Strain effects on semiconducting two-dimensional crystals

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2016

Wang, Y. (2016). Strain effects on semiconducting two-dimensional crystals. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/65945>

<https://doi.org/10.32657/10356/65945>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

STRAIN EFFECTS ON SEMICONDUCTING
TWO-DIMENSIONAL CRYSTALS

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TWO-DIMENSIONAL CRYSTALS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2015

2015

STRAIN EFFECTS ON SEMICONDUCTING TWO-DIMENSIONAL CRYSTALS

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

2015

Acknowledgements

I would like to make use of this opportunity to acknowledge the people who made a contribution to my dissertation over the past four years. It is their selfless help that strengthened my determination to conquer all the difficulties during my PhD journey.

To begin with, I would like to express my sincere appreciation to my supervisor, Professor Yu Ting who led me to the research field of the fantastic nanomaterials and made me have opportunities to study the emergent two-dimensional materials. I truly thank him for constantly pushing me to probe deeper when I felt complacent about my little progress and encouraging me not to give up when I got stuck on my projects. He not only sets me a good example on how to do research, but also inspires me by his strong willingness to learn from others. His rigorous attitude towards research and spirit of dedication to science will be my permanent goals in my future research career.

Next, I want to give my cordial thanks to Prof Shen Zexiang for sharing the Raman facilities with our group and facilitating the characterizations of my sample.

Furthermore, I plan to convey my special gratitude to Dr. Cong Chunxiao who always tries to help me in all respects. She is an experienced and accomplished experimentalist, who patiently trained me many optical techniques, such as Raman spectroscopy and atomic force microscopy. Chunxiao often encouraged me to be strict with myself and gave many insightful comments when I discussed my preliminary results with her. She has much research experience and imparted all the valuable first-hand experience to me without reservation, which I benefit a lot from.

I am thankful to all of my current group members and former colleagues, Dr. Yang Weihuang, Dr. Shang Jingzhi, Ms. Namphung Peimyoo, Mr. Cao Bingchen, Mr.

Chen Yu, Dr. Mustafa Eginligil, Mr. Zou Chenji, Dr. Qiu Caiyu, Dr. Hu Hailong, Dr. Shen Xiaonan, Mr. Parviz Hajiyevev, *etc.* for their kind help and constructive suggestions.

I feel appreciative of Professor Yang Li and Mr. Fei Ruixiang for their calculation assistance, which greatly contributed to my understanding of the experimental results.

Last but not least, I hope to thank my parents and grandparents for their selfless love and utmost solicitude. They are my strong backing and provide me a lot of support to get through the tough time in my PhD life.

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Abstract

Two-dimensional (2D) semiconducting layered materials have attracted widespread research interest recently not only from the fundamental point of view, but also because of their great possibilities in next-generation electronic devices, valleytronics, photodetectors, and flexible optoelectronics applications due to their as-born bandgaps and other unique properties. Strain, which can be used to alter and control the properties of these 2D semiconducting materials, thus enables the exploration of novel fundamental physics and applications of these materials. In this thesis, we present the band structure evolutions and lattice vibrational responses in 2D MS_2 ($M=Mo, W$) and BP crystals under uniaxial tensile strain through a combination of *in situ* photoluminescence and Raman spectroscopy studies, as well as density functional theory (DFT) calculations.

As uniaxially strained monolayer WS_2 is theoretically predicted to undergo a direct-indirect bandgap transition which may limit its optoelectronic applications, it is important to accurately determine the critical strain to induce such transition. We have experimentally demonstrated the possibility of tuning different optical transition energies and their relative spectral weight in monolayer WS_2 by applying uniaxial strain. This tuneable optical property is attributed to the strain-induced direct-indirect bandgap transition and confirmed by DFT calculations. In addition, slight lowering of the trion dissociation energy with increasing uniaxial strain is observed.

Not only the band structure engineering, but also the crystallographic orientation determination could be achieved by the strain in TMDs. Crystal orientation can significantly determine the properties of TMD materials, which necessitates a convenient and reliable way to identify it. Our *in situ* Raman spectroscopy study reveals uniaxial tensile strain can soften the in-plane E' phonon mode and even lift its two-fold degeneracy as reflected by a doublet splitting. We further show that the polarizations of the scattered light from these two splitted modes are linear and orthogonal. Moreover, the polarization dependence of the two sub-bands could be adopted to identify the crystal orientation and confirms the observed zigzag-oriented edge of monolayer WS_2 grown by chemical vapour deposition method in previous studies.

BP possesses the remarkably anisotropic mechanical properties as a result of its unique puckered structure, so it is critical to understand how the anisotropic behaviors can be modulated by strain for the better integration of BP into various technologies, such as flexible electronics. It is found that the out-of-plane A_g^1 mode is sensitive to uniaxial tensile strain along the armchair direction while the in-plane B_{2g} and A_g^2 modes are susceptible to the zigzag direction strain. Our DFT calculation results clearly illustrate the anisotropic influence of uniaxial strain on structural properties of few-layer BP owing to its unique puckered crystal structure and could be used to elucidate the striking dependence of strained phonon frequencies on crystal orientations.

Our work suggests that strain engineering holds a promising future for extensive modulation of optical and mechanical properties in semiconducting layered materials. This study indeed enriches our understanding of strained states of 2D crystals and further lays a foundation for developing various applications of such emerging semiconducting layered materials based on their strain dependent properties, such as flexible optoelectronic devices.

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2. **Y. Wang**,* C. Cong,* W. Yang, J. Shang, N. Peimyoo, Y. Chen, J. Kang, J. Wang, W. Huang and T. Yu, Strain-induced direct–indirect bandgap transition and phonon modulation in monolayer WS₂, *Nano Res.* 8, 2562, 2015.
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Citations to published work

Majority of Chapter 3 and minority of Chapter 4 appear as:

“Strain-induced direct–indirect bandgap transition and phonon modulation in monolayer WS₂” Y. Wang*, C. Cong*, W. Yang, J. Shang, N. Peimyoo, Y. Chen, J. Kang, J. Wang, W. Huang, and T. Yu. *Nano Res.*, *Nano Res.* **8**, 2562-2572 (2015)

Majority of Chapter 4 appears as:

“Raman spectroscopy study of lattice vibration and crystallographic orientation of monolayer MoS₂ under uniaxial strain” Y. Wang*, C. Cong*, C. Qiu, and T. Yu. *Small* **9**, 2857-2861 (2013)

Majority of Chapter 5 appears as:

“Remarkable Anisotropic Phonon Response in Uniaxially Strained Few-layer Black Phosphorus” Y. Wang*, C. Cong*, R. Fei, W. Yang, Y. Chen, B. Cao, L. Yang, and T. Yu *Nano Res.* **8**, 3944-3953 (2015)

Chapter 1 Introduction

1.1 Introduction to two-dimensional layered materials

The successful isolation of atomically thin carbon sheets (also called graphene) from graphite by micromechanical exfoliation in 2004 was quite encouraging, because before that time it was hard to imagine two-dimensional (2D) crystals could be stable in reality from the perspective of thermodynamic instability [1]. This exciting discovery made Konstantin Novoselov and Andre Geim win the 2010 Nobel Prize in physics without controversy. Though a variety of exotic properties have been subsequently demonstrated, such as relativistic Dirac fermion behaviors of electrons [2], extremely high intrinsic strength [3], superior electrical and thermal conductivity [4, 5], and impermeability to any standard gas molecule [6], graphene is undoubtedly not perfect. It has a fatal flaw that graphene-based transistors suffer from an unsatisfactory on-off ratio due to the absence of as-born bandgap, which hinders its applications in electronics [7, 8]. Consequently, it is still necessary to continue searching for alternative 2D materials and explore the rich physics inside them. Recently, atomic thin layers of semiconducting transition metal dichalcogenides (TMDs) with the as-born bandgap have attracted much research interest. The indirect bandgap for thick layers of semiconducting TMDs becomes a direct bandgap in monolayer TMDs [9-11], which makes them hold promise for various applications, such as next-generation electronic devices, optoelectronics, and so on. Unfortunately,

the semiconducting TMD materials possess the low carrier mobility, in spite of their high on-off ratio [12, 13]. Black phosphorus (BP), the most stable allotrope of phosphorus, possesses a direct bandgap for any thickness, which is tuneable from 2.15 eV for monolayer to 0.3 eV for bulk [14]. This energy gap range bridges the gap between graphene and TMDs, making BP perfectly appropriate for near- and mid-infrared optoelectronics [15]. Moreover, the on/off ratio and mobility combination of BP happens to fill the blank region unreachable by graphene and TMDs [15]. Last but not least, its unique puckered structure results in many anisotropic electrical [16, 17], optical [17-19], thermal [20, 21], and mechanical [22-25] properties. All of these properties greatly inspire and motivate researches working on 2D materials. Researches have made a lot of progress in bringing semiconducting 2D crystals to the strict standards of contemporary technology based on the experience of graphene studies, though there is still a long way to go. In this section, an introduction to 2D TMDs and BP will be given, which are the two kinds of atomically thin semiconducting materials studied in this thesis.

1.1.1 Semiconducting MX_2 (M=Mo, W; X=S, Se) crystals

1.1.1.1 The crystal structure of semiconducting MX_2 materials

TMD materials possess a general form MX_2 , where M symbolizes a group-IV (Hf, Zr, Ti, *etc.*), group V (V, Nb, and so on) or group-VI (for instance W and Mo) transition metal element, while X represents a group-VIA chalcogen. TMDs can be

classified based on their different properties; some show charge density wave states, such as TaSe₂ and TaS₂ [26], some display semiconductor properties, *e.g.* MoS₂ [27], and some TMDs, including NbSe₂ and NbS₂, exhibit superconductivity phases [28]. Here, we focus on semiconducting MX₂ (M=Mo, W; X=S, Se) which attracts special research interest and holds promise for next generation electronics [29].

There are various kinds of structural polytypes in MX₂, *e.g.* 1T, 2H, and 3R. 1T denotes tetragonal symmetry with each layer serving as repeat unit and chalcogen atoms in this polytype have octahedral coordination [29]. 3R-MX₂ possesses rhombohedral symmetry with the nonmetal atoms in trigonal prismatic coordination and comprises the repeat unit of three layers [29]. 1T phase mainly exists in chemically exfoliated samples [30] and 3R-polytype could be transformed into 2H-polymorph upon heating. Therefore, we only consider the most dominant and stable 2H-polytype in the remaining part of this thesis. 2H-MX₂ exhibits hexagonal symmetry and its repeat unit comprises two layers. From its schematic representation in Figure 1.1(a), the metal atom is at the center and its nearest six chalcogen atoms have trigonal prismatic coordination [29, 31]. The bulk structure is formed with the adjacent layers vertically arranged, as shown in Figure 1.1(b) [29]. Atoms are held together by the covalent force within the layers, while between layers the van der Waals (vdW) interaction dominates, which leads to the easy cleavage of planes [32]. As can be seen from the top view of 2H-MX₂ (Figure 1.1(c)), metal atoms overlap with chalcogenide atoms in the adjacent layers and vice versa.

