meanwhile, exfoliated graphene on 100 nm SiO₂/Si was prepared. The two exfoliated samples were aligned on an optical microscopy. Remove the PDMS (together with the glass slide) with a blade when the two samples were contacted well (which needs some time). (b, c) Two heterostructures samples fabricated with the method mentioned above. From top to bottom, it is MoS₂ - graphene - 100 nm SiO₂ - Si. The red lines highlighted the shape of graphene beneath.

Figure 3-5 (a) demonstrated the schematics of making a heterostructure sample in our lab. Exfoliated MoS₂ and exfoliated graphene were prepared separately on PDMS-glass slide and 100 nm SiO₂/Si, respectively. The alignment of the two thin films was conducted on an optical microscope, with graphene put on the sample stage and

MoS₂ placed upside down with a holder. Move the position of glass slide until the two samples are seen aligned along the *z*-axis, out-of-plane direction. Lower down the height of glass slide (with MoS₂) and increase the height of sample stage (with graphene), in order to make the two samples contact and attach firmly to each other (which takes some time). After the removal of upper substrate (PDMS-glass slide), the preparation of a heterostructure is done, as shown in Figure 3-5 (b, c). The interface barrier, possibly caused by air/bubble, is hard to be completely avoided, while further annealing can help to ease even remove the problem [169].

3.2 Thermal Annealing Thinning

As we have discussed in Chapter 1 that thinning methods of MoS₂ include laser-thinning [31], plasma-thinning [32], and annealing-thinning [33, 34]. Laser thinning is fast, but the layer-by-layer process cannot be achieved. Thinning of MoS₂ layer-by-layer was first achieved by using Ar⁺ plasma, but this method is much easier to cause damage than other thinning methods because of the energetic plasma. Next, I am going to introduce the thermal annealing method developed in our lab.

The Thermal annealing experiments were conducted in a CVD furnace which has been described in Chapter 2. The thinning mechanism is believed to be related to heat-induced sublimation, similar to that in laser thinning [31]. By placing the exfoliated few- and multi-layer samples with SiO₂/Si substrate beneath in the center of a quartz tube, we can make sure the temperature on the samples is the same as (or very close to) the set point. In this case, temperature of 650 °C and pressure of 10 Torr were set. Argon gas with

flowing rate of 5 standard cubic centimeters per minute (sccm) was used to stabilize the pressure and gas component inside the chamber, as oxygen in air might cause oxidation of MoS_2 . One hour is set as one cycle, during which one layer was removed, thus achieving layer-by-layer process. As a matter of fact, the above mentioned parameters gave us the optimized results, considering the surface quality, the thinning rate, and the remaining size of the thinned samples.

Figure 3-6. Optical images of the pristine (a, e), and thermal annealed MoS_2 samples (b–d) and (f–h). From (b) to (d), as well as from (f) to (h), the annealing times are 2 hours, 4 hours, and 7 hours, respectively. Scale bars correspond to 15 μm in (a–d) and 5 μm (e–h).

Samples in Figure 3-6 (a) (8 L) and Figure 3-6 (e) (7 L) are pristine MoS_2 flakes before annealing thinning. Figure 3-6 (b–d) and Figure 3-6 (f–h) show the gradual changes of the two few-layer samples. Because thicker MoS_2 flakes is capable of reflecting more light and showing a brighter color than the thinner ones, the variation of color, from bright to dark, suggests that the flakes are getting thinner and thinner. In the meantime, we also noticed a shrinkage of the surface area, which means that sublimation occurs not only perpendicularly on the surface, but also along the surface, therefore causing smaller areas.

To characterize the thinning process of the originally 7 L MoS_2 sample (shown in

Figure 3-6 (e)), we have conducted Raman scattering measurements. Compared with the high-frequency intralayer vibrational modes, the low-frequency interlayer breathing and shear modes are much more sensitive to thickness [118, 170, 171]. For example, B1 mode (interlayer breathing with the lowest frequency) shifts from 10 cm^{-1} in 9 L to 40 cm^{-1} in 2 L. However, the frequency difference between A_{1g} and E_{2g}^1 modes evolved from about $\sim 18 \text{ cm}^{-1}$ in 1 L to $\sim 24.5 \text{ cm}^{-1}$ in 5 L, and the value in 5 L is in fact very close to that in the bulk [120]. Original and thinning MoS₂ flakes after each cycle (one hour) were measured under both $\bar{z}(xy)z$ and $\bar{z}(xx)z$ polarization configurations.

Figure 3-7. Monitoring the thermal annealing process on Raman spectroscopy. (a, b) Raman spectra of thinned MoS₂ flake under $\bar{z}(xx)z$ configuration in the low-frequency (a) and high-frequency (b) regions. (c, d) Raman spectra of thinned MoS₂ flake under $\bar{z}(xy)z$ configuration in the low-frequency (c) and high-frequency (d) regions. (e, f) Raman shift of S1 & B1 modes (e) and A_{1g} & E_{2g}^1 modes (f) of few-layer MoS₂ as a function of thinning cycles. Spectra in (a, c) are normalized according to the intensity of S1 peak. Spectra in (b) and (d) are normalized according to the intensities of A_{1g} peak and E_{2g}^1 peak, respectively.

We can see from Figure 3-7 (a) that the interlayer breathing mode B1 peak shifts to

higher frequency and the interlayer shear mode E_{2g}^2 (labelled as S1 peak for convenience) down-shifts as annealing cycle increases, which indicates that the layer thickness is decreasing. The mixture surface is reflected from the spectra as well. The two B1 peaks after the 2nd and 3rd cycle of annealing confirm that the surface is a mixture of N layer and $N-1$ layer ($N = 6, 5$) even in a small area, within a laser spot. After the 7th cycle, interlayer shear mode S1 and breathing mode B1, which are mainly caused by the vdW interactions, disappear. The existence of fingerprint modes A_{1g} and E_{2g}^1 peaks in Figure 3-7 (b) suggests that the sample is in monolayer regime. In addition, shifts of A_{1g} and E_{2g}^1 modes, especially from the 4th cycle to the 7th cycle, are pronounced, which can be regarded as another evidence of thinning. This observation is in agreement with previous reports [118, 120].

Figure 3-7 (c) and (d) are the spectra from cross-polarized $\bar{z}(xy)z$ configuration, with shear modes detected only. Out-of-plane vibrational modes (such as A_{1g} at ~ 408 cm^{-1} and B1 mode < 50 cm^{-1}) are greatly suppressed under the $\bar{z}(xy)z$ configuration, which is consistent with that observed in exfoliated 2H-stacked MoS_2 [118]. The cross-polarized configuration enables better observation of low-frequency shear modes, because stray light is suppressed more under $\bar{z}(xy)z$ configuration than that of $\bar{z}(xx)z$ [147]. Through Figure 3-7 (c), two S1 peaks were observed after the 4th and 5th cycle, indicating the mixed surface of N and $N-1$ layer ($N = 4, 3$). Note that after the 6th cycle, A_{1g} peak was not as suppressed as other cycles, shown in Figure 3-7 (d). We believe there might be some heat-induced disorders or defects after this cycle, which primarily affects the out-of-plane vibration.

We summarize the shifts of B1, S1, A_{1g} , and E_{2g}^1 modes as a function of annealing

cycles in Figure 3-7 (e) and (f). General trend of shifts confirm that thermal annealing is effective in thinning down the few-layer MoS₂. The abnormal shift of B1 mode from ~40 cm⁻¹ to ~38 cm⁻¹ from the 5th to the 6th cycle is noticed, while the shift is expected to go to lower frequency with increasing time on annealing. Strain is a possible reason. Previous reports have shown that an in-plane strain can cause splitting of the double degenerate E_{2g}^1 mode and soften the A_{1g} mode [137, 172]. Similar effects can be expected on the S1 mode (split) and B1 mode (down-shift). While there is no splitting of both E_{2g}^1 and S1 modes, if there is strain effect, the applied strain is supposed to be along the out-of-plane direction, such that the out-of-plane vibrational modes are affected more than the in-plane ones. Meanwhile, the red-shifted A_{1g} mode is not a concrete evidence for strain, as the red-shift is mainly caused by thickness effect, supposedly. A recent report shows that the frequency of B1 mode in 3R-stacked 2 L MoS₂ is lower by ~2 cm⁻¹ than that in the 2H-stacked bilayer. Also, the intensity ratio between B1 and S1 increases a lot in 3R compared to that in 2H [173]. The above mentioned phenomena are very similar to what we have observed in Figure 3-7, which gives a possibility of stacking transition from 2H to 3R from the 5th to the 6th cycle. Recent papers show that 3R-stacked TMDs are accessible, and not as instable as people previous thought [133, 134, 173]. Still, we cannot make a conclusion yet, as high resolution transmission electron microscopy (TEM) images are needed to make the statement. We also remark that the counterpart monolayers of 2H-stacked and 3R-stacked MoS₂ are the same, also referred to 1H. In contrast, 1T monolayer is different from 1H monolayer. Structural inversion symmetry is kept in 1T and broken in 1H.

In Figure 3-7 (f) , we can see the frequency difference of A_{1g} and E_{2g}^1 is about 21.5

cm⁻¹ in 1 L, and close to 23 cm⁻¹ in 2 L, which is larger than that of most pristine MoS₂ produced by mechanical exfoliation [120]. Similar phenomena were observed in 1 L MoS₂ flakes fabricated by chemical exfoliation [30] and laser thinning [31]. Possible reasons such as the presence of unremoved MoS₂ on the surface during thinning [31], and local thickness variations [30] have been suggested to explain the larger value. On the other hand, smaller frequency difference in 1 L (16 cm⁻¹) and 2 L (21 cm⁻¹) MoS₂ is also reported in mechanically exfoliated MoS₂ in a previous paper [48]. These differing reports were mostly caused by the variation in the frequency of E_{2g}^1 mode, suggesting that surface effect might be a more reliable reason. The layer-dependent shift of E_{2g}^1 mode is a combined effect of thickness effect (downshift with decreasing thickness) and surface effect (upshifts with increasing thickness), as I have introduced in Chapter 1 [122]. Different methods in sample preparation can possibly cause different surface environment. It means that the thickness effect might be constant, but the magnitude of surface effect may differ. If we apply surface effect (referring the larger Mo-S force constant in the surface layer [122]) to explain the larger frequency difference, it indicates that the Mo-S force constant on the surface layer is smaller in (laser-, thermal annealing-) thinning samples than that in pristine exfoliated samples.

We further use atomic force microscopy (AFM) to check the homogeneity of the thinned MoS₂ flake, as shown in Figure 3-8. As expected, the inhomogeneous surface appears even after the first cycle (one-hour annealing time). During repeated experiment, although we have succeeded in thinning with homogeneous thickness, but just for a small portion of samples. We therefore consider defects as a possible factor to cause the non-uniform surface. Since the pristine exfoliated sample from nature is not totally

defect-free, defects can work as cores for sublimation. Hence, area around defects would probably disappear faster and the mixture of N layer and $N-1$ layer emerges. Interestingly, the rate of sublimation varies sometimes. For instance, N -layer MoS_2 can turn to the mixture of either N and $N-1$ layers (Figure 3-8 (c, d)), or $N-1$ and $N-2$ layers (Figure 3-8 (a, b)) after one cycle of annealing. Although the thinning experiment is not a perfect layer-by-layer process yet, we believe with the optimized parameters (mainly temperature and pressure), thinned MoS_2 flakes with homogenous rate is achievable by thermal annealing. Therefore, we still consider this low-cost and easy approach as a promising top-down method in obtaining mono- and few-layer MoS_2 , as well as facilitating future *in situ* measurements on optical properties and electrical performance. This thinning method may be applied to other TMD materials as well.

Figure 3-8. AFM images of few-layer MoS_2 . (a, b) Pristine 8 L flake (a) and thinned MoS_2 after one cycle (b). (c, d) Pristine 7 L flake (c) and thinned MoS_2 after one cycle (d). The corresponding optical images of (a) and (c) are shown in Figure 3-6 (a) and (e), respectively. Height profiles are taken from the indicated arrows.

Chapter 4 CVD Synthesis of Atomically Thin MSe₂ (M = Mo, W)

Films and Flakes

The most popular and probably the most effective bottom-up method in the synthesis of group IV TMD materials MX₂ (M = Mo, W; X = S, Se) is sulfurization/selenization in a CVD furnace. In this chapter, I am going to introduce how I used the CVD system to growth atomically thin MoSe₂ and WSe₂, as well as discussing their optical properties and electrical performance.

4.1 Synthesis of Mono- and Few-layer MoSe₂ Film

4.1.1 CVD-growth and STEM Imaging

Up to now, it has been proven that CVD growth is one of the most promising methods in obtaining large-area monolayer TMDs with high quality on various substrates, such as mica, sapphire, copper foil, and even silicon [44, 46, 48, 51, 52, 59, 62, 64, 65]. Previous reports show that sulfurization/selenization of MoO₃/WO₃ can produce large scale, high quality mono- and few-layer TMDs [46, 52, 59, 62]. When I started on CVD synthesis of MoSe₂ in June 2013, the majority of papers at that time were reporting on the synthesis of MoS₂ only. It is true that the lower chemical reactivity [174] of selenium (Se) makes it more difficult to synthesize large-area and atomically thin Se- based TMDs (MSe₂, where M = Mo, W) than to grow large-scale thin MS₂. Therefore, longer reaction time is indispensable for large-scale synthesis of MSe₂; nonetheless, it is inevitable to avoid thicker films with longer time on synthesis, since the growth is not self-limiting. This is different from graphene, whose synthesis on copper foil is a self-limited process thanks to the low solubility of carbon on copper. Thus it is very suitable to use Cu in the

growth of monolayer graphene [175]. Consequently, it is still challenging to synthesize large-area transition metal diselenides on conventional amorphous SiO₂ substrate which does not have self-limiting properties. We believe the key to solve the challenge of reproducibly synthesizing large-scale and atomically thin Se-based TMD films on SiO₂ substrates is the careful tuning and optimization of the synthesis parameters. Meanwhile, Yu *et al.* have reported that by using MoCl₅ precursor, instead of MoO₃+S/Se, the self-limiting mechanism is achievable in growing thin film MoS₂ [80].

We use a home-built vapor transport CVD system with single-zone furnace for the synthesis. First of all, two quartz boats were put inside the quartz tube reactor, which contained MoO₃ powder and Se powder, respectively. MoO₃ was at the center of the heating zone, and Se was ~17 cm away on the upstream. A Si substrate capped with 100 nm oxide layer was placed on the downstream for deposition. Since H₂ is necessary in the reaction of selenization due to the low chemical reactivity [174] of Se, it was used as the carrier gas to transport the Se and MoO₃ vapors and deposit MoSe₂ film on the substrate. The substrate is put at the downstream position. It is worth noting that there is one paper reporting on the growth of MoSe₂ by selenization without H₂ involved [58], although almost every group used hydrogen gas in the (selenization) synthesis of MoSe₂ or WSe₂ [54-56, 62, 176-178].

The temperature was elevated to 800 °C in 10 minutes, maintained constant for 8 minutes, and reduced to room temperature naturally. When the temperature on MoO₃ reaches 800 °C, the temperature on Se powder is estimated to be around 350 °C. During growth, the pressure was kept stable at 20 Torr inside the tube reactor. The relation between vapor pressure and temperature of Se is given by: $\log P = 8.0886 - \frac{4989.5}{T}$ (P

in the unit of mmHg; T in the unit of K), measured with quartz Bourdon gages in 1952 [179]. Following the equation, the vapor pressure of Se at 350 °C is 12 Torr, a little smaller than the pressure we used. The as-grown MoSe₂ film is usually 4-6 cm away from the center, where the MoO₃ boat is placed.

Figure 4-1. CVD-synthesized thin MoSe₂ film on 100 nm SiO₂/Si substrate. (a) a photograph showing the comparison of the CVD-grown MoSe₂ and a bare SiO₂ substrate. (b) An optical microscopy image of the CVD-grown MoSe₂ film. The scratch was made by a tweezer, in order to show the apparent contrast. (c) AFM image of the CVD-grown MoSe₂ film, which suggests the grain size is of ~100 nm. (d) Height profile from sections as indicated by the black and blue lines in (c). The thickness of 1 L MoSe₂ is ~0.7 nm.

Our CVD-grown mono- and few-layers MoSe₂ film on SiO₂/Si substrate has relatively homogenous area (in majority mono- and bilayer) which can reach 1×1 cm². Figure 4-1 (a) shows the difference between a bare substrate and MoSe₂ thin film on 100 nm SiO₂/Si substrate. As the thickness of 1 L MoSe₂ is only ~0.7 nm, the relative contrast on Si substrate with 100 SiO₂ is not very distinct. Yet we can see the 1 L MoSe₂ exhibits a dark green color as compared to the substrate which has a purple hue. In addition, the optical image in Figure 4-1 (b) displays a homogenous color, indicating the uniformity of thickness. AFM image reveals that the film is consisted of many small triangular grains,

as displayed in Figure 4-1 (c). AFM images of other areas are similar to Figure 4-1 (c), except that there are more single-layers in the high temperature region, and the film is less continuous; while thicker layers are in relatively high density within the low temperature region. Figure 4-1 (d) displays two section profiles indicated by the blue and black lines in Figure 4-1 (c), showing the predominating bilayer and monolayer with thicknesses of 1.5 nm and ~0.8 nm, respectively.

For further characterization, the CVD-grown MoSe₂ thin film was transferred from the SiO₂/Si substrate onto a lacey carbon grid by using a wet-chemistry etching method. Firstly, we spin-coated PMMA layer on top of the sample. The PMMA-coated sample was immersed into NaOH solution after baking. Wait until the PMMA layer with MoSe₂ film floated on the surface of NaOH solution. Afterwards, a TEM grid (or a sapphire substrate for optical absorption measurement which will be discussed later) was used to fish the PMMA film. Eventually, the PMMA layer can be dissolved by acetone, and the MoSe₂ thin film is left on the TEM grid (or new substrate).

Figure 4-2 (a) displays the general morphology of the as-transferred MoSe₂ thin film. The film is homogeneous and continuous in large scale. At random locations, there are some small wrinkles and cracks (indicated by green arrows in Figure 4-2 (a)), which are probably introduced during the transfer process. To obtain further information on the thin films down to the atomic level, annular dark field (ADF) imaging on an aberration-corrected scanning transmission electron microscope (STEM) was utilized. ADF imaging is capable of providing an in-depth analysis of the grain boundary structures and the crystallinity of the film. Under the conditions our measurements, regions with different thickness are able to exhibit distinct contrast in the ADF images

(Figure 4-2 (b)). Moreover, the intensity shows a linear dependence on the number of layers in thin samples, up to at least 6 L, as demonstrated in Figure 4-2 (c). The linear relationship provides an accurate and facile method to identify the thickness by ADF imaging. Results show that the TEM sample contains mostly 1-3 L MoSe₂, in agreement with the measurements from AFM on the as-grown film. The fact that few-layers and monolayers coexist also indicates that the growth of MoSe₂ on SiO₂ substrate is not a self-limiting growth mechanism.

An ADF image with atomic resolution of the lattice structure in the monolayer MoSe₂ is shown in Figure 4-2 (e), which displays a hexagonal pattern with alternating dim and bright atomic sites. The intensity in ADF image is correlated to the number of atoms and the atomic number [180]. Therefore, the dimmer atomic sites are Mo columns and the brighter ones are Se₂ columns, which is indicated by the intensity profile displayed in the bottom right of Figure 4-2 (e). Meanwhile, point defects that are observed frequently in layered materials can be identified with ADF-STEM as well, such as the mono-Se vacancies (indicated by the green arrows in Figure 4-2 (e)) [181]. Electron energy loss spectroscopy (EELS) was further used to check the chemical identity of the MoSe₂ film, with results shown in Figure 4-2 (d). In the bilayer or trilayer regions, oriented stacking, *i.e.* no rotation between the two layers, is found to be dominant. Both 2H and 3R stacking configurations were observed, as seen in Figure 4-2 (f) and (g), respectively.

Figure 4-2. Grain boundaries and morphology and of as-grown MoSe₂ films. (a) Low-magnification bright field TEM image of the MoSe₂ film. (b) ADF image of the CVD-grown MoSe₂ film shows distinct contrast among 1 L, 2 L, and 3 L. (c) Dependence of the intensity in ADF image on the thickness of MoSe₂. (d) EEL spectrum taken at 1 L region, which shows typical Se and Mo edges. (e) ADF image of 1 L MoSe₂ with atomic resolution. Structural model is overlaid. Bottom-left: corresponding FFT pattern. Bottom-right: Profile of intensity taken along the dashed line. (f, g) ADF images of 2 L MoSe₂ with 3R (g) and 2H (f) stacking, respectively. (h) ADF image of a 21° tilted grain boundary in 1 L MoSe₂, which consists of 5|7 rings. Inset: FFT of the image. (i) ADF image of a 60° grain boundary. 4|4 rings with 8-member rings at the kinks can be observed. The orientation of the mirror symmetric grains is displayed with two triangles. Corresponding structural model for (h, i) are shown on the right. Orange and purple spheres represent the Se and Mo atoms, respectively. In order to reduce random noise, all ADF images have been low-pass filtered.

The atomic structure at the monolayer regions was also investigated by using ADF imaging, with mirror and tilted symmetric grain boundaries detected. A 21° grain boundary is shown in Figure 4-2 (h), with the corresponding Fourier pattern displayed as inset. The grain boundary consists of dislocation cores with distorted 6-fold rings and five- and seven-fold (5|7) rings in between, which is similar to those predicted and

observed in monolayer MoS₂ [52, 181, 182]. Due to the broken of 6-fold symmetry, a 60° grain boundary is observed in Figure 4-2 (i). The lower and upper parts of the monolayer region are in mirror symmetry, as illustrated by the two triangles. The two parts are connected by the chains of point-sharing four-fold rings (4|4P) with 8-fold rings serving as grain boundary kinks. This kind of 60° grain boundary has been reported in monolayer MoS₂ previously [181], and calculations on band structure suggest that it is metallic [182], providing intrinsic conductive channels within the semiconducting MoSe₂ layer.

Figure 4-3. CVD synthesis of MoSe₂ with non-optimized parameters. (a, b) Compared with the parameters used in Figure 4-1, growth with a lower temperature (700 °C) and growth with a lower pressure (10 Torr) are shown in (a) and (b), respectively.

Back to the CVD synthesis, it is very interesting to examine the dependence of growth on parameters, such as temperature and pressure. Growth with a lower temperature (700 °C. Other parameters remain the same.) and Growth with a lower pressure (10 Torr. Other parameters remain the same.) are shown in Figure 4-3, respectively. Generally speaking, a lower temperature reduces the growth rate, resulting in larger grain size; While a lower pressure can increase evaporation rate of source, and as-grown samples are smaller. However, the CVD-grown flakes from 700 °C (and 20 Torr) do not exhibit the fingerprint A_{1g} mode ($\sim 241\text{ cm}^{-1}$) from Raman spectroscopy,

indicating that the products are not MoSe₂, or with very bad crystallinity. Samples from (800 °C and) 10 Torr show a weak A_{1g} peak on Raman spectrum, also suggesting the poor quality. In contrast, the optimized parameter not only gives good morphology, but also introducing excellent optical properties, which will be discussed in the next section.

Figure 4-4. Optical images of CVD-grown MoSe₂ taken with different distances from the center. Black arrows indicate the scratches made by a tweezer, which shows the pronounced contrast between sample and substrate. Red circles highlight thick flakes (byproducts).

The distribution of as-grown samples as related to different positions (*i.e.*, closer or farther to the center where MoO₃ is placed) is shown in Figure 4-4. As the substrate is put very closed to the center where thermocouple is installed, temperature variation on the substrate is supposed to play a relatively minor role. Still, position closer to the substrate is at higher temperature, and the deposition rate is faster at lower temperature end, which is evident by the fact that thickness increases towards the downstream.

Figure 4-5. Morphology and density dependence on the distance from center. From (a) to (d), the distance between the as-grown samples and the center increases. As it goes farther away from the center, the samples change from irregular shape, triangle to film, and density increases in the meantime. The black arrow in (d) indicates the scratches intentionally made by a tweezer to show optical contrast under the optical microscopy and give height step under AFM.

The different contrast is not due to thickness, as all of the regions in Figure 4-4 do not have interlayer vibrational modes, indicating that they are in monolayer regime [118, 170, 171, 183]. We further used AFM to check the morphology and density (Figure 4-5, from a different batch of growth). As position moves closer to the downstream side, denser samples is observed, which can be explained by temperature effect. Meanwhile, the morphology changes from irregular shape, triangle to film. Wang *et al.* have studied the shape evolution of monolayer MoS₂ grown by CVD and observed similar phenomena [184]. According to their results, the dependence on position is related to the concentration of precursors (*i.e.*, MoO₃ and Se in my growth). When it moves towards to

the downstream, concentration decreases and the rate of growth reduces, thus leading to a stable growth under thermodynamic control [184]. Liu *et al.* also discussed that the growth may shift from thermodynamic control to kinetic control when the growth proceeds too fast [177]. Based on previous literature [177, 184], we speculate that as position moves from center to downstream, the growth is more thermodynamic-controlled and less kinetic-controlled, and different kinds of dynamics affect the morphology.

Figure 4-6. Schematic diagram displaying a possible growth mechanism in the growth of MoSe₂ on SiO₂/Si substrate. Black and red circles refer to holes and Se seeds, respectively. The blue triangle represents the MoSe₂ flake.

To further explore the growth mechanism, we have conducted some controlled experiments with even lower growth rate compared to the optimized parameters (*e.g.*, higher pressure and lower concentration of H₂), in order to see the intermediate states between precursor powder and the thin-film triangle flakes. The possible growth mechanism of MoSe₂ thin film is shown in Figure 4-6. First of all, the Se powder evaporates and goes into the pinholes on the substrate. Se particles on these pinholes can serve as seeds in the following growth. The MoSe₂ flake grows with a Se seed as the core subsequently. Afterwards, the seed is either detached or melted, leaving a hole. The flake then grows from the outside to the inside and fills in the hole eventually. In fact, we have seen, *via* AFM, flakes with a hole in the middle, flakes with a detached “seed”, and flakes

with a melted “seed” from the slower growth. CVD-grown samples with a seed in the middle have been widely observed and reported [52, 185]. However, concrete evidence is still needed to support this speculated mechanism.

4.1.2 Optical Properties: Photoluminescence and Raman Scattering

Dependence on substrate position not only affects morphology, density, and thickness, but also influences photoluminescence properties. Figure 4-7 (a) and (b) have shown two examples from different batches of synthesis with the same growth parameters. In general, with increasing distance from the center where temperature is the highest, the PL peak position down-shifts to the low energy side; the change of PL intensity, however, is not monotonic. Instead, it increases first and then decreases, reaching maximum somewhere along the sweep. Comparison between Figure 4-7 (a) and (b) also indicates the variation between batches of growth, which is supposed to be related to the small growth window of atomically thin TMD materials. Nevertheless, sample with the best morphology and the strongest PL intensity always locates between 4 to 6 cm, as mentioned in the previous section.

The strongest PL peak always has its energy located at 1.56 eV, even from different batches of growth. According to previous reports [186-189], it corresponds to the energy of A excton in MoSe₂ ($1.56 \text{ eV} \pm 0.01$). While other positions with weaker intensity are possibly due to poorer crystalline quality (thus more non-radiative recombination) and thickness effect, such as sample #4.8 cm in Figure 4-7 (b). The much weaker intensity as well as peak position (inset of Figure 4-7 (b)) indicates the sample is bilayer MoSe₂. Therefore, sample #4.4 cm is possibly a mixed region with majority monolayers and less

bilayers. However, the shift of energy in Figure 4-7 (a) cannot be caused by thickness.

Figure 4-7. Dependence on substrate positions of photoluminescence (PL) properties. (a, b) PL spectra ranging from 1.4 to 1.7 eV taken at different positions on the substrate, with length referred to the distance between where the sample was grown and the center of the furnace. (a) and (b) are from different batches of synthesis, while but the PL spectra were measured under the same circumstances (*i.e.*, the same setup, power, and acquisition time). Inset: zoom-in spectra of sample #4.0 cm (a) and sample #4.8 cm (b). 5.0 cm (1) and (2) indicate different positions where spectra were measured, while the distances from the center are the same. (c) PL spectrum of sample #5.0 cm_2 in (a) with range from 1.2 to 2.0 eV.

A previous paper has shown that dielectric environment has significantly effect on the PL peak and energy in monolayer MoS₂ [190]. With increasing dielectric constant, blue-shift of exciton or trion up to 40 meV was observed, which was explained by the dielectric screening effect of the Coulomb potential. In the meantime, stronger PL intensity is detected. By comparison, PL peak redshifts with increasing intensity in Figure 4-7 (a), different trend from the above observation. Moreover, the samples are in the same dielectric environment. Here, my speculation is that weaker intensity towards the upstream may be related to sample density, and higher energy is possibly related to quantum confinement effect (closer to the center, smaller grain size).

The full range PL spectrum is shown in Figure 4-7 (c). Both B and A excitons can be observed with energies of 1.76 eV and 1.56 eV, respectively, which are in consistent with previous experimental results [188]. Theoretical calculations predict that the splitting energy of B and A excitons is 183 meV in MoSe₂, which is caused by the strong

spin-orbit interaction [86]. To have a further analysis on the emission properties, we have done fitting on the PL spectrum, as shown in Figure 4-8.

Figure 4-8. Fitting of A exciton peak by using different functions: Gaussian (a), Lorentzian (b), and Voigt (c). Black line and red line represent raw data and fitting curve, respectively.

Analyzing the PL lineshape helps to understand the intrinsic properties. Bergman et al. explored the impurity distribution in diamond thin film by the analysis of PL spectra, in which line defects and point defects are expected to be Gaussian and Lorentzian, respectively [191]. Gaussian function ($y = y_o + \frac{A}{\omega\sqrt{\pi/2}} e^{-\frac{(x-x_c)^2}{\omega^2}}$) and Lorentzian function ($y = y_o + \frac{2A}{\pi} \frac{\omega}{4(x-x_c)^2 + \omega^2}$) are widely used in the analysis of PL spectra. Homogeneous broadening, such as natural lifetime broadening resulted from spontaneous decay of an excited state and collision broadening caused by inter-particle collision, follows Lorentzian profile. Inhomogeneous broadening, including Doppler broadening and power broadening, has a Gaussian line shape. Meanwhile, the broadening due to spectrometer usually exhibits a Gaussian profile. Gaussian fitting in the PL spectra of TMDs have been reported [82, 192, 193]. Using Lorentzian function to do fitting in the PL spectra of group IV TMDs is also common [83, 99, 169, 190, 194-198]. Here, I presented the fitting with Gaussian function and Lorentzian function of A exciton in Figure 4-8 (a) and (b), respectively. Comparison shows that Lorentzian function matches better.

Voigt function ($V(x; \omega_G, \omega_L) = \int G(x'; \omega_G) L(x-x'; \omega_L) dx'$) is the convolution of a

Gaussian profile and a Lorentz profile. When $\omega_G = 0$, the Voigt function exhibits a Lorentzian profile; when $\omega_L = 0$, the Voigt profile is pure Gaussian. Fitting with Voigt function is displayed in Figure 4-8 (c), with $\omega_G = 30.6$ meV and $\omega_L = 36.2$ meV. It is also worth mentioning that Voigt profile matches the best among the three functions. Voigt profile has also been used in atomically thin TMDs before [199, 200].

Furthermore, temperature-dependent PL and optical absorption measurements were carried out (Figure 4-9). Absorption related to A and B excitons exhibit comparably intensity from the spectra (red in Figure 4-9 (a)), while the emission from A exciton is much stronger than that from B exciton due to their difference in PL quantum yield (black in Figure 4-9 (a)). The asymmetric line shape of the complex A exciton becomes pronounced with decreasing temperature. Following existing literatures [188, 194], we assign the peak with higher energy as the neutral exciton A^0 , and the one with lower energy, which only appears at low temperature, as the negatively charged exciton A^- . A^- is considered as a trion; that is, bound states of two electrons to one hole [194]. From absorption spectra, the asymmetry of complex A exciton begins to appear when the temperature was lowered to 220 K, which indicates the binding energy of A^- trion is supposed to be between 22.5 meV ($T = 260$ K) and 19.1 meV ($T = 220$ K). Otherwise, once the thermal energy $k_B T$ exceeds the binding energy, it will be less likely to observe the A^- charged exciton due to dissociation. According to previous papers [194, 201], the energy difference between A^0 and A^- from PL spectrum can be used to characterize the difficulty in removing one electron from the trion, as well as the binding energy of A^- with infinitesimal doping. $E(A^0) - E(A^-)$ extracted from fitting is shown to be 23.5 ± 1.5 meV between 77 to 180 K (30 meV in exfoliated monolayer MoSe₂ measured at 20 K

[188]), and it is 14 meV at 220 K (Figure 4-9 (d)). As a matter of fact, trion emission at 220 K is very weak and rather broad, which affects the accuracy in the interpretation. Meanwhile, it is very possible that the trion of CVD-MoSe₂ monolayer film ionizes around 220 K. By comparison, most previous reports focused at low temperature < 77 K where trion exhibits substantial intensity [188, 194, 202].

Figure 4-9. Temperature-dependent emission properties of CVD-grown monolayer MoSe₂ film. (a) Temperature-dependent PL spectra (black) and optical absorption spectra (red) of CVD-grown monolayer MoSe₂ film. Both spectra are normalized. (b) Temperature-dependent PL spectra with Voigt function fitting. (c) Comparison of fitting with Gaussian, Lorentzian, and Voigt functions on PL spectrum of monolayer MoSe₂ at 77 K. (d-f) Extracted temperature-dependent excitonic energies (d) and width (e) of neutral exciton A⁰ and charged exciton A⁻. (f) Integrated intensity ratio of A⁻/A⁰.

The temperature-dependent PL spectra with fitting by Voigt function have been plotted in Figure 4-9 (b), where we have found several interesting features: The emission of neutral exciton A⁰ is best captured by the combination of Gaussian and Lorentzian functions at room temperature, as demonstrated in Figure 4-8, while the weight of Gaussian profile increases with decreasing temperature. It is pure Gaussian at 100 K and

77 K in the spectra. On the other hand, the emission of trion A^- is always Lorentzian. Comparison of fitting with Gaussian, Lorentzian, and Voigt functions at 77 K is displayed in Figure 4-9 (c). Only Voigt profile, which uses Gaussian and Lorentz for A^0 and A^- , respectively, can well describe the emission feature. Previously, Zhu *et al.* have also used Gaussian for neutral exciton and Lorentz for trion when discussing PL from 2 L WS₂ [203].

The temperature-dependent excitonic energy and width were extracted and plotted in Figure 4-9 (d, e). The width of Voigt profile is calculated through $\omega_v \approx 0.5346 * \omega_L + \sqrt{0.2166 * \omega_L^2 + \omega_G^2}$, where ω_v , ω_L , and ω_G are the corresponding widths of Voigt, Lorentzian, and Gaussian profiles. The above approximation is exactly correct for a pure Gaussian, but has an error of about 0.000305% for a pure Lorentzian profile [204]. The ratio of A^-/A^0 in terms of integrated intensity is also shown in Figure 4-9 (f), in agreement with previous result [188].

Power-dependent PL measurements were conducted as well, in order to explore the relation between peak intensity (I) and excitation power (P), $I \sim P^\alpha$. According to previous results [195, 199, 202], both A^0 and A^- should have a linear relation between I and P ; that is, the parameter α is supposed to be close to 1. The power-dependent measurements at 77 K are also crucial for the understanding of the broad and weak peak (labelled as L in Figure 4-10 (a)) located around 1.56 eV, which only appears at low temperature (100 K and 77 K in Figure 4-9 (b)). If $\alpha < 1$, the peak is supposed to be related to defects or localized states, which has been widely reported in TMDs [98, 195, 199, 202].

Dependence of intensity on excitation power is plotted in Figure 4-10 (b, c), with both the commonly-used logarithmic scale and the linear scale. The parameter α is

extracted to be 0.94 and 0.81 for A^- and A^0 , respectively, in the logarithmic scale. While in the linear scale, α is just 0.81 and 0.75 for A^- and A^0 , respectively. The fitting in linear scale is by using power law function, $y = a * x^b$, and the main advantage of linear scale is that it can include the zero point (*i.e.*, when power is zero, intensity is zero). If Guassian function, instead of Voigt function, is used in the fitting, α is 0.95 and 0.84 for A^- and A^0 , respectively [55]. Meanwhile, the value α for L peak is 0.66 (under Gaussian fitting), suggesting that it is indeed related to localized states/defects [55, 205].

Figure 4-10. Power-dependent PL spectra of CVD-grown MoSe₂ monolayer film at 77 K. (a) Power-dependent PL spectrum at 77 K. Zoom-in view with vertical axis plotted in logarithmic scale is shown as inset. A^0 and A^- are neutral and charged excitons, respectively. L peak is supposed to be related to localized states or defects. (b, c) Dependence of intensity on excitation power in logarithmic scale (b) and linear scale (c). Dots are experimental data extracted from (a) and lines are fitting results. (d, e) PL spectra with fitting of Voigt profile under excitation power of 0.02 mW (d) and 2.15 mW (e), respectively.

The value K obtained from fitting suggests that A^- is more sensitive to excitation power than A^0 . At low power (such as 0.02 mW in Figure 4-10 (d)), photo-generated electrons are in low concentration and they are more likely to be compensated by holes, so the neutral exciton A^0 is in dominance [206]. Increasing the excitation power can introduce a higher concentration of photo-excited electrons, which can be regarded as

optical doping. Reversible optical doping effect has been observed in graphene on SiO₂/Si substrate, in which the down-shifted 2D band and up-shifted G band confirm the electron doping [207]. The charged exciton A⁻, in our case, thus becomes stronger with increasing electron concentration due to higher power. When power keeps increasing to 3.40 mW, a saturation plateau zone will be reached, as Figure 4-10 (c) indicates [206]. The results from power-dependent PL measurements are a little bit deviated from previous reports [195, 199]: The value α is not that close to 1. This might be due to the non-uniform distribution of photo-excited carriers or to competitive nonlinear and non-radiative processes [208]. Further experiments need to be conducted to understand the reason.

Meanwhile, we also performed the Raman scattering measurements to check the lattice vibrational properties. Figure 4-11 (a) presents the atomic displacement in vibrational modes of 1 L and 2 L 2H-stacked MoSe₂. Figure 4-11 (b) presents the Raman spectra taken from the as-grown 1 L and 2 L MoSe₂. The out-of-plane vibrational mode A_{1g} is stronger as compared to the fingerprint peak from Si (520.7 cm⁻¹), which suggests the quality of the CVD-grown MoSe₂ thin films is not bad. Furthermore, we show the zoom-in view to check the thickness-dependent shift of A_{1g} and E_{2g}^1 in Figure 4-11 (c). As expected, A_{1g} mode is stiffened and E_{2g}^1 mode is softened from 1 L to 2 L, in agreement with previous results from exfoliated samples [118, 186].

In MoS₂ thin film, the layer-dependent shifts of the high-frequency intralayer vibrational modes are less sensitive compared to the low-frequency interlayer shear and breathing modes. Take out-of-plane vibrational modes as an example: from 2 L to 9 L, the shift of high-frequency A_{1g} mode is less than 5 cm⁻¹, while the low-frequency B1 mode shifts by ~30 cm⁻¹ [186]. In our CVD-grown 2 L MoSe₂, we have observed the interlayer

shear mode E_{2g}^2 at 18 cm^{-1} . Figure 4-11 (d) shows the zoom-in view of E_{2g}^2 mode and a high frequency breathing mode at 352 cm^{-1} , which is another difference between mono- and bi-layer. This peak corresponds to the optically-inactive B_{2g}^1 mode in the bulk, which evolves into a Raman-active mode with A_{1g} symmetry in bilayer and an infrared-active (Raman-inactive) A_2^* mode in the monolayer case, due to the symmetry change [118, 121]. The detailed discussion on Raman scattering of CVD-grown MoSe₂ will be shown in Chapter 5.

Figure 4-11. Raman spectra of CVD-grown MoSe₂. (a) Vibrational normal modes of 1 L and 2 L 2H-stacked MoSe₂. Orange and blue spheres represent Se and Mo atoms respectively. Monolayer MoSe₂ is consisted of two layers of Se and one intermediate layer of Mo. (b) Raman spectra taken from the CVD-grown mono- and bi-layer MoSe₂. (c, d) Zoom-in spectra show the difference between monolayer and bilayer.

4.1.3 SU-8 Patterning and Electrical Performance

Before fabricating a device on the CVD-grown MoSe₂ film, SU-8 patterning is

indispensable. The narrower effective channel length resulted patterning makes it easier to avoid the defects staying on the substrate which might affect the device performance by constraining the current flow into the channel. Defects on the substrate, such as pinholes in the gate oxide, may form because of the high temperature during CVD growth (also observed in the MoS₂ FET synthesized by CVD [209]), imperfection in the production of the substrate, or during the device fabrication and processing steps.

Figure 4-12. Schematic diagram of the patterning process.

The schematic diagram of SU-8 patterning process is shown in Figure 4-12. After CVD-synthesis, the patterning was carried out on an EBL system, with 30 kV as the acceleration voltage. For SU-8 patterning, we used the negative epoxy-based SU-8 2002 (Micro Chem). Firstly, SU-8 was spin-coated on the sample at 4000 rpm for 40 seconds, followed by soft-baking (65 °C) on a hot-plate for 1 minute and another 1 minute at 95 °C subsequently. Afterwards, the sample was immersed into SU-8 developer (Micro Chem) for 1 minute after the EBL exposure. To completely remove the SU-8 pattern, the sample is baked post-exposure at 95 °C for 1 minutes, immersed into Remover PG (Micro Chem) at ~65 °C for 10-30 minutes, and then blow-dried with N₂ flow. After SU-8 patterning,

the gate leakage current was suppressed by two orders of magnitude [57], enabling the correct interpretation of the electrical performance on CVD-grown MoSe₂ films, as shown in Figure 4-13.

Figure 4-13 (a) shows transfer characteristics of the device at room temperature. Ambipolar field-effect was demonstrated and the n-type behavior is more prominent. With 37.5 V gate overdrive, the on-off current ratio of $\sim 10^2$ was measured for the n-type conductance. It is evident that higher on-off current ratio is achievable with a larger gate overdrive. In the meantime, the subthreshold swing is measured to be 15.2 V/dec. Figure 4-13 (b) demonstrates the transport properties of the device with several drain voltages. The inset of Figure 4-13 (b) shows that the leakage current is about 100 pA at $V_g = -30$ V, several orders smaller than the drain current even at $V_d = 1$ V, which indicates that the ambipolar behavior of the device is not resulted from gate leakage. The field-effect mobility of the CVD-grown sample is estimated by using the equation $\mu = (dI_{ds}/dV_g) \times (L/WC_{ox}V_{ds})$, where L and W are the channel length and width of the device, respectively. C_{ox} is the areal capacitance of the oxide gate (3.45×10^{-8} F/cm² for 100 nm SiO₂). The mobility is calculated to be 0.012 cm²V⁻¹S⁻¹ for hole and 0.020 cm²V⁻¹S⁻¹ for electron at the linear regime of the transfer curve. The value of electronic mobility for the MoSe₂ device is comparable with the typical range of mobility from as-synthesized 1 L MoS₂ (~ 0.003 - 0.8 cm²V⁻¹S⁻¹) [44, 46, 48, 51]. Figure 4-13 (d) and (c) show the output characteristics of the device at several negative and positive gate voltages, respectively. The ambipolar behaviour of the device is demonstrating, as current level increases with increasing $|V_g|$. The I_{ds} - V_{ds} plot is linear, although minor asymmetry between positive and negative V_{ds} interval suggests the presence of Schottky barrier at the

Ni-MoSe₂ contact [210].

Figure 4-13. Electrical properties of the MoSe₂ film grown *via* CVD. (a) I_{ds} - V_g curves plotted in linear and semi-log scale at $V_{ds} = 5$ V. Inset: Scanning electron microscopy (SEM) image of the device. D and S denotes the drain and source electrode pads. (b) I_{ds} - V_g curves for various V_{ds} . Inset: gate leakage current as a function of V_g . (c) and (d) show the I_{ds} - V_{ds} curves of the device for various positive and negative gate voltage ranges, respectively.

Further measurements [57] of temperature-dependent conductance show that the mobility of CVD-grown MoSe₂ film increases with temperature, and the transport properties follow variable range hopping (VRH) mechanism. Normally, VRH mechanism is applied in strongly disordered systems with localized charge-carrier states. The occurrence of VRH transport properties further confirm that the L peak observed in low temperature PL spectra is related to the localized states. Improvements on the device performance is achievable either by depositing high-k top gate dielectric to screen Coulomb scattering, or by enhancing the sample quality. In addition, Hall measurements can be utilized to eliminate contact resistance and deduce the gate capacitance [211, 212].

4.2 Synthesis of Few-layer MoSe₂ Nanoflakes

Increasing the grain size of CVD-grown MoSe₂ will help on the electrical performance, as scattering due to grain boundary within the effective channel length will be reduced. Meanwhile, our previous growth on MoSe₂ thin film has shown that 2H and 3R stacking orders can coexist within the same batch of growth (Figure 4-2). Nonetheless, further study of stacking-dependent optical and electrical properties was limited by the small grain size (~100 nm), which can only proceed with larger samples (at least ~3 μm).

4.2.1 Parameters Optimization in CVD-growth of MoSe₂ flakes

Figure 4-14. CVD-grown few-layer MoSe₂ flakes on 285 nm SiO₂ in low (a) and high magnification (b-h). Thickness, confirmed from AFM, is indicated in each sub-figure. Scale bars correspond to 10 μm in (b-h).

Through numerous trials on optimizing the growth parameters, few-layer MoSe₂ flakes with grain size of more than 10 μm have been obtained, in a relatively large density, as shown in Figure 4-14. Figure 4-15 shows the schematic of the synthesis, with MoO₃ powder put in the center boat and Se power on the upstream. The separation distance between two the boats is 15.5 cm. 285 nm SiO₂/Si substrate was chosen to be the growth

substrate, which was put upside down on the center boat. CVD-growth of film/flakes on 100 nm SiO₂/Si or 285 nm SiO₂/Si is actually very similar, meaning that the density, morphology, and thickness resemble. Selection of 285 nm SiO₂ is mainly for electrical performance, as larger leakage current is observed in substrate with thinner oxide layer. In contrast, the choice of 100 nm SiO₂ is in favor of PL measurement, because 285 nm SiO₂ has destructive interference effect of light ~800 nm (A exciton of MoS₂ has energy of 1.56 eV, corresponding to 795 nm.). The temperature was ramped up to 750 °C within 15 minutes, kept for 5 minutes, and reduced naturally to room temperature. During the CVD-synthesis, the whole quartz tube reactor was kept constant at 810 Torr with 20 sccm of 5% H₂/Ar as the carrier gas.

Figure 4-15. Schematic of the CVD-synthesis of MoSe₂ few-layer flakes. The tube was heated to 750°C in the center, where the MoO₃ powder was placed (~50°C/min ramp rate), and kept for 5 minutes at this temperature for sample growth. Chamber pressure is 810 Torr. The flow of 20 sccm 5% H₂ in Argon was used to carry the vaporized Se and MoO₃ powder for the formation of MoSe₂. Before sample retrieval, the whole CVD system is allowed to cool to room temperature naturally.

Next, I am going to introduce how I optimized the critical parameters, including pressure, H₂ concentration and so forth. Growth pressure of 810 Torr was adopted from the comparison in pressure-dependent growth. The corresponding controlled experiments were conducted with 750 Torr (atmosphere pressure), 810 Torr, and 870 Torr.

Figure 4-16. Pressure-dependent CVD growth of few-layer MoSe₂ flakes. The chamber pressure was kept at 750 Torr, 810 Torr, and 870 Torr in (a, b), (c, d), and (e, f), respectively. Other growth parameters are kept the same: Annealing temperature is 750°C and time is 5 minutes. Flow gas is 70 sccm 5% H₂ diluted in Ar. Scale bars correspond to 20 μm. (b) and (f) are in relatively low magnification.

In general, density (seen from comparison between Figure 4-16 (b) and (f)) and grain size increase with higher growth pressure. The grain size from 810 Torr and 870 Torr are similar, and both pressures produce larger flakes than those from 750 Torr, as shown in Figure 4-16 (a, c, d, e), which is consistent with previous report on pressure-dependent CVD growth of monolayer MoS₂ [52]. Further comparison between 810 Torr and 870 Torr shows that the as-grown flakes from 870 Torr are thicker (white color instead of blue color), so 810 Torr was chosen. Nevertheless, the sample surface is dirtier at higher pressure. The small particles, which can act as scattering center, would deteriorate electrical performance. Controlled experiments on flow rate (70, 40, and 20 sccm) show that this can be solved by reducing flow rate, and thus 20 sccm was selected as the final growth parameter. A previous paper on CVD-synthesis of MoS₂ has reported that the high flow rate may promote the mass transfer process, which contributes to the increase in the crystal growth rate. In this case, instability may occur as atoms do not have enough time

to move into the right lattice locations, and the probability of defect formation increases [184].

Figure 4-17. Dependence on H₂ concentration in CVD-growth of MoSe₂. (a) A photo of three pieces of substrates after growth. From left to right, H₂ concentration varies from 0%, 5%, to 100%. Bottom: Illustration on sample distribution of growth with 5% H₂. (b-d) Optical microscopy images from growths with different concentration of H₂.

The concentration of H₂ is another crucial factor. Controlled experiments were performed with 20 sccm 100% Argon, 5% H₂ in Argon, and 100% H₂ as flow gas, and all other parameters remain unchanged: Annealing temperature is 750 °C; Growth pressure is

810 Torr; Substrate is 285 nm SiO₂/Si with width of 1.5 cm and placed upside down on the center boat of MoO₃. From the photo in Figure 4-17 (a), we see from naked eyes that there is almost no deposition on the substrate when the growth was without H₂. Zoom-in optical images in Figure 4-17 (b) shows that there are only black particles, further confirming that H₂ is necessary in the synthesis of MoSe₂ [174]. When H₂ is introduced, the morphology differs from film-like samples (100% H₂) and nanoflakes (5% H₂) depending on concentration. The thickness of film goes from thin to thick when the location on substrate gets closer to the center (MoO₃), indicating the growth in this case is more kinetic controlled as it relies a lot on the concentration of MoS₂ vapour. In contrast, the growth with 5% H₂ did not show a similar trend. The sample distribution is displayed in the bottom of Figure 4-17 (a). MoSe₂ flakes are inclined to grow close to the edge as well as along the flow direction of the gas. However, unlike that with 100% H₂, the distribution of thin samples does not localize in a certain region.

The synthesis of atomically thin TMD materials in large-area with highly crystalline quality and uniform thickness is not trivial, especially when the field just started (from 2012 to early 2014). Using various kinds of aromatic molecules as seeding promoters, such as PTAS and tris(4-carbazoyl-9-ylphenyl) amine (TCTA), can help during growth [51, 77]. I have also compared the syntheses with and without PTAS catalyst. PTAS powder was first dissolved in deionized water (50 μM), and then the solution was drop-casted on the substrate for 30 minutes, which was later dried with N₂ flow and heated on a hot plate at 50 °C. During CVD-growth, the same parameters were adopted for both PTAS-seeded and unseeded substrates. The low magnification optical images of as-grown samples were shown in Figure 4-18, with scale bars corresponding to 0.4 mm.

Figure 4-18. Comparison on the CVD-growth of MoSe₂ flakes with and without PTAS catalyst. (a, b) CVD-growth with PTAS catalyst (a) and without PTAS catalyst (b). Growth with catalyst has higher density and better repeatability. (c, d) Further comparison of synthesis with (c) and without catalyst (d) in a “clean” environment, which shows almost no discrepancy in density. The explanation on “clean” is described in the main text. Scale bars correspond to 0.4 mm.

In an “ordinary” environment, growth with PTAS gives better repeatability and has higher yield; while some very large flakes (with lateral width up to 80 μm compared to average size of 10-20 μm) usually occur on substrate without catalyst, though density is very low. The PTAS particle can function as a nucleation during synthesis, which accelerates the growth. In contrast, large flakes tend to grow in a slow speed, thus emerging on non-catalyst substrates. The reason for using the word “ordinary” here is for the comparison of “clean”. A previous report has shown that a “clean” environment benefits the CVD-growth of monolayer MoS₂, in which the size grows bigger and bigger in cleaner system [53]. However, they did not specify “clean” in their paper. Here, what I mean by writing “clean” is the status of a CVD system after being thoroughly cleaned,

including the components on the upstream (referred to where after flow rate controller and before quartz tube) and downstream (referred to where after quartz tube and before pump). Besides, a complete cleanness of substrate is also necessary: The substrates were cleaned through acetone, UV-ozone, and piranha solution ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$) in orders. From Figure 4-18 (c) and (d) we can see that in terms of morphology and density are similar on substrates with and without PTAS catalyst. Unfortunately, flake with size up to $80\ \mu\text{m}$ is still rare in the CVD synthesis with “clean” environment.

4.2.2 Electrical Performance: Catalyst VS Non-catalyst

The usage of PTAS catalyst induces formation of particles aggregated on the substrate, in agreement to previous reports [60, 77]. We also observed that the particles have an average diameter of $65 \pm 9\ \text{nm}$. Such PTAS particles may stay on the substrate after the growth of MoS_2 flakes and even after the removal of the flakes [60], according to previous report. The PTAS particles do not have significant effect on phonon modes, while it is another story on electrical performance.

Figure 4-19 (a) contrasts the gate sweep curve between the FET from PTAS-seeded and unseeded MoSe_2 bilayer flakes. In general, unseeded flakes outperformed the PTAS-seeded flakes in terms of subthreshold swing and on-off ratio. The low on-off ratio on seeded samples were not only due to relatively lower on-state current. We also saw a high off-state current level ($\sim\text{nA}$, dashed black curve) in some devices, which suggests that there is current leakage in the FET.

Figure 4-19 (b-d) further show the comparison of FET device performance between PTAS-seeded and unseeded MoSe_2 flakes on field-effect mobility, on-off ratio, and

subthreshold swing. The measurements were performed on 178 devices from multiple batches of growth to show that the effect that we observed is statistically significant. The data is grouped according to thickness to rule out any dependence on layer number. Here, we see that the unseeded MoSe₂ FETs consistently performed better: higher mobility, higher on-off ratio, and lower subthreshold swing. Increasing average mobility with respect to thickness is also observable, which is in consistent with previous work on MoS₂ [213].

Figure 4-19. Comparison of electrical performance between PTAS-seeded and unseeded MoSe₂ FETs. (a) I_{ds} vs V_g curves of representative from PTAS-seeded and unseeded 2 L MoSe₂. PTAS-seeded MoSe₂ has not only lower on-off ratio, but high off-current level as well at $\sim nA$. Red arrows denote the direction of the hysteresis in the curve of unseeded MoSe₂. (b-d) We further compared the electrical performance of PTAS-seeded and unseeded MoSe₂ FETs in terms of mobility (b), on-off ratio (c), and subthreshold swing (d). In all cases, unseeded MoSe₂ exhibited better performances.

It is safe to draw a conclusion that PTAS acts negatively on device performance. The existence of PTAS particles may be considered as an additional impurity on the substrate. When the flakes were formed, the impurity on the flake-substrate interface will work as a Coulomb scattering center. Moreover, the incorporation of the particles on a flake [78]

will also interfere with the charge transport on the sample by increasing the scattering rate. The above mentioned two factors will add up to decrease the carrier mobility and the conductivity (hence reducing the on-state current) of PTAS-seeded MoSe₂ devices. The large subthreshold swing in seeded flakes also implies that the impurity due to PTAS particles may also add the interface trap density at the flake-substrate interface. In addition, the application of PTAS seeds into the MoSe₂ flakes after the synthesis might create new localized defect states within the bandgap of the MoSe₂ devices.

4.3 Synthesis of WSe₂ Thin Film and Flakes

After the synthesis of MoSe₂ film and flakes, I have attempted to grown WSe₂ *via* CVD system also by using selenization. As the melting point of WO₃ is higher than that of MoO₃, most CVD-growth of WSe₂ needs higher temperature [62, 176, 177, 214, 215].

4.3.1. CVD-Growth of WSe₂ Thin Film

Both samples in Figure 4-20 (a) and (b) were grown with temperature on WO₃ powder set to be 1000 °C, and the boat for Se powder was placed 18 cm away on the upstream. Substrates are both 100 nm SiO₂/Si, but the position differs: The substrate was put upside down on the center for the film in Figure 4-20 (a), and for that in Figure 4-20 (b), substrate was placed 14 cm away from the center on the downstream. Pressures are different as well. *Sample a* (film in Figure 4-20 (a)) was grown under 100 Torr, while 20 Torr was adopted for the synthesis of *sample b* (film in Figure 4-20 (b)).

Figure 4-20. CVD-synthesis of atomically WSe₂ film. (a, b) Optical images of as-grown thin film from two batches of growth with different parameters described in the main text. Scale bars correspond to 20 μm . (c, d) Raman spectra (c) and PL spectra (d) from *sample a* (in Figure 4-20 (a)) and *sample b* (in Figure 4-20 (b)), respectively. Raman spectra were normalized according to the Si peak located at $\sim 520 \text{ cm}^{-1}$.

From optical images we can see that *sample a* has better morphology than *sample b*. However, further characterization on Raman spectroscopy and PL measurements show that *sample a* exhibits stronger fingerprint Raman peaks and much higher PL intensity. The absence of interlayer vibrational modes in the low frequency region suggests that both samples are monolayers [118]. The strong luminescence from *sample a* locates at $\sim 1.62 \text{ eV}$, which is assigned to be the emission of A exciton [176, 186, 200]. Meanwhile, the asymmetric lineshape was also observed in Figure 4-20 (d). A recent paper [200] has observed similar shoulder and they suspected the peak is due to biexciton due to the super-linear intensity dependence. Since my growth parameters have not been fully optimized, I tentatively believe that the small shoulder on the low energy side of A exciton might be related to defects. Still, further experiments need to be conducted before

making a conclusion. On the other hand, *sample b* does not have luminescence in the range of 1.5-1.9 eV. Possibly there are defects states or localized states within the band gap, contributing a lot on non-radiative recombination, thus PL is not observed.

4.3.2. CVD-Growth of WSe₂ Flakes

The as-grown few-layer WSe₂ flakes were shown in Figure 4-21. Same as that in MoSe₂ flakes, the pressure is also 810 Torr and substrate is put upside down on the center boat. Temperature on WO₃ is 980 °C and Se powder is 18.5 cm away from the center. Flow gas is 70 sccm 5% H₂ in Argon. The growth of WSe₂ flakes is obviously not as successful as MoSe₂, as most flakes are in whit color (thick). Yet few-layer flakes (2-5 L) with size of ~3 μm are sufficiently large for optical studies on micro-Raman spectroscopy.

Figure 4-21. CVD-grown WSe₂ flakes. (a, b) Optical images in low magnification (a) and high magnification (b). (c, d) SEM image of a flake exhibiting petal-like pattern on the corner (c). (d) Zoom-in view. (e, f) SEM (e) and AFM (f) images of a 2 L WSe₂ flake, which shows that the petal-like can also exist in the middle of the flake. Height profile in (f) was taken along the black line in (f).

Scanning electron microscopy (SEM) was used to check the morphology. A petal-like pattern was observed, which can appear both on the corner (Figure 4-21 (c, d))

and in the middle (Figure 4-21 (e, f)) of the flake, regardless of the thickness. Wang *et al.* have explored polymorphism of dislocation core structures by using STEM [216], and the type I dislocation they have observed is very similar to the pattern in Figure 4-21 (e, f). This indicates that the petal-like pattern might result from partial dislocations. Partial dislocations are referred to dislocations with Burgers vectors (the magnitude and direction of the lattice distortion. They are not translation vectors of the lattice). They appear as a pair and must border a two-dimensional defect (usually a stacking fault).

Figure 4-22. SEM images of three types of morphologies in the CVD-grown WSe₂ flakes, including screw dislocation (a), petal-like pattern (b), and sample with flat surface (c).

Besides the petal-like pattern we just discussed, there are two other types of morphologies common in the CVD-grown WSe₂ flakes, shown in Figure 4-22. Screw dislocation has been observed in CVD-grown WSe₂ before [214], suggesting the growth mechanism follows the Screw-Dislocation-Driven (SDD) spiral growth fashion. Spirals in MoS₂ has also been reported [217]. The spirals composed of several connected MoS₂ layers with decreasing areas: each basal plane has a triangular shape and shrinks gradually to the summit. Although dislocations are widely seen, flakes with flat surface are not in minority, as shown in Figure 4-22 (c). These flat flakes are not necessarily free of dislocations; high resolution TEM images are needed for further investigation. Nevertheless, these three types of morphology coexist in the same batch growth, it is very

possible that the growth mechanisms are the same (at least similar).

We performed Raman scattering measurements on CVD-grown WSe₂ flakes with flat surface (such as the flake in Figure 4-22 (c)). The intralayer vibrational modes, E_{2g}^1 and A_{1g} , in WSe₂ are both around 250 cm⁻¹. Polarization-dependent measurements help to resolve the two peaks [218]. The two modes are degenerate in monolayer WSe₂. With increasing thickness, E_{2g}^1 mode down-shifts and A_{1g} mode up-shifts, thus the degeneracy is lifted. The frequency difference between E_{2g}^1 and A_{1g} modes is observed to be ~3 cm⁻¹ in bulk WSe₂ [218]. Compare the CVD-grown and exfoliated WSe₂ samples, there is no observable difference on E_{2g}^1 and A_{1g} modes. In contrast, the low frequency Raman spectra demonstrate something new as shown in Figure 4-23: (1) Absence of interlayer shear modes. (2) Frequencies of B1 and B2 modes in CVD-grown samples are relatively lower than those of exfoliated ones. We have measured 10 bilayers and 8 trilayers from two batches of growth, and the results are consistent.

Figure 4-23. Low-frequency interlayer vibrational modes of CVD-grown WSe₂ flakes with flat surface. (a, b) Raman spectra taken under $\bar{z}(xx)z$ (a) and $\bar{z}(xy)z$ (b) configurations, respectively. (c) Comparison of frequency of B1 and B2 modes between exfoliated and CVD-grown samples. B1 and B2 refer to the interlayer breathing mode branch with the lowest and 3rd lowest frequency, respectively.

We supposed the new features might be related to dislocations, and utilized STEM techniques to further check the as-grown samples. Results show that screw dislocations

are only seen on flakes with layer number > 10 , such as the ~ 18 L in Figure 4-24 (a). On thin layers, stacking transition within a short range (several nanometers) is observed. This leads to a new question: Is there any correlation between short-range stacking transition and absence of interlayer shear modes? A paper published on *Nature* in 2014 has revealed that such kind of stacking transition (*e.g.* from Bernal stacking to rhombohedral stacking in 3 L graphene) can be resulted from partial dislocations [219]. Follow the conventional pathway that one batch of samples follow the same grow mechanism, especially when the samples are located nearby, it is intuitive to infer that the stacking transition we observed is also related to partial dislocation. Apart from the alteration of the stacking, Butz *et al.* have detected the pronounced buckling (by around 1 nm) of the graphene membrane [219]. The buckling is associated with the dislocation lines as the driving force for the buckling is release of strain energy in the dislocation strain field. Through strain analysis, they found that the buckling can alter strain states in bilayer graphene: Localized strain in one layer and uniform strain on the other layer. We have also found localized strain on the bilayers in Figure 4-24 (c). Although our observation resembles what have been found in graphene, it is still very difficult to make a conclusion on what causes the absence of the interlayer shear modes. Maybe it is the partial dislocations or the localized strain. Further experiments and analysis have to be done.

Figure 4-24. STEM images of CVD-grown WSe₂ flakes. (a) An ~18 L flake with screw dislocation. (b) A 9 L flake without obvious spiral feature. (c) A 2 L flake with stacking transitions within several nanometers.

4.4 Summary

I have introduced how we used selenization of trioxide in producing mono- and few-layer MoSe₂ and WSe₂ *via* a CVD system. Detailed discussion on the dependence of substrate position, pressure, and concentration of H₂ was presented. Optical images and STEM images are shown to demonstrate the morphology. Optical properties, including measurements on PL spectroscopy and Raman spectroscopy, are discussed on both MoSe₂ and WSe₂, in the form of not only film but also individual flake. Electrical performance was briefly introduced, in order to give a full view of the properties on the CVD-grown TMD materials.