Figure 1.1 (a) Schematic diagram and (b) perspective view of 2H polytype. Adapted from ref. [29]. (c) Top view of 2H-MX₂.

1.1.1.2 The electronic band structure of semiconducting MX₂ materials

The thickness-dependent electronic properties of semiconducting MX₂ (M=Mo, W; X=S, Se) have attracted tremendous attention. Because semiconducting MX₂ possess similar crystal structure, their thickness-dependent electronic characteristics are quite similar [33]. Here, we take WS₂ as an example to demonstrate how the band structure changes with the layer number. Figure 1.2 shows the calculated band structure of single-layer, few-layer, and bulk WS₂. The bulk WS₂ has an indirect bandgap of 1.3 eV originated from the valence band maximum (VBM) located at Γ point and the conduction band minimum (CBM) situated halfway between K and Γ points. The direct bandgap of the bulk WS₂ is located at K point. When the layer number decreases, the indirect bandgap energy keeps increasing while the direct bandgap energy remains nearly unchanged, which leads to indirect-direct bandgap transition in single-layer limit [33].

Figure 1.2 Band structure of WS_2 with different thicknesses. Adapted from ref. [33].

1.1.1.3 The phonon structure of semiconducting MX_2 materials

The general phonon features of semiconducting MX_2 ($\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{S}, \text{Se}$) are similar though the phonon frequencies are different for each individual MX_2 [34]. MoS_2 is used as an example to detail the phonon properties of semiconducting MX_2 . The phonon dispersion curves of monolayer and bulk MoS_2 calculated by the density functional theory (DFT) method are shown in Figure 1.3. Because the primitive unit cell of monolayer MoS_2 contains three atoms, there are nine phonon dispersion branches, among which three are acoustic branches and the remaining six are optical ones. The three acoustic branches correspond to the in-plane transverse acoustic (TA), longitudinal acoustic (LA), and out-of-plane acoustic (ZA) modes. In addition, the six optical branches are assigned to two in-plane transverse optical (TO), two in-plane longitudinal optical (LO), and two out-of-plane optical (ZO) phonon modes [35]. In bulk MoS_2 , the number of phonon branches increases to 18 as a result of the enlarged

unit cell compared with that of the monolayer counterpart. A comparison of calculated phonon dispersion curves and the experimental data obtained by neutron inelastic scattering spectroscopy demonstrates the good consistency between theory and experiments. Overall, the phonon dispersions of monolayer and bulk MoS₂ share a similarity [34]. In the bulk, all modes originally belonging to single-layer now split into two branches, but the splitting is not obvious as a consequence of the weak interlayer interaction [34]. The only prominent exception is the mode splitting around Γ point, where there are no low-frequency optical modes in monolayer MoS₂.

Figure 1.3 Phonon dispersion curves (left) and density of states (right) of (a) monolayer and (b) bulk MoS₂. Black points are experimental data by neutron-inelastic-scattering techniques extracted from Ref. [36]. Adapted from ref. [34].

1.1.2 Black phosphorus

1.1.2.1 The crystal structure of BP

Orthorhombic BP, the most stable allotrope of phosphorus, possesses a unique puckered structure, which can be clearly seen in Figure 1.4(a). Each unit layer

comprises covalently bonded phosphorus atoms from two sub-planes, which form a hinge-like structure [37]. X -axis is set to be zigzag direction along the ridge orientation and z -axis denotes the armchair one parallel to the hinge direction. Along the out-of-plane y direction, layers are arranged in Bernal (AB) stacking sequence by vdW force. As can be seen from the top view of BP shown in Figure 1.4(b), unlike graphene, BP exhibits a hexagonal structure in the x - z plane, comprising two kinds of edges with significantly different lengths [15].

Figure 1.4 (a) Perspective and (b) top views of bi-layer BP with puckered structure.

The yellow and grey colors are used to distinguish top and bottom layers, respectively.

1.1.2.2 The electronic band structure of BP

BP possesses a direct bandgap for any thickness, as shown in the band structure evolution of BP with different thickness (Figure 1.5(a)). According to Figure 1.5(b), though different calculation methods yield different calculated bandgap energies, they all follow a power-law dependence with the form of $(A/N^\alpha + B)$, where N is the layer number [38]. The significant thickness dependent bandgap energies, *e.g.* from 2.0 eV

in the monolayer form to 0.3 eV in its bulk counterpart from GW-calculated results, indicate the wide range of tunability for the bandgap in BP.

Figure 1.5 (a) Calculated band structure for BP with different thicknesses. Adapted from ref. [39]. (b) The evolution of bandgap energy calculated by different methods as a function of the layer number of BP. The measured absorption peak energy of monolayer BP read from ref. [40] is also shown here. The dashed lines present power-law fitting curves. Adapted from ref. [38].

1.1.2.3 The phonon structure of BP

Figure 1.6 presents the phonon dispersion of monolayer BP. It has four phosphorous atoms per unit cell, and thus there are 12 lattice vibrational modes at the Γ point, which can be written as $\Gamma = B_{1g} + B_{2g} + 2B_{3g} + 2A_g + 2B_{1u} + 2B_{2u} + B_{3u} + A_u$. Similar to graphene and semiconducting MX_2 , the frequency of the out-of-plane ZA mode shows a quadratic dependence on the wave vector near the Γ point [41], which is a typical behavior of layered materials [42].

Figure 1.6 Phonon dispersion of monolayer BP. Adapted from ref. [22].

1.2 Introduction to Raman spectroscopy

Raman spectroscopy is one important technique to probe the lattice vibrations of molecules or atoms. Raman scattering describes the creation or annihilation of one or more phonons during the interaction between the incident light and matter. The corresponding phonon energy is compensated by the decrease or increase in the energy of the scattered light compared to the incident one. This inelastic scattering process was first theoretically predicted in 1923 by Smekal [43], and then experimentally discovered simultaneously in 1928 by Raman in liquids [44] and by Landsberg in crystals [45]. In this section, we introduce fundamental concepts of Raman scattering and review some related literatures about Raman spectroscopic studies on TMD and BP layers.

1.2.1 Fundamentals of Raman scattering

(1) Basic concepts of Raman scattering process

Figure 1.7 illustrates the schematic diagram of Rayleigh and Raman scatterings. When the molecular or atomic system is irradiated by an incoming light with frequency ν_0 , the electron is excited from a low-energy vibrational state to an intermediate virtual state with higher energy. The majority of photons are elastically scattered, *i.e.* the scattering light has the same frequency ν_0 as that of the incoming light. This elastic scattering of incident photon is called Rayleigh scattering, which results from scattering centres much smaller than the wavelength of the incoming light. In addition, there also exist some other kinds of elastic scattering, such as Mie and Brillouin scatterings, which are beyond the scope of this introduction. On the other hand, the minority of photons (about 10^{-6} of the incident radiation) experience either energy gain or energy loss in inelastic Raman scattering process. The Stokes Raman scattering originates from the transitions which finally end at a higher energy level compared to the starting one, accompanied by creation of a phonon. In the case of anti-Stokes scattering, the scattered light gains the energy and a phonon with this energy is annihilated. The electron population at each energy state follows the Boltzmann distribution, so the excited state has a much smaller population compared with that of the ground state, which makes the probability of Stokes scattering much larger than that of anti-Stokes scattering.

Figure 1.7 Schematics of the Rayleigh and Raman scattering processes.

(2) Raman spectroscopy selection rules

Based on classical theory, Raman scattering can be clarified in this way [46]: consider the electric field strength E of the electromagnetic wave (incident light) which fluctuates with time t in the form of

$$E = E_0 \cos 2\pi\nu_0 t \quad (1-1)$$

where ν_0 is the frequency of electromagnetic wave.

Suppose that a diatomic molecule is illuminated by this light, which induces an electric dipole moment P :

$$P = \alpha E \quad (1-2)$$

where α is the polarizability of the molecule. Assuming that the molecule has a vibrational frequency of ν_m and vibrational amplitude of q_0 , the nuclear displacement q can be expressed as

$$q = q_0 \cos 2\pi\nu_m t \quad (1-3)$$

If q_0 is small, α is linearly dependent on q . Therefore, we can write

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_0 q + \dots \quad (1-4)$$

Combining Equations (1-1) to (1-4), we can obtain

$$P = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \{\cos[2\pi(\nu_0 - \nu_m)t] + \cos[2\pi(\nu_0 + \nu_m)t]\} \quad (1-5)$$

In this expression, the first term denotes an oscillating dipole that scatters light with the frequency same as the incoming beam (inelastic Rayleigh scattering) and the second term denotes lights with the frequencies of $\nu_0 - \nu_m$ and $\nu_0 + \nu_m$, corresponding to the Stokes and anti-Stokes Raman scatterings, respectively. Therefore, the vibration can be Raman-active only if $\left(\frac{\partial \alpha}{\partial q}\right)_0$ is nonzero.

Besides, the Raman scattering intensity can be calculated based on the following expression [47]:

$$I_s \propto |e_i \cdot R \cdot e_s^T|^2 \quad (1-5)$$

where e_i and e_s represent the electric polarization vectors of incoming and scattered lights, respectively. R is the Raman tensor of the lattice vibrational mode. Therefore, we can use the Equation (1-5) to determine whether a phonon mode can be observed by Raman spectroscopy under a certain polarization geometry.

1.2.2 Raman spectroscopic study of semiconducting MX₂ materials

(1) Evolution of phonon frequencies with layer number

Because semiconducting MX₂ (M=Mo, W; X=S, Se) share similar thickness dependent phonon behaviors as a result of the same crystal structure, MoS₂ is adopted

as an example to demonstrate the evolution of phonon frequencies with layer number in TMD materials. Bulk MoS₂ belongs to the D_{6h}^4 space group and possesses 12 phonon modes at the Γ point [48, 49]. Four of them are first-order Raman-active modes, including E_{2g}^2 (32 cm⁻¹), E_{1g} (286 cm⁻¹), E_{2g}^1 (383 cm⁻¹), and A_{1g} (408 cm⁻¹), as shown in Figure 1.8(a) [50, 51]. In the widely used backscattering configuration with laser beam propagating along the out-of-plane direction of the MoS₂ sample, A_{1g} and E_{2g} modes are allowed while E_{1g} is forbidden [48, 49]. The denotations of these modes in even (E_g and A_{1g}) and odd (E' and A'_1) numbers of layers are different from the bulk due to their different symmetries. When discussing the evolution of the high-frequency phonon modes from the monolayer to bulk MoS₂, we will simply denote the corresponding modes as E_{2g}^1 and A_{1g} in the bulk, which is a common practice in the literature [34, 52].

Figure 1.8 (a) Atomic displacements of vibration modes for MoS₂. (b) Raman spectra of bulk and thin layers of MoS₂. (c) Phonon frequencies of A_{1g} and E_{2g}^1 modes (left

axis) and their frequency difference (right axis) as a function of layer number. Adapted from ref. [52].

Raman spectra of bulk and thin layers of MoS₂ are shown in Figure 1.8(b). The vibrational frequencies of E_{2g}¹ and A_{1g} exhibit opposite trends with increasing thickness from the monolayer to bulk, with the former softening and the latter hardening as shown in Figure 1.8(c). The blueshift of the A_{1g} mode is due to the existence of interlayer vdW interactions which act as additional "spring" on the sulphur atoms as expected [52] while the anomalous redshift behaviour of the E_{2g}¹ mode is successfully attributed to enhancement of the dielectric screening which weakens long-range Coulomb interactions between the effective charges when the layer thickness increases [34].

(2) Temperature dependence and thermal effects

Figure 1.9(a) shows the temperature dependence of Raman spectra of monolayer WS₂ reported by Peimyoo *et al.* [53]. Both of these two mode redshift with increasing temperature and their frequency trends with temperature are demonstrated in Figure 1.9(b). The softening triggered by elevated temperature can be ascribed to the volume contribution caused by the thermal expansion and the intrinsic temperature contribution because of the anharmonicities of the phonon modes [53]. In addition, the negative temperature coefficients of two phonon modes obtained by linear fitting indicate that the frequency of the A₁' mode is more sensitive to temperature than that

of the E' mode, which could be explained by unrestraint of the vibration away from the basal plane due to the absence of the interlayer interaction [54].

Figure 1.9 (a) Raman spectra of single-layer WS₂ as a function of temperature. (b) Fitted temperature dependent phonon frequencies of E' and A₁' modes. Adapted from ref. [53].

Thermal effects on MoS₂ with different thickness have also been studied [55]. Significant redshift of E' and A₁' modes is observed in monolayer MoS₂ as the laser power increases (Figure 1.10(a)). As shown in Figure 1.10(b), the A_{1g} mode softens more obviously with increasing laser power than E_{2g}¹ in thin layers of MoS₂, which is consistent with the temperature dependent results [53]. Besides, the less sensitivity of the E_{2g}¹ mode to thickness has been observed, which is explained by the less efficient interlayer coupling of this in-plane mode.

Figure 1.10 (a) Raman spectra of single-layer MoS₂ under different laser powers. (b) The frequency change of E_{2g}¹ and A_{1g} modes in MoS₂ samples with different thicknesses when the laser power increases from 2 mW to 20 mW. Adapted from ref. [55].

(3) Other characteristics of TMD probed by Raman spectroscopy

In addition to the optical investigations on thin layers of TMD mentioned above, other phonon and electronic properties of TMD layers have also been revealed by Raman spectroscopy. Raman scattering has been widely employed to study the interlayer coupling [56-60], alloy composition [61, 62], spin-orbital splitting [63], and phonon properties modified by various external perturbations, such as electrical field [64] and pressure [65] in TMDs.

1.2.3 Raman spectroscopic study of BP

(1) Raman characterization of BP with different thicknesses

Bulk BP belongs to point group D_{2h}^{18} (mmm) and space group $Cmce$ [66]. It possesses 12 lattice vibrational modes at the Γ point and six of them are Raman active

[66, 67]. In the normal backscattering configuration, only A_g (containing both A_g^1 and A_g^2) and B_{2g} modes have a non-zero Raman scattering intensity [18, 19]. The symmetry classification of Raman modes and corresponding Raman tensors apply to BP with any thickness, because thin layers (whether odd or even numbers) share the identical point group (D_{2h}) with the bulk [66]. The atomic displacements of three phonon modes are plotted in Figure 1.11(a) [18, 19, 67]. While the A_g^1 mode involve atoms which oscillate out of the layer plane, B_{2g} and A_g^2 are in-plane vibrational modes.

Figure 1.11 (a) Schematic diagrams of the atomic displacements for different phonon modes in BP. (b) Raman spectra measured in different regions of a BP sample with different thicknesses. (c) The integrated intensity ratio between the A_g^1 and Si peaks as a function of BP thickness. Adapted from ref. [14].

Figure 1.11(b) shows the Raman spectra a BP sample with different thicknesses. It is found that the frequencies of the phonon modes slightly depend on the layer thickness of the BP flakes and therefore are not good parameters to determine the layer numbers. Instead, the intensity ratio between the A_g^1 mode and the silicon peak can be adopted to determine the sample thickness within 1–2 nm accuracy, as shown in Figure 1.11(c). It should be noted that the silicon peak intensity is sensitively dependent on its crystal orientation relative to the polarization of incoming light, so the substrate must be carefully aligned for precise comparisons between different samples when identifying the thickness by this method. The intensity ratio between the A_g^2 (or B_{2g}) and silicon peaks, on the other hand, strongly varies from sample to sample. This large variation might be caused by different crystal orientations of the samples relative to the polarization of incident light, because the A_g^2 and B_{2g} modes involve atomic vibrations within the layer plane [14].

(2) Crystal orientation determination by polarized Raman spectroscopy

Through the polarization dependent Raman spectroscopy, Wu *et al.* demonstrated the unique anisotropic nature of BP [18]. They first calculated the scattering efficiency of A_g and B_{2g} modes under parallel and cross polarization configurations based on their Raman tensors as a function of the sample rotation angle between the zigzag direction and polarization of scattered light (θ) [18]. As shown in Table 1.1 (a and c are Raman tensor elements), only the A_g mode under parallel polarization configuration can be adopted to determine the crystal orientation, because it exhibits a

180 ° variation period. Since the value of c is calculated to be larger than that of a [66], the A_g mode reaches a comparatively larger local maximum intensity when θ is 90 ° and the relatively smaller local maximum intensity can be obtained when θ is 0 °. The B_{2g} mode under both polarization configurations and the A_g mode under cross polarization configuration show a variation period of 90 °, which makes them fail to achieve the same goal.

Table 1.1 Raman scattering efficiency of A_g and B_{2g} modes. Adapted from ref. [18].

A_g mode		B_{2g} mode	
parallel	cross	parallel	cross
$(a\cos^2\theta + c\sin^2\theta)^2$	$0.25(a-c)^2\sin^22\theta$	$e^2\sin^22\theta$	$e^2\cos^22\theta$

Then, Wu *et al.* investigated the polarization dependent phonon intensities combined with the angle-resolved conductance [18]. The conductance measurements were first performed on the BP sheet with 12 electrodes on top, as shown in Figure 1.12(a). Because the hole conductance of BP along the zigzag direction has been reported to be smaller than that along the armchair direction [17], the zigzag orientation happens to be near the horizontal direction by fitting the angle-resolved conductance in Figure 1.12(b). Next, the corresponding angle-resolved polarized Raman measurements were conducted on this sample under parallel polarization configuration. Figure 1.12(c) shows the polarization dependent intensities of the A_g^2 mode as a function of θ , which can be well fitted by the function in Table 1.1. Besides, the zigzag direction obtained here is in good agreement with that deduced from the

angle-resolved conductance measurement. As expected, the angle-dependent intensities of the B_{2g} mode (Figure 1.12(d)) cannot be used to determine the crystal orientation because of its same intensity corresponding to both armchair and zigzag directions.

Figure 1.12 (a) Optical image of the BP device. (b) Angle-dependent conductance measured along different directions on the BP sample. (c) and (d) are polar plots of peak intensities of A_g^2 and B_{2g} modes under parallel polarization configuration. Adapted from ref. [18].

Very recently, Ribeiro *et al.* claimed that the angle-dependent intensities of phonon modes in the parallel and cross-polarization configurations cannot be simultaneously fitted well by the functions shown in Table 1.1 [19]. Therefore, imaginary parts should be taken into consideration when calculating the polarization dependent Raman scattering intensities of anisotropic BP [19]. Specifically speaking, after the complex values of the Raman tensor elements are taken account of, the

expressions for two A_g modes will differ while that for the B_{2g} mode will remain the same. The revised expressions for the intensities of A_g modes under parallel and perpendicular configurations are given by:

$$I_{A_g}^{//} \propto (|a| \sin^2 \theta + |c| \cos \phi_{ca} \cos^2 \theta)^2 + |c|^2 \sin^2 \phi_{ca} \cos^4 \theta \quad (1-1)$$

$$I_{A_g}^{\perp} \propto [(|a| - |c| \cos \phi_{ca})^2 + |c|^2 \sin^2 \phi_{ca}] \sin^2 \theta \cos^2 \theta \quad (1-2)$$

where ϕ_{ca} is the phase difference between a and c .

Figure 1.13 shows the angle-dependent intensities of the two A_g modes, together with the best fits provided by (1-1) and (1-2). All the angular dependencies of the A_g modes are nicely fitted, which demonstrates the necessity of introducing the phase difference ϕ_{ca} to calculation expressions.

Figure 1.13 Polarization dependent Raman intensities measured with the (a-d) 633, (e-f) 532, and (g-h) 488 nm laser lines. The polarization configurations and the phonon modes are marked in each panel. Dots indicate experimental data and solid curves correspond to the best fits to the data using equations obtained after complex values of the Raman tensor elements are taken account of. Adapted from ref. [19].

(3) Study of the crystal degradation by Raman spectroscopy

The crystal degradation of the BP flakes induced by photo-oxidation can be probed by Raman spectroscopy, as demonstrated by Favron *et al.* [68]. A typical atomic force microscopy (AFM) image of a multilayer BP with the thickness of 2.8 nm is presented in Figure 1.14(a). Degradation is noted by the homogeneous distribution of small bumps or defects at the surface of the layer in AFM images taken shortly after exfoliation. The degradation becomes obvious after several days from the AFM image (Figure 1.14(b)), with a severe transformation observed along with new droplets distributed in the vicinity of the initial position of the flakes. Figure 1.14(c) shows Raman spectra of a BP flake at different time intervals between exfoliation and measurements under continuous exposure to fluence of $2 \times 10^4 \text{ Wcm}^{-2}$ with the 532 nm laser line. As Raman scattering intensity is very sensitive to crystal quality, the quenching of the intensity is another indication of a fast degradation of the multilayer BP exposed to light. The experiment was carried out in vacuum in order to verify whether the mere presence of visible light is sufficient to induce degradation. To minimize the influence of the hydrophilicity of the SiO_2/Si substrate, a multilayer BP flake was mechanically exfoliated and transferred onto a SiO_2/Si substrate coated with 20 nm of parylene C. Figure 1.14(d) shows Raman spectra taken as a function of time under different conditions. No change in the Raman signal is observed for samples kept in vacuum or exposed separately to oxygen and water (results not shown here). Samples in vacuum exposed to a higher flux of photons up to $6 \times 10^4 \text{ Wcm}^{-2}$ also

showed no sign of degradation. The light-induced degradation of the multilayer BP is however instantly activated by introducing air or a mixture of pure water and vapor oxygen. Furthermore, the integrated Raman intensity as a function of time indicates that degradation in air is monoexponential, $\sim e^{-t/\tau}$, where t and τ indicate the time and decay time, respectively. All of these results reveal that water, oxygen, and visible light are three key environmental parameters simultaneously required for the degradation of multilayer BP.