Although CVD-growth has been called as a “dark magic” by some people as it is definitely not trivial to synthesize high quality atomically thin samples with good

reproducibility, CVD-synthesis can offer us lots of new possibilities and opportunities. For instance, samples with non-2H stacking, even stacking faults and stacking transition are more easily obtained through CVD synthesis. In the next chapter, I will discuss the relationship between interlayer shear modes and stacking orders based on CVD-grown MoSe₂ flakes. On the other hand, defects (*e.g.* dislocation), impurities, and grain boundaries in CVD-grown samples have provided a platform for the study and engineering defects for device applications. That is the beauty of CVD synthesis.

Chapter 5 Stacking Sequences and Interlayer Shear Modes

In this chapter, I will first discuss about the principles governing the thickness-dependent evolutionary trends for both interlayer breathing modes and interlayer shear modes. The trend for interlayer breathing mode is predominantly associated with thickness, while that for interlayer shear modes will be shown to be related to stacking orders/sequences. Furthermore, I will take CVD-grown MoSe₂ as a case study to demonstrate the relation between stacking and interlayer shear modes.

5.1 Thickness-Dependent Evolutional Trends for Interlayer Vibrational Modes

Figure 5-1. Normal mode displacements for interlayer breathing mode B1 (the branch with the lowest frequency) and a spring model. (a) Normal mode displacements for B1 mode in 2-5 L thin films. One blue rectangle represents one layer. The length of the arrow is related to the displacement value. (b) Simple harmonic motion in a spring. The mass of the two spheres is m_1 and m_2 , respectively. The force constant of the spring is K . The upper layer(s) and the bottom layer(s) displace in opposite directions in Figure 5-1 (a), which suggests that the simple harmonic motion shown in Figure 5-1 (b) can be applied to explain the displacements of B1 mode.

By comparing the frequency evolutionary trends of the interlayer vibrational modes in 2H-stacked TMDs and the rhombohedral Bi₂X₃ (X = Se or Te) few-layers [118, 128, 170, 171, 183], it is found that the trends for breathing modes in both systems are the same (*i.e.*,

redshift in thicker samples), while trends of the shear modes behave differently: as the thickness increases, shear modes blue-shift in 2H-TMDs, but red-shift in Bi_2X_3 .

The downshifting interlayer breathing modes with increasing thickness can be understood by considering the simple harmonic motion in a spring. Take B1 mode as an example, which is the interlayer breathing mode with the lowest frequency and usually the strongest in each thickness [118]. It is also referred to layer breathing mode (LBM) in some papers [148, 168, 171]. The displacement of each layer for B1 mode in 2-5 L thin films (*e.g.* TMDs, Bi_2X_3 , graphene, and black phosphorus) is shown in Figure 5-1 (a). We can see that the upper layer(s) and the bottom layer(s) displace in opposite directions. This suggests that the simple harmonic motion with only two spheres and one spring demonstrated in Figure 5-1 (b) can be applied. The frequency of the simple harmonic motion can be calculated by $\omega = \sqrt{K/\mu}$, where K refers to the force constant of the spring and μ is the effective mass ($\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$, m_1 and m_2 represent the masses of the two spheres). In B1 mode, K means the out-of-plane interlayer force constant K_z , which shows negligible change from bulk to bilayer. μ is related to the mass of the thin films: μ increases in thicker layers, resulting in the smaller frequency; Also, μ varies for different samples. Although K_z is similar, B1 mode in bilayer graphene and MoS_2 locates at $\sim 80 \text{ cm}^{-1}$ and $\sim 40 \text{ cm}^{-1}$, as a result of different mass.

The discrepancy in the evolutionary trend of interlayer shear modes is an interesting topic to study. This evolution trends are determined by the Raman active modes with the largest Raman intensity. It is natural to ask what determines the direction of the trend. In other words, is there any general rule to govern the largest Raman intensity of the interlayer modes? A bond polarizability model will be introduced, in order to find out the

rule on determining the evolutionary trend. This theoretical aspect of the bond polarizability model is mainly developed from our collaboration with theoretical physicist Professor Quek Su Ying's group from National University of Singapore.

Since Raman activity is determined by the space group and symmetry of the material, it is important to first discuss the symmetry of the different material polytypes. The space group (symmetry) of few-layered graphene, MoS₂ (TMDs) and Bi₂Se₃ (Bi₂Te₃) has been summarized in Table 5-1, with different thickness and stacking orders. It is obvious from the table that symmetry (space group) cannot explain the Raman intensities of the interlayer shear modes. For example, both AB (Bernal) and ABC stacked four-layer graphene (4 LG) have the same symmetry (D_{3d}^3), but the highest frequency interlayer shear mode (C mode) has large Raman intensity only in AB-stacked 4 LG [147]. In contrast, there is negligible Raman intensity of C mode in ABC-stacked 4 LG [220]. Likewise, for films with an even number of layers, ABC-stacked Bi₂Te₃ and Bi₂Se₃ share the same space group (D_{3d}^3) with 4 LG, either AB- or ABC-stacked graphene. The frequency trend of ABC-stacked Bi₂Te₃ and Bi₂Se₃ is the same as that in ABC-stacked graphene, instead of that in AB-stacked graphene. On the other hand, even though ABC-stacked graphene (D_{3d}^3) and ABC-stacked (3R phase) MoS₂ and MoSe₂ (C_{3v}^1) have different symmetries, their interlayer shear modes have the same frequency trend in the Raman spectra (red-shifts in thicker samples). Therefore, it seems that the stacking order, rather than space group, affects the evolution trends of the observed interlayer shear mode in the Raman spectra.

The observed frequency trends arise from which interlayer shear modes have the largest Raman intensity. For AB-stacked materials, it is the highest frequency shear mode

(maximum out-of-phase displacements in adjacent layers) which has the largest Raman intensity, while for ABC-stacked materials, the lowest frequency shear mode (minimum out-of-phase displacements in adjacent layers) has the largest Raman intensity. These observations would seem consistent with the physical intuition that a maximum out-of-phase displacement would result in the largest change in polarizability (and therefore largest Raman intensity) in AB-stacked materials, while the opposite is true for ABC-stacked materials. This physical intuition can be confirmed more quantitatively using the bond polarizability model [221].

Table 5-1. Space group and stacking orders of graphene, black phosphorus, MX_2 ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{Se}$), and Bi_2X_3 ($\text{X} = \text{Se}, \text{Te}$) under AB and ABC stacking order. “Odd (Even) number of layers” is abbreviated to “Odd (Even) N ” in the table.

	AB stacking			ABC stacking	
	Single Layer	Odd N $N = 3, 5, 7 \dots$	Even N $N = 2, 4, 6 \dots$	Odd N $N = 3, 5, 7 \dots$	Even N $N = 2, 4, 6 \dots$
Multi-layered Graphene	D_{6h}^1	D_{3h}^1	D_{3d}^3	D_{3d}^3	D_{3d}^3
MX_2 ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{S}, \text{Se}$)	D_{3h}^1	D_{3h}^1	D_{3d}^3	C_{3v}^1	C_{3v}^1
Bi_2X_3 ($\text{X} = \text{Se}, \text{Te}$)	D_{3d}^3	--	--	D_{3d}^3	D_{3d}^3

Within the Placzek approximation, if the incident frequency of laser light is smaller than any absorption frequency but much larger than the Raman transition frequency, the intensity of the Stokes Raman peak can be calculated by [222]: $I^k = |e_i \cdot \tilde{R}^k \cdot e_s|^2 \propto \frac{(n_k + 1)}{\omega_k} \left| \sum_{\alpha\beta} e_{i\alpha} e_{s\beta} P_{\alpha\beta,k} \right|^2$, where $\tilde{R}^k$ is the Raman tensor, and $P_{\alpha\beta,k}$ is the Raman susceptibility, n is the Bose-Einstein distribution $n_k = 1/\{\exp(\eta\omega_k / k_B T) - 1\}$. For the anti-Stokes process, $n_k + 1$ is replaced by n_k . $P_{\alpha\beta,k}$ can be calculated with an empirical bond polarizability model. In first principles calculations, $P_{\alpha\beta,k}$ is obtained using density functional perturbation theory using the formula $P_{\alpha\beta,k} = \sum_{l\gamma} \frac{\partial^3 E_{\text{tot}}}{\partial \varepsilon_m \partial \varepsilon_n \partial u_{l\gamma}} \chi_{l\gamma}^k$ where ε is the electric field, $\frac{\partial}{\partial u_{l\gamma}}$ refers to the

derivative (of the polarizability $\frac{\partial^2 E_{tot}}{\partial \epsilon_m \partial \epsilon_n}$) with respect to the γ^{th} spatial coordinate of atom l , and $\chi_{l\gamma}^k$ is the displacement of atom l in the γ direction for eigenmode k [223]. Within the bond polarizability model, the electronic polarizability is written as a sum of individual bond polarizabilities, which are assumed to be roughly independent of the chemical environment [224]:

$$P_{\alpha\beta} = \frac{1}{2} \sum_{l,B} \left\{ \frac{1}{3} (\alpha_{||} + 2\alpha_{\perp}) \delta_{\alpha\beta} + (\alpha_{||} - \alpha_{\perp}) \left(R_{\alpha} R_{\beta} - \frac{1}{3} \delta_{\alpha\beta} \right) \right\}$$

where $\mathbf{R}(l,B)$ is the bond vector connecting atom l to one of its nearest neighbour atoms l' connected by bond B , the vector being normalized to unity. $\alpha_{\perp}$ and $\alpha_{||}$ are the static perpendicular and longitudinal bond polarizability, respectively, which are further assumed to depend on the bond length R only. The derivative of the bond polarizability in the $\bar{z}(xx)z$ configuration, which determines the Raman intensity in most of our measurement, can be written as:

$$P_{xx,k} = - \sum_{lB} \left\{ \frac{\alpha'_{||} + 2\alpha'_{\perp}}{3} \mathbf{R}_0 \cdot \bar{\chi}_l^k + (\alpha'_{||} - \alpha'_{\perp}) R_{0x}^2 \mathbf{R}_0 \cdot \bar{\chi}_l^k - \frac{1}{3} (\alpha'_{||} - \alpha'_{\perp}) \mathbf{R}_0 \cdot \bar{\chi}_l^k + 2R_{0x} \chi_{lx}^k \frac{\alpha_{||} - \alpha_{\perp}}{R_0} - 2 \frac{\alpha_{||} - \alpha_{\perp}}{R_0} R_{0x}^2 \mathbf{R}_0 \cdot \bar{\chi}_l^k \right\}$$

where R_0 is the bond length at equilibrium, R_{0x} is the x component of the vector $\mathbf{R}$ defined above, the “primes” on the polarizabilities refer to radial derivatives with respect to atomic displacement, and χ_l^k is the eigenvector of phonon mode k .

Using the bond polarizability model, we can see that the Raman intensity in the $\bar{z}(xx)z$ configuration is zero for the lowest frequency interlayer shear mode and largest for the highest frequency interlayer shear mode in AB-stacked systems, while the opposite is true for ABC-stacked systems. These different Raman intensities determine the frequency evolution trends observed in Raman spectra.

5.2 Stacking and Polytypism in CVD-grown MoSe₂

Figure 5-2. Schematics of 1T, 2H, and 3R the structures in 3 L MX₂ (M = Mo, W; X = S, Se).

There is structural polytypism in group VI TMDs MX₂ (M = Mo, W; X = S, Se, Te). For S- and Se-based MX₂ (M = Mo, W; X = S, Se), the most common and stable phase is 2H (trigonal prismatic coordination), with H referring to hexagonal structure and two as the layer number per unit cell. Other common phases of MX₂ (M = Mo, W; X = S, Se) also include 1T and 3R. 1T stacking (octahedral coordination) has tetragonal symmetry, and one layer per repeat unit; 3R stacking (trigonal prismatic coordination) has rhombohedral symmetry and three layers per repeat unit [2]. The corresponding schematics are shown in Figure 5-2, with trilayer as an example. 1T phase has been reported to be metastable in MoS₂ [30] and MoSe₂ [225], which can be converted to the stable 2H phase when heated at low temperature for MoS₂ (complete transfer at 300 °C [30]), or dried in air for MoSe₂ (1T-MoSe₂ is stable if dispersed in water [225]). It is worth noting that the monolayer counterpart of 2H and 3R are the same, also referred to

1H. 1T, however, is different, as one of the S/Se atoms has 180° rotation. Therefore, the spatial inversion symmetry is reserved in 1T stacking, but it is broken in 1H structure. Further comparison between 2H and 3R structures in different thickness shows discrepancy: 3R stacking is noncentrosymmetric from 1 L to bulk, and valley polarization is expected regardless of layer number [100]. In contrast, the 2H stacking with even layer number has an inversion symmetry point and that with odd layer number is noncentrosymmetric.

The following discussion on the correlation between interlayer shear modes and stacking orders will be focused on stable structures, such as 2H phase (AB-stacked) and 3R phase (ABC-stacked). Interlayer vibrational modes, including the in-plane shear modes (atoms moving in the basal plane) and out-of-plane breathing modes (atoms moving perpendicular to the basal plane), are also called as “rigid-layer” or “quasi-acoustical” modes, because the entire layers of atoms vibrate rigidly against the neighbouring layers [125].

Figure 5-3. Normal mode displacements of all the interlayer shear modes in 3 L MX_2 ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}$) with 2H & 3R structure (Only 2 interlayer shear modes in 3 L). Orange and blue balls represent S/Se and Mo/W atoms, respectively. S_1 mode is Raman-active and S_2 mode is Raman-inactive in 2H phase. In contrast, the opposite is true for 3R phase.

There are $N-1$ 2-fold degenerate interlayer shear modes and $N-1$ interlayer breathing modes in N layer TMDs, graphene, black phosphorus, and most of other layered materials. The “ N ” in “ N layer”, in most cases, refers to a number smaller than ten and starts from two when discussing about interlayer vibration. But not all of the interlayer shear and breathing modes can be detected on Raman spectrometer. Take interlayer shear modes as an example for further illustration. In the following, we will call the interlayer shear modes as $S_1, S_2, S_3, \dots$ counting from the highest frequency in the sequence of decreasing frequency. In 2H phase, only the interlayer shear modes with the odd-highest frequency ($S_1, S_3, S_5, \dots$) are observable. The even-highest modes ($S_2, S_4, \dots$) cannot be detected, but reasons differ in odd layers and even layers: S_2 and S_4 modes are inactive on Raman spectroscopy (*i.e.*, there is no non-zero matrix elements in the corresponding Raman tensor) in even layers (2 L, 4 L, ...); in the opposite, though S_2 and S_4 modes are Raman active in odd few-layers (3 L, 5 L, ...), they cannot be seen on the commonly-used back-scattering configuration because of polarization (it might be possible to observe these modes in other scattering configurations) [118]. In addition, the peak intensity of all the observable interlayer shear modes in 2H stacking follows the trend of $I(S_1) > I(S_3) > I(S_5) > \dots$ relative to each other. The same principles also apply for interlayer breathing modes.

The relative peak intensity in 3R phase obey the opposite trend to 2H phase because observable modes at lower frequency have stronger intensities, and the lowest frequency mode (S_{N-1}) exhibits the highest intensity. Take 5 L as an example of odd layer, the trend of intensity is supposed to be $I(S_1) > I(S_3)$ in 2H phase and $I(S_4) > I(S_2)$ in 3R phase. A simpler example (3 L) is demonstrated in Figure 5-3. Take 6 L as an example of even

layer, the trend of intensity follows $I(S_1) > I(S_3) > I(S_5)$ in 2H phase and $I(S_5) > I(S_3) > I(S_1)$ in 3R phase. Meanwhile, the alternate modes starting from the second lowest frequency (S_{N-2} , for $N > 2$) are unobservable in 3R phase on the back-scattering configuration (*e.g.*, S_4 and S_2 modes cannot be seen in 6 L). A simpler example of even layer number (4 L) is demonstrated in Figure 5-4. Although Raman-active modes are the same, the relative intensities are different, which will be shown later.

Figure 5-4. Normal mode displacements of all three interlayer shear modes in 4 L MoSe₂ with 2H & 3R structure. S_1 (S_3) means the highest (lowest) frequency interlayer shear mode. Orange and blue balls represent Se and Mo atoms, respectively.

Before demonstrating results on CVD-grown MoSe₂ with multiple types of stacking orders, I will first show the properties of phonon modes on exfoliated 2H-stacked MoSe₂ few-layers in Figure 5-5. We observed that A_{1g} mode blue-shifts and E_{2g}^1 red-shifts as thickness increases, in agreement with existing literatures on TMDs [120, 186, 218]. It is believed that the surface effect, which refers to the larger M-X (M=Mo, W; X=S, Se)

force constants at the surface layer [122], causes the opposite shifting direction. In addition, the absence of B_{2g}^1 mode under cross-polarized $\bar{z}(xy)z$ configuration (Figure 5-5 (b)) indicates that the peak is from an out-of-plane vibration [121]. Previous literatures have shown that the lattice vibrational modes on Raman spectroscopy have polarization dependence: In-plane (shear) modes are Raman-active under both parallel $\bar{z}(xx)z$ and cross $\bar{z}(xy)z$ polarization configurations, but out-of-plane (breathing) modes are suppressed a lot in the $\bar{z}(xy)z$ configuration [118, 218]. Yet, Raman spectra on exfoliated 2H-MoSe₂ exhibit the same number of low-frequency peaks with both configurations (Figure 5-5 (c) and (d)), indicating the “absence” of all interlayer breathing modes in exfoliated MoSe₂ samples. In the meantime, the interlayer shear modes show the same trends to previous studies on MoS₂, WS₂, and WSe₂ with 2H stacking [118, 135, 170, 171].

According to calculations, the interlayer breathing modes in MoSe₂ should be Raman-active. We, unfortunately, did not see any of them, on either exfoliated or CVD-grown samples. However, Lui *et. al.* [168] and Chen *et. al.* [135] have managed to observe the modes in few-layer MoSe₂. Our explanation is that compared to those in MoS₂, WS₂, and WSe₂, the interlayer breathing modes in MoSe₂ are relatively weaker, which are not accessible (in terms of signal/noise ratio) on our spectrometer. Similarly, Puretzky *et al.* also barely observed the interlayer breathing modes in few-layer MoSe₂ on Raman spectroscopy [133].

Figure 5-5. Intralayer and interlayer vibrational modes in MoSe₂. (a-d) Raman spectra of exfoliated mono- and few-layer MoSe₂, in the range from 220 to 360 cm⁻¹ (a, b) and in the region with frequency < 40 cm⁻¹ (c, d) under both parallel- and cross-polarized configurations. In (a-d), experimental data are shown in black lines/dots, and blue lines are fitting results by using Lorentzian function. (e) Raman spectra of few-layer CVD-MoSe₂ in the low frequency region under $\bar{z}(xy)z$ configuration.

Our goal is to make a correlation between the stacking sequence and interlayer shear modes, and first of all, we measured the Raman spectra from CVD-grown MoSe₂ flakes under the cross-polarized configuration. The advantage of this configuration over the parallel polarization is that the stray light is suppressed more significantly [147] (seen in Figure 5-5 (c) and (d)). In the relatively high frequency region, intralayer modes are almost identical to those from exfoliated 2H-stacked MoSe₂. The shifts of A_{1g} and E_{2g}¹ modes with changing thickness are not very pronounced, because the intralayer vibrational modes are not as sensitive as the interlayer ones [118, 183]. As various Raman

features can be seen on flakes with the same thickness, we only show the maximum number of observable interlayer shear modes in each thickness in Figure 5-5 (e). A comparison is made afterwards, between the exfoliated sample and CVD-grown MoSe₂. Spectra from CVD-MoSe₂ unambiguously show additional peaks. Some modes, which are Raman-inactive in 2H stacking have appeared in CVD-MoSe₂, suggesting the non-2H stacking.

The difference in terms of crystal structure between 3R and 2H phases starts from the bilayer. Figure 5-6 (a) demonstrates the schematic of 2H and 3R stacking structures in bilayer MoSe₂. Besides the shift of layer, which also occurs in 3R phase, the N^{th} layer of 2H stacking is rotated with respect to the $N-1^{\text{th}}$ layer. Though the observable modes are different in 3R and 2H stacking orders, the energies of phonon modes will not necessarily change. According to our DFT calculations (Figure 5-6 (b-e)), the frequencies in 3R and 2H stacking orders have negligible difference in all S₁-S₄ modes. The similar frequencies in 3R and 2H phases suggest that the mass per unit area and force constant are not sensitive to stacking. In addition, Raman-shifts of the extra peaks in Figure 5-5 (e) match very well with the calculated frequencies of the S₂ and S₄ modes, but DFT calculations are incapable of explaining the origin of some modes, such as the S₂ mode in 4 L. Neither 3R-stacked or 2H-stacked 4 L can possess a Raman-active S₂ mode. We thus use the bond polarizability model discussed in the previous section to predict the Raman modes and intensity in MoSe₂ with stacking faults [221]. Results show that stacking faults can induce new features on the interlayer shear modes. For instance, a strong S₂ mode can emerge in both ABAC and ABCB stacking orders in 4 L, *i.e.*, one layer or two deviated from the

positions in the perfect-3R stacking (ABCA). First principles calculations also support these predictions.

Figure 5-6. Structure of 2H and 3R in bilayer MoSe₂ and layer-dependent frequencies of interlayer shear modes in MoSe₂. (a) Schematic of 3R and 2H stacking structures in bilayer. (b)-(e) Layer-dependent frequencies of interlayer shear modes obtained from experiments and first principles calculations. "DFT 3R" (2H) denotes to the frequencies from DFT calculations on 3R (2H) phase, as shown in red (black) in the figures. Exfoliated 2H-stacked (magenta) samples and experimental results from CVD-grown (blue) samples are also included.

Furthermore, we have conducted controlled experiments on Raman spectroscopy from flakes with different thickness to substantiate our analysis. On bilayer MoSe₂, all the CVD-grown bilayers exhibit a strong shear mode (S_1) around 19 cm⁻¹, with linewidth of 1.5 cm⁻¹, similar to 1.0 cm⁻¹ observed in the exfoliated 2H-stacked bilayer (Figure 5-7 (a)). Both 3R and 2H stacking structures have an active S_1 mode, which cannot be used to tell the stacking in 2 L. Nonetheless, in trilayers and even thicker layers, the appearance of interlayer shear modes begins to show strong dependence on stacking sequence. From our theoretical analysis as previously discussed, trilayer MoSe₂ has only observable S_2 mode in 3R stacking and only observable S_1 mode in 2H stacking. Indeed, we observed flakes which show such spectral features from CVD-grown MoSe₂ (Figure 5-7 (b)), which

allows us to attribute the stacking of these flakes to be either 3R (~35%) or 2H (~28%), seen in Figure 5-7 (f).

Figure 5-7. Stacking sequences and interlayer shear modes in few-layer MoSe₂. (a) Raman spectra (frequency < 40 cm^{-1}) of exfoliated 2H-stacked and CVD-grown MoSe₂ bilayers. (b-d) Raman spectra (frequency < 50 cm^{-1}) of CVD-grown 3 L (b), 4 L (c), and 5 L (d) MoSe₂ flakes with different stacking configurations. Experimental data in (a-d) are expressed in dots and solid lines are fitting results based on Lorentzian function. (e-h) Pie charts of 3 L (f), 4 L (g), and 5 L (h), showing the proportion of different stacking sequences in a given thickness. The legend is shown in (e).

We have also observed the coexistence of S₁ and S₂ modes from approximately 37% of all the trilayer samples, which are attributed to the in-plane mixture of 3R and 2H phases within one individual flake (*i.e.*, polytypism). The mixture can be connected either through a gradual transition in lateral direction or with a sharp boundary. In fact, the mixture of 3R and 2H stacking configurations with atomically sharp boundary has been previously observed in our CVD-synthesized 2 L MoSe₂ films (see Figure 5-8). Detailed discussion on STEM imaging of different stacking sequences will be presented in next section. The origin and the mechanism of polytypism in our samples are not completely understood yet. We speculate that polytypism is accessible at high temperature synthesis because previous literatures reported that the formation energy between 2H and 3R phase is very close, with difference of ~1 meV/atom [226-228].

In the following, we are going to address the low-frequency features in 4 L MoSe₂ (Figure 5-7 (c)). As expected from theoretical calculations, the highest frequency mode (S₁) is in dominance from 2H-stacked samples; the lowest frequency peak (*i.e.*, S₃ in 4 L) has the strongest intensity in 3R phase. The appearance of S₂ mode is shown to be related to stacking fault. Both ABAC and ABCB stacking configurations can lead to an observable S₂ peak, and 9.5% of all the measured 4 L samples are categorized to be of ABAC/ABCB stacking. Yet 59.5% of the 4 L CVD-MoSe₂ showed Raman features which cannot be simply attributed to only one type of stacking (blue lines in Figure 5-7 (c)). Therefore, we believe that these flakes consist of mixture. The 59.5% flakes were grouped into “3R-based (~29%)” and “2H-based (~30.5%)” mixture, with major difference in the intensity of S₃ mode. Because S₃ mode is the weakest in both ABCB/ABAC and 2H stacking configurations, extremely low intensity or even invisible signal is expected in the measured spectra [118]. In contrast, S₃ mode exhibits the strongest intensity among the low-frequency modes in 3R stacking. The flakes with phase mixed with 3R stacking may still have appreciable intensity of S₃ mode.

We have to consider more stacking combinations when the thickness increases to reach 5 L (Figure 5-7 (d)). Similar to that in trilayer, 3R (S₄-dominant) and 2H (S₁-dominant) can be assigned unambiguously. A few different combinations of spectral features, however, still remain. For example, S₃-dominant samples constitute 17% of all the 5 L CVD-MoSe₂. Based on our calculations, we believe that ABCBA stacking has an enhanced S₃ mode, with negligible contribution from S₁ peak, and Raman-inactive S₂ and S₄ modes. Similarly, we have detected the ABACA stacking (S₂-dominant) and ABABC/ABCBC stacking with $I(S_1) > I(S_2) > I(S_3) > I(S_4)$ in Figure 5-7 (h).

Figure 5-8. Z-contrast images of the co-existence of 2H and 3R stacking configurations in 2 L MoSe₂. (a) Top: Side-view scheme of 2H & 3R stacked bilayer. Bottom: Sharp boundary of 2H and 3R in CVD-grown bilayer MoSe₂ film grown at low pressure [55].

5.3 STEM Imaging on Various Stacking Sequences

To further study the atomic structure of the CVD-MoSe₂ few-layers, we have conducted ADF Z-contrast imaging on an aberration-corrected STEM, with collaboration from Oak Ridge National Laboratory in USA. In the meantime, we need evidence from STEM to confirm our analysis on the correlation between interlayer shear modes and stacking sequences. Figure 5-9 (a) presents a Z-contrast image of 3R-stacked MoSe₂ bilayer. From the Z-contrast images, the intensity at each atomic site can be correlated to the number of atoms and the atomic number in the imaged atomic columns [180]. With the image intensity, 3R phase in 2 L MoSe₂ can be unambiguously determined, where the overlapping sites (bright spots: Mo+Se₂) are surrounded by Se₂ and Mo columns (dim

spots), as displayed in the intensity profile. By comparison, 2H-stacked 2 L samples maintain the hexagonal shape and every atomic site has equal intensity [226].

Figure 5-9. Z-contrast images of different stacking configurations in the few-layer CVD-MoSe₂. (a) Image of 3R-stacked MoSe₂ bilayer with atomic resolution and side-view scheme. The bottom plot shows the intensity profile of the highlighted columns in (a). Schematic of the imaged region is shown as inset. (b, c) 3R-stacked few-layers: 3 L (b) and 4 L (c). Lower row: Simulated images. (d) Shifted-2H stacking in an 8 L MoSe₂ sample. (e) Shifted-3R stacking in a flake with region of 1-5 L. FFT of the image is shown in the top inset, and simulated image of the shifted-3R stacking with 0.4 Å interlayer shift from the perfect 3R stacking is displayed in the lower inset. (f) Continuous shifting of one layer (or more layers) away from the perfect-3R stacking (right side) in a 5 L flake. Such shift might generate mixtures of different stacking orders within one individual flake. FFT of the image is shown as inset.

Z-contrast images of 3R-stacked 4 L and 3 L MoSe₂ are displayed in Figure 5-9 (c) and (b), which are in consistent with the simulated images by using the perfect 3R phase model. We found that 2H phases are less frequently observed than 3R phases in the

few-layer flakes, in agreement with the statistical analysis in Figure 5-7 (e-h). In addition, it is also an indication that even though 2H stacking is more commonly seen in nature, 3R phase is slightly more preferable than 2H phase during our synthesis.

Besides the perfect 3R and 2H stacking orders, “shifted” 3R (Figure 5-9 (e): a flake with region of 1–5 L) and “shifted” 2H (Figure 5-9 (d): 8 L) stacking configurations have been observed as well. The term “shifted” refers to a slight interlayer in-plane shift of one layer (or more layers) in the few-layer samples from the perfect 3R or 2H stacking positions, but no misorientation is observed within the “shifted” flake, which is confirmed by the FFT of the ADF image. For instance, by comparing the experimental observation with the simulated image, we found that in the edge region of a flake (shown in Figure 5-9 (e)) shifting occurred in the $\langle 100 \rangle$ direction with different amount of shifting distance in each layer. The amount of shift was estimated to be 0.4 Å in the 2nd L, 0.8 Å in the 3rd L, 1.2 Å in the 4th L, and 1.6 Å in the 5th L. Although the 5th layer is ~57% away from the perfect 3R stacking positions (The lattice spacing along $\langle 100 \rangle$ direction in MoSe₂ is 2.8 Å, where the lattice constant a : 3.3 Å [229]), our theoretical calculations show that the relatively small interlayer shifting in 3R stacking (*i.e.*, 0.4 Å between adjacent layer, ~14% of 2.8 Å) would not cause significant changes in the interlayer shear modes on the Raman spectra. These results suggest that the observed Raman spectrum labeled with 3R and 2H may also involve the contribution from “shifted” 3R and 2H stacking orders. Evidence showing the coexistence of “shifted” 3R and 2H stacking (*i.e.*, polytypism) is provided in Figure 5-10.

If the interlayer shifting keeps increasing, the layer may register into another atomic sites and cause the emergence of local stacking faults. New Raman features thus appear.

For instance, if all the atoms in the 4th layer in a 3R-stacked 4 L MoSe₂ flake shift from A sites to B sites, ABCB stacking fault is formed. ABCB stacking leads to the observation of S₂ mode in the Raman spectra, which cannot be detected in 3R-stacked 4 L MoSe₂. Indeed, transition regions between different stacking were observed in our CVD-MoSe₂ sample. Figure 5-9 (f) demonstrates a Z-contrast image of one side of the transition region in a 5 L flake with the well-aligned 3R stacking on the right. The image shows that one layer or more is shifting gradually (either stretching or compressing) without misorientation and rotation, as confirmed by the FFT. The transition regions have a typical width of hundreds of nanometers. Such gradual transition of stacking which generates local stacking faults may be resulted from the out-of-plane fluctuations between layers [230]. This observation confirms our analysis of the new Raman features which can be correlated to a mixture of phases and polytypism.

Figure 5-10. Co-existence of “shifted” 2H and 3R stacking. (a) Low-magnification Z-contrast image of a large area in an 8 L MoSe₂ flake. The “shifted” 2H stacking have brighter intensity than the “shifted” 3R stacking due to the aligned atomic registry. (b-d) Zoom-in image showing the atomic structure of the highlighted regions: “shifted” 2H stacking (b), “shifted” 3R stacking (c) and the transition region (d).

It is significant to point out that because of the projective nature of STEM imaging, identification of the exact stacking sequence in thicker layers is very difficult. For example, 4 L MoSe₂ with ABCA and ABAC stacking configurations can produce very similar images on STEM-ADF measurements (Figure 5-11 (b) and (a)). Nevertheless, ABCA and ABAC can be unambiguously distinguished from their distinct features on low frequency Raman scattering: S₃ mode dominates ABCA stacking, while S₂ mode is the strongest in ABAC stacking. The comparison further establishes that Raman spectroscopy is an important and powerful technique in studying the stacking configuration of layered materials.

Figure 5-11. Simulated Z-contrast images. ABAC (a) and ABCA (b) in 4 L. ABCAB (c, *i.e.*, perfect 3R stacking) and ABCBA (d) in 5 L.

5.4 Summary

We remark that the above analysis is not only applicable to MoSe₂ [133, 134], but also suitable for graphene [149, 220], as demonstrated by experimental results. Puretzky

et al. have reported similar results to ours almost at the same time. Besides what have been discussed in this chapter, they also found that in bilayer MoSe₂, the Raman intensity of interlayer shear mode in 2H phase is approximately 6 times of that in 3R phase [133], which we did not observe in our CVD-grown samples. All the 2 L MoSe₂ samples exhibit similar Raman intensity around 19 cm⁻¹ in our measurements, with small variations. Nevertheless, we both found the frequencies of interlayer shear modes show negligible differences in few-layers. Subsequently, stacking-dependent interlayer vibrational modes were studied in few-layer MoS₂ by two different groups as well [173, 231]. Further experiments by Piretzky *et al.* [130] have revealed that the interlayer breathing modes in MoSe₂ are very sensitive to twisted angles. From their results, the 2H-stacked bilayer MoSe₂ (60° between adjacent layers) do not exhibit interlayer breathing mode, but the peak does appear within a large range of twisting angle (*e.g.* from 34° to 58°). This observation can possibly explain why we cannot observe the interlayer breathing in few-layer MoSe₂. It is supposed to due to twisting angle, rather than the signal/noise ratio.

Studies on stacking-dependent and twisting angle-related phonon modes are very active in recent years, which even extends to heterostructures [168]. Besides Raman spectroscopy, PL spectroscopy has been utilized to explore the luminescence from twisted bilayers [228] and heterostructures [163] with different stacking angles. Stacking (sequences/angles) is not only important to lattice vibration and PL. The metallic 1T-MoS₂ has been used as electrodes, which can help to improve device performance in 2H-MoS₂ by reducing the contact resistance [129]. 3R-MoS₂ crystal has provided another new platform for the study on valley physics [100]. More interesting features and potential applications are still under investigation.

Chapter 6 Gate-Tunable Phonon Properties in Atomically Thin MoS₂

6.1 Introduction

Study on gate-tunable properties in 2D materials has always been an active field, especially in recent years. These studies on electrical control have many aspects, including gate-tunable conductance [232, 233], phase transition [234, 235], photocurrent [236] and *etc.* Research on gate-tunable topological valley transport in graphene [237] and valley polarization in TMDs [98, 238] has appeared in recent years. The successful manipulation of physical properties through electrical control is not only important for fundamental study but also significant to the realization of real-world applications. For example, optical nano-imaging of graphene plasmons controlled by a gate voltage promotes the development of active subwavelength-scale optics, benefiting biosensing applications [239]; The observation of gate-tunable memristive phenomena, which is mediated by grain boundaries in monolayer MoS₂ [240], also enables new functionality that is not observed in previous memristive devices.

Yan *et al.* [241] and Pisana *et al.* [242] first reported the electrical control of phonon properties on graphene in two separate papers. The schematic for the measurement was shown in Figure 6-1 (a). A gate voltage (V_g) can be applied from the back side of the substrate (degenerately doped Si wafer with 300 nm SiO₂). A positive value of $V_g - V_0$ can introduce excess electrons in the sample, with V_g and V_0 referred to gate voltage and charge-neutral Dirac point, respectively; The negative $V_g - V_0$ will induce excess holes. In both cases, Fermi level E_f will be shifted in the graphene sample. Evolutions of G band

and D* band (also referred to 2D band [117]) on Raman spectra in the function of gate voltage were demonstrated in Figure 6-1 (b) and (d).

Figure 6-1. Gate-modulated Raman spectroscopy of graphene. (a) Schematic diagram of the setup in Ref. [242]. A similar back-gate setup is used in Ref. [241] as well, with 488 nm laser as excitation line. (b-d) Raman spectra measured at low temperature and fitting results by using Lorentzian function (curves in the figure) [241]. (b) Evolution of G peak in a monolayer graphene with gate voltage V_g . The inset in the upper left shows the displacement of carbon atoms for G band. (c) Spectrum of G band from a thick (> 10 nm) graphite layer. (d) Evolution of D* band (2D band) of a monolayer graphene with V_g .

Results show that G band is more sensitive to gate voltage, while the reduced impact of electric field effect is observed in 2D band. Doping by either electron or hole in graphene prohibits the formation of phonon-induced electron-hole pairs and thus affecting the self-energy of G phonon. Distortion of the structure with atomic displacements in a G band phonon leads to a shift of the Dirac cone center and a change on Fermi surface. If the adiabatic Born-Oppenheimer approximation applies, the energy cost would not change with doping; and therefore doping is incapable of causing the frequency of G band to shift [242, 243]. While G band is actually hardened with both electron and hole doping. This is due to the breakdown of adiabatic approximation. Electrons do not obey the nuclear motion and remain in their ground state. The Fermi surface is the same as in the

unperturbed case and does not follow the Dirac-cone displacement. Overall, the electron energy increases, leading to a stiffening G mode [242, 243].

The sharper linewidth in higher doping is also observed along with the upshifting frequency [241, 242], which indicates a longer lifetime of G phonon. The change of lifetime is related to the decay channel for G phonon. Landau damping of G phonon is only allowed when $|E_F| < \hbar\omega_G/2$, due to Pauli exclusion principle. The interaction of the G phonon with small wave vector particle-hole pairs has critical dependence on the onset energy for vertical transitions (zero momentum transfer), in which an electron transfers from a π valence band to a π^* conduction band. As higher concentration of doping induces larger change of E_f , the regime in which G band phonons are damped *via* decay into vertical particle-hole pairs is in lower density, causing the narrower G peak. Details can be seen in Figure 6-2 and Ref. [241, 242].

Figure 6-2. Band width and decay channel of G band in graphene [241]. (a) Dependence of G bandwidth on Fermi energy. The inset is Feynman diagram for electron-phonon coupling, which is applicable to the case of the G phonon. (b, c) Decay channel in graphene. (b) Broadened bandwidth of the G phonon because of the decay into particle-hole pairs. (c) The decay into electron-hole pair for G and phonon is forbidden by the Pauli principle, when high electric field induces the shift of E_f .

Later, top-gated graphene by using a solid polymer electrolyte was demonstrated [244]. Compared to the standard SiO₂ back gating, a much higher hole and electron

doping is achieved. The concentration is approximately one order higher. The 2D band shows pronounced change, which was not observed in back gating. Under electron doping, the position (frequency) of 2D band does not change much ($< 1 \text{ cm}^{-1}$) until gate voltage reaches $\sim 3 \text{ V}$ (The corresponding concentration is estimated to be $\sim 2.5 \times 10^{13} \text{ cm}^{-2}$). At higher gate voltage, a pronounced softening of $\sim 20 \text{ cm}^{-1}$ is observed. While for hole doping, 2D band upshifts by more than 10 cm^{-1} , as shown in Figure 6-3 (c).

Figure 6-3. Raman scattering measurements on top-gated graphene with gate modulation [244]. (a) Schematic of the experimental setup. The layer of polymer electrolyte (PEO + LiClO₄) was indicated by the black dotted box between the source and drain electrode contacts, and the graphene samples was shown in blue stripe between the electrodes. Inset on the left shows the optical microscopy image of a monolayer graphene connected between drain and source electrodes. Scale bar is 5 μm . Inset on the right is a schematic illustration on top gating, with ClO₄⁻ and Li⁺ ions, as well as the Debye layers near each electrode. (b, c) Positions (frequencies) of G band (b) and 2D band (c) as a function of doping.

The nature of the 2D band is a second-order, double-resonant Raman scattering [245].

Frequency of the 2D peak can be estimated by computing the energy of the phonons involved in the double-resonant Raman scattering process. Due to the angular dependence

of the electron-phonon coupling matrix elements and the trigonal warping of the π - π^* bands, only phonons oriented along the Γ -K-M direction and with $q > K$ give a considerable contribution to the 2D band. The precise value of q is fixed by the constraint that the energy of an incoming photon has to match a real electronic transition exactly. For the 2D peak measured by a 514.5 nm (2.41 eV) laser, the influence of dynamic effects is expected to be negligible, since the phonons contributing to the 2D peak are far away from the Kohn anomalies [242, 243] at K point. In general, calculations match with experiment qualitatively, showing a down-shift on frequency with higher electron doping. Discussion on the difference between calculations and experiments are shown with details in Ref. [244].

Figure 6-4. Gate-tunable phonon properties in monolayer MoS₂ [138]. (a) Raman spectra measured on 1 L MoS₂ under different top-gate voltages V_{TG} . Experimental data are expressed with open circles. Curves are fitting with Lorentzian function to the spectra. (b, c) Change in frequency (b) and FWHM (c) of A_{1g} and E_{2g}^1 modes as a function of V_{TG} . (d, e) Comparison between experimental results (d) and DFT calculations (e) on the change of frequency under different electron concentration n . (f) Electron-phonon coupling of E_{2g}^1 and A_{1g} modes as a function of n . (g) As electron concentration increases, ratio of electron-phonon coupling [$\lambda_{A_{1g}}(n \neq 0) / \lambda_{A_{1g}}(n = 0)$] is displayed in open squares and phonon linewidth [$\text{FWHM}_{A_{1g}}(n \neq 0) / \text{FWHM}_{A_{1g}}(n = 0)$] is shown in solid squares.

Research on gate-tunable phonon properties has extended to monolayer MoS₂ in 2012 [138]. By using a top-gated MoS₂ transistor, an *in situ* carrier-dependent Raman

study was carried out. Raman spectra were taken under different gate voltage V_{TG} , with focus on the fingerprint intralayer vibrational modes, A_{1g} and E_{2g}^1 , as shown in Figure 6-4 (a). The A_{1g} mode shows stronger dependence on V_{TG} compared to E_{2g}^1 mode, both on Raman shift and the peak width.

To make a detailed analysis, Chakraborty *et al.* [138] estimated the doping concentration by using $n_e = C_{TG}(V_{TG} - V_{TH})$. C_{TG} refers to the top-gate capacitance, and the top-gated material is solid polymer electrolyte, a mixture of polyethylene oxide (PEO) and LiClO_4 in a weight ratio of 8:1. The value of C_{TG} is determined to be $1.5 \mu\text{F}/\text{cm}^2$ in a dual gate measurement without considering quantum capacitance [246]. V_{TG} and V_{TH} are the applied gate voltage and the threshold voltage of the transistor, respectively. The maximum electron doping they can reach is $\sim 1.8 \times 10^{13} \text{ cm}^{-2}$ when $V_{TG} = 2.0 \text{ V}$.

Under the maximum electron concentration, A_{1g} mode is down-shifted by 4 cm^{-1} . By comparison, the shift is merely $\sim 0.6 \text{ cm}^{-1}$ for E_{2g}^1 mode. Raman shift towards the lower frequency is because of the occupation of antibonding states in the conduction band of MoS_2 , resulted from electron doping. In this case, the Mo-S bonds are weaker, thus frequency softened. In the meantime, the width of A_{1g} peak increases significantly by $\sim 6 \text{ cm}^{-1}$ under the maximum electron concentration, whereas the full width at half maximum (FWHM) of E_{2g}^1 mode hardly shows any change. There are two factors which can alter the linewidth of a phonon: interaction between electron and phonon (Γ^{EPC}), and anharmonic effects (Γ^{an}) [247, 248]. That is, $\Gamma = \Gamma^{\text{EPC}} + \Gamma^{\text{an}}$. The increased linewidth in A_{1g} mode is resulted from the strengthening electron-phonon coupling with electron doping. Calculations also indicate that A_{1g} mode couples with electrons much more strongly than the E_{2g}^1 mode, shown in Figure 6-4 (f). This explains why E_{2g}^1 mode is

insensitive to electron doping.

6.2 Device Fabrication and Setup

We first prepared the mono- and few-layer MoS₂ flakes on Si wafer capped with 285 nm SiO₂ by mechanical exfoliation. The general procedure of device fabrication can be summarized as: spin-coating, electron beam lithography (EBL) exposure, development, metal deposition, and lift-off. Two kinds of resists will be spin-coated before EBL. Firstly, copolymer MMA (MMA (8.5) MMA EL9, Micro Chem; concentration: 9% solid ethyl lactate, molecular mass) was spin-coated on the sample/substrate at 4000 rpm for 60 seconds and then baked on a hot plate at 180 °C for 5 minutes. Subsequently, PMMA (950 PMMA A4, Micro Chem; concentration: 4% solid in anisole, molecular mass) is spin-coated also with spinning rate of 4000 rpm for 60 seconds, followed by baking at 180 °C for 8 minutes. The thickness of MMA and PMMA is ~300 nm and ~200 nm, respectively.

Next, we designed the marker patterns, either Arabic number or electrode contact, according to requirements. After EBL, the substrate was developed for 1 minute, while the developer solution is a mixture of IPA and methyl isobutyl ketone (MIBK) with a ratio of 3:1. After being rinsed by IPA and blown dry by a nitrogen gun, the substrate was placed into the thermal evaporator. 30 nm Ti and 80 nm Au films were chosen as contact materials. Lift-off was conducted after deposition, in which the whole substrate was immersed into ~50 °C acetone for about 30 minutes. Take out the substrate and blow dry it with a nitrogen gun. The device with back-gate is ready, as shown in Figure 6-5. It is

important to note that not every sample has two contacts on the surface. Gate-tunable Raman measurements only need one contact electrode, which will be grounded during measurements. However, the correct interpretation of transport properties can only be done on the *device d* among all in Figure 6-5.

Figure 6-5. Optical images of MoS₂ devices. (a, b) As-exfoliated 2 L and 3 L MoS₂ before (a) and after (b) device fabrication. (c) A large MoS₂ flake containing 1-3 L regions with contact electrodes. (d) An individually 2 L flake with uniform thickness. Side gate is used in applying the top-gate voltage, similar to that in a previous paper [234].

Previous literature has already demonstrated that top-gate is more effective than back-gate [244], such as on the concentration of doped electrons/holes, which is resulted from the higher capacitance of top-gate materials. The 2D band of graphene under polymer electrolyte (PEO + LiClO₄) top-gating shows appreciable Raman shift as the concentration of doped electrons reached the threshold, $\sim 2.5 \times 10^{13} \text{ cm}^{-2}$. The peak can red-shift by $\sim 20 \text{ cm}^{-1}$ when the concentration is $\sim 3.5 \times 10^{13} \text{ cm}^{-2}$ [244]. In contrast, a back-gated graphene transistor on Si substrate with 300 nm oxide layer is very difficult to

achieve electron concentration above $1.0 \times 10^{13} \text{ cm}^{-2}$ [241, 242]. Measurements of charge transport properties on 1-3 L MoS₂ have also confirmed the effective gating by using top-gate [249]. The comparison is shown with top-gate material being PS-PMMA-PS + EMIM-TFSI, and back-gate material being 300 nm SiO₂/Si. The ratio $\Delta V_{\text{bg}}/\Delta V_{\text{tg}}$ is taken as an indicator, where ΔV_{bg} and ΔV_{tg} denote to the difference in back-gate and top-gate voltage to reach the same change in conductivity. The ratio $\Delta V_{\text{bg}}/\Delta V_{\text{tg}}$ is obtained to be ~86 for 1 L, ~64 for 2 L, and ~43 for 3 L MoS₂ device [249].

Figure 6-6. Preparation of polymer ionic gel top-gated MoS₂ device for gate-tunable Raman scattering measurements. (a) The optical image of device in Figure 6-5 (d) after being drop-casted gel. (b, c) Photographs of the setup inside (b) and outside (c) the cryostat. The substrate was attached on a home-made chip carrier with silver paste in (b).

We thus chose to use ionic gel top-gating in the gate-tunable Raman study. The gated material is PS-PEO-PS + EMIM-TFSI, with acetonitrile as solution and EMIM-TFSI is the effective elements which works for gating. PS-PEO-PS is believed to be useful for reducing the leakage current. The preparation of ionic gel is straightforward. Mix the

three components, EMIM-TFSI, acetonitrile, and PS-PEO-PS with ratio of 33%, 66.5%, and 0.5% in a weight percentage. The ionic gel is placed in a glove box for better storage. Before top-gating measurements, the gel was drop-casted on the MoS₂ device by a micropipette. The top-gate device later will be put in a cryostat, which will be pumped down by a turbo pump. We usually waited ~12 hours or even longer before measurements, in order to make sure the moisture is fully removed.

The schematic of setup on Raman spectroscopy is depicted in Figure 6-7. When we apply a positive potential ($V_g > 0$) to the side gate, the negative TFSI (-) ions will accumulate around the side gate pad (electrode), forming a thin layer. This layer of charge is called as the Debye layer. Meanwhile, the EMIM (+) ions become dominant in the Debye layer formed at the surface on the MoS₂ sample. The Debye layer works like a parallel-plate capacitor. The thickness of Debye layer in polymer electrolyte gating is reported to be 1-5 nm [250]. It is assumed to be 2 nm in previous experiments on Raman spectroscopy of top-gated graphene [244].

Figure 6-7. Schematic of the measurement setup on Raman spectroscopy.

Basic electrical characterization has been conducted, with one of the important purposes of obtaining the threshold voltage V_{th} , which is crucial in calculating the concentration of doping electrons. Figure 6-8 has shown an example of a 2 L MoS₂ device, with corresponding optical image in Figure 6-5 (d). Under back-gating of SiO₂, V_{tg} is shown to be -27.7 V when sweeping from negative to positive, and -20.7 V when the sweeping direction is reverse. We take the average value, -24.2 V, as V_{th} . The gate capacitance of 285 nm SiO₂ is $\sim 1.2 \times 10^{-8}$ F/cm². With $n_e = C_g(V_g - V_{th})$, we can roughly estimate the largest concentration of doped electrons when using back-gate. The largest positive voltage we can apply on our setup is 40 V, and $\sim 5.0 \times 10^{12}$ cm⁻² is the highest doping level we can achieve with back-gate voltage.

Figure 6-8. Comparison of a 2 L MoS₂ device with back-gating and top-gating. (a, b) I_{ds} vs V_g curves when $V_{ds} = 10$ mV under back-gated voltage (a) and top-gated voltage (b). (c, d) Output curves of the device under back-gated voltage (c) and top-gated voltage (d). The linear curves are resulted from quasi-ohmic contact within the sample. Optical image of the corresponding device is shown in Figure 6-5 (d).

Similar calculations can be performed on top-gate device as well. The capacitance of EMIM-TFSI gel has been measured to be 1.07×10^{-5} F/cm² at 0.1 Hz by Yu *et. al.* [251],

which is almost 1000 times of that in SiO₂. However, quantum capacitance cannot be simply neglected, which is different from back-gate. *If screening effect is ignored*, gate capacitance C_g is given by: $C_g = (\frac{1}{C_q} + \frac{1}{C_x})^{-1}$, with C_q and C_x referring to the quantum capacitance of the sample and the capacitance of gated materials (*i.e.*, SiO₂ for back-gate and ionic gel for top-gate), respectively. When $C_q \gg C_x$, $C_g \approx C_x$, which is the case in back-gating with 285 nm SiO₂. For top-gate, it has to be divided into two condition: (1) When E_f is within the band gap and the sample is low-doped, $C_q \ll C_x$, thus $C_g \approx C_q$ [249]; (2) When the sample is highly doped and E_f is within the conduction band, C_q increases a lot [252], and both C_q and C_x contribute to C_g . By using a simple relation $C_g^{top} \Delta V_{tg} = C_g^{back} \Delta V_{bg}$, the C_q of 1 L, 2 L, and 3 L MoS₂ is roughly estimated to be 1.0×10^{-6} F/cm², 0.8×10^{-6} F/cm², and 0.5×10^{-6} F/cm², respectively in a previous paper [249]. While the calculated C_q of 1 L MoS₂ is reported to be $\sim 4.0 \times 10^{-6}$ F/cm² by another group [252].

On the other hand, *if the screening effect is considered and neglected the contribution from quantum capacitance*, the capacitance of LiClO₄ + PEO is determined to be 1.5×10^{-6} F/cm² in a dual gate measurement [246]. Another approach is to take the Debye screening layer as a parallel-plate capacitor, and the capacitance of LiClO₄ + PEO is obtained to be 2.2×10^{-6} F/cm² [244]. So far, I have not seen any papers carefully considered both *screening effect* and *quantum capacitance*, partially due to the complexity. Neither did any report on the capacitance of EMIM-TFSI by seriously considering the screening effect.

If we take 0.8×10^{-6} F/cm² as the quantum capacitance C_q of *bilayer* MoS₂ [249] into calculation, the obtained maximum doping concentration is merely $\sim 7.7 \times 10^{12}$ cm⁻², only a bit higher than that with SiO₂. Experimental results, which I will introduce later when

discussing about gate-tunable PL, strongly oppose this value, because the gating effect in our measurements is far better than that has been reported with SiO₂ back-gating [83, 253, 254]. Similarly, when we take 1.0×10^{-6} F/cm² as C_q of *monolayer* MoS₂ [249] into calculations, the maximum doping is approximately 9.0×10^{12} cm⁻² only.

If we consider another value, 4.0×10^{-6} F/cm² (C_q of *monolayer* MoS₂ from Ref. [252]), the maximum doping concentration is calculated to be $\sim 2.3 \times 10^{13}$ cm⁻², similar to what have been previously achieved in monolayer MoS₂ [138]. While it is still important to note that $\sim 7.7 \times 10^{12}$ cm⁻² in 2 L and $\sim 9.0 \times 10^{12}$ cm⁻² in 1 L are indeed underestimated, but $\sim 2.3 \times 10^{13}$ cm⁻² in 1 L is possibly overrated.

In addition, I would like to point out two important points. Firstly, the positive voltage used in top-gated measurements is usually no more than 2.0 V. On one hand, top-gating is more effective, and high voltage such as 100 V is not that necessary. On the other hand, high voltage such as 2.5 V can lead to a large leakage current in the top-gate setup, which we have observed in our experiments. Secondly, unlike that in graphene where doping of electron and hole are both possible. MoS₂ is an intrinsic n-type semiconductor, with E_f very close to the CBM. And the gap of MoS₂ is not small; The direct optical gap is ~ 1.9 eV and quasi-particle gap is no smaller than 2 eV [255]. Therefore, it is impossible to achieve hole-doping in our experiments.

6.3 Gate-Tunable PL in Bilayer and Trilayer

As we have discussed in the previous section that the maximum electron doping level might be either underestimated or overestimated, but at least we have a range now, from

$7.7 \times 10^{12} \text{ cm}^{-2}$ to $2.3 \times 10^{13} \text{ cm}^{-2}$. The reason for which $7.7 \times 10^{12} \text{ cm}^{-2}$ is an underestimation comes from the experimental data on gate-tunable PL measurements in bilayer MoS₂. Three papers have reported on the gate-tunable PL from 2 L MoS₂, at both room temperature and low temperature [83, 253, 254]. All of them failed in mediating the PL from 2 L MoS₂ with SiO₂ as back-gated material before decreasing the temperature. The maximum change in the carrier density due to V_g is reported to be $n_e = C_g \Delta V_g \sim 7.0 \times 10^{12} \text{ cm}^{-2}$, with $\Delta V_g = 50 \text{ V} - (-50 \text{ V}) = 100 \text{ V}$. This change in the carrier density translates into a shift of the Fermi energy by $\pi \hbar^2 n / m_e \sim 45 \text{ meV}$, where $m_e \sim 0.4 m_0$ is the effective electron mass in 2 L MoS₂ [254, 255]. The failure in mediating emission (of A exciton) is because most back-gated experiments are only tuning E_f within the Λ valley of CBM (lowest point in CB for 2 L, 3 L, ...), but the dominant direct-gap emission of A/B exciton comes from the K point, which is hardly affected. The indication I obtained is that: If we can succeed in tuning the PL within a small range of V_{tg} (e.g., from -0.5 V to + 0.5 V), the change of carrier density Δn_e should be no smaller than $7.0 \times 10^{12} \text{ cm}^{-2}$. The maximum doped electron at $V_{tg} = 1.5 \text{ V}$ or 2 V can be calculated accordingly. At least the range we estimated (from $7.7 \times 10^{12} \text{ cm}^{-2}$ to $2.3 \times 10^{13} \text{ cm}^{-2}$) can be narrower.

Still, it is worth mentioning that by using dual-gate (top-gate: HfO₂/graphene; back-gate: SiO₂), Chu *et al.* have recently achieved the tunable band gap in bilayer MoS₂ [256], which is beyond the discussion of this thesis. Figure 6-9 shows the room temperature PL spectra of 2 L and 3 L MoS₂ before being applied a gate voltage. Except that the energies of A and B excitons are slightly lower than previous reports [190, 194], the PL features are expected with splitting energy of $\sim 150 \text{ meV}$ between the two excitons. Note that the negative charged exciton A⁻ is not supposed to appear in 2 L and 3 L at room

temperature due to thermal dissociation, which is related to the band structure [253].

Figure 6-9. PL spectra of few-layer MoS₂ with Lorentzian fitting, including bilayer (a) and trilayer (b). 532 nm laser is used for excitation, and the lines around ~2.3 eV are Raman peaks of MoS₂. The PL spectra were measured with ionic gel on the MoS₂ samples. The samples were put into a cryostat and pumped for ~12 hours before measurements.

Figure 6-10 shows the Gate-tunable PL spectra of bilayer MoS₂. From 0 V to 1.5 V, the change in PL intensity is negligible, while a slight red-shift is observed on the emission, including both A and B excitons, as well as luminescence from the indirect-gap. As shown in Figure 6-10 (b), the energy of A exciton is red-shifted by approximately 30 meV (The more accurate value is obtained after fitting.) with V_{tg} increasing from 0 to 1.5 V. This is resulted from the many-body effect. On one hand, Pauli exclusion principles will cause the observed PL peak blue-shifted. On the other hand, the doped electron induced by a positive gate voltage narrows the band gap due to renormalization. Our observation on PL spectra is in consistent with previous results [194, 253]. For the negative V_{tg} , the increased PL intensity is detected, which is expected. As V_{tg} changes from 0 V to -1.5 V, the amount of electrons in the sample becomes less and less, causing E_f moving down towards the neutral line. Note that MoS₂ is n-type intrinsically, with E_f close to the CB. Previous papers [257, 258] have demonstrated that for an n-type

semiconductor, p-type dopants can increase PL intensity, but n-type dopants would decrease the PL intensity. This effect is very dramatic for the neutral exciton.

Figure 6-10. Gate-tunable PL spectra of bilayer MoS₂. (a) PL spectra of 2 L MoS₂ with V_{tg} ranging from 0 V to +1.75 V. There is almost no change in intensity, but a slight red-shift is observed. The spectrum with +1.75 V resembles that with +1.5 V, indicating saturation. (b) Zoom-in PL spectra from 1.78 to 1.92 eV, which shows a red-shift of ~30 meV between $V_{tg} = 0$ V and $V_{tg} = +1.5$ V. (c) PL spectra of 2 L MoS₂ with V_{tg} ranging from 0 V to -1.5. The increased intensity is observed.

After careful fitting by using Lorentzian function, we have extracted the peak positions of A exciton, B exciton, and emission from the indirect gap (I peak). Results were plotted in Figure 6-11 (c). As expected, the shift of I peak is more than that of A and B excitons, because I peak originates from the Λ point in CB, which is more affected by the doped electrons than K point. We also plotted the intensity ratio of $I/(A+B)$ in Figure 6-11 (d), which can reflect the carrier distribution in k-space qualitatively, but not quantitatively. As V_{tg} changes from positive to negative, the ratio increases in general.

This is because the electron concentration is reduced in the sample, and the lowest point in the CB is more easily affected. That is, the weight of electron in Λ point increases dramatically, compared to that in the K point of CB. However, as the probability of radiative recombination from an indirect gap is *far smaller* than that of the direct-gap recombination, the intensity ratio is thus not proportional to the weight distribution. Experimental data plotted in Figure 6-11 (d) is just for the rough estimation.

Figure 6-11. Analysis on gate-tunable PL of bilayer MoS₂ after all the spectra are fitted by using Lorentzian function. (a, b, c) PL spectra with Lorentzian fitting under gate voltage of +1.5 V (a), 0.0 V (b), and -1.5 V (c), respectively. (d) Extracted peak positions of A, B, and I, as a function of V_{tg} . (e) The Intensity ratio of $I/(A+B)$ as a function of V_{tg} .

As I have mentioned in the very beginning of this section that a change of electron concentration by $\sim 7.0 \times 10^{12} \text{ cm}^{-2}$ cannot introduce any change on PL spectrum of 2 L MoS₂ at room temperature [254], now that our gate-tunable PL measurements have achieved the change even with the smallest step, 0.5 V. This suggests that the effective C_g in our setup is at least $2.24 \times 10^{-6} \text{ F/cm}^2$, according to the relation $\Delta n_e = C_g \Delta V_g$.

The V_{th} in our top-gated devices have ranged from 0 V to 0.5 V. If we take the average, $V_{th} = 0.25$ V as a general case, the maximum electron doping level when $V_{tg} = 1.5$ V is calculated to be $\sim 1.75 \times 10^{13} \text{ cm}^{-2}$. To this step, we have obtained a range in terms of maximum concentration of doped electron in 2 L MoS₂, from $1.75 \times 10^{13} \text{ cm}^{-2}$ to $2.3 \times 10^{13} \text{ cm}^{-2}$, which is comparable to that in top-gated 1 L MoS₂ ($1.8 \times 10^{13} \text{ cm}^{-2}$) [138].

Similar to that in 2 L MoS₂, we have performed the gate-tunable PL measurements on 3 L MoS₂, also at room temperature. We observed the dependence on gate voltage of PL spectra, although the V_{tg} -dependent change is not as pronounced as that in bilayer. This is probably related to the larger quantum capacitance in trilayer, thus causing the effective C_g to be smaller. Figure 6-12 shows the gate-tunable PL spectra with V_{tg} ranging from 0 V to 1.5 V. A slight red-shift of ~ 20 meV is observed as V_{tg} increased to 1.5 V.

Figure 6-12. Gate-tunable PL spectra of 3 L MoS₂. (a) PL spectra of 3 L MoS₂ with V_{tg} ranging from 0 V to 1.5 V. (b) Zoom-in PL spectra from 1.79 to 1.90 eV, which shows a red-shift of ~ 20 meV between $V_{tg} = 0$ V and $V_{tg} = 1.5$ V.

All PL spectra presented in this section were measured on a Jobin-Yvon HR800 Raman system, excited by a 532 nm laser. The signal was collected *via* a long working distance (10.6 mm) 50 $\times$ objective and dispersed by a 300 g/mm grating before reaching the liquid nitrogen cooled charge-coupled detector.

6.4 Raman Spectra Excited by Non-Resonant Lasers

The gate-tunable PL measurements have already confirmed the effective gating effect. However, this does not necessarily guarantee the modulation of phonon properties because PL is more sensitive to electron concentration compared to Raman peaks, which has been recently demonstrated [259]. In this newly published paper, Li *et al.* cannot observe the obvious change of A_{1g} mode in 1 L MoS₂ when carrier density varies from $\sim 0.5 \times 10^{13} \text{ cm}^{-2}$ to $\sim 3 \times 10^{13} \text{ cm}^{-2}$ (Shift occurs only when concentration is below $\sim 0.5 \times 10^{13} \text{ cm}^{-2}$), while the change of PL is always robust [259]. By comparison, the shift of A_{1g} mode from experiment in Ref. [138] is $\sim 2 \text{ cm}^{-1}$ and $\sim 4 \text{ cm}^{-1}$ when electron concentration is $\sim 0.6 \times 10^{13} \text{ cm}^{-2}$ and $\sim 1.8 \times 10^{13} \text{ cm}^{-2}$, respectively. There are two possibilities: (1) Inaccuracy in estimating the concentration of doped electrons. (2) There might be extra unknown modification on the 1 L MoS₂ in the heterostructure sample (*e.g.* MoS₂/graphene) reported in Ref. [259].

Our gate-tunable Raman scattering measurements were conducted on Horiba-JY T64000 Raman spectrometer. The objective is also the long working distance 50 $\times$ objective, but the Raman signal was dispersed by a 1800 g/mm grating (instead of 300 g/mm used in PL) before reaching the detector. Both 514 nm laser (2.41 eV) and 532 nm laser (2.33 eV) have been used with resolution of $\sim 0.6 \text{ cm}^{-1}$ and $\sim 0.7 \text{ cm}^{-1}$, respectively. As expected, no observable difference is seen between the two lasers. Figure 6-13 shows the experimental results of gate-tunable Raman spectra of 1-3 L MoS₂. From the raw data, we can see that the signal/noise ratio is very poor for 1 L. Note that the similar weak

signal is also observed in a previous top-gated Raman study of monolayer MoS₂ [259]. The broadened A_{1g} mode with V_{tg} changing from -1.5 V to 2.0 V is very clear for 1 L and 2 L. Yet further conclusion can only be drawn after careful fitting by using Lorentzian function.