Figure 1.14 (a) and (b) are AFM images measured instantly after exfoliation on a SiO₂/Si substrate and after several days under ambient conditions, respectively. (c) Raman spectra measured in air 24, 48, 96, and 120 min after exfoliation with the 532 nm laser line. (d) The evolution of the intensity of the A_{2g}² mode as a function of time under different conditions. Adapted from ref. [68].

(3) Other Raman spectroscopic studies of BP

Moreover, Raman spectroscopy has also been employed to probe the interlayer interaction of BP layers [66, 69] and the thermal effect on BP sheets [70].

1.3 Introduction to photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is an effective technique to study light emission properties of semiconductors, whose signals normally come from the charge carrier recombination [71]. In this part, we introduce the mechanism of PL spectra and review some relevant literatures about PL spectroscopic studies on TMD materials.

1.3.1 Basic principle of PL spectroscopy

In the electronic band structure of a semiconductor, the bandgap refers to the energy difference between the conduction band (CB) and the valence band (VB) [71]. There exist some sub-bands located in the bandgap, which are closely associated with surface states and/or surface defects. Figure 1.15 shows the schematic diagram of PL and non-radiative processes when semiconductors are excited by light with energies no less than the bandgap energy. Process I demonstrates the photo-excited process in which the electrons are excited from the VBM to the different energy states in the CB, and holes (h^+) are simultaneously generated in the VB after excitation [72]. After that, the excited electrons can easily return to the VB through a certain course and recombine with the holes, because they are energetically unstable. During this process, a certain amount of the chemical energy is released, which can be further converted to

the light or heat energy. The light energy can be emitted in the form of photons, which leads to the light emission called PL. Actually, the electrons located at different excited states in the CB can easily transfer to the CBM first via non-radiative transitions and afterwards, the processes II, III or IV will probably occur. Process II describes the band-to-band PL process in which the electron transits to the VBM from the CBM, accompanied by releasing of a photon with the energy equivalent to the bandgap energy. Occasionally, the photon energy can exceed the bandgap energy, which mainly comes from the transitions of excited electrons from higher energy states in the CB band to the VBM directly. Process III demonstrates the excitonic PL process in which the excited electrons transit from the CBM to different sub-bands in a non-radiative procedure first, and then proceeds to the VBM with the emission of a photon [71]. The energy of the emitted photon in this case is lower than the bandgap energy. Generally, the excitonic PL signal originates from defects of semiconductors and surface oxygen vacancies. Additionally, the excited electrons at the CBM can return to the VB either directly or indirectly through non-radiative transitions, as indicated in process IV.

Figure 1.15 Schematic diagram of PL and non-radiative processes. Adapted from ref. [71].

1.3.2 PL spectroscopic study of semiconducting MX₂ materials

(1) Thickness-dependent light emission properties

In this section, we take MoS₂ as an example to demonstrate how the light emission changes with the layer number. As mentioned in section 1.1.1.2, thick MoS₂ undergoes an indirect-direct bandgap transition when thinned to monolayer [27]. According to Figure 1.16(a), a much higher PL quantum yield is observed in monolayer MoS₂ compared with those of the few-layer counterparts, which confirms this bandgap transition. As presented in Figure 1.16(b), the observed peaks in PL spectra are marked as A, B, and I, respectively. A and B peaks originate from direct excitonic transitions at the K point in the Brillouin zone due to the spin-orbital splitting in the VBM [9]. The A peak redshifts and broadens slightly with increasing thickness. The broad I peak only appears in the PL spectrum of MoS₂ thicker than

monolayer and is attributed to phonon-assisted indirect-gap luminescence. As can be seen in Figure 1.16(c), the bandgap systematically shifts to higher energy when MoS₂ gets thinner, which is due to perpendicular quantum confinement [10].

Figure 1.16 PL spectra of single-layer and bi-layer MoS₂. The inset shows the PL quantum yield as function of layer numbers. (b) Normalized PL spectra (by the intensity of A exciton peak) of MoS₂ thin layers. (c) The variations of bandgap energy with layer numbers. Adapted from ref. [10].

(2) Tunable light emissions of neutral and charged excitons in single-layer TMD via doping

The switch between spectral weights of neutral and charged excitons at different Fermi levels in monolayer MoS₂ has been reported by Mak *et al.* [73]. Figure 1.17(a) presents the PL and absorption spectra of monolayer MoS₂ at different back gate voltages, ranged from the charge neutral to an electron concentration of around 10¹³ cm⁻². For positive gate voltages, the neutral exciton A peak nearly vanishes in the absorption and PL spectra. On the other hand, the A⁻ negative trion peak, understood as the combination of an exciton and one electron, becomes completely dominant. As the negative gate voltage increases, the spectral weight of neutral exciton gradually

increases due to the decrease in the electron concentration, which limits the formation of trion. At the gate voltage of -80 V, the trion peak appears at the higher-energy side shoulder and can be clearly resolved from the fitted PL spectrum. From Figure 1.17(b), it can be seen that when the Fermi energy increases from 0 to 30 meV, the neutral exciton energy blueshifts, while the energy of the trion keeps nearly unchanged after a slight initial redshift. These dependences are in agreement with the calculation results and could be ascribed to the combined effects of many-body interactions and Pauli blocking [73]. The trion dissociation energy, defined as the minimum energy for removing one electron from the trion, can be obtained by calculating the difference between the neutral exciton and trion energies. As demonstrated in Figure 1.17(c), the trion dissociation energy linearly depends on Fermi energy and its value at infinitesimal electron concentration is the trion binding energy, which is the energy required for promoting one of the two electrons from the trion up to the CB edge.

Figure 1.17 (a) Absorption and PL spectra of monolayer MoS₂ as a function of the gate voltage. (b) The energies of the neutral exciton and trion, extracted from the absorption spectra, as a function of the Fermi energy and gate voltage. (c) The energy difference between the neutral exciton and trion as a function of the Fermi energy. The red line indicates the linear fit. The inset shows the process of the trion dissociation into an electron and a neutral exciton at the Fermi level. Adapted from ref. [73].

(3) Other properties of TMD investigated by PL spectroscopy

In addition to the optical investigations on thin layers of TMD introduced above, PL spectroscopy has also been used to study valley confinement [74, 75], alloy composition [61], crystal quality [76], and effects of various external perturbations on band structure, such as strain [77-79], temperature [80] and α -particle irradiation [81] in TMDs.

1.3.3 PL spectroscopic study of BP

Figure 1.18(a) shows the PL spectra of BP with different thicknesses. The marked PL feature can be observed in all thin layered BP samples, corresponding to the direct bandgap transition at the Γ point. As shown in Figure 1.18(b), the measured optical bandgap decreases when BP gets thicker, which confirms the trend predicted by the theoretical calculation [82]. This thickness dependence of PL peaks is consistent with that observed in MoS₂ [10], which is attributed to perpendicular quantum confinement [82].

Figure 1.18 (a) PL spectra of bi-layer, tri-layer, quadruple-layer, and quinary-layer (5L) BP. (b) Layer dependent optical bandgaps of BP from both PL spectra and theoretical simulation. Adapted from ref. [82].

1.4 Strain engineering in semiconducting 2D crystals

It is important to understand strain effects on 2D materials both for fundamental studies and developing various applications. In this section, several examples of how strain can be utilized to tune the properties of atomically thin materials will be given.

1.4.1 Electronic band structure engineering via strain in 2D semiconducting MX_2 materials

The first systematic study of strain effects on monolayer TMD was conducted by transferring thin layers of MoS_2 onto flexible substrates and applying homogeneous tensile uniaxial strain in a bending test experimental configuration [78]. As shown in Figure 1.19, it is found that the excitonic features linearly redshift when the tensile strain increases, indicating the narrowing of the bandgap upon tensile uniaxial strain. Similar redshift rates are obtained for the A and B excitons, which suggests that the A-B exciton splitting is strain independent. This is because the spin-orbit coupling originates from the inner parts of the atoms, which is insensitive to bond lengths of the atoms [78]. Besides, the PL peak of A exciton shows a similar redshift rate compared with its absorption peak, which indicates the insensitivity of Stokes shift to strain.

Figure 1.19 (a) Absorption and PL spectra of monolayer MoS₂ under uniaxial strain along the zigzag direction. (b) Strain dependent peak energies extracted from the absorption and PL measurements. Adapted from ref. [78].

For comparison, the strain effects on the electronic band structure of bi-layer MoS₂ were also investigated by the same group [78]. As shown in Figure 1.20(a), absorption and PL spectra of bi-layer MoS₂ are significantly modified by the application of uniaxial strain. Linear redshift trends were observed for the A, B, and I peaks from the absorption and PL measurements when uniaxial strain was applied (Figure 1.20(b) and (c)). Unlike monolayer MoS₂, the Stokes shift of the A exciton becomes larger with increasing strain, possibly owing to strain-induced defects [78]. The relative spectral weight of the I and A peak, together with the overall PL intensity,

decreases with increasing strain, which is again attributed to strain-induced defects [78].

Figure 1.20 (a) Absorption and PL spectra of bi-layer MoS₂ under uniaxial strains along the zigzag direction. (b) and (c) are strain dependent peak energies extracted from the absorption and PL measurements, respectively. Adapted from ref. [78].

1.4.2 Theoretical study on phonon frequencies of strained BP

The evolution of phonon modes under uniaxial strain has been calculated by Fei *et al.* [22]. As shown in Figure 1.21, the frequency shifts are dependent on atomic displacements of phonon modes, strain orientation and strength. The authors took the B_{2g} mode as an example and attributed its obvious redshift under uniaxial strain along the zigzag direction to the increase of the bond length between two nearby phosphorus

atoms in the same sub-plane. To our best knowledge, experimental investigations of strain effects on the BP are still lacking.

Figure 1.21 Frequencies of phonon modes for monolayer BP under uniaxial strain applied along both armchair and zigzag directions. Adapted from ref. [22].

1.5 Motivations and significances of the thesis

The exceptionally high stretchability of atomically thin semiconducting materials enables extensive manipulation of their properties and exploration of the rich physics through the application of external strain. The study of strain engineering in 2D semiconducting crystals is still at a relatively early stage, in spite of some pioneering theoretical and experimental explorations. Because of the as-born direct bandgap and the indirect-direct bandgap transition in single-layer limit, semiconducting TMDs have recently attracted much research interest. The high on/off ratio in monolayer semiconducting TMDs makes them hold promise for flexible optoelectronic applications; however, their carrier mobility is low. The application of strain can be used to improve the mobility of monolayer semiconducting TMDs as a common practice in modern microelectronics, but strain may also cause some unintended

consequences, such as the direct-indirect bandgap transition which may hinder its optoelectronic applications. As a result, it is necessary to quantify the strain in a convenient and non-destructive way and accurately determine the critical strain to induce such transition. Besides, the crystal orientation can significantly determine the properties of TMD materials, which necessitates a reliable way to identify it. When the strain is high enough to make symmetry lower, the doubly degenerate phonon mode will split and the polarization dependence of the splitted modes will be closely related to the crystal orientation in monolayer semiconducting TMDs, as predicted by theory. Thus, the polarization response of phonon modes under uniaxial strain may be used to determine the crystal orientation. BP, which has been revisited from the perspective of the 2D form, possesses a direct bandgap for any layer number, with the thickness dependent bandgaps bridging the gap between graphene and TMDs, making BP perfectly appropriate for near- and mid-infrared optoelectronics. Moreover, the on/off ratio and mobility combination of BP happens to fills the blank region unreachable by graphene and TMDs. Of particular interest is the unique puckered structure of BP, which results in many anisotropic properties. Therefore, it is important to understand strain effects on the anisotropic properties of BP for its better integration into various technologies, such as flexible electronics.

Motivated by what is mentioned above, this thesis focuses on investigating band structure evolutions and lattice vibrational responses in 2D MS_2 ($M=Mo, W$) and BP crystals under uniaxial tensile strain by *in situ* PL and Raman spectroscopy, together

with the DFT calculations. The main objective of this thesis is to gain a better understanding of strain effects on atomically thin semiconducting crystals and provide insights into their prospective future in flexible optoelectronics and photonics.

1.6 Organization of the thesis

This thesis is organized as follows:

Chapter 1 introduces the adopted techniques (Raman and PL spectroscopy), as well as the optical properties of studied materials (TMDs and BP) in this thesis and reviews recent advances in optical studies and strain engineering of these two kinds of semiconducting layered materials.

Chapter 2 describes sample preparation methods, our Raman system, and the technique to induce strain.

Chapter 3 systematically investigates the strain dependent light emission properties of atomically thin WS_2 . Both the bandgap-energy tuning and direct-indirect bandgap transition achieved by strain are revealed from *in situ* strained PL spectra of monolayer WS_2 and confirmed by DFT calculations. Furthermore, trion behaviors subject to strain are discussed.

Chapter 4 focuses on the modulation of phonon properties by uniaxial tensile strain in monolayer MoS_2 and WS_2 . The uniaxial tensile strain is shown to soften the in-plane E' phonon mode and even lift its two-fold degeneracy as reflected by a doublet splitting. Moreover, the different polarization dependence of the two splitted

sub-peaks proves to be an effective pointer of the crystal orientation for monolayer MS_2 (M= Mo, W).

Chapter 5 reveals the remarkable anisotropic response of phonon frequencies to uniaxial strain in few-layer BP. Each phonon mode is shown to be sensitive to uniaxial tensile strain along either the zigzag or armchair direction while inert to strain applied perpendicular to the previous direction. The observed direction dependent phonon behaviors under uniaxial strain are explained by anisotropic influence of tensile strain on structural parameters of BP by means of DFT calculations.

Chapter 6 includes a summary of this thesis and future work on the research of 2D materials.

Chapter 2 Experimental techniques and calculation method

2.1 Sample preparation

The semiconducting 2D crystals studied in this thesis are fabricated by two methods: mechanical exfoliation of bulk crystals (MoS_2 and BP) and chemical vapor deposition (CVD) growth (WS_2) followed by transfer process.

2.1.1 Mechanical exfoliation

After mechanical exfoliation was demonstrated to be an effective way to obtain thin layers of graphene by Novoselov *et al.* [1], this top-down method has been widely used to fabricate various 2D materials [83]. Because mechanical cleavage is a simple way to produce high quality flakes that are appropriate for general characterization [83], we adopt this method to obtain thin layers of MoS_2 and BP.

The polyethylene terephthalate (PET) substrates are thoroughly cleaned by successive supersonic bath treatments in acetone, water, and isopropyl alcohol (IPA) (each for 10 min) and then blow dried by ultra-high-purity nitrogen gas after each step. The fresh surface of bulk crystal is rubbed against the scotch tape and then peeling is repeated on the tape to make the transferred flakes thinner. After that, scotch tape/thin crystal (WS_2 , MoS_2 or BP) is pressed evenly onto the washed PET substrates and peeled off gently after several minutes. The whole process can leave many thin layers

with different thicknesses on the PET substrates, which could be easily identified by under the optical microscope.

2.1.2 Chemical vapor deposition growth and transfer of monolayer WS₂

Though mechanical exfoliation has enabled fabrication of high-quality flakes, much time needs to be spent on searching for desired samples due to its low yield. As a method to synthesize large-area and uniform 2D materials, CVD has been employed to grow several TMD materials in previous reports [76, 84-86].

Figure 2.1 presents the schematic diagram of our CVD system to obtain monolayer WS₂ [76], which is very different from the one previously reported to fabricate the same material [87]. In our setup, WO₃ thin film is not pre-deposited on the SiO₂/Si wafer in the high-vacuum chamber; instead, large-area monolayer WS₂ is fabricate by one step, that is using sulfur powders to directly sulfurize WO₃ powders [76]. To be more specific, after being cleaned by the same method adopted to wash the PET substrates, two 300 nm SiO₂/Si substrates are placed face to face with the top wafer upside down [76]. Appropriate quantities of WO₃ powders (normally around 1 mg, >99.5%, Sigma Aldrich) are sandwiched in the middle of the two substrates and loaded in a small one-end airtight quartz tube, which is pre-cleaned by deionized water and IPA. The small quartz tube, combined with sulfur powders of around 100 mg (>99.95%, Sigma Aldrich) placed near the non-sealed end, is introduced inside a big-diameter quartz tube and heated up by a tube furnace. The temperature of the furnace is raised first to 550 °C, then to 750 °C with a ramping speed of 20 °C/min

and 3 °C/min, respectively, and finally cooled down to the room temperature after the temperature is stable at 750 °C for 5 min. The flow rate of ultra-high-purity argon gas is 100 sccm throughout the entire growing process [76].

Figure 2.1 Schematic diagram of the CVD-growth process to fabricate WS₂ flakes.

Adapted from ref. [76].

After the quality of the as-grown WS₂ is confirmed by a quick optical characterization including Raman and PL spectroscopy, the samples are transferred from SiO₂/Si substrates to PET substrates by the widely used method reported by Ruoff *et al.* [88]. Firstly, the polymethyl-methacrylate (PMMA) is spin coated on the as-grown monolayer WS₂ film, which is then cured on a hot plate at 100 °C for 2 min. The SiO₂/Si substrate is subsequently etched away by an aqueous of potassium hydroxide solution (4 mol/L) after around 14 h. After that, the PMMA/WS₂ stack is repeatedly washed with deionized water and then transferred to the washed PET substrates. When the stack becomes dried after 1 hour, a drop of liquid PMMA solution is redeposited onto the PMMA/WS₂ to melt the predeposited PMMA. The newly formed PMMA film is then gradually cured at ambient condition for about 1 hour and dissolved by acetone and IPA, respectively.

Figure 2.2 compares the optical images of monolayer WS₂ before and after transfer, which demonstrates that the perfect triangle shape can be preserved after transfer process.

Figure 2.2 Comparison of optical images of CVD-grown monolayer WS₂ before and after transfer. (a–c) show optical images before transfer and (d–f) are the corresponding images of samples taken after being transferred onto the PET substrate.

2.2 Sample characterization

2.2.1 Micro-Raman spectroscopy

All the Raman spectra shown in this thesis are collected by the WITec CRM200 Confocal Raman system. Its schematic diagram and beam path are shown in Figure 2.3 [89]. A tungsten halogen lamp is adopted as the white light excitation source to illuminate and focus the sample with the wavelength ranged between 350 nm and 850 nm. The laser beam is coupled into the microscope via a single-mode optical fiber and then collimated with an adjustable optics to a parallel beam. The parallel beam is then

directed by the beam splitter to the microscope objective, through which it is focused onto the sample. The diameter of laser spot on the sample is around 500 nm after passing through a 100x objective lens of numerical aperture (NA) = 0.95 (Olympus). The measured sample is placed on the XYZ stage, which can be coarsely moved in the x - y plane by hand and finely shifted with the piezo stage. The scattered light is collected under backscattering configuration and detected by a charge-coupled device (CCD) after the majority of Rayleigh light is blocked by an edge filter. Three different excitation sources are used, which are 457, 532, and 488 nm laser, with 1800 and 2400 grooves/mm gratings. Sample damage is avoided by extremely careful control of laser power and integration time. For polarization dependent Raman measurements, the polarization of incident beam is adjusted by a half wave plate, while that of the scattered light is tuned by an analyzer placed on top of the edge filter.

Figure 2.3 Schematic diagram of WITec CRM200 Confocal Raman system.

Adapted from ref. [89].

2.2.2 Micro-PL spectroscopy

The PL spectroscopy measurements in this dissertation are performed by the same WITec CRM200 system with 457 nm excitation laser. Here, 150 grooves/mm grating is adopted to split and diffract the emission light from the sample into several streams of light travelling in different directions.

2.3 Strain application

The samples are first fixed onto a strain stage and the desired areas are ensured to be located on the gap area of the stage as shown in Figure 2.4. Once the sample firmly adheres to the stage (which generally takes around 10 hours), *in situ* strained Raman and/or PL measurements can be conducted. By elongating the PET film in the horizontal direction, uniaxial tensile strain is applied. The controllable strain strength is determined by calculating the ratio of the extra length and the pristine one. The vdW interaction between the substrate and atomically thin materials should be strong enough to exert the strain on them because the studied samples are ultrathin [90].

Figure 2.4 Schematic diagram of how uniaxial strain is applied to the sample.

2.4 Calculation method

The electronic band structures and atomic structures of the 2D semiconducting materials are calculated based on the DFT method within the local density approximation (LDA). The studied material is modeled by its corresponding unit cell and the introduced vacuum spacing between periodic replicas along the c axis is large enough to make the structure effectively isolated along the out-of-plane direction. For strained geometries, the lattice vector along the strain direction is enlarged according to strain strength while those along the other two directions are kept constant and all the atoms are allowed to be fully relaxed.

Chapter 3 Electronic band structure engineering of 2D WS₂ via uniaxial strain

3.1 Introduction

Strain engineering plays a key role in tuning properties of 2D crystals. Strain effects on monolayer graphene have been widely studied. The lattice vibration, the magnetism, and even the electronic band structures of graphene could be remarkably influenced by applying strains [90-96]. Owing to the as-born bandgap and extremely high breaking strength [97, 98], atomically thin semiconducting TMDs provide a good opportunity to further study strain effects on 2D materials. Phonon softening [99, 100], crystal orientation determination [99], bandgap narrowing [78, 79], valley polarization decrease [77], and giant valley drift [101] under tensile strain have been reported in monolayer MoS₂. However, influences of strain on the direct bandgap feature, the most interesting and important property of 2D TMDs, such as a direct-indirect bandgap transition under strain predicted by the theoretical calculations [102-105], have not been systematically studied by any experimental approach. Moreover, the strain effects on trion feature which was recently assigned in several monolayer TMDs [73, 75, 106, 107] remain unstudied experimentally to our best knowledge. 2D tungsten disulphide (WS₂), one kind of TMD material, has been demonstrated to hold potential for optoelectronics, photonics, and nanoelectronics both in independent forms and heterostructures [108-111], and CVD method has been employed to

successfully grow monolayer WS₂ in large area with high quality in our recent reports [76, 112]. A study of strain dependent properties could help us gain further insight into the opportunity for applications of this material, especially the flexibility-related ones [113]. However, experimental investigations of strain effects on the light emission and lattice vibration of 2D WS₂ are still lacking, in stark contrast to the 2D MoS₂ counterpart [77-79, 99, 100].