Figure 6-13. Raman spectra of MoS₂ as a function of different V_{tg} , with thickness of samples ranging from monolayer (a), bilayer (b), to trilayer (c). The excitation line is 532 nm laser. All spectra were measured on the same day (same setup) and under the same laser power. The acquisition times in (a), (b), and (c) are 300 s, 200 s, and 180 s, respectively. The displayed data are raw data without normalization. Some spectra are offset vertically for clarity.

From Figure 6-14, we can see that the E_{2g}^1 mode in 1-3 L MoS₂ is insensitive to gate voltage, both in Raman shift and in width, which matches with previous reports [138, 259]. In contrast, A_{1g} mode is softened and broadened with V_{tg} changes from -1.5 V to 2.0 V in mono- and bi-layer. There is negligible change of A_{1g} mode in trilayer MoS₂ due to less effective gating effect, consistent with the observation on PL spectra. We have measured 1 monolayer, 8 bilayers, and 4 trilayers. Only on one trilayer sample, we can see a slight red-shift of ~ 1 cm⁻¹ for A_{1g} mode by using a non-resonant laser. That is to say, Figure 6-14 (e, f) represents the general case in trilayer.

Figure 6-14. Raman shift and FWHM as a function of V_{tg} (data extracted from Figure 6-13 after fitting). (a, b) Raman shift (a) and FWHM (b) as a function of V_{tg} in 1 L MoS₂. (c, d) Raman shift (c) and FWHM (d) as a function of V_{tg} in 2 L MoS₂. (e, f) Raman shift (e) and FWHM (f) as a function of V_{tg} in 3 L MoS₂. The peak positions were aligned according to the Si peak at 520.70 cm⁻¹. Blue dash lines indicate the frequency and width measured before the first attempt on the application of gate voltage.

From 1 L MoS₂, we can see that there is “saturation” on 2.0 V, which is probably due to the large leakage induced by an increasing positive V_{tg} . Thus, less effective gating effect is observed on 2.0 V than on 1.5 V. Note that the “saturation V_{tg} ” varies from sample to sample, ranging from 1.75 V to 2.75 V, but it is safe to claim that 1.5 V is still within the range of effective gating from our repeated experiments. Compared with the initial frequency (blue lines in Figure 6-14), the largest red-shift of A_{1g} mode in 1 L and 2 L are both ~ 2 cm⁻¹, but larger shift is actually expected in thinner layers due to more effective gating. While the ~ 2 cm⁻¹ in 1 L MoS₂ is comparable to that in Ref. [259], but it is about $\frac{1}{2}$ smaller than that in Ref. [138]. However, in terms of FWHM, our observation is similar to the results in Ref. [138].

Since we have only measured one monolayer sample, it is hard to draw a conclusion based on the exact value of red-shift yet. Nonetheless, the trend is meaningful: As V_{tg}

changes from negative to positive (crossing the zero point), A_{1g} mode is red-shifted and broadened in mono- and bi-layers. This is resulted from the increasing electron-phonon coupling (wider linewidth) and weakened Mo-S bond (smaller force constant and thus peak down-shifted), which has been discussed in Ref. [138] and introduced in section 6.1. However, Ref. [138] did not measure the negative V_{tg} region. Our results in Figure 6-14 show a stiffened A_{1g} mode in 1 L and 2 L, as V_{tg} changes from 0 V to -1.5 V. Meanwhile, some other bilayer samples exhibit no variation on Raman shift in the negative V_{tg} region (*e.g.* Figure 6-19). Sample variation might be related to the sufficient/insufficient electron depletion or the off-state current. Bilayer MoS₂ samples which have no change in the negative V_{tg} region usually exhibit low off-state current. In general, the frequency of A_{1g} mode up-shifts when the electron concentration decreases. As less electrons occupy the unstable antibonding states in the conduction band, the Mo-S is supposed to be stronger, leading to a larger force constant and an up-shifted A_{1g} mode. The narrower peak width as V_{tg} drives towards negative (shown in Figure 6-14 (d)) also indicates less electron-phonon interaction as a result of electron depletion.

The observation on splitting of A_{1g} mode in a few 2 L MoS₂ samples with a non-resonant laser is unexpected, as shown in Figure 6-15. Splitting of A_{1g} mode in few-layer WS₂ has been reported recently [260]. The counterpart of A_{1g} mode in monolayer is A_1' mode. There are N zone-center phonons evolving from the A_1' monolayer mode in N -layer WS₂. As for bulk WS₂, the A_1' monolayer mode evolves to be the in-phase and out-of-phase A_{1g}/B_{1u} pair, called as Davydov pair. The conjugate pairs of A_{1g} and B_{1u} modes have very similar frequency, and the degeneracy is related to the weak vdW interlayer interaction [106, 109]. A_{1g} and B_{1u} are supposed to be the

Raman-active and IR-active modes, respectively. The counterpart of B_{1u} mode has A_{2u} symmetry in bilayer, as shown in Figure 6-15 (b). Staiger *et al.* reported that in few-layer WS_2 , all of the N components evolved from the monolayer out-of-plane A_1' mode can be observed irrespective of their Raman activity, when the incident photon has energy close to that of A exciton [260]. Similarly, A_{1g}/B_{1u} pair is observed in MoS_2 by using 633 nm as excitation [261], but not as pronounced as that in WS_2 [260] and $MoSe_2$ [186].

Figure 6-15. Splitting of A_{1g} mode in 2 L MoS_2 . (a) Raman spectrum of 2 L MoS_2 in the range of 365-420 cm^{-1} when $V_{lg} = -1.5$ V. Experimental data is shown in black dots and lines represent fitting results by using Lorentzian profile. (b) Atomic displacement of A_{2u} mode and A_{1g} mode in 2 L MoS_2 .

This is the first time that the Davydov splitting of A_{1g} mode is observed in few-layer MoS_2 with a non-resonant laser. The observation relies on a negative gate voltage, which indicates that electron depletion is capable of relaxing Raman selection rule (A_{2u} mode in bilayer is inactive). Staiger *et al.* attributed the strong splitting of A_1' mode in WS_2 to exciton-phonon coupling. Under the specific case of resonant (to A exciton) Raman process, the N layers in few-layer WS_2 are to be treated approximately as N individual monolayers. Thus there are N Raman-allowed modes to be expected in the region of the monolayer A_1' Raman mode, and these modes are split in frequency [260].

Apply the explanation in WS₂ on our gated 2 L MoS₂, the observation of splitting indicates that the exciton-phonon coupling increases when $V_{tg} = -1.5$ V (Note that the enhanced PL intensity from A exciton can be seen in Figure 6-10 (c) when $V_{tg} < 0$ V.), and the bilayer can thus be treated as two quasi-independent layers under effective electron depletion. It is well-known that electron doping due to gating effect can cause uneven distribution of carriers in bilayer, and the two layers are not in parity. In this case, the major contribution of CBM and VBM are from two different layers [99, 256, 262], which renders the two layers “separated” in band structure but they are also very related to each other as a unity. Electron depletion, an opposite effect to electron doping, leads to the detection of A_{2u} mode as shown in our experiments, which is a new observation.

6.5 Resonance and Dependence on Excitation Lasers

Conventionally, most resonance Raman studies on MoS₂ were done by using a 633 nm laser [115, 261, 263, 264]. Therefore, this section will be started by discussing about gate-tunable Raman spectra excited by a 633 nm laser (1.96 eV), as shown in Figure 6-16.

There is a dramatic change in the Raman intensity of E_{2g}^1 and A_{1g} modes, which was not observed when using 514 nm and 532 nm lasers. Considering that the intensity of Si peak (~ 520 cm⁻¹) does not show appreciable variation, the increasing intensity from MoS₂ with V_{tg} changing from 2.0 V to -2.0 (-2.5) V cannot be attributed to gate-induced change on the ionic gel. The dependence of Raman intensity on V_{tg} (with 633 nm laser) is a solid phenomenon as it is observed in all the 8 bilayers and 4 trilayers. We have attempted to do corresponding measurements on monolayer by the 633 nm laser, but we

failed due to the extremely weak signal even when $V_{tg} = -2.5\text{V}$. Previous results on wavelength-dependent Raman spectra have already confirmed that the intensity from 1 L MoS₂ decreases rapidly as the excitation energy red-shifts [140, 261]. Plus, the Raman signals measured by a 532 nm laser are already weak (Figure 6-13 (a)).

Figure 6-16. Gate-tunable resonant Raman spectra excited by a 633 nm laser. (a) Gate-tunable Raman spectra measured on 2 L MoS₂ with V_{tg} changing from 2.0 V to -2.0 V. (b) Gate-tunable Raman spectra measured on 3 L MoS₂ with V_{tg} changing from 2.0 V to -2.5 V. All the spectra were measured with the same acquisition time and under the same laser power. Spectra are upshifted for clarity.

Also note that the 3 L MoS₂ is supposed to exhibit stronger Raman intensity than the 2 L MoS₂, but it is actually the opposite in Figure 6-16. Since the thickness of ionic gel which was drop-casted on the substrate is related to the Raman intensity, locally thicker region will block more signal. Currently, I have not figured out an effective way to control and decrease the thickness, other than dropping smaller amount of gel. However, I found that experiments done by using the freshly prepared gel in general exhibit stronger intensity than those with gel stored in the glove box for months. Except intensity, there is no observable difference between new and old gels. Probably longer storage time will cause a smaller wetting angle between the gel and the substrate, which prohibits the spread of the gel and induces poor Raman signal. Based on the aforementioned factor, it

is unfair to compare the experiments done from different samples even with the same thickness.

Although the observation on changing intensity is valid on more than 10 samples, it is still very interesting to check whether this effect is reversible. If it is not, the change in intensity might occur due to some gate-induced modification on the sample (such as damage), rather than a genuine “*tunable*” effect. Thus, several sweeps (either from “+” to “-” or from “-” to “+”, during which the maximum change of carrier density is achieved) have been conducted on a single bilayer (or trilayer) sample. Spectra presented in Figure 6-16 are from the 1st sweep. The 2nd sweep is from -2.0 V (-2.5 V) to 2.0 V, and the 3rd sweep is from 2.0 V to -2.0 V (-2.5 V), same as that in the 1st sweep. With all the measured Raman spectra, I have done a careful Lorentzian fitting based on previous literatures [115, 261, 263, 264], as shown in Figure 6-17.

Figure 6-17. Raman spectrum of 3 L MoS₂ excited by a 633 nm laser when $V_{lg} = -1.5$ V. Dots are experimental results and lines are from Lorentzian fitting.

Peaks around ~ 408 cm⁻¹ are resulted from the Davydov splitting of A_{1g} mode, and the split mode at lower frequency has different symmetries in odd or even layer numbers.

For instance, it is A_{2u} in bilayer, and A_1 in trilayer. We take the annotation from bulk, B_{1u} , during assignment for convenience. Similarly, E_{2g}^1 and E_{1u}^2 are another Davydov pairs. Sekine *et al.* have assigned the peak *a* in Figure 6-17 as the E_{1u}^2 mode [265]. However, a few recent reports [261, 264, 266] have kept a conservative attitude towards this peak, because from reflection spectroscopy, E_{1u}^2 mode is supposed to have higher frequency than E_{2g}^1 mode [107]. The peak at $\sim 420 \text{ cm}^{-1}$ (labelled as peak *b*) appears when the excitation laser energy is just above the 1s level of the A exciton and shows a strong dispersion with incident laser photon energies. It occurs due to a two-phonon Raman process, involving the successive emission of a dispersionless TO phonon and a dispersive quasi-acoustic phonon [115, 264]. The peaks around 456 cm^{-1} and 468 cm^{-1} are 2LA (M) and A_{2u} modes, respectively. Literature shows that the frequencies of 2LA(M) and A_{2u} peaks increase in thicker layers. On the other hand, the relative intensity of the 2LA(M) with respect to the A_{2u} peak decreases with increasing thickness [261]. This resembles the intensity ratio dependence on the size of the MoS₂ nanoparticles [115].

We have put our focus on E_{2g}^1 and A_{1g} modes. Detailed analysis on frequency, width, and intensity (referred to height or counts, not integrated intensity) is given based on the extracted data after Lorentzian fitting. The frequency discussed in the following is aligned according to the Si peak at 520.70 cm^{-1} . The intensity is normalized according to the intensity of Si peak as well, in order to minimize the influence of other factors which affect the measured Raman intensity.

Figure 6-18. Detailed analysis on intensity, FWHM, and Raman shift of E'_{2g} mode. Black, red, and blue lines are from the 1st, 2nd, and 3rd sweep, respectively. (a-c) Intensity of E'_{2g} mode as a function of V_{tg} from the 1st (a), 2nd (b), and 3rd (c) sweep. (d-f) FWHM of E'_{2g} mode as a function of V_{tg} from the 1st (d), 2nd (e), and 3rd (f) sweep. (g-i) Raman shift of E'_{2g} mode as a function of V_{tg} from the 1st (g), 2nd (h), and 3rd (i) sweep.

Figure 6-18 shows the change of intensity, width, and wavenumber of E'_{2g} mode from bilayer MoS₂ during the three times of sweeps. Unlike the results from non-resonant lasers (Ref. [138] and our data in section 6.4), E'_{2g} mode exhibits considerable dependence on gate voltage, especially for Raman intensity. The reversible change also confirms the gate tunability. The slightly broadened peak width (Figure 6-18 (d-f)) and down-shifted frequency (Figure 6-18 (g-i)) at a large electron concentration resemble the behavior of A_{1g} mode under 532 nm and 514 nm excitation, which indicates that it is the enhanced electron-phonon coupling that leads to the change in FWHM and Raman shift of E'_{2g} mode. Meanwhile, it suggests that the electron-phonon interaction has dependence on excitation wavelength. Thus we also expect a more dramatic change on

A_{1g} mode.

The dramatic change of Raman intensity as a function of V_{tg} is a new phenomenon in MoS₂ and graphene, but similar phenomenon was observed before in single-walled carbon nanotube with electrochemical charging [142]. The charging of a nanotube caused the first electronic states of the particular tube filled or depleted, similar to electron doping or depletion induced by a gate voltage. The bleaching of Raman signal observed in carbon nanotube under certain range of electrode potential was explained by the filling of the van Hove singularities which are resonant to the excitation energy. When the filled van Hove singularities are resonant to the excitation energy, the bleaching effect is stronger than in the case where the electronic states are off resonance with the excitation energy. In MoS₂, van Hove singularity in the band structure is calculated [144]. However, 633 nm laser with an energy less than 2.0 eV is impossible to cross the quasiparticle gap and resonates with these electronic states. Meanwhile, it is unknown yet whether there is van Hove singularity in the optical states which a visible laser is capable of producing resonance effect. Nevertheless, the explanation on carbon nanotube might still be helpful in explaining the quenched E_{2g}^1 mode at large electron concentration.

The doped electrons induced by V_{tg} first occupy the Λ valley (where CBM is in bilayer MoS₂). As V_{tg} increases, doped electrons will be distributed into the K valley as well. 633 nm laser has an energy resonant to the direct gap transition at K point. The absorption cross section will become infinitely large mathematically, which means the absorption of 633 nm light will predominantly occur close to/at the K point. When doping concentration is high and K valley are occupied by doped electron, Pauli exclusion principle will forbid the transition at K point, also referred as absorption bleaching. In

comparison, the absorption of 514.5 nm or 532 nm light can take place on the VBM at Γ point (phonon-assisted indirect-gap transition), band nesting region along the Γ - Λ line [144, 267], or around the K point. Even if the channel at K point is blocked, the absorption of 514.5/532 nm light is hardly affected. Therefore, one of the possibilities to explain the quenched E_{2g}^1 mode at high electron concentration on resonance is related to absorption. If this is the true case, the Raman intensity of A_{1g} mode will become zero simultaneously.

Figure 6-19. Detailed analysis on intensity, FWHM, and Raman shift of A_{1g} mode. Black, red, and blue lines are from the 1st, 2nd, and 3rd sweep, respectively. (a-c) Intensity of A_{1g} mode as a function of V_{tg} from the 1st (a), 2nd (b), and 3rd (c) sweep. (d-f) FWHM of A_{1g} mode as a function of V_{tg} from the 1st (d), 2nd (e), and 3rd (f) sweep. (g-i) Raman shift of A_{1g} mode as a function of V_{tg} from the 1st (g), 2nd (h), and 3rd (i) sweep.

We extracted the intensity, line width, and frequency of A_{1g} mode from the same spectra in which Figure 6-18 (E_{2g}^1 mode in 2 L MoS₂) was from, with data plotted in Figure 6-19. The change in intensity for A_{1g} mode shows the same trend as that in E_{2g}^1

mode, but the magnitude is different: E_{2g}^1 mode is already quenched when $V_{tg} = 1.0$ V, but A_{1g} mode did not fully disappear when $V_{tg} = 2.0$ V, although the intensity is very weak (almost unobservable in Figure 6-16 (a)). Note that for different samples (either 2 L or 3 L), as electron concentration increases, it is always the intensity of E_{2g}^1 mode decreases more significantly (faster) than that of A_{1g} mode. The consistency between bilayer and trilayer indicates that there is no dependence on odd/even layer number. This shows that absorption bleaching may explain the decreased intensity, but it is probably not the only reason.

Figure 6-20. Comparison of gate-tunable Raman study of 2 L MoS₂ by using different excitation lasers. (a, b) FWHM of E_{2g}^1 mode (a) and A_{1g} mode (b) as a function of V_{tg} . (c, d) Raman shift of E_{2g}^1 mode (c) and A_{1g} mode (d) as a function of V_{tg} . Black lines and red lines are results from spectra excited by 532 nm laser and 633 nm laser, respectively. Blue dashed lines indicate the values measured before the application of gate voltage.

A surprising effect has been observed in Figure 6-19. With increasing doping of electron (a more “positive” V_{tg}), A_{1g} mode broadens due to the enhanced electron-phonon coupling. Supposedly, A_{1g} mode should down-shift in the meantime, as

a result of smaller force constant caused by electron occupation of antibonding states; while it is not the case, as seen in Figure 6-19 (g-i).

Comparisons between off- and on-resonance are shown in Figure 6-20, the frequencies of E_{2g}^1 mode within the electron depletion region ($V_{tg} < -0.5$ V) are similar excited by both 532 nm and 633 nm lasers. E_{2g}^1 mode is observed to be softened and broadened with increasing electron doping under 633 nm excitation, but the mode does not change with 532 nm laser. The broadened linewidth extracted from the spectra excited by 633 nm laser (Figure 6-20 (a)) is an indication of stronger electron-phonon coupling. Moreover, the peak shift for E_{2g}^1 mode on resonance can also be attributed to the enhanced electron-phonon coupling. By comparison, the FWHM of A_{1g} mode shows no dependence on excitation energy (Figure 6-20 (b)). The appreciable peak shift with increasing electron doping, either blue-shift or red-shift, occurs along with the broadened peak width. The V_{tg} -dependent Raman shift for A_{1g} mode is complicated. Take Figure 6-20 (d) as an example. The A_{1g} mode blue-shifts when V_{tg} increases from 0 V to 1 V, but it red-shifts when V_{tg} changes from 1V to 2 V. Meanwhile, I also notice that the frequency of A_{1g} mode red-shifts by ~ 2 cm^{-1} when $V_{tg} \leq 0$ V. This is not supposed to happen, because first order phonon modes (such as A_{1g}) reflect the vibrational properties in the ground state, and the Raman shift should not change with excitation laser.

To obtain an explanation on the complicated V_{tg} -dependent Raman shift for A_{1g} mode, we think the first step is to figure out why A_{1g} mode is red-shifted on resonance. Therefore, we considered the situations without gating effect and electron doping. Also, we would like to confirm the red-shifted frequency is a true phenomenon, instead of an occasion. It is worth noting that the frequency of zone-center phonon A_{1g} mode is

measured to be down-shifted when the sample is excited by a red laser, as shown in Figure 6-21 (a) from Ref. [140]; while E_{2g}^i mode is dispersionless as expected. The authors also remarked that due to the poorer resolution when using laser of higher energy (3.81 eV), the results from this wavelength might be less reliable. Meanwhile, another group has also reported on the down-shifted A_{1g} mode when excitation is 633 nm in Ref. [268]. In fact, I have found the same wavelength-dependent Raman shift during my experiments as well, as shown in Figure 6-21 (b, c). That is to say, the red-shifted A_{1g} mode in few-layer MoS₂ on resonance is a reproducible phenomenon. However, the softened A_{1g} mode under resonance has not yet been explained by previous papers.

Figure 6-21. Dependence on excitation laser energy of the zone-center phonons, E_{2g}^i and A_{1g} modes. (a) Experimental results from Ref. [140]. (b, c) Wavelength-dependent Raman shift of E_{2g}^i and A_{1g} modes in 1-5 L (b) and 1-7 L (c) MoS₂. E_{2g}^i mode of 1 L MoS₂ in (c) is too weak to be resolved when excitation is 633 nm. The corresponding Raman scattering measurement was conducted at ambient condition with a 100× objective. (b) Normal mode displacement for A_{1g} mode in bilayer MoS₂. ω_0 refers to the Raman shift of A_{1g} mode in monolayer, and $\Delta\omega$ is related to the interlayer coupling (the interlayer breathing mode of bilayer, ~39.5 cm⁻¹ in 2H-MoS₂).

Here we take bilayer, the simplest case, for further illustration. Figure 6-21 (d) shows the normal mode displacement for A_{1g} in bilayer MoS₂. The neighbouring S atoms (with van der Waals (vdW) gap in between) displace in the opposite direction. If we regard each layer as one spring, the second spring in A_{1g} mode can accumulate restoring force and thus increase the frequency compared to the case when there is only one spring. Quantitatively, the frequency of two identical coupled oscillator ω_l (A_{1g} in bilayer) can be determined by $\sqrt{\omega_0^2 + \Delta\omega^2}$, where ω_0 represents the frequency of the isolated oscillator (A_{1g} in monolayer, *i.e.*, A_1') and $\Delta\omega$ is related to the interlayer coupling (the interlayer breathing mode of bilayer, $\sim 39.5 \text{ cm}^{-1}$ in 2H-MoS₂). This analysis match well with the experimentally measured Raman shift in MoS₂ [118, 120]. When the excitation laser switched from 457/514.5 nm to 633 nm in Figure 6-21 (c), ω_l decreases, which means either ω_0 or $\Delta\omega$ becomes smaller (or both). Figure 6-21 (c) shows the change of ω_0 is negligible, indicating that the interlayer coupling strength ($\Delta\omega$) decreases when the excitation energy is resonant to A exciton. The weaker interlayer coupling on resonance to A exciton leads to the decoupling effect between the two layers in the bilayer sample. Our analysis is consistent with the discussion on N quasi-independent layers as mentioned above in WS₂ [260]. So far, it is believed that the orientation/distribution of the exciton is associated with the resonance-related decoupling effect. Schuller *et al.* found that A/B exciton is highly confined in-plane, with negligible expansion in the neighbouring layer(s) [269], which may be the reason for decoupling.

In total, I have measured 8 bilayers, 6 of them exhibit the anomalous blue-shift in A_{1g} mode with increasing electron concentration. One of the rest two bilayers was further measured by using other excitation lines, as shown in Figure 6-22. The ionic gel

used in the measurement of Figure 6-22 was freshly-prepared, which leads to higher collection efficiency. From the raw data in Figure 6-22, we can see that except the spectrum excited by 514.5 nm laser, spectra excited by the rest 5 laser lines all show the dependence of Raman intensity on gate voltage, though the magnitude differs. All the 5 laser lines are resonant or near resonant to either A/B exciton, which further confirms that the change in intensity is closely related to resonance. Meanwhile, the asymmetric A_{1g} peak is clearly seen in Figure 6-22 (c-e), indicating the occurrence of Davydov splitting. In fact, the wavelength-dependent Raman spectra can also help to test our analysis on the anomalous blue-shift of A_{1g} mode with increasing electron doping, when the excitation laser is resonant to A/B exciton. Besides, we also expect that there is a wavelength which can cause the frequency of A_{1g} mode to be V_{tg} -independent. The competing effect between red-shift and blue-shift as carrier concentration increases, should be counterbalanced at this certain wavelength.

Figure 6-23 (a) shows the V_{tg} -dependent energies of A and B excitons, which were extracted after Lorentzian fitting to the PL spectra. V_{tg} -dependent PL measurements were performed on the same bilayer MoS₂ sample from which the V_{tg} -dependent Raman scattering measurements were done. As V_{tg} increases (when $V_{tg} > 0$), excitation energy is more resonant to B exciton for 632.9 nm laser, while it is less resonant when 612.2 nm is used. From Figure 6-23 (e) (612.2 nm) and Figure 6-23 (f) (632.9 nm), we see that in the electron depletion and low electron doping regions, Davydov splitting of A_{1g} mode appears, and the split Raman-inactive A_{2u} mode is displayed in red empty triangles. The Davydov splitting is more pronounced under resonance, in consistent with previous reports on WS₂ and MoTe₂ [260, 270].

Figure 6-22. Dependence on excitation wavelength of gate-tunable Raman spectra of 2 L MoS₂. The used laser lines are 514.5 nm (a), 580.6 nm (b), 595.5 nm (c), 612.2 nm (d), 632.9 nm (e), and 671.0 nm (f).

In the moderate/heavy electron doping region when there is no splitting, as V_{tg} increases, A_{1g} mode blue-shifts when excitation wavelength is 612.2 nm while red-shifts when 632.9 nm is used. Note that the influence from antibonding electrons which weaken the Mo-S bond and thus causing softened frequency is ought to be the same under the same electron concentration (*i.e.* the same V_{tg}). What makes the V_{tg} -dependent Raman shift opposite between 612.2 nm excitation and 632.9 nm excitation is the decoupling effect related to resonance. For the 612.2 nm excitation laser, with increasing electron doping, the energy difference between excitation and exciton becomes larger, the resonance decoupling effect is weaker, causing A_{1g} mode shifts to higher frequency. On the other hand, the antibonding electron causes A_{1g} mode shifts to lower frequency. The combined effect for 612.2 nm excitation is A_{1g} mode blue-shifts when V_{tg} increases,

indicating that it is the excitation energy related-decoupling effect plays a dominant role over the antibonding electron for this specific excitation energy. Nevertheless, A_{1g} mode red-shifts when V_{tg} increases for the 632.9 nm excitation. Both antibonding electron and the decoupling effect cause the peak to soften in this case.

Figure 6-23. V_{tg} -dependent excitonic energy (The corresponding PL spectra were excited by a 532 nm laser.) and Raman shift of A_{1g} mode measured with different excitation wavelengths. (a) V_{tg} -dependent energy of A and B excitons. Data was extracted after Lorentzian fitting on the result in Figure S2. The dash lines indicate the energy of resonant excitation lines. As V_{tg} increases (when $V_{tg} > 0$), excitation energy is more resonant to B exciton for 632.9 nm laser, while it is less resonant when 612.2 nm is used. (b-g) V_{tg} -dependent Raman shift of A_{1g} mode with excitation wavelength of 514.5 nm (b), 580.6 nm (c), 595.5 nm (d), 612.2 nm (e), 632.9 nm (f), and 671.0 nm (g). The splitting of A_{1g} mode tends to occur during electron depletion or light electron doping, especially under resonance condition. The peak positions in (b-g) were obtained after Lorentzian fitting. The wavenumber of A_{1g} mode is shown in black solid square when there is no splitting. When there is splitting, the peak positions of A_{1g} and A_{2u} modes are shown in black triangles and red triangles, respectively.

When the excitation laser is 580.6 nm or 595.5 nm, there is not a clear trend on V_{tg} -dependent Raman shift for A_{1g} mode. This is the counterbalance effect between blue-shift and red-shift as we expected. Furthermore, the V_{tg} -dependent Raman shifts in Figure 6-235 (g) (671.0 nm) and Figure 6-23 (b) (514.5 nm) are very similar, despite that the excitation of 671.0 nm is resonance to A exciton. Photoluminescence excitation spectroscopy of bilayer MoS₂ [271] has suggested that both 671.0 nm and 514.5 nm lasers cannot cause the emission of A exciton to be dominant over that from the indirect gap, unlike the 612.2 nm excitation line. This result indicates that the decoupling effect is related to the formation of A exciton.

To have a brief summary, there are mainly three new features: (1) Electron-phonon coupling is stronger during resonance, mainly evidenced by the behavior of E_{2g}^1 mode. (2) Significant gate-tunable Raman intensity is observed. Absorption bleaching may play an important role in affecting the intensity. (3) Anomalous blue-shift of A_{1g} mode is observed with increasing electron concentration, when the excitation energy is on resonance with A/B exciton.

Besides bilayer and trilayer samples, I have further done experiments on a 6 L MoS₂ flake to see whether the interesting features still persist. On the other hand, Davydov splitting is more pronounced in thicker layers (The two peaks are not well-resolved in thin layers) [261]. Will the anomalous shift appear if A_{1g} mode is split (while there is no anomalous shift when splitting appears from 2 L MoS₂, shown in Figure 6-23)? As expected, there is no observable change when excitation is 532 nm laser from the 6 L MoS₂ flake. The dramatic change in intensity is very robust when the spectra were excited by a 633 nm laser, as shown in Figure 6-24.

Figure 6-24. Gate-tunable Raman spectra of 6 L MoS₂ measured by using 633 nm laser as excitation (raw data without normalization). The gate voltage was changed from 2.0 V to -1.5 V, during which intensities of Raman peaks in MoS₂ dramatically increase.

With focus on the A_{1g} mode at $\sim 407 \text{ cm}^{-1}$, I have fitted the spectra by using Lorentzian function. Before comparing the Raman shift, I have aligned all the spectra according to the Si peak at 520.70 cm^{-1} . As expected, the splitting is more pronounced at a negative gate voltage (already discussed in Figure 6-15). There is almost no V_{tg} -dependent shift when the peak is split (From -1.5 V to -0.5 V: $\sim 0.3 \text{ cm}^{-1}$ and $\sim 0.4 \text{ cm}^{-1}$ for lower and higher branches, respectively), consistent with the case in bilayer. However, when $V_{tg} > 0$, A_{1g} mode blue-shifts by $\sim 1 \text{ cm}^{-1}$ as V_{tg} increases from 0.5 V to 1.5 V, and there is no more splitting. It is worth mentioning that the peak width of A_{1g} and B_{1u} modes hardly change with different V_{tg} , but the V_{tg} -dependence still preserves on E_{2g}^1 mode. In general, result on 6 L is in agreement with those on 2 L and 3 L. The splitting occurs when $V_{tg} < 0$, but peak shift is not pronounced at this electron depletion regime.

Figure 6-25. Extracted frequencies of A_{1g} and B_{1u} modes as a function of V_{tg} from 6 L MoS₂. Blue line indicates the peak position of A_{1g} mode measured by 532 nm laser, which does not shift when carrier density varies. The comparison of Raman shift was based on the alignment of Si peak at 520.70 cm^{-1} .

6.6 Summary

We have demonstrated the effective gating effect on top-gated mono- and few-layer MoS₂ device, with gated material to be PS-PEO-PS + EMIM-TFSI. PL spectra of bilayer and trilayer MoS₂ have been shown to be controllable by a gate voltage. This is the first time that the energy and intensity of A exciton in 2 L MoS₂ can be tuned by a gate voltage at room temperature. Also this is the first report on electric control of luminescence properties of 3 L MoS₂. The above results further confirm that our setup is able to tune the carrier density of few-layer MoS₂ sample within a large range. By comparison, most previous papers failed to tune the PL due to insufficient electron concentration.

On the studies of phonon properties, I first repeated what have been done in a previous report (gate-tunable Raman spectra excited by 532/514.5 nm laser), but extended the thickness to 3 L. Our experimental data is consistent with previous results, and thus we have proceeded to the next step, gate-tunable Raman scattering measurements excited

by a 633 nm laser, the resonance condition. There are mainly three new features: (1) Electron-phonon coupling is stronger under resonance condition, mainly evidenced by the behavior of E_{2g}^1 mode. (2) Significant gate-tunable Raman intensity is observed. Absorption bleaching may play an important role in affecting the intensity, but it is not the only factor. (3) Anomalous blue-shift of A_{1g} mode with increasing electron concentration.