In this work, we report our observation of tunable light emissions of CVD-grown monolayer and mechanically exfoliated bilayer WS₂ under uniaxial tensile strain. Both the bandgap-energy tuning and direct-indirect transition achieved by strain can be revealed from strained PL spectra of monolayer WS₂. Furthermore, trion behaviors subject to strain are discussed. Finally, we observe the linear redshift of both direct and indirect bandgap energies of bilayer WS₂ with uniaxial strain.

3.2 Experimental methods

Mechanical exfoliation: Bi-layer WS₂ samples were fabricated by mechanical exfoliation of bulk WS₂ crystals (2D Semiconductors, CAS #12138-09-9, USA).

Growth and transfer: The CVD method as previously described [76] was employed to grow single-layer WS₂. Desired areas were located, with corresponding optical and fluorescence (FL) images taken by an optical microscope (BX 51). Then, the grown samples were transferred to the PET substrate adopting the improved method proposed by Li *et al.* [88].

Strain application: The samples were mounted on a strain stage with the desired areas in the middle of the stage gap and could be controllably elongated to apply uniaxial tensile strain (see section 2.3 for details).

Optical characterization: Raman spectra were collected by a Raman system (WITec CRM200) with 1800 lines/mm grating under 457 nm excitation laser. PL measurements were conducted in the same WITec system with 150 lines/mm grating under both 457 and 532 nm laser lines. The laser spot is around 500 nm in diameter. The PL spectra before and after transfer process were taken under the same condition. Raman spectrum of single-layer WS₂ transferred to PET substrate was measured with higher integration time and power compared with that of as-grown one for better comparison. In each strain loading process, at least three different points were studied to ensure the observed spectrum change is typical. Both Raman and PL measurements under different strain were performed under the same condition with a low laser power to avoid damaging the sample. Under some specific strain strengths, several spectra on the same spot were taken and compared to confirm the validity of measurement results.

3.3 Results and discussion

A CVD-grown monolayer WS₂ sample on a SiO₂/Si substrate was firstly identified by its intense light emission, and this was confirmed by the frequency difference between the E' and A'₁ Raman modes. As shown by the FL image in

Figure 3.1(b), the triangle area with monolayer thickness exhibits an obviously stronger light emission than the center, which is thicker than the monolayer. This is due to the indirect–direct bandgap transition when the sample is thinned to a monolayer limit [11, 114]. In addition, by fitting the Raman peaks of the as-grown monolayer WS₂ sample on the SiO₂/Si substrate displayed in Figure 3.2(c), a frequency difference of 59.3 cm⁻¹ between the E' and A₁' Raman modes was obtained, which verifies the monolayer identification, as this quantity is thickness-dependent in the thin layers of WS₂ [115, 116].

Figure 3.1 (a) Optical and (b) FL images of CVD-grown monolayer WS₂ sample on SiO₂/Si substrate. The green dot in the FL image represents the position where spectra shown in Figure 3.3(a) were taken.

As can be seen from the FL image in Figure 3.1(b), the light emission from the sample near the edge is enhanced compared with that near the body. The PL quenching in certain areas of the CVD-grown monolayer WS₂ has been reported and attributed to the defect-induced electron doping [76, 112]. Considering this non-uniformity, we studied the evolution of the PL spectra under different strain

strengths by shining the laser at exactly the same position on the sample. We compared the PL behaviors at different points to ensure that the observed spectrum change was typical. The green dot in Figure 3.1(b) indicates the point where the spectra shown in Figure 3.3(a) were measured.

To effectively apply uniaxial strain to single-layer WS₂, the as-grown CVD WS₂ thin layers on SiO₂/Si substrate are needed to be transferred onto the flexible PET substrate. Optical images of monolayer WS₂ before and after transfer shown in Figure 3.2(a) and (b) reveal that the transferred sample maintained its original perfect triangle shape. As a unique and powerful tool for investigations of layer number [52, 117, 118], stacking order [119-121], local oxidation [122], and doping effects [64, 123], Raman spectroscopy is adopted to characterize the samples before and after transferring with 457 nm excitation laser line. As shown in Figure 3.2(c), under this excitation condition, one second-order zone-edge phonon mode (2LA(M), 347 cm⁻¹) plus two zone-center modes (E', 357cm⁻¹ and A'₁, 417cm⁻¹) dominate in the range of 300 to 480 cm⁻¹ [115]. No obvious spectral change is observed, confirming that the transferred sample maintained its quality.

Figure 3.2 Optical images of CVD-grown monolayer WS₂ on (a) SiO₂/Si substrate and (b) PET substrate after transfer process. (c) Raman and (d) PL spectra of monolayer WS₂ before and after transfer with fitted curves.

Benefitting from a direct bandgap, single-layer TMDs usually possess strong PL emissions. For our CVD-grown single-layer WS₂, a strong and symmetric peak usually presents [76, 112]. As can be seen from Figure 3.2(d), an obvious peak splitting occurs after the transfer process. Considering that the transfer process may cause some non-intentional doping to the single-layer WS₂, we attribute the doublet split two peaks to neutral exciton (higher energy) and charged exciton or trion (lower energy), respectively. The similar excitonic emission features have also been previously observed in WS₂ and other 2D TMDs [73, 75, 106, 107]. Such excitonic emissions are originated from the direct bandgap transition at the K point in the Brillouin zone [114] and there is a switch between neutral exciton (A) and trion (A⁻ or

A^+ depending on extra carrier type) at different Fermi levels [73, 75, 106, 107]. From our previous studies, our CVD-grown WS_2 exhibits an n-type doping property [112]. The existence of excessive electrons in such n-type WS_2 could facilitate the formation of negative charged exciton (A^-). For the transferred samples, the spectral-weight transformation from A^- to A in the PL spectra is caused by a decrement of the n-type doping level resulted from the trapped molecules during the transfer process. The molecular doping effects on the light emissions of monolayer WS_2 have been discussed in the previous report [124].

To further probe the strain modulated electronic band structures revealed by our DFT calculation, the detailed *in situ* strain PL spectra measurements were conducted. Figure 3.3(a) displays the evolution of PL spectra in single-layer WS_2 as a function of uniaxial tensile strain. With increasing strain ranged from 0 to 2.2%, there is an obvious redshift of PL emission while the line shape keeps unchanged, similar to the previous observation for strained single-layer MoS_2 [77, 78]. A discernible PL peak broadening can be observed under 2.5% strain (see Figure 3.4), after which PL spectrum continues to broaden and entirely redshifts with increasing strain. Considering that our DFT observation of the direct-indirect bandgap transition arises under *ca.* 2.6% (see section 3.4.2 for details), such broadening, especially at the longer wavelength tail, may arise from the extra contribution of the light emission from the indirect bandgap (Γ -K).

Figure 3.3 (a) PL spectra, fitted light-emission (b) integrated intensities and (d) energies of A, A⁻, and I peaks for CVD-grown monolayer WS₂ as a function of the uniaxial strain under 532 nm laser line. The intensities of all peaks are normalized by the I peak intensity under 3.7% strain, which is the largest one of the sub peaks in measured strain range. (c) and (e) are intensity ratios of direct-indirect transition peak and position-distance trend of A and A⁻ peak with increasing strain, respectively. The dashed lines in (b) and (e) act as guides for the corresponding trend under strain and the solid lines in (c) show linear fit.

To test this speculation, we fitted the PL spectra with strain below 2.5% by two Gaussian peaks while the PL spectra under strain beyond 2.5% were fitted by three Gaussian peaks. Excellent fittings could be achieved by using this fitting strategy, as demonstrated by the representative spectra shown in Figure 3.4. It is noteworthy that the newly appearing peak under strain no less than 2.5% (expressed as I, standing for

indirect thereafter) is always broader than the other two, which agrees with the feature of the indirect gap emission peak in few-layer WS₂ [11, 114]. This broadening is contributed by the phonon which participates in the recombination process of the indirect transition to satisfy momentum conservation by providing appropriate momentum [125]. As can be seen in Figure 3.3(b), I peak intensity has a rising trend with increasing strain contrary to those of A and A⁻ peaks. The simultaneous reduction of two intensity ratios (A/I and A⁻/I) (see Figure 3.3(c)) shows direct-indirect spectral-weight conversion with increasing strain, as a result of strain-induced faster energy narrowing rate of the indirect transition than that of the direct one. The fitted light-emission energies as a function of uniaxial strain are given in Figure 3.3(d). In addition to the expected linear redshift of A exciton peak with strain (-0.0114 eV/%), which is also found in single-layer MoS₂ [77-79], I peak is linearly redshifted at a higher rate of -0.0187 eV/%. Notably, under 2.5% strain, the energy of I peak is 35 meV smaller than that of A peak. This contrasts the observation of the approximate energy degeneracy of these two transitions near the critical strain to transform the bandgap type. It can be explained by the larger binding energy of the indirect transition compared to that of the direct one. The light-emission energy measured by PL spectroscopy represents the fundamental bandgap subtracted by the binding energy of the corresponding transition. The exciton binding energy is linearly dependent on the effective exciton mass [126], and the latter is jointly determined by the effective electron and hole mass at the band edge with the expression $\mu_{\text{ex}} = m_e m_h / (m_e + m_h)$.

Since the direct and indirect transitions share the same effective electron mass, the much larger hole mass at Γ than at K [127] lead to the stronger binding for the indirect transition. This different binding energy and the near-degenerate fundamental energy gap lead to the lower energy of I peak, which makes them distinguishable in the PL spectrum. Furthermore the trion dissociation energy evolution under strain can be estimated by extracting the strain dependent energy distances of A and A⁻ peaks. A slightly decreasing trend is observed, as shown in Figure 3.3(e). The decrease of trion dissociation energy under applying an increasing tensile strain has been noticed and explained by the changes of effective exciton mass and polarizability caused by varying strain [127, 128]. In detail, increasing strain could effectively reduce the effective exciton mass meanwhile enlarge the polarizability [127]. The smaller effective exciton mass and the larger polarizability consequently lead to a reduction of the trion dissociation energy [128]. To further prove that the indirect transition peak does contribute to the observed PL spectra, we show the results obtained by fitting all PL spectra under strain with two Gaussian peaks in Figure 3.5. In this way, the fitted intensity of A⁻ peak increases remarkably in the high strain region where the shortest transition is indirect and the dissociation energy decreases slightly with increasing strain. Those do not agree with the expected strain-induced light emission change as discussed before and provide additional evidence for the assignment of I peak in PL spectra under high strain.

Figure 3.4 PL spectra of CVD monolayer WS_2 transferred onto PET substrate with fitted curves under certain strain strengths.