We focused on the anomalous blue-shift of A_{1g} mode with increasing electron concentration, which is shown to be a reversible phenomenon and really gate-controllable. Meanwhile, the shift is repeated on 6 out of 8 bilayers, 4 trilayers, and a 6 L flake. One of the two “failed” 2 L is further checked by using multiple laser lines, including 514.5 nm, 580.6 nm, 595.5 nm, 612.2 nm, 632.9 nm, and 671.0 nm. Result shows that the anomalous shift on this flake occurs when excitation is 612.2 nm (2.025 eV), with energy very close to 632.9 nm (1.959 eV). The subtle difference is attributed to sample variation.

The anomalous blue-shift of A_{1g} mode with increasing electron concentration is related to the decoupling effect. The occurrence of decoupling effect is related to resonance, or rather the formation of A exciton. Further evidence was demonstrated with the *in situ* correlation between excitonic energy and excitation laser energy (Figur 6-23). So far, we can conclude that there are two major factors that affect the Raman shift of A_{1g} mode in our measurments. On one hand, doped electrons cause the Mo-S bond to be weaker with increasing electron doping. Thus A_{1g} mode should red-shift as V_{lg} increases. On the other hand, the excitonic energies are changing with different gate voltages, resulted from many-body effects. The resonance-related decoupling effect will cause A_{1g} mode to red-shift. If the energy difference between incident light and A exciton increases

(decreases), A_{1g} mode blue-shifts (red-shifts).

The detailed discussion on the softened A_{1g} mode under resonance condition is presented for the first time, with a simple oscillator model. The softened A_{1g} mode is related to the decreased interlayer coupling on resonance. Direct measurement on low-frequency interlayer breathing mode is very challenging (especially in thin layers) even on the triple grating Raman spectroscopy, because of the large resonance background. Here we have shown an indirect method to probe the interlayer coupling. Besides, we have pointed out the selection of incident laser affects the observation of carrier doping on Raman spectroscopy. We believe our work on gate-tunable resonant Raman spectroscopy is essential for future study on many-body effect.

Chapter 7 Conclusions and Future Work

7.1 Conclusions

During my PhD study, I mainly worked on synthesis and optical properties of atomically thin layered transition metal dichalcogenides MoX_2 ($X = \text{S}, \text{Se}$). The first half, Chapter 3 and Chapter 4, is sample-driven, which introduces several top-down methods and CVD-growth (a typical bottom-up way to obtain nanomaterials). The top-down methods I have used include the conventional mechanical exfoliation and thermal annealing thinning. Mechanical exfoliation can be applied to a variety of 2D layered materials, with examples shown on graphene, MoS_2 , WSe_2 , black phosphorus, GaSe and *etc.* Thermal annealing, in principle, should also be a common method to get thin film samples. In this thesis, I have taken MoS_2 as a case study on layer-by-layer thinning. After optimizing parameters, I have roughly achieved layer-by-layer thinning by annealing the sample at 650 °C in argon with pressure of 10 Torr. It takes one hour to remove one layer, which is due to heat-induce sublimation. The changing color from bright blue to dark blue (on 285 nm SiO_2/Si substrate) with increasing annealing time is an indication of thinning. Meanwhile, AFM data further confirms the decreased thickness. Raman spectroscopy is also used to monitor the thermal thinning. As annealing time increases, the pronounced blue-shift of interlayer breathing mode in the low frequency region suggests that the layer number has decreased. It is worth noting that inhomogeneous surface is also observed, both on AFM and on Raman spectrometer.

Sulfurization and selenization of metal trioxide inside a CVD chamber has become a very popular way to get mono- and few-layer MX_2 ($M = \text{Mo}, \text{W}; X = \text{S}, \text{Se}$). My focus in

this thesis is CVD-synthesis of MoSe₂. Different morphologies are obtained, in the form of either thin film with size of $\sim 1 \times 1 \text{ cm}^2$ or individual flake with grain size of $\sim 10 \text{ }\mu\text{m}$. The key factor in my growth is pressure: Low pressure (20 Torr) favors large area film but grain size is small, $\sim 100 \text{ nm}$; High pressure (810 Torr), however, promotes the flakes to enlarge size to $\sim 10 \text{ }\mu\text{m}$, while only few-layer (2-8 L in majority) can be obtained. Details on how to optimize the growth parameters are shown by discussing about the controlled experiments which include dependence on temperature, H₂ concentration and *etc.* In addition, STEM imaging and Raman spectroscopy confirm that the as-grown samples are MoSe₂ with good quality.

The emission properties of CVD-grown thin film are investigated in detail, with temperature-dependent PL spectra, optical absorption spectra, power-dependent measurements, as well as comparison on the PL fitting by using different functions. Electrical performance was studied, in which we found that the performance is poor on thin film, but improves a lot on flake with size of $\sim 10 \text{ }\mu\text{m}$. Meanwhile, the usage of catalyst affects the device performance, evidenced on 178 devices. Furthermore, I also showed that the selenization growth in CVD can even extend to WSe₂, both in film and flake as well. Interesting features, such as dislocation, are observed.

The second half consists of Chapter 5 and Chapter 6, with focus on the lattice vibrational properties. Chapter 5 investigated the relation between stacking sequence and the low-frequency interlayer shear modes. Through bond polarizability model, we found that AB-stacked layered materials (such as 2H-stacked MoS₂) exhibit blue-shifted interlayer shear mode as layer number increases, while the trend is opposite in ABC-stacked samples (*e.g.* 3R-stacked MoS₂). Experimental evidence is shown on

CVD-grown few-layer MoSe₂ flakes with multiple types of stacking orders. Besides the commonly-known 2H and 3R phases, mixture in the basal plane is found as well, which is evidenced not only from the low-frequency Raman spectra (co-existence of the fingerprints of both 3R and 2H stacking orders), but also STEM imaging. Stacking fault, such as ABCB stacking 4 L, is also assigned with the help of theoretical calculations. We have demonstrated that Raman spectroscopy can work in a rapid and nondestructive way to identify stacking in this chapter.

Chapter 6 is devoted to explore the influence of electric field gating effect on the phonon properties of MoS₂. By applying a gate voltage through the top-gated ionic gel, we can achieve electron doping with maximum concentration around $\sim 1.75 \times 10^{13} \text{ cm}^{-2}$ on 2 L MoS₂. Gate-tunable PL measurements and non-resonant Raman scattering measurements with different electron doping level have been conducted. The new features, however, were observed by using a resonant laser, 633 nm: First, electron-phonon coupling is stronger during resonance, mainly evidenced by the behavior of E_{2g}^1 mode. Second, significant gate-tunable Raman intensity is observed. Absorption bleaching may play an important role in affecting the intensity, but it is probably not the only factor. Last but not the least, it is the anomalous blue-shift of A_{1g} mode with increasing electron concentration, which is red-shifted when the excitation laser is 532 nm. In particular, we focused on the anomalous blue-shift of A_{1g} mode and have done further experiments (*e.g.* wavelength-dependent measurements). We believe there are two major factors affecting the V_{tg} -dependent Raman shift of A_{1g} mode: The antibonding electrons cause the Mo-S bond to be weaker and thus A_{1g} mode softened; While the resonance-related decoupling effect also influences the frequency of A_{1g} mode. If the energy difference

between incident light and A exciton increases (decreases), A_{1g} mode blue-shifts (red-shifts).

7.2 Future Work

Figure 7-1. The low-frequency mode 38 cm⁻¹ in MoS₂ under 633 nm (1.96 eV) excitation. (a) Peak positions for breathing (circle) and shear (square) modes as functions of layer number. The peak at 38 cm⁻¹ only shows up when excitation energy is 1.96 eV [140]. (b) Low-frequency Raman spectra of MoS₂ thin films at different thicknesses under excitation of 633 nm. The broad feature around 38 cm⁻¹ is observed only under resonance condition [170].

Except the interlayer shear and breathing modes in few-layer MX₂ (M = Mo, W; X = S, Se), there is one more low-frequency mode observed and common among the four layered materials, which only appears when the excitation energy is in/near resonance to the exciton energy. For MoS₂, this peak is located at 38 cm⁻¹ (~4.7 meV), and its energy is not dependent on thickness, as shown in Figure 7-1. The broad peak at 38 cm⁻¹, which is observed under both parallel- and cross-polarized configurations, is rather broad compared to the interlayer shear and breathing modes. Zeng *et al.* thinks this peak might be related to the splitting of conduction band at K point due to the strong spin-orbit coupling [170]. Coincidentally, the splitting energy is calculated to be 3-4 meV [87]. However, Lee *et al.* later found that the peak at 38 cm⁻¹ is always observable no matter the

polarization is $\sigma^-\sigma^-$ or $\sigma^-\sigma^+$, indicating that the peak is not resulted from the splitting [140]. This is because if it is due to spin-flip scattering process, the peak is unobservable when the polarization is $\sigma^-\sigma^-$.

The origin of this peak is unknown yet. Our group has previously suspected that it has something to do with electron-phonon scattering, and Raman scattering measurements have been conducted on a few-layer sample with SiO_2 back-gating. There is no appreciable progress, possibly due to the insufficient doping level. Along with the experiments in Chapter 6, I have done some measurements in the low-frequency region, as shown in Figure 7-2.

Figure 7-2. Gate-tunable low-frequency Raman spectra of a top-gated 3 L MoS_2 excited by 633 nm laser. (a, b, c) Spectra taken at $V_{tg} = -1.5$ V (a), 0 V (b), and 1.0 V (c), respectively. Grey lines are experimental data and red (& blue) lines are results from Lorentzian fitting.

The low-frequency peak is measured to locate at 37.6 cm^{-1} when $V_{tg} = 0$ V, in agreement with previous reports [140, 170]. When $V_{tg} = 1.0$ V, the signal is relatively weaker (read from the y-axis). It is possibly due to the absorption bleaching which we have mentioned in Chapter 6. Within the electron depletion region ($V_{tg} = -1.5$ V), the peak is softened to 36.3 cm^{-1} , and it exhibits stronger intensity. Meanwhile, the peak at 79.7 cm^{-1} is supposed to be the second-order overtone. At ambient condition, Lee *et al.* have obtained the two peaks to be located at 38 cm^{-1} and 76 cm^{-1} , respectively [140]. The

V_{tg} -dependent behavior of peak at $\sim 38 \text{ cm}^{-1}$ is different from all the other peaks, as it shows a true blue-shifted trend with increasing electron doping. While the anomalous blue-shifted A_{1g} mode we have discussed in Chapter 6 is just “*shifting back to the original frequency*”. More investigation has to proceed to understand the low-frequency peak at $\sim 38 \text{ cm}^{-1}$ (and its overtone). So far, we can only say that the peak is gate-tunable and very different from all the other modes.

Figure 7-3. Low-frequency interlayer vibrational modes from MoS₂-based heterostructures from literatures. (a, b) LBM (layer breathing mode; *i.e.*, interlayer breathing mode) of MoSe₂/MoS₂ hetero-bilayer at selected stacking angles: 45°, 32°, and 5° (a). (b) The LBM frequencies of 58 MoSe₂/MoS₂ hetero-bilayer samples as a function of the layer rotational angle (θ). The inset shows the schematic rotational angle between single-crystal MoS₂ and MoSe₂ monolayers [168]. (c) Low-frequency Raman spectra of LBM and shear mode from as-grown continuous MoS₂ films on WS₂ with AA and AB stacking orders, and as-transferred twisting-stacked MoS₂/WS₂ heterostructures [198].

Besides, studying low-frequency vibrational modes in heterostructures is also a very interesting topic to me. As far as I know, there are only two papers [168, 198] reporting on the low-frequency modes of atomically thin heterostructures, as shown in Figure 7-3. In contrast, there are considerable literatures on PL from TMDs-based 1+1 hetero-bilayers [163, 166, 169, 198, 272], in which stacking angle was shown to have critical effect on the luminescence [163, 228]. The slow progress on low-frequency mode from

heterostructures is probably related to several difficulties, including techniques on low-frequency Raman spectroscopy, sample preparation, and poor repeatability.

The poor repeatability can be seen in Figure 7-3 (b). For example, when the stacking angle is $\sim 30^\circ$, the frequency of LBM can vary from 31 to 33 cm^{-1} . The trend which Lui *et al.* have observed in Figure 7-3 (b) has to rely on a large amounts of samples [168]. The poor repeatability is related to the interlayer coupling. Even with the same technique, the same bulk samples (batch of growth), and the same person in sample preparation, it is still very difficult to make sure the interlayer distance/coupling is the same, or the deviation is within a small range. Based on a simple model, the hetero-bilayer can be treated as two spring-coupled masses with a frequency of $\omega = \sqrt{k/m}$. k is the out-of-plane force constant, and m is the reduced mass per unit area. In fact, this is actually a simplified linear chain model [118]. The calculated frequency in $\text{MoSe}_2/\text{MoS}_2$ hetero-bilayer is 34.5 cm^{-1} . However, most of the data points in Figure 7-3 (b) are smaller than the calculated value [168], because it is very difficult to completely avoid the interlayer gap between the two monolayers. Once there is a little gap, the interlayer coupling will be weaker, leading to a smaller k and ω .

I have some preliminary data shown in Figure 7-4. All the samples prepared for Raman scattering measurements were annealed beforehand. The new modes, N1 and N2, only appear under parallel-polarized polarization, which suggests the nature of N1 and N2 is interlayer breathing mode. N1 is tentatively believed to be the derivative of B1 mode in the heterostructure. N2, in most of cases, only appear when the thickness of graphene is comparable or thicker than MoS_2 . Meanwhile, from Figure 7-4 we can see that interlayer shear mode is less sensitive to the addition of graphene onto MoS_2 sample. Nevertheless,

we are also suffering from the problem of sample variation. Research investigation is still going on and more samples are needed to draw a concrete conclusion.

Figure 7-4. Low-frequency modes from MoS₂/graphene heterostructures. (a, b) 2 L MoS₂ (a) and 4 L MoS₂ (b) on graphene layers with different thickness. 2LG means two layers of graphene. Dots are experimental data and lines are results from Lorentzian fitting. S1 and B1 refer to interlayer shear and breathing mode with the strongest intensity, respectively. N1 is short for “new mode 1”.

References

- [1] Geim, A. K.; Novoselov, K. S. The rise of graphene. *Nature Mater.* **2007**, *6*, 183-191.
- [2] Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature Nanotech.* **2012**, *7*, 699-712.
- [3] Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L. J.; Loh, K. P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chem.* **2013**, *5*, 263-275.
- [4] Xu, X.; Yao, W.; Xiao, D.; Heinz, T. F. Spin and pseudospins in layered transition metal dichalcogenides. *Nature Phys.* **2014**, *10*, 343-350.
- [5] Liu, H.; Du, Y.; Deng, Y.; Ye, P. D. Semiconducting black phosphorus: synthesis, transport properties and electronic applications. *Chem. Soc. Rev.* **2015**, *44*, 2732-2743.
- [6] Ling, X.; Wang, H.; Huang, S.; Xia, F.; Dresselhaus, M. S. The renaissance of black phosphorus. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 4523-4530.
- [7] Geim, A. K.; Grigorieva, I. V. Van der Waals heterostructures. *Nature* **2013**, *499*, 419-425.
- [8] Zhang, Y.; He, K.; Chang, C.-Z.; Song, C.-L.; Wang, L.-L.; Chen, X.; Jia, J.-F.; Fang, Z.; Dai, X.; Shan, W.-Y.; Shen, S.-Q.; Niu, Q.; Qi, X.-L.; Zhang, S.-C.; Ma, X.-C.; Xue, Q.-K. Crossover of the three-dimensional topological insulator Bi₂Se₃ to the two-dimensional limit. *Nature Phys.* **2010**, *6*, 584-588.
- [9] Hasan, M. Z.; Kane, C. L. Colloquium: Topological insulators. *Rev. Mod. Phys.* **2010**, *82*, 3045-3067.
- [10] Qi, X.-L.; Zhang, S.-C. Topological insulators and superconductors. *Rev. Mod. Phys.* **2011**, *83*, 1057.
- [11] Novoselov, K. S.; Jiang, Z.; Zhang, Y.; Morozov, S. V.; Stormer, H. L.; Zeitler, U.; Maan, J. C.; Boebinger, G. S.; Kim, P.; Geim, A. K. Room-temperature quantum hall effect in graphene. *Science* **2007**, *315*, 1379-1379.
- [12] Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271-1275.
- [13] Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.
- [14] Gutierrez, H. R.; Perea-Lopez, N.; Elias, A. L.; Berkdemir, A.; Wang, B.; Lv, R.; Lopez-Urias, F.; Crespi, V. H.; Terrones, H.; Terrones, M. Extraordinary Room-Temperature Photoluminescence in Triangular WS₂ Monolayers. *Nano Lett.* **2013**, *13*, 3447-3454.
- [15] Li, L.; Yu, Y.; Ye, G. J.; Ge, Q.; Ou, X.; Wu, H.; Feng, D.; Chen, X. H.; Zhang, Y. Black phosphorus field-effect transistors. *Nature Nanotech.* **2014**, *9*, 372-377.
- [16] Liu, H.; Neal, A. T.; Zhu, Z.; Luo, Z.; Xu, X.; Tomanek, D.; Ye, P. D. Phosphorene: An Unexplored 2D Semiconductor with a High Hole Mobility. *ACS Nano* **2014**, *8*, 4033-4041.
- [17] Wang, X.; Jones, A. M.; Seyler, K. L.; Tran, V.; Jia, Y.; Zhao, H.; Wang, H.; Yang, L.; Xu, X.; Xia, F. Highly anisotropic and robust excitons in monolayer black phosphorus. *Nature Nanotech.* **2015**, *10*, 517-521.
- [18] Xia, F.; Wang, H.; Jia, Y. Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics. *Nat. Commun.* **2014**, *5*, 4458.
- [19] Zhang, J.; Peng, Z.; Soni, A.; Zhao, Y.; Xiong, Y.; Peng, B.; Wang, J.; Dresselhaus, M. S.; Xiong, Q. H. Raman spectroscopy of Few-quintuple layer topological insulator Bi₂Se₃ nanoplatelets. *Nano Lett.* **2011**, *11*, 2407-2414.

- [20] Cui, X.; Lee, G.-H.; Kim, Y. D.; Arefe, G.; Huang, P. Y.; Lee, C.-H.; Chenet, D. A.; Zhang, X.; Wang, L.; Ye, F.; Pizzocchero, F.; Jessen, B. S.; Watanabe, K.; Taniguchi, T.; Muller, D. A.; Low, T.; Kim, P.; Hone, J. Multi-terminal transport measurements of MoS₂ using a van der Waals heterostructure device platform. *Nature Nanotech.* **2015**, *10*, 534-540.
- [21] Wu, S.; Huang, C.; Aivazian, G.; Ross, J. S.; Cobden, D. H.; Xu, X. Vapor–Solid Growth of High Optical Quality MoS₂ Monolayers with Near-Unity Valley Polarization. *ACS Nano* **2013**, *7*, 2768-2772.
- [22] Frindt, R. F. Single crystals of MoS₂ several molecular layers thick. *J. Appl. Phys.* **1966**, *37*, 1928.
- [23] Nicolosi, V.; Chhowalla, M.; Kanatzidis, M. G.; Strano, M. S.; Coleman, J. N. Liquid exfoliation of layered materials. *Science* **2013**, *340*, 1226419.
- [24] Coleman, J. N.; Lotya, M.; O'Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J.; Shvets, I. V.; Arora, S. K.; Stanton, G.; Kim, H. Y.; Lee, K.; Kim, G. T.; Duesberg, G. S.; Hallam, T.; Boland, J. J.; Wang, J. J.; Donegan, J. F.; Grunlan, J. C.; Moriarty, G.; Shmeliov, A.; Nicholls, R. J.; Perkins, J. M.; Grieveson, E. M.; Theuvsen, K.; McComb, D. W.; Nellist, P. D.; Nicolosi, V. Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* **2011**, *331*, 568-571.
- [25] Brent, J. R.; Savjani, N.; Lewis, E. A.; Haigh, S. J.; Lewis, D. J.; O'Brien, P. Production of few-layer phosphorene by liquid exfoliation of black phosphorus. *Chem. Commun.* **2014**, *50*, 13338-13341.
- [26] Woomer, A. H.; Farnsworth, T. W.; Hu, J.; Wells, R. A.; Donley, C. L.; Warren, S. C. Phosphorene: Synthesis, Scale-Up, and Quantitative Optical Spectroscopy. *ACS Nano* **2015**, *9*, 8869-8884.
- [27] Joensen, P.; Frindt, R. F.; Morrison, S. R. Single-layer MoS₂. *Mater. Res. Bull.* **1986**, *21*, 457-461.
- [28] Zeng, Z.; Yin, Z.; Huang, X.; Li, H.; He, Q.; Lu, G.; Boey, F.; Zhang, H. Single-layer semiconducting nanosheets: High-yield preparation and device fabrication. *Angew. Chem. Int. Ed.* **2011**, *50*, 11093-11097.
- [29] Zheng, J.; Zhang, H.; Dong, S.; Liu, Y.; Nai, C. T.; Shin, H. S.; Jeong, H. Y.; Liu, B.; Loh, K. P. High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide. *Nat. Commun.* **2014**, *5*, 2995.
- [30] Eda, G.; Yamaguchi, H.; Voiry, F.; Fujita, T.; Chen, M.; Chowalla, M. Photoluminescence from chemically exfoliated MoS₂. *Nano Lett.* **2011**, *11*, 5111-5116.
- [31] Castellanos-Gomez, A.; Barkelid, M.; Goossens, A. M.; Calado, V. E.; van der Zant, H. S. J.; Steele, G. A. Laser-Thinning of MoS₂: On Demand Generation of a Single-Layer Semiconductor. *Nano Lett.* **2012**, *12*, 3187-3192.
- [32] Liu, Y. L.; Nan, H. Y.; Wu, X.; Pan, W.; Wang, W. H.; Bai, J.; Zhao, W. W.; Sun, L. T.; Wang, X. R.; Ni, Z. H. Layer-by-Layer Thinning of MoS₂ by Plasma. *ACS Nano* **2013**, *7*, 4202-4209.
- [33] Lu, X.; Utama, M. I. B.; Zhang, J.; Zhao, Y.; Xiong, Q. H. Layer-by-layer thinning of MoS₂ by thermal annealing. *Nanoscale* **2013**, *5*, 8904-8908.
- [34] Wu, J.; Li, H.; Yin, Z.; Liu, J.; Cao, X.; Zhang, Q.; Zhang, H. Layer Thinning and Etching of Mechanically Exfoliated MoS₂ Nanosheets by Thermal Annealing in Air. *Small* **2013**, *9*, 3314-3319.
- [35] Peng, Y.; Meng, Z.; Zhong, C.; Lu, J.; Yu, W.; Jia, Y. B.; Qian, Y. Hydrothermal synthesis and characterization of single-molecular-layer MoS₂ and MoSe₂. *Chem. Lett.* **2001**, *30*, 772-773.
- [36] Koma, A.; Sunouchi, K.; Miyajima, T. Fabrication and characterization of heterostructures with subnanometer thickness. *Microelec. Eng.* **1984**, *2*, 129-136.
- [37] Koma, A. van der Waals Epitaxy for Highly Lattice-mismatched Systems. *J. Cryst. Growth* **1999**, *201*, 236-241.
- [38] Utama, M. I. B.; Belarre, F. J.; Magen, C.; Peng, B.; Arbiol, J.; Xiong, Q. H. Incommensurate van der Waals Epitaxy of Nanowire Arrays: A Case Study with ZnO on Muscovite Mica Substrates. *Nano*

Lett. **2012**, *12*, 2146-2152.

- [39] Utama, M. I. B.; Peng, Z.; Chen, R.; Peng, B.; Xu, X.; Dong, Y.; Wong, L. M.; Wang, S.; Sun, H.; Xiong, Q. H. Vertically Aligned Cadmium Chalcogenide Nanowire Arrays on Muscovite Mica: A Demonstration of Epitaxial Growth Strategy. *Nano Lett.* **2011**, *11*, 3051-3057.
- [40] Pan, J.; Utama, M. I. B.; Zhang, Q.; Liu, X.; Peng, B.; Wong, L. M.; Sum, T. C.; Wang, S.; Xiong, Q. H. Composition-Tunable Vertically Aligned CdS_xSe_{1-x} Nanowire Arrays via van der Waals Epitaxy: Investigation of Optical Properties and Photocatalytic Behavior. *Adv. Mater.* **2012**, *24*, 4151-4156.
- [41] Zhu, Y.; Zhou, Y.; Utama, M. I. B.; de la Mata, M.; Zhao, Y.; Zhang, Q.; Peng, B.; Magen, C.; Arbiol, J.; Xiong, Q. H. Solution phase van der Waals epitaxy of ZnO wire arrays. *Nanoscale* **2013**, *5*, 7242-7249.
- [42] Schlaf, R.; Lang, O.; Pettenkofer, C.; Jaegermann, W. Band lineup of layered semiconductor heterointerfaces by van der Waals epitaxy: Charge transfer correction term for the electron affinity rule. *J. Appl. Phys.* **1999**, *85*, 2732.
- [43] Zhang, Y.; Chang, T.-R.; Zhou, B.; Cui, Y.-T.; Yan, H.; Liu, Z.; Schmitt, F.; Lee, J.; Moore, R.; Chen, Y.; Lin, H.; Jeng, H.-T.; Mo, S.-K.; Hussain, Z.; Bansil, A.; Shen, Z.-X. Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoSe₂. *Nature Nanotech.* **2014**, *9*, 111-115.
- [44] Zhan, Y.; Liu, Z.; Najmaei, S.; Ajayan, P. M.; Lou, J. Large-area vapor-phase growth and characterization of MoS₂ atomic layers on a SiO₂ substrate. *Small* **2012**, *8*, 966-971.
- [45] Kang, K.; Xie, S.; Huang, L.; Han, Y.; Huang, P. Y.; Mak, K. F.; Kim, C.-J.; Muller, D.; Park, J. High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity. *Nature* **2015**, *520*, 656-660.
- [46] Lin, Y. C.; Zhang, W.; Huang, J. K.; Liu, K. K.; Lee, Y. H.; Liang, C. T.; Chu, C. W.; Li, L. J. Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization. *Nanoscale* **2012**, *4*, 6637-6641.
- [47] Elias, A. L.; Perea-Lopez, N.; Castro-Beltran, A.; Berkdemir, A.; Lv, R.; Feng, S.; Pradhan, N. R.; Balicas, L.; Mallouk, T. E.; Lopez-Urias, F.; Terrones, H.; Terrones, M. Controlled synthesis and transfer of large-area WS₂ sheets: from single layer to few layers. *ACS Nano* **2013**, *7*, 5235-5242.
- [48] Liu, K. K.; Zhang, W.; Lee, Y. H.; Lin, Y. C.; Chang, M. T.; Su, C. Y.; Chang, C. S.; Li, H.; Shi, Y.; Zhang, H.; Lai, C. S.; Li, L. J. Growth of large-area and highly crystalline MoS₂ thin layers on insulating substrates. *Nano Lett.* **2012**, *12*, 1538-1544.
- [49] Song, J.-G.; Park, J.; Lee, W.; Choi, T.; Jung, H.; Lee, W. W.; Hwang, S.-H.; Myoung, J. M.; Jung, J.-H.; Kim, S.-H.; Lansalot-Matras, C.; Kim, H. Layer-controlled, wafer-scale, and conformal synthesis of tungsten disulfide nanosheets using atomic layer deposition. *ACS Nano* **2013**, *7*, 11333-11340.
- [50] Wang, X.; Feng, H.; Wu, Y.; Jiao, L. Controlled synthesis of highly crystalline MoS₂ flakes by chemical vapor deposition. *J. Am. Chem. Soc.* **2013**, *135*, 5304-5307.
- [51] Lee, Y. H.; Zhang, X. Q.; Zhang, W.; Chang, M. T.; Lin, C. T.; Chang, K. D.; Yu, Y. C.; Wang, J. T.; Chang, C. S.; Li, L. J.; Lin, T. W. Synthesis of large-area MoS₂ atomic layers with chemical vapor deposition. *Adv. Mater.* **2012**, *24*, 2320-2325.
- [52] Najmaei, S.; Liu, Z.; Zhou, W.; Zhou, X.; Shi, G.; Lei, S.; Yakobson, B. I.; Idrobo, J.-C.; Ajayan, P. M.; Lou, J. Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nature Mater.* **2013**, *12*, 754-759.
- [53] van der Zande, A. M.; Huang, P. Y.; Chenet, D. A.; Berkelbach, T. C.; You, Y. M.; Lee, G. H.; Heinz, T. F.; Reichman, D. R.; Muller, D. A.; Hone, J. C. Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide. *Nature Mater.* **2013**, *12*, 554-561.
- [54] Shaw, J. C.; Zhou, H.; Chen, Y.; Weiss, N. O.; Liu, Y.; Huang, Y.; Duan, X. Chemical vapor deposition growth of monolayer MoSe₂ nanosheets. *Nano Res.* **2014**, *7*, 1-7.