As shown in Figure 3.4, a comparison between the PL spectra of the monolayer WS_2 obtained at different strain-loading stages clearly indicates that the PL shape after the strain release is similar to that in the zero-strain case and can be well fitted by two Gaussian peaks. The disappearance of the I peak when the strain is released further confirms that this peak originates from the indirect bandgap transition. In addition, after the strain release, the sample exhibits a PL emission comparable to that of the as-transferred one. This, together with the absence of defect-related bound exciton peaks, indicates that our sample is defect-free throughout the whole process and available for a new round of strain measurement.

Figure 3.5 Results obtained by fitting all PL spectra under strain with two Gaussian peaks. (a) Light-emission integrated intensities of A and A⁻ peaks of CVD monolayer WS₂ as a function of the uniaxial tensile strain. The intensities of all peaks are normalized by the A⁻ peak intensity under 3.7% strain. (b) The position-distance trend of A and A⁻ peaks with increasing strain.

For comparison, we next investigate the bandgap modification of bi-layer WS₂ via uniaxial strain. Figure 3.6(a) presents the optical image of the WS₂ sample which contains both single-layer and bi-layer regions, with the layer numbers determined by Raman spectroscopy [115, 116]. Owing to the different symmetry (D_{3h}^1 for single-layer and D_{3d}^3 for bi-layer), the high-frequency zone-center phonon modes are characterized by E_g and A_{1g} for bi-layer WS₂, corresponding to E' and A_1' modes for the single-layer counterpart [57]. By fitting the Raman spectra shown in Figure 3.6(b), the frequency differences between these two zone-center modes were obtained to be 60.0 and 62.3 cm^{-1} in the two regions, which provide a rapid identification of single-layer and bi-layer WS₂ nanosheets [115, 116]. The much lower light emission yield of bi-layer WS₂ compared with that of the single-layer counterpart can be clearly

reflected in the FL image (Figure 3.6(c)) and attributed to indirect-direct bandgap transition from few-layer to monolayer WS₂ [11, 114]. As shown in Figure 3.6(d), contrary to the PL spectrum of monolayer WS₂ where only direct gap transitions can be observed, the I peak at 1.76 eV also appears in the case of the bi-layer sample. This feature is originated from the indirect bandgap transition (Γ -K) [33, 129] and has larger intensity relative to that of the hot luminescence A peak in bi-layer WS₂.

Figure 3.6 (a) Optical and (c) FL images of the mechanically exfoliated WS₂ sample with both single-layer (1L) and bi-layer (2L) regions on PET substrate. (b) Raman and (d) PL spectra of 1L and 2L WS₂.

The strain dependent PL spectra of bi-layer WS₂ are displayed in Figure 3.7(a). Both A and I peaks redshift with increasing strain and no obvious change occurs to the line shape of bi-layer WS₂ throughout the applied strain range until 2.8% strain. This is because the uniaxial tensile strain does not induce transition of the bandgap type,

which further verifies our previous interpretation of the observed spectrum change in strained monolayer WS_2 . Figure 3.7(b) plots the dependence of light emission energies of A and I peaks on uniaxial strain. The linear dependence is observed for both of these two peaks, with the redshift rates of -0.0271 and -0.0361 eV/% extracted for A and I peaks, respectively. The more sensitivity of I peak to strain compared with that of A exciton peak is observed in bi-layer MoS_2 and attributed to different strain dependent orbital composition and orbital hybridization involved in these two transitions [78].

Figure 3.7 (a) PL spectra and (b) fitted light-emission energies of A and I peaks of bi-layer WS_2 as a function of the uniaxial strain under 457 nm laser line.

3.4 Calculation of electronic structure

3.4.1 Calculation methods

The electronic band structure calculations of unstrained and strained monolayer WS_2 based on the DFT were performed by the projector augmented wave

pseudopotentials method with a plane-wave basis set as implemented in the widely used code of Vienna *ab initio* simulation package (VASP) [130-132]. The plane-wave cutoff energy was 500 eV and the exchange–correlation functional was treated with the LDA based on the Ceperlay Alder (CA) parameterization. The 1H-WS₂ single-layer was modeled by 1×1 unit cell that contains three atoms. A vacuum spacing larger than 22 Å was introduced to hinder the interaction between periodic replicas along the *c* axis, making the single-layer structure effectively isolated. The convergence condition for the energy was chosen as 10^{−6} eV and the structures were fully relaxed until the forces on each atom were less than 0.01 eV/Å. The Monkhorst–Pack scheme was used as the sampling method for Brillouin-zone integration. To obtain the unstrained configuration, the atomic positions and lattice vectors were fully relaxed with a mesh of 15×15×1, and the optimized (relaxed) coordinates were then used for the self-consistent and density of state (DOS) calculations with the mesh of *k* space accumulated to 25×25×1. Band structures were calculated along the path Γ –M–K– Γ connecting high symmetry points. Since the uniaxial strain effects on band structure (especially the band edge parts) of single-layer TMD materials have been shown to be nearly direction independent [77, 79, 102], we only considered the strain along the [010] direction. More specifically, the lattice vector along this direction was enlarged according to strain strength while those along the other two directions were kept constant.

3.4.2 Band structure of monolayer WS₂ under different uniaxial strain

To better understand the observed strain-dependent light-emission behaviors shown in section 3.3, we calculated the band structure of single-layer WS₂ under different uniaxial strain by the DFT method and presented our findings in Figure 3.8 (see section 3.4.1 for details). One remarkable change of the band structure induced by applying uniaxial tensile strain is the direct-indirect bandgap transition, as also theoretically predicted in other single-layer TMD materials [79, 101, 102, 104, 105]. In unstrained state as shown in Figure 3.8(a), both VBM and CBM locate at K point. As the strain increases, the energy difference between the local maxima of K and Γ points in the VB becomes smaller and the maxima are nearly degenerate under 2.4% strain (Figure 3.8(b)). A uniaxial strain of 2.6% can move the VBM of monolayer WS₂ from K to Γ while keep the CBM unchanged, resulting in the narrowest gap between the transition from Γ to K, as can be seen in Figure 3.8(c). With the continuous increase of strain, the indirect bandgap feature becomes more obvious (see the band structure with 3.8% strain in Figure 3.8(d)). In addition, the zoom-in view of the band structure near the K point (the inset of Figure 3.8(d)) show that the strain can move the local VBM and CBM slightly away from the K point and this so-called “valley drift” has recently been observed in uniaxially strained monolayer MoS₂ [101].

Figure 3.8 Calculated band structure of monolayer WS_2 under (a) 0%, (b) 2.4%, (c) 2.6%, and (d) 3.8% uniaxial strain. Inset: zoomed-in band structure near CBM and VBM around the K point.

3.5 Summary

In summary, we have systematically investigated the strain dependent light emission properties of CVD-grown single-layer and mechanically exfoliated bi-layer WS_2 . For monolayer samples, we have experimentally demonstrated the possibility of tuning different optical transition energies and their relative spectral weight by applying uniaxial strain. This tuneable optical property is attributed to the strain-induced direct-indirect bandgap transition and confirmed by DFT calculations. We have also shown that uniaxial tensile strain can decrease the trion dissociation energy. In bi-layer WS_2 , the indirect bandgap transition redshifts with a larger shift

rate than the A exciton under tensile strain. These findings extend previous experimental studies of strained TMDs, corroborating theoretical predictions regarding strain effects on band structural evolution and providing insights into strain dependent trion behaviors. The observed sensitivity of the light emission to strain in single-layer WS_2 caused by the strain-induced bandgap type and energy change further indicates that this atomically thin semiconducting TMD material holds promise for various applications such as strain detection and optoelectronics.

Chapter 4 Raman spectroscopy study of lattice vibration and crystallographic orientation of monolayer MS_2 (M=Mo, W) under uniaxial strain

4.1 Introduction

Edges of 2D materials, such as TMDs and graphene, possess significantly different physical behaviors compared with the body counterpart because the structural discontinuity makes the edge atoms reconstruct structurally and electronically [133]. Consequently, edges have drawn considerable research interest with a variety of edge-related physical properties discovered, including high stability [134], anomalous magnetic responses [135-137], broadly tunable energy gaps [138, 139], and anisotropic optical polarization [140]. The properties of TMD materials are closely related to their edge chirality, especially for TMD nanoribbons. For example, MoS_2 armchair nanoribbons are nonmagnetic and semiconducting, while zigzag nanoribbons are ferromagnetic and metallic [141]. Moreover, the physical properties of 2D heterostructures are largely dependent on the relative orientation between two individual layers [142-144]. Thus, accurate identification of the edge chirality or crystal orientation is important for both fundamental studies and practical applications in TMDs.

Nowadays, to identify the edge chirality, researches commonly adopt second harmonic microscopy [145, 146] and electron-spectroscopy techniques such as transmission electron microscopy (TEM) or scanning transmission electron microscopy (STEM) [76, 84, 86]. The edges of CVD-grown 2D TMDs have been reported to be the zigzag termination by TEM and STEM observations though they are not atomically sharp [76, 114]. However, these techniques require specialized equipment and/or ultrahigh vacuum conditions [92], which makes the characterization not convenient. In addition, defect formation [84] and edge reconstruction [147] have been observed during TEM measurements, which makes the results possibly unreliable. For graphene, the intensity of the D band and polarization dependence of the G mode in Raman spectroscopy can be used to identify the edge chirality [148, 149]. Unfortunately, this method fails to achieve the same purpose in TMD materials. Therefore, an accurate, non-destructive, and simple technique is desired to effectively determine the edge or crystal orientation of TMD materials.

In this project, we carry out Raman spectroscopy measurements of monolayer mechanically exfoliated monolayer MoS₂ and CVD-grown monolayer WS₂ flakes on flexible PET substrate under controllable uniaxial tensile strain. We have shown that uniaxial tensile strain can soften the in-plane E' phonon mode followed by lifting its two-fold degeneracy, which makes the frequency of the E' mode a good choice for quantifying the amount of strain. Moreover, the different polarization dependence of the two splitted sub-peaks, E'⁺ and E'⁻, is an effective pointer of the crystal orientation

for monolayer MS_2 (M= Mo, W) and confirms the observed zigzag-oriented edge of CVD-grown WS_2 in previous studies.

4.2 Experimental methods

Sample preparation: the MoS_2 samples were fabricated by micromechanical exfoliation of a bulk MoS_2 (SPI Supplies, CAS #1317-33-5, USA) followed by transfer onto flexible PET substrates. Monolayer WS_2 samples were obtained by transferring as-grown WS_2 from SiO_2/Si substrates to PET substrates by the same method as presented in the last chapter.

Raman and PL spectroscopy characterization: the Raman spectra were obtained by a WITec confocal Raman microscope CRM200 with 2400 and 1800 lines/mm grating under 488 and 532 nm excitation laser, respectively. PL measurements were conducted in the same WITec system with 150 lines per mm grating under 532 laser line. The laser spot size is about 0.5 μm . To achieve a good signal to noise ratio and avoid laser-induced damaging, laser power was finely tuned. *In situ* strained Raman measurements were conducted by the method as described in section 2.3.