- [55] Lu, X.; Utama, M. I. B.; Lin, J.; Gong, X.; Zhang, J.; Zhao, Y.; Pantelides, S. T.; Wang, J.; Dong, Z.; Liu, Z.; Zhou, W.; Xiong, Q. H. Large-area synthesis of Monolayer and Few-layer MoSe₂ Films on Silicon Substrates. *Nano Lett.* **2014**, *14*, 2419-2425.
- [56] Wang, X.; Gong, Y.; Shi, G.; Chow, W. L.; Keyshar, K.; Ye, G.; Vajtai, R.; Lou, J.; Liu, Z.; Ringe, E.; Tay, B. K.; Ajayan, P. M. Chemical Vapor Deposition Growth of Crystalline Monolayer MoSe₂. *ACS Nano* **2014**, *8*, 5125-5131.
- [57] Utama, M. I. B.; Lu, X.; Zhan, D.; Ha, S. T.; Yuan, Y.; Shen, Z.; Xiong, Q. H. Etching-free patterning method for electrical characterization of atomically thin MoSe₂ films grown by chemical vapor deposition. *Nanoscale* **2014**, *6*, 12376-12382.
- [58] Xia, J.; Huang, X.; Liu, L.-Z.; Wang, M.; Wang, L.; Huang, B.; Zhu, D.-D.; Li, J.-J.; Gu, C.-Z.; Meng, X.-M. CVD synthesis of large-area, highly crystalline MoSe₂ atomic layers on diverse substrates and application to photodetectors. *Nanoscale* **2014**, *6*, 8949-8955.
- [59] Zhang, Y.; Ji, Q.; Ju, J.; Yuan, H.; Shi, J.; Gao, T.; Ma, D.; Liu, M.; Chen, Y.; Song, X.; Hwang, H. Y.; Cui, Y.; Liu, Z. Controlled Growth of High-Quality Monolayer WS₂ Layers on Sapphire and Imaging Its Grain Boundary. *ACS Nano* **2013**, *7*, 8963-8971.
- [60] Lee, Y. H.; Yu, L.; Wang, H.; Fang, W.; Ling, X.; Shi, Y.; Lin, C. T.; Huang, J. K.; Chang, M. T.; Chang, C. S.; Dresselhaus, M.; Palacios, T.; Li, L. J.; Kong, J. Synthesis and transfer of single-layer transition metal disulfides on diverse surfaces. *Nano Lett.* **2013**, *13*, 1852-1857.
- [61] Cong, C.; Shang, J.; Wu, X.; Cao, B.; Peimyoo, N.; Qiu, C.; Sun, L.; Yu, T. Synthesis and Optical Properties of Large-Area Single-Crystalline 2D Semiconductor WS₂ Monolayer from Chemical Vapor Deposition. *Adv. Opt. Mater.* **2014**, *2*, 131-136.
- [62] Huang, J.-K.; Pu, J.; Hsu, C.-L.; Chiu, M.-H.; Juang, Z.-Y.; Chang, Y.-H.; Chang, W.-H.; Iwasa, Y.; Takenobu, T.; Li, L.-J. Large-Area Synthesis of Highly Crystalline WSe₂ Monolayers and Device Applications. *ACS Nano* **2014**, *8*, 923-930.
- [63] Zhou, H.; Wang, C.; Shaw, J. C.; Cheng, R.; Chen, Y.; Huang, X.; Liu, Y.; Weiss, N. O.; Lin, Z.; Huang, Y.; Duan, X. Large Area Growth and Electrical Properties of p-Type WSe₂ Atomic Layers. *Nano Lett.* **2015**, *15*, 709-713.
- [64] Shi, Y.; Zhou, W.; Lu, A. Y.; Fang, W.; Lee, Y. H.; Hsu, A. L.; Kim, S. M.; Kim, K. K.; Yang, H. Y.; Li, L. J.; Idrobo, J. C.; Kong, J. van der Waals epitaxy of MoS₂ layers using graphene as growth templates. *Nano Lett.* **2012**, *12*, 2784-2791.
- [65] Ji, Q.; Zhang, Y.; Gao, T.; Ma, D.; Liu, M.; Chen, Y.; Qiao, X.; Tan, P. H.; Kan, M.; Feng, J.; Sun, Q.; Liu, Z. Epitaxial Monolayer MoS₂ on Mica with Novel Photoluminescence. *Nano Lett.* **2013**, *13*, 3870-3877.
- [66] Mann, J.; Ma, Q.; Odenthal, P. M.; Isarraraz, M.; Le, D.; Preciado, E.; Barroso, D.; Yamaguchi, K.; Palacio, G. v. S.; Andrew, N.; Tai, T.; Wurch, M.; Ariana, N.; Klee, V.; Bobek, S.; Sun, D.; Heinz, T. F.; Rahman, T. S.; Kawakami, R.; Bartels, L. 2-Dimensional Transition Metal Dichalcogenides with Tunable Direct Band Gaps: MoS_{2(1-x)}Se_{2x} Monolayers. *Adv. Mater.* **2014**, *26*, 1399-1404.
- [67] Gong, Y.; Liu, Z.; Lupini, A. R.; Shi, G.; Lin, J.; Najmaei, S.; Lin, Z.; Elias, A. L.; Berkdemir, A.; You, G.; Terrones, H.; Terrones, M.; Vajtai, R.; Pantelides, S. T.; Pennycook, S. J.; Lou, J.; Zhou, W.; Ajayan, P. M. Band Gap Engineering and Layer-by-Layer Mapping of Selenium-Doped Molybdenum Disulfide. *Nano Lett.* **2014**, *14*, 442-449.
- [68] Tongay, S.; Narang, D. S.; Kang, J.; Fan, W.; Ko, C.; Luce, A. V.; Wang, K. X.; Suh, J.; Patel, K. D.; Pathak, V. M.; Li, J.; Wu, J. Two-dimensional semiconductor alloys: Monolayer Mo_{1-x}W_xSe₂. *Appl. Phys. Lett.* **2014**, *104*, 012101.
- [69] Li, H.; Duan, X.; Wu, X.; Zhuang, X.; Zhou, H.; Zhang, Q.; Zhu, X.; Hu, W.; Ren, P.; Guo, P.; Ma, L.; Fan, X.; Wang, X.; Xu, J.; Pan, A.; Duan, X. Growth of Alloy MoS_{2x}Se_{2(1-x)} Nanosheets with Fully

- Tunable Chemical Compositions and Optical Properties. *J. Am. Chem. Soc.* **2014**, *136*, 3756-3759.
- [70] Su, S.-H.; Hsu, Y.-T.; Chang, Y.-H.; Chiu, M.-H.; Hsu, C.-L.; Hsu, W.-T.; Chang, W.-H.; He, J.-H.; Li, L.-J. Band Gap-Tunable Molybdenum Sulfide Selenide Monolayer Alloy. *Small* **2014**, *10*, 2589-2594.
- [71] Zheng, S.; Sun, L.; Yin, T.; Dubrovkin, A. M.; Liu, F.; Liu, Z.; Shen, Z. X.; Fan, H. J. Monolayers of $W_xMo_{1-x}S_2$ alloy heterostructure with in-plane composition variations. *Appl. Phys. Lett.* **2015**, *106*, 063113.
- [72] Duan, X.; Wang, C.; Shaw, J. C.; Cheng, R.; Chen, Y.; Li, H.; Wu, X.; Tang, Y.; Zhang, Q.; Pan, A.; Jiang, J.; Yu, R.; Huang, Y.; Duan, X. Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions. *Nature Nanotech.* **2014**, *9*, 1024-1030.
- [73] Huang, C.; Wu, S.; Sanchez, A. M.; Peters, J. J. P.; Beanland, R.; Ross, J. S.; Rivera, P.; Yao, W.; Cobden, D. H.; Xu, X. Lateral heterojunctions within monolayer $MoSe_2$ - WSe_2 semiconductors. *Nature Mater.* **2014**, *13*, 1096-1101.
- [74] Gong, Y.; Lin, J.; Wang, X.; Shi, G.; Lei, S.; Lin, Z.; Zou, X.; Ye, G.; Vajtai, R.; Yakobson, B. I.; Terrones, H.; Terrones, M.; Tay, B. K.; Lou, J.; Pantelides, S. T.; Liu, Z.; Zhou, W.; Ajayan, P. M. Vertical and in-plane heterostructures from WS_2 / MoS_2 monolayers. *Nature Mater.* **2014**, *13*, 1135-1142.
- [75] Li, M.-Y.; Shi, Y.; Cheng, C.-C.; Lu, L.-S.; Lin, Y.-C.; Tang, H.-L.; Tsai, M.-L.; Chu, C.-W.; Wei, K.-H.; He, J.-H.; Chang, W.-H.; Suenaga, K.; Li, L.-J. Epitaxial growth of a monolayer WSe_2 - MoS_2 lateral p-n junction with an atomically sharp interface. *Science* **2015**, *349*, 524-528.
- [76] Gong, Y.; Lei, S.; Ye, G.; Li, B.; He, Y.; Keyshar, K.; Zhang, X.; Wang, Q.; Lou, J.; Liu, Z.; Vajtai, R.; Zhou, W.; Ajayan, P. M. Two-Step Growth of Two-Dimensional WSe_2 / $MoSe_2$ Heterostructures. *Nano Lett.* **2015**, *15*, 6135-6141.
- [77] Ling, X.; Lee, Y.-H.; Lin, Y.; Fang, W.; Yu, L.; Dresselhaus, M. S.; Kong, J. Role of the Seeding Promoter in MoS_2 Growth by Chemical Vapor Deposition. *Nano Lett.* **2014**, *14*, 464-472.
- [78] Utama, M. I. B.; Lu, X.; Yuan, Y.; Xiong, Q. H. Detrimental influence of catalyst seeding on the device properties of CVD-grown 2D layered materials: A case study on $MoSe_2$. *Appl. Phys. Lett.* **2014**, *105*, 253102.
- [79] Jeon, J.; Jang, S. K.; Jeon, S. M.; Jang, G. Y. H.; Park, J.-H.; Lee, S. Layer-controlled CVD growth of large-area two-dimensional MoS_2 films. *Nanoscale* **2015**, *7*, 1688-1695.
- [80] Yu, Y.; Li, C.; Liu, Y.; Su, L.; Zhang, Y.; Cao, L. Controlled scalable synthesis of uniform, high-quality monolayer and few-layer MoS_2 films. *Sci. Rep.* **2013**, *3*, 1866.
- [81] Baroni, S.; Corso, A. D.; de Gironcoli, S.; Giannozzi, P.; Cavazzoni, C.; Ballabio, G.; Scandolo, S.; Chiarotti, G.; Focher, P.; Pasquarello, A.; Laasonen, K.; Trave, A.; Car, R.; Marzari, N.; Kokaji, A. Plane-Wave Self-Consistent Field Home Page. <http://www.pwscf.org>.
- [82] Zhao, W.; Ribeiro, R. M.; Toh, M.; Carvalho, A.; Kloc, C.; Castro Neto, A. H.; Eda, G. Origin of Indirect Optical Transitions in Few-Layer MoS_2 , WS_2 , and WSe_2 . *Nano Lett.* **2013**, *13*, 5627-5634.
- [83] Pei, J.; Yang, J.; Xu, R.; Zeng, Y.-H.; Myint, Y. W.; Zhang, S.; Zheng, J.-C.; Qin, Q.; Wang, X.; Jiang, W.; Lu, Y. Exciton and Trion Dynamics in Bilayer MoS_2 . *Small* **2015**, *11*, 6384-6390.
- [84] Kang, J.; Tongay, S.; Zhou, J.; Li, J.; Wu, J. Band offsets and heterostructures of two-dimensional semiconductors. *Appl. Phys. Lett.* **2013**, *102*, 012111.
- [85] Xiao, D.; Liu, G.-B.; Feng, W.; Xu, X.; Yao, W. Coupled Spin and Valley Physics in Monolayers of MoS_2 and Other Group-VI Dichalcogenides. *Phys. Rev. Lett.* **2012**, *108*, 196802.
- [86] Zhu, Z. Y.; Cheng, Y. C.; Schwingenschlögl, U. Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors. *Phys. Rev. B* **2011**, *84*, 153402.
- [87] Kosmider, K.; Gonzalez, J. W.; Fernandez-Rossier, J. Large spin splitting in the conduction band of transition metal dichalcogenide monolayers. *Phys. Rev. B* **2013**, *88*, 245436.
- [88] Mak, K. F.; He, K.; Shan, J.; Heinz, T. F. Control of valley polarization in monolayer MoS_2 by optical

- helicity. *Nature Nanotech.* **2012**, *7*, 494-498.
- [89] Xiao, D.; Yao, W.; Niu, Q. Valley-contrasting physics in graphene: Magnetic moment and topological transport. *Phys. Rev. Lett.* **2007**, *99*, 236809.
- [90] Yao, W.; Xiao, D.; Niu, Q. Valley-dependent optoelectronics from inversion symmetry breaking. *Phys. Rev. B* **2008**, *77*, 235406.
- [91] Cao, T.; Wang, G.; Han, W.; Ye, H.; Zhu, C.; Shi, J.; Niu, Q.; Tan, P.; Wang, E.; Liu, B.; Feng, J. Valley-selective circular dichroism of monolayer molybdenum disulphide. *Nat. Commun.* **2012**, *3*, 887.
- [92] Kioseoglou, G.; Hanbicki, A. T.; Currie, M.; Friedman, A. L.; Gunlycke, D.; Jonker, B. T. Valley polarization and intervalley scattering in monolayer MoS₂. *Appl. Phys. Lett.* **2012**, *101*, 221907.
- [93] Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X. Valley polarization in MoS₂ monolayers by optical pumping. *Nature Nanotech.* **2012**, *7*, 490-493.
- [94] Li, P.; Song, Y.; Dery, H. Intrinsic spin lifetime of conduction electrons in germanium. *Phys. Rev. B* **2012**, *86*, 085202.
- [95] Wakabayashi, N.; Smith, H. G.; Nicklow, R. M. Lattice-dynamics of hexagonal MoS₂ studied by neutron-scattering. *Phys. Rev. B* **1975**, *12*, 659-663.
- [96] Sandoval, S. J.; Yang, D.; Frindt, R. F.; Irwin, J. C. Raman-study and lattice-dynamics of single molecular layers of MoS₂. *Phys. Rev. B* **1991**, *44*, 3955-3962.
- [97] Parsons, R. R. Band-to-band optical pumping in solids and polarized photoluminescence. *Phys. Rev. Lett.* **1969**, *23*, 1152-1154.
- [98] Wu, S.; Ross, J. S.; Liu, G.-B.; Aivazian, G.; Jones, A.; Fei, Z.; Zhu, W.; Xiao, D.; Yao, W.; Cobden, D.; Xu, X. Electrical tuning of valley magnetic moment through symmetry control in bilayer MoS₂. *Nature Phys.* **2013**, *9*, 149-153.
- [99] Jones, A. M.; Yu, H.; Ross, J. S.; Klement, P.; Ghimire, N. J.; Yan, J.; Mandrus, D. G.; Yao, W.; Xu, X. Spin-layer locking effects in optical orientation of exciton spin in bilayer WSe₂. *Nature Phys.* **2014**, *10*, 130-134.
- [100] Suzuki, R.; Sakano, M.; Zhang, Y. J.; Akashi, R.; Morikawa, D.; Harasawa, A.; Yaji, K.; Kuroda, K.; Miyamoto, K.; Okuda, T.; Ishizaka, K.; Arita, R.; Iwasa, Y. Valley-dependent spin polarization in bulk MoS₂ with broken inversion symmetry. *Nature Nanotech.* **2014**, *9*, 611-617.
- [101] Li, Y.; Rao, Y.; Mak, K. F.; You, Y.; Wang, S.; Dean, C. R.; Heinz, T. F. Probing Symmetry Properties of Few-Layer MoS₂ and h-BN by Optical Second-Harmonic Generation. *Nano Lett.* **2013**, *13*, 3329-3333.
- [102] Yu, H.; Talukdar, D.; Xu, W.; Khurgin, J. B.; Xiong, Q. Charge-Induced Second-Harmonic Generation in Bilayer WSe₂. *Nano Lett.* **2015**, *15*, 5653-5657.
- [103] Seyler, K. L.; Schaibley, J. R.; Gong, P.; Rivera, P.; Jones, A. M.; Wu, S. F.; Yan, J. Q.; Mandrus, D. G.; Yao, W.; Xu, X. D. Electrical control of second-harmonic generation in a WSe₂ monolayer transistor. *Nat. Nanotech.* **2015**, *10*, 407-411.
- [104] Levine, B. F. Bond-charge calculation of nonlinear optical susceptibilities for various crystal-structures. *Phys. Rev. B* **1973**, *7*, 2600-2626.
- [105] Wilson, J.; Yoffe, A. The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Adv. Phys.* **1969**, *18*, 193-335.
- [106] Verble, J. L.; Wieting, T. J. Lattice mode degeneracy in MoS₂ and other layer compounds. *Phys. Rev. Lett.* **1970**, *25*, 362-365.
- [107] Wieting, T. J.; Verble, J. L. Infrared and Raman studies of long-wavelength optical phonons in hexagonal MoS₂. *Phys. Rev. B* **1971**, *3*, 4286-4292.
- [108] Wieting, T. J. Long-wavelength lattice-vibrations of MoS₂ and GaSe *Solid State Commun.* **1973**, *12*,

931-935.

- [109] Ghosh, P. N.; Maiti, C. R. Interlayer force and Davydov splitting in 2H-MoS₂ *Phys. Rev. B* **1983**, *28*, 2237-2239.
- [110] Boker, T.; Severin, R.; Muller, A.; Janowitz, C.; Manzke, R.; Voss, D.; Kruger, P.; Mazur, A.; Pollmann, J. Band structure of MoS₂, MoSe₂, and alpha-MoTe₂: Angle-resolved photoelectron spectroscopy and ab initio calculations. *Phys. Rev. B* **2001**, *64*, 235305.
- [111] Sugai, S.; Ueda, T. High-pressure Raman-spectroscopy in the layered materials 2H-MoS₂, 2H-MoSe₂ and 2H-MoTe₂. *Phys. Rev. B* **1982**, *26*, 6554-6558.
- [112] Sekine, T.; Nakashizu, T.; Toyoda, K.; Uchinokura, K.; Matsuura, E. Raman-scattering in layered compound 2H-WS₂. *Solid State Commun.* **1980**, *35*, 371-373.
- [113] Sourisseau, C.; Cruege, F.; Fouassier, M.; Alba, M. Second-order Raman effects, inelastic neutron-scattering and lattice-dynamics in 2H-WS₂. *Chem. Phys.* **1991**, *150*, 281-293.
- [114] Chen, J. M.; Wang, C. S. Second-order Raman-spectrum of MoS₂. *Solid State Commun.* **1974**, *14*, 857-860.
- [115] Frey, G. L.; Tenne, R.; Matthews, M. J.; Dresselhaus, M. S.; Dresselhaus, G. Raman and resonance Raman investigation of MoS₂ nanoparticles. *Phys. Rev. B* **1999**, *60*, 2883-2892.
- [116] Frey, G. L.; Tenne, R.; Matthews, M. J.; Dresselhaus, M. S.; Dresselhaus, G. Optical properties of MS₂ (M = Mo, W) inorganic fullerene-like and nanotube material optical absorption and resonance Raman measurements. *J. Mater. Res.* **1998**, *13*, 2412-2417.
- [117] Ferrari, A. C.; Basko, D. M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nature Nanotech.* **2013**, *8*, 235-246.
- [118] Zhao, Y.; Luo, X.; Li, H.; Zhang, J.; Araujo, P. T.; Gan, C. K.; Wu, J.; Zhang, H.; Quek, S. Y.; Dresselhaus, M. S.; Xiong, Q. H. Interlayer breathing and shear modes in few-trilayer MoS₂ and WSe₂. *Nano Lett.* **2013**, *13*, 1007-1015.
- [119] Michel, K. H.; Verberck, B. Theory of rigid-plane phonon modes in layered crystals. *Phys. Rev. B* **2012**, *85*, 094303.
- [120] Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂. *ACS Nano* **2010**, *4*, 2695-2700.
- [121] Luo, X.; Zhao, Y.; Zhang, J.; Toh, M.; Kloc, C.; Xiong, Q.; Quek, S. Y. Effects of lower symmetry and dimensionality on Raman spectra in two-dimensional WSe₂. *Phys. Rev. B* **2013**, *88*, 195313.
- [122] Luo, X.; Zhao, Y.; Zhang, J.; Xiong, Q.; Quek, S. Y. Anomalous frequency trends in MoS₂ thin films attributed to surface effects. *Phys. Rev. B* **2013**, *88*, 075320.
- [123] Mrstik, B.; Kaplan, R.; Reinecke, T.; Van Hove, M.; Tong, S. Surface-structure determination of the layered compounds MoS₂ by low-energy electron diffraction. *Phys. Rev. B* **1977**, *15*, 897-900.
- [124] Nemanich, R.; Lucovsky, G.; Solin, S. Long Wavelength Lattice Vibrations of Graphite. *Proc. of the International Conference on Lattice Dynamics* **1977**, Flammarion, Paris, France, pp 619-621.
- [125] Verble, J.; Wietling, T.; Reed, P. Rigid-layer lattice vibrations and van der waals bonding in hexagonal MoS₂. *Solid State Commun.* **1972**, *11*, 941-944.
- [126] Sekine, T.; Izumi, M.; Nakashizu, T.; Uchinokura, K.; Matsuura, E. Raman-scattering and Infrared reflectance in 2H-MoSe₂ *J. Phys. Soc. Jpn* **1980**, *49*, 1069-1077.
- [127] Mead, D. G.; Irwin, J. C. Long wavelength of optic phonons in WSe₂. *Can. J. Phys.* **1977**, *55*, 379-382.
- [128] Zhao, Y.; Luo, X.; Zhang, J.; Wu, J.; Bai, X.; Wang, M.; Jia, J.; Peng, H.; Liu, Z.; Quek, S. Y.; Xiong, Q. Interlayer vibrational modes in few-quintuple-layer Bi₂Te₃ and Bi₂Se₃ two-dimensional crystals: Raman spectroscopy and first-principles studies. *Phys. Rev. B* **2014**, *90*, 245428
- [129] Kappera, R.; Voiry, D.; Yalcin, S. E.; Branch, B.; Gupta, G.; Mohite, A. D.; Chhowalla, M.

- Phase-engineered low-resistance contacts for ultrathin MoS₂ transistors. *Nature Mater.* **2014**, *13*, 1128–1134.
- [130] Poretzky, A. A.; Liang, L.; Li, X.; Xiao, K.; Sumpter, B. G.; Meunier, V.; Geohegan, D. B. Twisted MoSe₂ Bilayers with Variable Local Stacking and Interlayer Coupling Revealed by Low-Frequency Raman Spectroscopy *ACS Nano* **2016**, *10*, 2736–2744.
- [131] Tan, P.-H.; Wu, J.-B.; Han, W.-P.; Zhao, W.-J.; Zhang, X.; Wang, H.; Wang, Y.-F. Ultralow-frequency shear modes of 2-4 layer graphene observed in scroll structures at edges. *Phys. Rev. B* **2014**, *89*, 235404.
- [132] Cong, C.; Yu, T. Enhanced ultra-low-frequency interlayer shear modes in folded graphene layers. *Nat. Commun.* **2014**, *5*, 4709.
- [133] Poretzky, A. A.; Liang, L.; Li, X.; Xiao, K.; Wang, K.; Mahjouri-Samani, M.; Basile, L.; Idrobo, J. C.; Sumpter, B. G.; Meunier, V.; Geohegan, D. B. Low-Frequency Raman Fingerprints of Two-Dimensional Metal Dichalcogenide Layer Stacking Configurations. *ACS Nano* **2015**, *9*, 6333–6342.
- [134] Lu, X.; Utama, M. I. B.; Lin, J.; Luo, X.; Zhao, Y.; Zhang, J.; Pantelides, S. T.; Zhou, W.; Quek, S. Y.; Xiong, Q. H. Rapid and Nondestructive Identification of Polytypism and Stacking Sequences in Few-Layer Molybdenum Diselenide by Raman Spectroscopy. *Adv. Mater.* **2015**, *27*, 4502–4508.
- [135] Chen, S.-Y.; Zheng, C.; Fuhrer, M. S.; Yan, J. Helicity-Resolved Raman Scattering of MoS₂, MoSe₂, WS₂, and WSe₂ Atomic Layers. *Nano Lett.* **2015**, *15*, 2526–2532.
- [136] Wu, J.; Mao, N.; Xie, L.; Xu, H.; Zhang, J. Identifying the Crystalline Orientation of Black Phosphorus Using Angle-Resolved Polarized Raman Spectroscopy. *Angew. Chem. Int. Ed.* **2015**, *54*, 2366–2369.
- [137] Wang, Y.; Cong, C.; Qiu, C.; Yu, T. Raman Spectroscopy Study of Lattice Vibration and Crystallographic Orientation of Monolayer MoS₂ under Uniaxial Strain. *Small* **2013**, *9*, 2857–2861.
- [138] Chakraborty, B.; Bera, A.; Muthu, D. V. S.; Bhowmick, S.; Waghmare, U. V.; Sood, A. K. Symmetry-dependent phonon renormalization in monolayer MoS₂ transistor. *Phys. Rev. B* **2012**, *85*, 161403(R).
- [139] Carvalho, B. R.; Malard, L. M.; Alves, J. M.; Fantini, C.; Pimenta, M. A. Symmetry-Dependent Exciton-Phonon Coupling in 2D and Bulk MoS₂ Observed by Resonance Raman Scattering. *Phys. Rev. Lett.* **2015**, *114*, 136403.
- [140] Lee, J.-U.; Park, J.; Son, Y.-W.; Cheong, H. Anomalous excitonic resonance Raman effects in few-layered MoS₂. *Nanoscale* **2015**, *7*, 3229–3236.
- [141] Ribeiro, H. B.; Pimenta, M. A.; de Matos, C. J. S.; Moreira, R. L.; Rodin, A. S.; Zapata, J. D.; de Souza, E. A. T.; Castro Neto, A. H. Unusual Angular Dependence of the Raman Response in Black Phosphorus. *ACS Nano* **2015**, *9*, 4270–4276.
- [142] Kalbac, M.; Farhat, H.; Kavan, L.; Kong, J.; Sasaki, K.-i.; Saito, R.; Dresselhaus, M. S. Electrochemical Charging of Individual Single-Walled Carbon Nanotubes. *ACS Nano* **2009**, *3*, 2320–2328.
- [143] Britnell, L.; Ribeiro, R. M.; Eckmann, A.; Jalil, R.; Belle, B. D.; Mishchenko, A.; Kim, Y. J.; Gorbachev, R. V.; Georgiou, T.; Morozov, S. V.; Grigorenko, A. N.; Geim, A. K.; Casiraghi, C.; Castro Neto, A. H.; Novoselov, K. S. Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films. *Science* **2013**, *340*, 1311–1314.
- [144] Carvalho, A.; Ribeiro, R. M.; Castro Neto, A. H. Band nesting and the optical response of two-dimensional semiconducting transition metal dichalcogenides. *Phys. Rev. B* **2013**, *88*, 115205.
- [145] Utama, M. I. B.; Zhang, Q.; Zhang, J.; Yuan, Y.; Belarri, F. J.; Arbiol, J.; Xiong, Q. H. Recent developments and future directions in the growth of nanostructures by van der Waals epitaxy. *Nanoscale* **2013**, *5*, 3570–3588.

- [146] Loudon, R. The Raman effect in crystals. *Adv. Phys.* **2001**, *50*, 813-864.
- [147] Tan, P. H.; Han, W. P.; Zhao, W. J.; Wu, Z. H.; Chang, K.; Wang, H.; Wang, Y. F.; Bonini, N.; Marzari, N.; Pugno, N.; Savini, G.; Lombardo, A.; Ferrari, A. C. The shear mode of multilayer graphene. *Nature Mater.* **2012**, *11*, 294-300.
- [148] Lui, C. H.; Ye, Z.; Keiser, C.; Xiao, X.; He, R. Temperature-Activated Layer-Breathing Vibrations in Few-Layer Graphene. *Nano Lett.* **2014**, *14*, 4615-4621.
- [149] Lui, C. H.; Ye, Z.; Keiser, C.; Barros, E. B.; He, R. Stacking-dependent shear modes in trilayer graphene. *Appl. Phys. Lett.* **2015**, *106*, 041904
- [150] Blake, P.; Hill, E. W.; Castro Neto, A. H.; Novoselov, K. S.; Jiang, D.; Yang, R.; Booth, T. J.; Geim, A. K. Making graphene visible. *Appl. Phys. Lett.* **2007**, *91*, 063124.
- [151] Ni, Z. H.; Wang, H. M.; Kasim, J.; Fan, H. M.; Yu, T.; Wu, Y. H.; Feng, Y. P.; Shen, Z. X. Graphene thickness determination using reflection and contrast spectroscopy. *Nano Lett.* **2007**, *7*, 2758-2763.
- [152] Wang, Y. Y.; Gao, R. X.; Ni, Z. H.; He, H.; Guo, S. P.; Yang, H. P.; Cong, C. X.; Yu, T. Thickness identification of two-dimensional materials by optical imaging. *Nanotechnology* **2012**, *23*.
- [153] Wang, X.; Zhao, M.; Nolte, D. D. Optical contrast and clarity of graphene on an arbitrary substrate. *Appl. Phys. Lett.* **2009**, *95*, 081102.
- [154] Yoon, D.; Moon, H.; Son, Y.-W.; Choi, J. S.; Park, B. H.; Cha, Y. H.; Kim, Y. D.; Cheong, H. Interference effect on Raman spectrum of graphene on SiO₂/Si. *Phys. Rev. B* **2009**, *80*, 125422.
- [155] Xu, K.; Heath, J. R. WETTING Contact with what? *Nature Mater.* **2013**, *12*, 872-873.
- [156] Chow, P. K.; Singh, E.; Viana, B. C.; Gao, J.; Luo, J.; Li, J.; Lin, Z.; Elias, A. L.; Shi, Y.; Wang, Z.; Terrones, M.; Koratkar, N. Wetting of Mono and Few-Layered WS₂ and MoS₂ Films Supported on Si/SiO₂ Substrates. *ACS Nano* **2015**, *9*, 3023-3031.
- [157] Castellanos-Gomez, A.; Vicarelli, L.; Prada, E.; Island, J. O.; Narasimha-Acharya, K. L.; Blanter, S. I.; Groenendijk, D. J.; Buscema, M.; Steele, G. A.; Alvarez, J. V.; Zandbergen, H. W.; Palacios, J. J.; van der Zant, H. S. J. Isolation and characterization of few-layer black phosphorus. *2D Mater.* **2014**, *1*.
- [158] Island, J. O.; Steele, G. A.; van der Zant, H. S. J.; Castellanos-Gomez, A. Environmental instability of few-layer black phosphorus. *2D Mater.* **2015**, *2*.
- [159] Luo, X.; Lu, X.; Koon, G. K. W.; Neto, A. H. C.; Oezylmaz, B.; Xiong, Q. H.; Quek, S. Y. Large Frequency Change with Thickness in Interlayer Breathing Mode-Significant Interlayer Interactions in Few Layer Black Phosphorus. *Nano Lett.* **2015**, *15*, 3931-3938.
- [160] Ling, X.; Liang, L.; Huang, S.; Piretzky, A. A.; Geohegan, D. B.; Sumpter, B. G.; Kong, J.; Meunier, V.; Dresselhaus, M. S. Low-Frequency Interlayer Breathing Modes in Few-Layer Black Phosphorus. *Nano Lett.* **2015**, *15*, 4080-4088.
- [161] Castellanos-Gomez, A.; Agrait, N.; Rubio-Bollinger, G. Optical identification of atomically thin dichalcogenide crystals. *Appl. Phys. Lett.* **2010**, *96*, 213116.
- [162] Li, H.; Wu, J.; Huang, X.; Lu, G.; Yang, J.; Lu, X.; Xiong, Q. H.; Zhang, H. Rapid and Reliable Thickness Identification of Two-Dimensional Nanosheets Using Optical Microscopy. *ACS Nano* **2013**, *7*, 10344-10353.
- [163] Fang, H.; Battaglia, C.; Carraro, C.; Nemsak, S.; Ozdol, B.; Kang, J. S.; Bechtel, H. A.; Desai, S. B.; Kronast, F.; Unal, A. A.; Conti, G.; Conlon, C.; Palsson, G. K.; Martin, M. C.; Minor, A. M.; Fadley, C. S.; Yablonovitch, E.; Maboudian, R.; Javey, A. Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 6198-6202.
- [164] Withers, F.; Del Pozo-Zamudio, O.; Mishchenko, A.; Rooney, A. P.; Gholinia, A.; Watanabe, K.; Taniguchi, T.; Haigh, S. J.; Geim, A. K.; Tartakovskii, A. I.; Novoselov, K. S. Light-emitting diodes by

- band-structure engineering in van der Waals heterostructures. *Nature Mater.* **2015**, *14*, 301-306.
- [165] Lee, C.-H.; Lee, G.-H.; van der Zande, A. M.; Chen, W.; Li, Y.; Han, M.; Cui, X.; Arefe, G.; Nuckolls, C.; Heinz, T. F.; Guo, J.; Hone, J.; Kim, P. Atomically thin p-n junctions with van der Waals heterointerfaces. *Nature Nanotech.* **2014**, *9*, 676-681.
- [166] Rivera, P.; Schaibley, J. R.; Jones, A. M.; Ross, J. S.; Wu, S.; Aivazian, G.; Klement, P.; Seyler, K.; Clark, G.; Ghimire, N. J.; Yan, J.; Mandrus, D. G.; Yao, W.; Xu, X. Observation of long-lived interlayer excitons in monolayer MoSe₂-WSe₂ heterostructures. *Nat. Commun.* **2015**, *6*, 6242.
- [167] Hong, X.; Kim, J.; Shi, S.-F.; Zhang, Y.; Jin, C.; Sun, Y.; Tongay, S.; Wu, J.; Zhang, Y.; Wang, F. Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures. *Nature Nanotech.* **2014**, *9*, 682-686.
- [168] Lui, C. H.; Ye, Z.; Ji, C.; Chiu, K.-C.; Chou, C.-T.; Andersen, T. I.; Means-Shively, C.; Anderson, H.; Wu, J.-M.; Kidd, T.; Lee, Y.-H.; He, R. Observation of interlayer phonon modes in van der Waals heterostructures. *Phys. Rev. B* **2015**, *91*, 165403.
- [169] Tongay, S.; Fan, W.; Kang, J.; Park, J.; Koldemir, U.; Suh, J.; Narang, D. S.; Liu, K.; Ji, J.; Li, J.; Sinclair, R.; Wu, J. Tuning Interlayer Coupling in Large-Area Heterostructures with CVD-Grown MoS₂ and WS₂ Monolayers. *Nano Lett.* **2014**, *14*, 3185-3190.
- [170] Zeng, H.; Zhu, B.; Liu, K.; Fan, J.; Cui, X.; Zhang, Q. M. Low-frequency Raman modes and electronic excitations in atomically thin MoS₂ films. *Phys. Rev. B* **2012**, *86*, 241301(R).
- [171] Zhang, X.; Han, W. P.; Wu, J. B.; Milana, S.; Lu, Y.; Li, Q. Q.; Ferrari, A. C.; Tan, P. H. Raman spectroscopy of shear and layer breathing modes in multilayer MoS₂. *Phys. Rev. B* **2013**, *87*, 115413.
- [172] Zhu, C. R.; Wang, G.; Liu, B. L.; Marie, X.; Qiao, X. F.; Zhang, X.; Wu, X. X.; Fan, H.; Tan, P. H.; Amand, T.; Urbaszek, B. Strain tuning of optical emission energy and polarization in monolayer and bilayer MoS₂. *Phys. Rev. B* **2013**, *88*, 121301(R).
- [173] Yan, J.; Xia, J.; Wang, X.; Liu, L.; Kuo, J.-L.; Tay, B. K.; Chen, S.; Zhou, W.; Liu, Z.; Shen, Z. X. Stacking-Dependent Interlayer Coupling in Trilayer MoS₂ with Broken Inversion Symmetry. *Nano Lett.* **2015**, *15*, 8155-8161.
- [174] Tsirlina, T.; Feldman, Y.; Homyonfer, M.; Sloan, J.; Hutchison, J. L.; Tenne, R. Synthesis and characterization of inorganic fullerene-like WSe₂ material. *Fullerene Sci. Technol.* **1998**, *6*, 157-165.
- [175] Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* **2009**, *324*, 1312-1314.
- [176] Huang, J.; Yang, L.; Liu, D.; Chen, J.; Fu, Q.; Xiong, Y.; Lin, F.; Xiang, B. Large-area synthesis of monolayer WSe₂ on a SiO₂/Si substrate and its device applications. *Nanoscale* **2015**, *7*, 4193-4198.
- [177] Liu, B.; Fathi, M.; Chen, L.; Abbas, A.; Ma, Y.; Zhou, C. Chemical Vapor Deposition Growth of Monolayer WSe₂ with Tunable Device Characteristics and Growth Mechanism Study. *ACS Nano* **2015**, *9*, 6119-6127.
- [178] Chen, J.; Liu, B.; Liu, Y.; Tang, W.; Nai, C. T.; Li, L.; Zheng, J.; Gao, L.; Zheng, Y.; Shin, H. S.; Jeong, H. Y.; Loh, K. P. Chemical Vapor Deposition of Large-Sized Hexagonal WSe₂ Crystals on Dielectric Substrates. *Adv. Mater.* **2015**, *27*, 6722-6727.
- [179] Brooks, L. S. The Vapor Pressures of Tellurium and Selenium. *J. Am. Chem. Soc.* **1952**, *74*, 227-229.
- [180] Nellist, P. D. The principles of STEM imaging. In *Scanning transmission electron microscopy: Imaging and analysis*. S. J. Pennycook; P. D. Nellist, Eds.; Springer; New York, 2011; pp 91-115.
- [181] Zhou, W.; Zou, X.; Najmaei, S.; Liu, Z.; Shi, Y.; Kong, J.; Lou, J.; Ajayan, P. M.; Yakobson, B. I.; Idrobo, J.-C. Intrinsic Structural Defects in Monolayer Molybdenum Disulfide. *Nano Lett.* **2013**, *13*, 2615-2622.

- [182] Zou, X.; Liu, Y.; Yakobson, B. I. Predicting Dislocations and Grain Boundaries in Two-Dimensional Metal-Disulfides from the First Principles. *Nano Lett.* **2013**, *13*, 253-258.
- [183] Zhang, X.; Qiao, X.-F.; Shi, W.; Wu, J.-B.; Jiang, D.-S.; Tan, P.-H. Phonon and Raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material. *Chem. Soc. Rev.* **2015**, *44*, 2757-2785.
- [184] Wang, S.; Rong, Y.; Fan, Y.; Pacios, M.; Bhaskaran, H.; He, K.; Warner, J. H. Shape Evolution of Monolayer MoS₂ Crystals Grown by Chemical Vapor Deposition. *Chem. Mater.* **2014**, *26*, 6371-6379.
- [185] Zhao, Y.; de la Mata, M.; Qiu, R. L. J.; Zhang, J.; Wen, X.; Magen, C.; Gao, X. P. A.; Arbiol, J.; Xiong, Q. Te-seeded growth of few-quintuple layer Bi₂Te₃ nanoplates. *Nano Res.* **2014**, *7*, 1243-1253.
- [186] Tonndorf, P.; Schmidt, R.; Boettger, P.; Zhang, X.; Boerner, J.; Liebig, A.; Albrecht, M.; Kloc, C.; Gordan, O.; Zahn, D. R. T.; de Vasconcellos, S. M.; Bratschitsch, R. Photoluminescence emission and Raman response of monolayer MoS₂, MoSe₂, and WSe₂. *Opt. Express* **2013**, *21*, 4908-4916.
- [187] Tongay, S.; Zhou, J.; Ataca, C.; Lo, K.; Matthews, T. S.; Li, J.; Grossman, J. C.; Wu, J. Thermally Driven Crossover from Indirect toward Direct Bandgap in 2D Semiconductors: MoSe₂ versus MoS₂. *Nano Lett.* **2012**, *12*, 5576-5580.
- [188] Ross, J. S.; Wu, S.; Yu, H.; Ghimire, N. J.; Jones, A. M.; Aivazian, G.; Yan, J.; Mandrus, D. G.; Xiao, D.; Yao, W.; Xu, X. Electrical control of neutral and charged excitons in a monolayer semiconductor. *Nat. Commun.* **2013**, *4*, 1474.
- [189] Han, H.-V.; Lu, A.-Y.; Lu, L.-S.; Huang, J.-K.; Li, H.; Hsu, C.-L.; Lin, Y.-C.; Chiu, M.-H.; Suenaga, K.; Chu, C.-W.; Kuo, H.-C.; Chang, W.-H.; Li, L.-J.; Shi, Y. Photoluminescence Enhancement and Structure Repairing of Monolayer MoSe₂ by Hydrohalic Acid Treatment. *ACS Nano* **2016**, *10*, 1454-1461.
- [190] Lin, Y.; Ling, X.; Yu, L.; Huang, S.; Hsu, A. L.; Lee, Y.-H.; Kong, J.; Dresselhaus, M. S.; T., P. Dielectric Screening of Excitons and Trions in Single-Layer MoS₂. *Nano Lett.* **2014**, *14*, 5569-5576.
- [191] Bergman, L.; Nemanich, R. J. Raman and photoluminescence analysis of stress state and impurity distribution in diamond thin-films. *J. Appl. Phys.* **1995**, *78*, 6709-6719.
- [192] Wang, Y.; Cong, C.; Yang, W.; Shang, J.; Peimyoo, N.; Chen, Y.; Kang, J.; Wang, J.; Huang, W.; Yu, T. Strain-induced direct-indirect bandgap transition and phonon modulation in monolayer WS₂. *Nano Res.* **2015**, *8*, 2562-2572.
- [193] Bellus, M. Z.; Ceballos, F.; Chiu, H.-Y.; Zhao, H. Tightly Bound Trions in Transition Metal Dichalcogenide Heterostructures. *ACS Nano* **2015**, *9*, 6459-6464.
- [194] Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J. Tightly bound trions in monolayer MoS₂. *Nature Mater.* **2013**, *12*, 207-211.
- [195] Shang, J.; Shen, X.; Cong, C.; Peimyoo, N.; Cao, B.; Eginligil, M.; Yu, T. Observation of Excitonic Fine Structure in a 2D Transition-Metal Dichalcogenide Semiconductor. *ACS Nano* **2015**, *9*, 647-655.
- [196] Peimyoo, N.; Yang, W.; Shang, J.; Shen, X.; Wang, Y.; Yu, T. Chemically Driven Tunable Light Emission of Charged and Neutral Excitons in Mono layer WS₂. *ACS Nano* **2014**, *8*, 11320-11329.
- [197] Conley, H. J.; Wang, B.; Ziegler, J. I.; Haglund, R. F., Jr.; Pantelides, S. T.; Bolotin, K. I. Bandgap Engineering of Strained Monolayer and Bilayer MoS₂. *Nano Lett.* **2013**, *13*, 3626-3630.
- [198] Zhang, J.; Wang, J.; Chen, P.; Sun, Y.; Wu, S.; Jia, Z.; Lu, X.; Yu, H.; Chen, W.; Zhu, J.; Xie, G.; Yang, R.; Shi, D.; Xu, X.; Xiang, J.; Liu, K.; Zhang, G. Observation of Strong Interlayer Coupling in MoS₂/WS₂ Heterostructures. *Adv. Mater.* **2016**, *28*, 1950-1956.
- [199] You, Y.; Zhang, X.-X.; Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R.; Heinz, T. F. Observation of biexcitons in monolayer WSe₂. *Nature Phys.* **2015**, *11*, 477-U138.
- [200] Park, K.-D.; Khatib, O.; Kravtsov, V.; Clark, G.; Xu, X.; Raschke, M. B. Hybrid Tip-Enhanced Nanospectroscopy and Nanoimaging of Monolayer WSe₂ with Local Strain Control. *Nano Lett.*

2016, *16*, 2621-2627.

- [201] Huard, V.; Cox, R. T.; Saminadayar, K.; Arnoult, A.; Tatarenko, S. Bound states in optical absorption of semiconductor quantum wells containing a two-dimensional electron gas. *Phys. Rev. Lett.* **2000**, *84*, 187-190.
- [202] Yan, T.; Qiao, X.; Liu, X.; Tan, P.; Zhang, X. Photoluminescence properties and exciton dynamics in monolayer WSe₂. *Appl. Phys. Lett.* **2014**, *105*, 101901.
- [203] Zhu, B.; Zeng, H.; Dai, J.; Gong, Z.; Cui, X. Anomalously robust valley polarization and valley coherence in bilayer WS₂. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 11606-11611.
- [204] Olivero, J. J.; Longbothum, R. L. Empirical fits to the Voigt line width: A brief review. *J. Quant. Spectrosc. Radiat. Transfer* **1977**, *17*, 233-236.
- [205] Schmidt, T.; Lischka, K.; Zulehner, W. Excitation-power dependence of the near-band-edge photoluminescence of semiconductors. *Phys. Rev. B* **1992**, *45*, 8989-8994.
- [206] Gomis-Bresco, J.; Munoz-Matutano, G.; Martinez-Pastor, J.; Alen, B.; Seravalli, L.; Frigeri, P.; Trevisi, G.; Franchi, S. Random population model to explain the recombination dynamics in single InAs/GaAs quantum dots under selective optical pumping. *New J. Phys.* **2011**, *13*, 023022.
- [207] Tiberj, A.; Rubio-Roy, M.; Paillet, M.; Huntzinger, J. R.; Landois, P.; Mikolasek, M.; Contreras, S.; Sauvajol, J. L.; Dujardin, E.; Zahab, A. A. Reversible optical doping of graphene. *Sci. Rep.* **2013**, *3*, 2355.
- [208] Cooper, D. E.; Bajaj, J.; Newman, P. R. Photoluminescence spectroscopy of excitons for evaluation of high-quality cdte crystals. *J. Cryst. Growth* **1988**, *86*, 544-551.
- [209] Schmidt, H.; Wang, S.; Chu, L.; Toh, M.; Kumar, R.; Zhao, W.; Castro Neto, A. H.; Martin, J.; Adam, S.; Özyilmaz, B.; Eda, G. Transport Properties of Monolayer MoS₂ Grown by Chemical Vapor Deposition. *Nano Lett.* **2014**, *14*, 1909-1913.
- [210] Larentis, S.; Fallahazad, B.; Tutuc, E. Field-effect transistors and intrinsic mobility in ultra-thin MoSe₂ layers. *Appl. Phys. Lett.* **2012**, *101*, 223104.
- [211] Radisavljevic, B.; Kis, A. Mobility engineering and a metal–insulator transition in monolayer MoS₂. *Nature Mater.* **2013**, *12*, 815-820.
- [212] Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS₂ transistors. *Nature Nanotech.* **2011**, *6*, 147-150.
- [213] Das, S.; Chen, H.-Y.; Penumatcha, A. V.; Appenzeller, J. High Performance Multilayer MoS₂ Transistors with Scandium Contacts. *Nano Lett.* **2012**, *13*, 100-105.
- [214] Chen, L.; Liu, B.; Abbas, A. N.; Ma, Y.; Fang, X.; Liu, Y.; Zhou, C. Screw-Dislocation-Driven Growth of Two-Dimensional Few-Layer and Pyramid-like WSe₂ by Sulfur-Assisted Chemical Vapor Deposition. *ACS Nano* **2014**, *8*, 11543-11551.
- [215] Chen, L.; Liu, B.; Ge, M.; Ma, Y.; Abbas, A. N.; Zhou, C. Step-Edge-Guided Nucleation and Growth of Aligned WSe₂ on Sapphire via a Layer-over-Layer Growth Mode. *ACS Nano* **2015**, *9*, 8368-8375.
- [216] Wang, Z.; Saito, M.; McKenna, K. P.; Ikuhara, Y. Polymorphism of dislocation core structures at the atomic scale. *Nat. Commun.* **2014**, *5*, 3239.
- [217] Zhang, L.; Liu, K.; Wong, A. B.; Kim, J.; Hong, X.; Liu, C.; Cao, T.; Louie, S. G.; Wang, F.; Yang, P. Three-Dimensional Spirals of Atomic Layered MoS₂. *Nano Lett.* **2014**, *14*, 6418-6423.
- [218] Zhao, W.; Ghorannevis, Z.; Amara, K. K.; Pang, J. R.; Toh, M.; Zhang, X.; Kloc, C.; Tan, P. H.; Eda, G. Lattice dynamics in mono- and few-layer sheets of WS₂ and WSe₂. *Nanoscale* **2013**, *5*, 9677-9683.
- [219] Butz, B.; Dolle, C.; Niekietel, F.; Weber, K.; Waldmann, D.; Weber, H. B.; Meyer, B.; Spiecker, E. Dislocations in bilayer graphene. *Nature* **2014**, *505*, 533-537.
- [220] Zhang, X.; Han, W.-P.; Qiao, X.-F.; Tan, Q.-H.; Wang, Y.-F.; Zhang, J.; Tan, P.-H. Raman characterization of AB- and ABC-stacked few-layer graphene by interlayer shear modes. *Carbon*

2016, *99*, 118-122.

- [221] Luo, X.; Lu, X.; Cong, C.; Yu, T.; Xiong, Q.; Quek, S. Y. Stacking sequence determines Raman intensities of observed interlayer shear modes in 2D layered materials - A general bond polarizability model. *Sci. Rep.* **2015**, *5*, 14565.
- [222] Brüesch, P. Phonons: Theory and Experiments II: Experiments and Interpretation of Experimental Results;. *Springer-Verlag: Berlin* **1986**.
- [223] Umari, P.; Pasquarello, A.; Dal Corso, A. Raman scattering intensities in alpha-quartz: A first-principles investigation. *Phys. Rev. B* **2001**, *63*, 094305.
- [224] Guha, S.; Menendez, J.; Page, J. B.; Adams, G. B. Empirical bond polarizability model for fullerenes. *Phys. Rev. B* **1996**, *53*, 13106-13114.
- [225] Gupta, U.; Naidu, B. S.; Maitra, U.; Singh, A.; Shirodkar, S. N.; Waghmare, U. V.; Rao, C. N. R. Characterization of few-layer 1T-MoSe₂ and its superior performance in the visible-light induced hydrogen evolution reaction. *APL Mat.* **2014**, *2*, 092802.
- [226] He, J.; Hummer, K.; Franchini, C. Stacking effects on the electronic and optical properties of bilayer transition metal dichalcogenides MoS₂, MoSe₂, WS₂, and WSe₂. *Phys. Rev. B* **2014**, *89*.
- [227] Liu, Q.; Li, L.; Li, Y.; Gao, Z.; Chen, Z.; Lu, J. Tuning Electronic Structure of Bilayer MoS₂ by Vertical Electric Field: A First-Principles Investigation. *J. Phys. Chem. C* **2012**, *116*, 21556-21562.
- [228] Huang, S.; Ling, X.; Liang, L.; Kong, J.; Terrones, H.; Meunier, V.; Dresselhaus, M. S. Probing the Interlayer Coupling of Twisted Bilayer MoS₂ Using Photoluminescence Spectroscopy. *Nano Lett.* **2014**, *14*, 5500-5508.
- [229] Coehoorn, R.; Haas, C.; Dijkstra, J.; Flipse, C. J. F.; Degroot, R. A.; Wold, A. Electronic-structure of MoSe₂, MoS₂, and WSe₂. I. Band-structure calculations and photoelectron-spectroscopy. *Phys. Rev. B* **1987**, *35*, 6195-6202.
- [230] Lin, J.; Fang, W.; Zhou, W.; Lupini, A. R.; Idrobo, J. C.; Kong, J.; Pennycook, S. J.; Pantelides, S. T. AC/AB Stacking Boundaries in Bilayer Graphene. *Nano Lett.* **2013**, *13*, 3262-3268.
- [231] Lee, J.-U.; Kim, K.; Han, S.; Ryu, G. H.; Lee, Z.; Cheong, H. Raman Signatures of Polytypism in Molybdenum Disulfide. *ACS Nano* **2016**, *10*, 1948-1953.
- [232] Zhang, Y.; Brar, V. W.; Wang, F.; Girit, C.; Yayon, Y.; Panlasigui, M.; Zettl, A.; Crommie, M. F. Giant phonon-induced conductance in scanning tunnelling spectroscopy of gate-tunable graphene. *Nature Phys.* **2008**, *4*, 627-630.
- [233] Craciun, M. F.; Russo, S.; Yamamoto, M.; Oostinga, J. B.; Morpurgo, A. F.; Tarucha, S. Trilayer graphene is a semimetal with a gate-tunable band overlap. *Nature Nanotech.* **2009**, *4*, 383-388.
- [234] Yu, Y.; Yang, F.; Lu, X. F.; Yan, Y. J.; Cho, Y.-H.; Ma, L.; Niu, X.; Kim, S.; Son, Y.-W.; Feng, D.; Li, S.; Cheong, S.-W.; Chen, X. H.; Zhang, Y. Gate-tunable phase transitions in thin flakes of 1T-TaS₂. *Nature Nanotech.* **2015**, *10*, 270-276.
- [235] Yoshida, M.; Zhang, Y.; Ye, J.; Suzuki, R.; Imai, Y.; Kimura, S.; Fujiwara, A.; Iwasa, Y. Controlling charge-density-wave states in nano-thick crystals of 1T-TaS₂. *Sci. Rep.* **2014**, *4*, 7302.
- [236] Yu, W. J.; Liu, Y.; Zhou, H.; Yin, A.; Li, Z.; Huang, Y.; Duan, X. Highly efficient gate-tunable photocurrent generation in vertical heterostructures of layered materials. *Nature Nanotech.* **2013**, *8*, 952-958.
- [237] Sui, M.; Chen, G.; Ma, L.; Shan, W.-Y.; Tian, D.; Watanabe, K.; Taniguchi, T.; Jin, X.; Yao, W.; Xiao, D.; Zhang, Y. Gate-tunable topological valley transport in bilayer graphene. *Nature Phys.* **2015**, *11*, 1027-1031.
- [238] Jones, A. M.; Yu, H.; Ghimire, N. J.; Wu, S.; Aivazian, G.; Ross, J. S.; Zhao, B.; Yan, J.; Mandrus, D. G.; Xiao, D.; Yao, W.; Xu, X. Optical generation of excitonic valley coherence in monolayer WSe₂. *Nature Nanotech.* **2013**, *8*, 634-638.

- [239] Chen, J.; Badioli, M.; Alonso-Gonzalez, P.; Thongrattanasiri, S.; Huth, F.; Osmond, J.; Spasenovic, M.; Centeno, A.; Pesquera, A.; Godignon, P.; Zurutuza Elorza, A.; Camara, N.; Javier Garcia de Abajo, F.; Hillenbrand, R.; Koppens, F. H. L. Optical nano-imaging of gate-tunable graphene plasmons. *Nature* **2012**, *487*, 77-81.
- [240] Sangwan, V. K.; Jariwala, D.; Kim, I. S.; Chen, K.-S.; Marks, T. J.; Lauhon, L. J.; Hersam, M. C. Gate-tunable memristive phenomena mediated by grain boundaries in single-layer MoS₂. *Nature Nanotech.* **2015**, *10*, 403-406.
- [241] Yan, J.; Zhang, Y.; Kim, P.; Pinczuk, A. Electric field effect tuning of electron-phonon coupling in graphene. *Phys. Rev. Lett.* **2007**, *98*, 166802.
- [242] Pisana, S.; Lazzeri, M.; Casiraghi, C.; Novoselov, K. S.; Geim, A. K.; Ferrari, A. C.; Mauri, F. Breakdown of the adiabatic Born-Oppenheimer approximation in graphene. *Nature Mater.* **2007**, *6*, 198-201.
- [243] Lazzeri, M.; Mauri, F. Nonadiabatic Kohn anomaly in a doped graphene monolayer. *Phys. Rev. Lett.* **2006**, *97*, 266407.
- [244] Das, A.; Pisana, S.; Chakraborty, B.; Piscanec, S.; Saha, S. K.; Waghmare, U. V.; Novoselov, K. S.; Krishnamurthy, H. R.; Geim, A. K.; Ferrari, A. C.; Sood, A. K. Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. *Nature Nanotech.* **2008**, *3*, 210-215.
- [245] Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **2006**, *97*.
- [246] Chakraborty, B.; Das, A.; Sood, A. K. The formation of a p-n junction in a polymer electrolyte top-gated bilayer graphene transistor. *Nanotechnology* **2009**, *20*, 365203
- [247] Lazzeri, M.; Piscanec, S.; Mauri, F.; Ferrari, A. C.; Robertson, J. Phonon linewidths and electron-phonon coupling in graphite and nanotubes. *Phys. Rev. B* **2006**, *73*, 155426.
- [248] Bonini, N.; Lazzeri, M.; Marzari, N.; Mauri, F. Phonon anharmonicities in graphite and graphene. *Phys. Rev. Lett.* **2007**, *99*, 176802.
- [249] Chu, L.; Schmidt, H.; Pu, J.; Wang, S.; Oezylmaz, B.; Takenobu, T.; Eda, G. Charge transport in ion-gated mono-, bi-, and trilayer MoS₂ field effect transistors. *Sci. Rep.* **2014**, *4*, 7293
- [250] Lu, C. G.; Fu, Q.; Huang, S. M.; Liu, J. Polymer electrolyte-gated carbon nanotube field-effect transistor. *Nano Lett.* **2004**, *4*, 623-627.
- [251] Pu, J.; Yomogida, Y.; Liu, K.-K.; Li, L.-J.; Iwasa, Y.; Takenobu, T. Highly Flexible MoS₂ Thin-Film Transistors with Ion Gel Dielectrics. *Nano Lett.* **2012**, *12*, 4013-4017.
- [252] Yoon, Y.; Ganapathi, K.; Salahuddin, S. How Good Can Monolayer MoS₂ Transistors Be? *Nano Lett.* **2011**, *11*, 3768-3773.
- [253] Kuemmel, T.; Quitsch, W.; Matthis, S.; Litwin, T.; Bacher, G. Gate control of carrier distribution in k-space in MoS₂ monolayer and bilayer crystals. *Phys. Rev. B* **2015**, *91*, 125305.
- [254] Newaz, A. K. M.; Prasai, D.; Ziegler, J. I.; Caudel, D.; Robinson, S.; Haglund, R. F., Jr.; Bolotin, K. I. Electrical control of optical properties of monolayer MoS₂. *Solid State Commun.* **2013**, *155*, 49-52.
- [255] Cheiwchanchamnangij, T.; Lambrecht, W. R. L. Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS₂. *Phys. Rev. B* **2012**, *85*, 205302.
- [256] Chu, T.; Ilatikhameneh, H.; Klimeck, G.; Rahman, R.; Chen, Z. Electrically Tunable Bandgaps in Bilayer MoS₂. *Nano Lett.* **2015**, *15*, 8000-8007.
- [257] Mouri, S.; Miyauchi, Y.; Matsuda, K. Tunable Photoluminescence of Monolayer MoS₂ via Chemical Doping. *Nano Lett.* **2013**, *13*, 5944-5948.
- [258] Liu, B.; Zhao, W.; Ding, Z.; Verzhbitskiy, I.; Li, L.; Lu, J.; Chen, J.; Eda, G.; Loh, K. P. Engineering

- bandgaps of monolayer MoS₂ and WS₂ on fluoropolymer substrates by electrostatically tuned many-body effects. *Adv. Mater.* **2016**, *x*, DOI: 10.1002/adma.201504876.
- [259] Li, Y.; Xu, C.-Y.; Qin, J.-K.; Feng, W.; Wang, J.-Y.; Zhang, S.; Ma, L.-P.; Cao, J.; Hu, P. A.; Ren, W.; Zhen, L. Tuning the Excitonic States in MoS₂/Graphene van der Waals Heterostructures via Electrochemical Gating. *Adv. Funct. Mater.* **2016**, *26*, 293-302.
- [260] Staiger, M.; Gillen, R.; Scheuschner, N.; Ochedowski, O.; Kampmann, F.; Schleberger, M.; Thomsen, C.; Maultzsch, J. Splitting of monolayer out-of-plane A₁' Raman mode in few-layer WS₂. *Phys. Rev. B* **2015**, *91*, 195419.
- [261] Chakraborty, B.; Matte, H. S. S. R.; Sood, A. K.; Rao, C. N. R. Layer-dependent resonant Raman scattering of a few layer MoS₂. *J. Raman Spectrosc.* **2013**, *44*, 92-96.
- [262] Ramasubramaniam, A.; Naveh, D.; Towe, E. Tunable band gaps in bilayer transition-metal dichalcogenides. *Phys. Rev. B* **2011**, *84*, 205325.
- [263] Fan, J.-H.; Gao, P.; Zhang, A.-M.; Zhu, B.-R.; Zeng, H.-L.; Cui, X.-D.; He, R.; Zhang, Q.-M. Resonance Raman scattering in bulk 2H-MX₂ (M = Mo, W; X = S, Se) and monolayer MoS₂. *J. Appl. Phys.* **2014**, *115*, 053527.
- [264] Livneh, T.; Sterer, E. Resonant Raman scattering at exciton states tuned by pressure and temperature in 2H-MoS₂. *Phys. Rev. B* **2010**, *81*, 195209.
- [265] Sekine, T.; Uchinokura, K.; Nakashizu, T.; Matsuura, E.; Yoshizaki, R. Dispersive raman mode of layered compound 2H-MoS₂ under the resonant condition. *J. Phys. Soc. Jpn.* **1984**, *53*, 811-818.
- [266] Molina-Sanchez, A.; Wirtz, L. Phonons in single-layer and few-layer MoS₂ and WS₂. *Phys. Rev. B* **2011**, *84*, 155413.
- [267] Gillen, R.; Maultzsch, J. Light-Matter Interactions in Two-Dimensional Transition Metal Dichalcogenides: Dominant Excitonic Transitions in Mono- and Few-Layer MoX₂ and Band Nesting. *IEEE J. Sel. Top. Quantum Electron.* **2016**, *23*, 1-12.
- [268] Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From Bulk to Monolayer MoS₂: Evolution of Raman Scattering. *Adv. Funct. Mater.* **2012**, *22*, 1385-1390.
- [269] Schuller, J. A.; Karaveli, S.; Schiros, T.; He, K.; Yang, S.; Kymissis, I.; Shan, J.; Zia, R. Orientation of luminescent excitons in layered nanomaterials. *Nature Nanotech.* **2013**, *8*, 271-276.
- [270] Song, Q. J.; Tan, Q. H.; Zhang, X.; Wu, J. B.; Sheng, B. W.; Wan, Y.; Wang, X. Q.; Dai, L.; Tan, P. H. Physical origin of Davydov splitting and resonant Raman spectroscopy of Davydov components in multilayer MoTe₂. *Phys. Rev. B* **2016**, *93*, 115409.
- [271] Kozawa, D.; Kumar, R.; Carvalho, A.; Amara, K. K.; Zhao, W. J.; Wang, S. F.; Toh, M. L.; Ribeiro, R. M.; Neto, A. H. C.; Matsuda, K.; Eda, G. Photocarrier relaxation pathway in two-dimensional semiconducting transition metal dichalcogenides. *Nat. Commun.* **2014**, *5*, 4543.
- [272] Yu, Y.; Hu, S.; Su, L.; Huang, L.; Liu, Y.; Jin, Z.; Purezky, A. A.; Geohegan, D. B.; Kim, K. W.; Zhang, Y.; Cao, L. Equally Efficient Inter layer Exciton Relaxation and Improved Absorption in Epitaxial and Nonepitaxial MoS₂/WS₂ Heterostructures. *Nano Lett.* **2015**, *15*, 486-491.

Publication List

1. **X. Lu**, M. I. B. Utama, J. Lin, X. Luo, Y. Zhao, J. Zhang, S. T. Pantelides, W. Zhou, S. Y. Quek, and Q. H. Xiong. Rapid and Nondestructive Identification of Polytypism and Stacking Sequences in Few-layer Molybdenum Diselenide by Raman Spectroscopy. **Adv. Mater.** 27 (30), 4502-4508, 2015.
2. **X. Lu**[#], M. I. B. Utama[#], J. Lin, X. Gong, J. Zhang, Y. Zhao, S. T. Pantelides, J. Wang, Z. Dong, Z. Liu, W. Zhou and Q. H. Xiong. Large-Area Synthesis of Monolayer and Few-Layer MoSe₂ Films on SiO₂ Substrates. **Nano Lett.** 14 (5), 2419-2425, 2014.
3. **X. Lu**, M. I. B. Utama, J. Zhang, Y. Zhao and Q. H. Xiong. Layer-by-layer thinning of MoS₂ by thermal annealing. **Nanoscale** 5, 8904-8908, 2013.
4. **X. Lu**[#], X. Luo[#], J. Zhang, S. Y. Quek, and Q. H. Xiong. Lattice vibrations and Raman scattering in two-dimensional layered materials beyond graphene (Invited Review). **Nano Res.** 9 (12), 3559-3597, 2016.
5. W. G. Xu, W. W. Liu, J. F. Schmidt, W. J. Zhao, **X. Lu**, T. Raab, C. Diederichs, W. B. Gao, D. V. Seletskiy, and Q. H. Xiong. Correlated Fluorescence Blinking in Two-dimensional Semiconductor Heterostructures. **Nature** 541, 62-67, 2017.
6. X. Luo, **X. Lu**, G. K. W. Koon, A. H. Castro Neto, B. Özyilmaz, Q. H. Xiong, and S. Y. Quek. Large Frequency Dependence on Thickness of Interlayer Breathing Mode - Significant Interlayer Interactions in Few Layer Black Phosphorus. **Nano Lett.** 15 (6), 3931–3938, 2015.
7. X. Luo, **X. Lu**, C. Cong, T. Yu, Q. H. Xiong, and S. Y. Quek. Stacking sequence and group symmetries determine Raman intensities of interlayer modes in 2D layered materials – A simple bond polarizability model. **Sci. Rep.** 5, 14565, 2015.
8. M. I. B. Utama[#], **X. Lu**[#], D. Zhan, S. T. Ha, Y. Yuan, Z. X. Shen, and Q. H. Xiong. Etching-free patterning method for electrical characterization of atomically thin MoSe₂ films grown by chemical vapor deposition. **Nanoscale** 6, 12376-12382, 2014.
9. M. I. B. Utama, **X. Lu**, Y. Yuan, and Q. H. Xiong. Detrimental influence of catalyst seeding on the device properties of CVD-grown 2D layered materials: A case study on MoSe₂. **Appl. Phys. Lett.** 105 (25), 253102, 2014.
10. J. Tao, J. Chai, **X. Lu**, L. M. Wong, T. I. Wong, J. Pan, Q. H. Xiong, D. Chi and S. Wang. Growth of wafer-scale MoS₂ monolayer by magnetron sputtering. **Nanoscale** 7, 2497-2503, 2015.
11. B. Peng, **X. Lu**, E. Mutlugun, S. Chen, C. H. A. Huan, S. F. Yu, H. V. Demir, and Q. H. Xiong. Exciton dynamics in luminescent carbon nanodots: electron-hole exchange interaction. **Nano Res.** 9 (2), 549-559, 2016.
12. Y. Yuan, L. Zhang, J. Xing, M. I. B. Utama, **X. Lu**, Y. Li, X. Hu, S. Wang, A. Genç, R. Dunin-Borkowski, J. Arbiol, and Q. H. Xiong. High-yield production and optical properties of g-C₃N₄. **Nanoscale** 7, 12343-12350, 2015.
13. H. Li, J. Wu, X. Huang, G. Lu, J. Yang, **X. Lu**, Q. H. Xiong and H. Zhang. Rapid and Reliable Thickness Identification of Two-Dimensional Nanosheets Using Optical Microscopy. **ACS Nano** 7, 10344-10353, 2013.

[#]Equally contributed.