4.3 Results and discussion

4.3.1 Strain-assisted phonon modification and crystallographic orientation determination of mechanically exfoliated monolayer MoS₂

Figure 4.1 shows the optical image, Raman spectra, fitted phonon frequency difference, and PL spectra of thin MoS₂ flakes with different layer numbers and bulk MoS₂. Two dominant peaks are observed at 384 cm⁻¹ and 403 cm⁻¹, corresponding to the E' and A'₁ modes, respectively (see Figure 4.1(b)). The vibrational frequencies of these two modes shift from bulk to monolayer, with a blueshift of 1 cm⁻¹ for the E' mode and a redshift of 5 cm⁻¹ for the A'₁ mode. The deviations are primarily attributed to the weakening of dielectric screening which enhances the long-range Coulomb interaction (for the E' mode) and decrease of the force constant originated from the weakening of the interlayer vdW interaction in MoS₂ layers (for the A'₁ mode) when the layer number decreases [52]. By reading the position difference between E' and A'₁ modes (Figure 4.1(c)), which is a commonly adopted method to identify the thickness of thin MoS₂ flakes [34, 52, 150], the layer numbers of the thin MoS₂ flakes were identified to be monolayer and trilayer as marked in Figure 4.1(a). It also can be seen from Figure 4.1(d) that the PL spectra further verify the identification of monolayer MoS₂ [9]. Two PL peaks marked in Figure 4.1(d) are established to come from A and B direct bandgap transitions at the K point in the Brillouin zone due to the spin-orbital interaction [9] and it is obvious that the PL emission from monolayer sample is much stronger than that from trilayer MoS₂. This

is due to the indirect-direct bandgap transition from few-layer to monolayer MoS₂ and consistent with the previous report [9].

Figure 4.1(a) Optical image of the monolayer, trilayer, and bulk MoS₂ (highlighted by red, green, and black dash lines, respectively) on PET. (b) Raman spectra and (c) the fitted frequency difference between E' and A₁' modes of monolayer, trilayer, and bulk MoS₂. (d) PL spectra normalized by the Raman intensity of MoS₂ samples with different thickness.

Optical contrast image and spectroscopy have been widely employed for identification of number of layers of graphene [151, 152]. Recently, it has been used for determination of the thickness of MoS₂ thin layers on typical SiO₂/Si [153, 154]. Here, we present the white light contrast spectra of monolayer MoS₂ and graphene on PET in Figure 4.2. The details of the white light contrast measurements have been

discussed in the previous report [151]. As can be seen from Figure 4.2, the contrast of single-layer MoS₂ on PET is much better than that of graphene, which is good for performing strain depended studies of MoS₂ thin layers.

Figure 4.2 White light contrast spectra of monolayer MoS₂ and graphene on PET substrates. Insets are the optical images of monolayer MoS₂ and graphene on PET.

Figure 4.3(a) shows the typical Raman spectrum of single-layer MoS₂ on the PET substrate in the range of 200 to 1250 cm⁻¹. In addition to the dominant E' and A'₁ modes, Raman peaks of MoS₂ were observed at 447, 564, 593, and 750 cm⁻¹, which could be assigned to 2LA(M), 2E'', E'+LA(M), and 2E' modes, respectively [51, 155]. To further determine the crystal orientation of single-layer MoS₂ by investigating polarization behaviours of E' and A'₁ modes under uniaxial strain, we carried out Raman measurements of the unstrained monolayer MoS₂ as a function of polarization angle. As displayed in Figure 4.3(b), the A'₁ mode exhibits significant polarization dependence and has nearly zero intensity when the polarizations of the incoming and

scattered lights are perpendicular, while the E'-mode intensities fluctuate very slightly. Our fitting results (Figure 4.3(c)) further clearly uncover the essence of polarization dependence for these two modes, which could be perfectly elucidated by the Raman selection rules according to their respective Raman tensors (see section 4.4.1 for details).

Figure 4.3 (a) Typical Raman spectrum of single-layer MoS₂ on PET. The phonon peaks marked by ▼ are phonon modes of single-layer MoS₂, including E' (384 cm⁻¹), A₁' (403 cm⁻¹), 2LA(M) (447 cm⁻¹), 2E'' (564 cm⁻¹), E'+LA(M) (593 cm⁻¹), and 2E' (750 cm⁻¹). Phonon modes labeled by * come from PET. (b) Raman spectra of the pristine single-layer MoS₂ on PET as a function of the angle between the polarization of the incoming light and that of the scattered light. (c) Polar plot of the fitted E'- and

A'_1 -mode intensities as a function of angles between the incoming and scattered light polarizations.

Figure 4.4(a) presents Raman spectra of E' and A'_1 modes of monolayer MoS_2 under increasing uniaxial strain. Though no obvious shift occurs to the A'_1 mode, the frequencies of the E' mode redshifts with increasing strain. This originally doubly degenerate optical E' mode further splits into two singlet sub-modes, termed E'^+ and E'^- , on the basis of their frequencies, under the strain larger than 1%, which lowers the original symmetry. As displayed in Figure 4.4(b), the E' mode involves opposite vibration of two sulphur atoms relative to the molybdenum atom in the basal plane while the A'_1 mode arises from the out-of-plane vibration of mere sulphur atoms in reverse directions [150]. Our experimental observations undoubtedly indicate that the dominated covalent bonding between sulphur and molybdenum atoms is rather sensitive to the in-plane uniaxial strain, which could indirectly evidence the modification of the electronic properties of single-layer MoS_2 through the strain-induced change in projected orbitals energy of molybdenum atom and the coupling between d orbital of the molybdenum atom and p orbital of the sulphur atom [102, 104].

Figure 4.4 (a) Evolution of the Raman spectra of monolayer MoS₂ under uniaxial strain. The peak positions are guided by the dash lines. (b) The schematic diagram of the atomic displacements of the E' and A₁' modes. The optical image of the single-layer MoS₂ (highlighted by red dashed rectangle) on PET is displayed in the inset. (c) Fitted vibrational frequencies of E' and A₁' modes under increasing uniaxial strain. The solid lines denote the linear fitting.

Figure 4.5 plots the Raman spectra of single-layer MoS₂ under some representative strain (0%, 1.0%, 2.4%, and 3.6%) simultaneously with fitted curves to specify the evolution of E' and A₁' modes under increasing strain. The fitted peak

positions of the A'_1 , E^+ and E^- modes are shown in Figure 4.4(c). We fitted the E' peak under strain of smaller than 1.0% and larger than 1.0% by single Lorentz and two Lorentz peaks, respectively, because the critical strain which makes E' mode begin to split into two singlet sub-modes is around 1.0%. The linear fittings give a shift rate of $-0.8 \text{ cm}^{-1}/\%$ for the $E^{'+}$ mode and $-2.5 \text{ cm}^{-1}/\%$ for the E'^{-} mode, which show much less significant dependence on strain compared with the G^+ and G^- modes of graphene [94]. To further comprehend the effects of uniaxial strain on the E' mode, the Grüneisen parameter ($\gamma_{E'}$) and the shear deformation potential ($\beta_{E'}$) are calculated based on the simplified equations (see section 4.4.2) [94]:

$$\gamma_{E'} = -\frac{P_{E'^+} + P_{E'^-}}{2\omega_{E'}^0 (1-\nu)} \quad (4-1)$$

$$\beta_{E'} = \frac{P_{E'^+} - P_{E'^-}}{\omega_{E'}^0 (1+\nu)} \quad (4-2)$$

where $P_{E'}$ is the shift rate, $\omega_{E'}^0$ is the zero-strain vibrational frequency of the E' mode, and $\nu = 0.33$ is the Poisson factor of the used PET substrate. From the Equations (4-1) and (4-2) together with the data in Figure 4.4(c), $\gamma_{E'}$ and $\beta_{E'}$ of monolayer MoS_2 are calculated to be 0.6 and 0.3, respectively, which are smaller compared with those of graphene [94].

Figure 4.5 Raman spectra of E' and A'_1 modes of monolayer MoS_2 with fitted curves under 0%, 1.0%, 2.4%, and 3.6% strain.

The polarization dependence of Raman spectroscopy has been successfully employed to investigate the crystal orientation of graphene [92, 94]. In this project, we used this technique to determine the crystal orientation of single-layer MoS_2 . Figure 4.6(a) demonstrates the configuration of our polarization dependent Raman measurements. We made the strain direction fixed along the x -axis (horizontal direction) and aligned the incoming laser polarization coincidently, meaning that the angle ψ is equal to 0° . The polarization of the scattered light compared with the strain direction (the angle ϕ) is rotated by an analyzer.

Figure 4.6 (a) Schematic diagram of the configuration for our polarization dependent Raman measurements. The strain direction ($\vec{\epsilon}$) is fixed along the x -axis, with a θ angle relative to the zigzag direction. e_i and e_s mark the polarization of the incoming and scattered lights, which deviate from the strain direction by angles of ψ and ϕ , respectively. (b) False-color image of the Raman spectrum intensity as a function of the angle ϕ and the Raman shift under uniaxial strain of 3.6%. (c) and (d) show polar plots of the fitted intensities of E^+ , E^- , and A_1' modes.

In this way, we can gain the Raman spectra of the monolayer MoS_2 under 3.6% uniaxial strain as a function of angle ϕ (see Figure 4.7) and plot the false-color image (3D type) of the spectrum intensity versus both polar angles and peak positions in

Figure 4.6(b). It can be seen that the strongest E^{+} and E^{-} peaks turn up at different polarization angles, revealed as the alternation of the intensity maxima within the E' mode frequency range while the maxima and minima of the A'_1 band appear in the same line of the Raman shift. To further comprehend the polarization dependence of the E^{+} , E^{-} , and A'_1 modes under the uniaxial strain and consequently determine the crystal orientation of single-layer MoS_2 , we implemented the Lorentz fitting and plotted the polarization dependent intensities of these three modes in Figure 4.6(c) and (d). Same as what is observed in pristine monolayer MoS_2 , the A'_1 mode follows a $\cos^2\varphi$ dependence as it is rather unsusceptible to in-plane uniaxial strain. Contrary to the non-polar behavior of the E' mode for the pristine single-layer MoS_2 (Figure 4.3(c)), the splitted E^{+} and E^{-} modes induced by applied strain are very sensitive to the polarization angle. For example, the E^{+} mode almost cannot be detected when the polarization of the scattered light is orthogonal to that of the incoming light ($\varphi = 90^\circ$), while the intensity of the E^{-} mode becomes strongest. After the analyzer is further rotated by 90 degrees which makes φ equal to 180° , the maximum of the E^{+} and the minimum of the E^{-} can be observed. This demonstrates that the polarizations of the scattered light from E^{+} and E^{-} modes are linear and perpendicular to each other.

Figure 4.7 The polar-dependent Raman spectra of monolayer MoS₂ on PET under 3.6% uniaxial strain.

The splitting of E' mode into E'⁺ and E'⁻ modes is induced by applied uniaxial strain, which could consequently change the symmetry or original crystal structure. Therefore, the measured intensities of the polarized scattered light from these two splitted modes depend on the strain direction with regard to the crystal lattice as

predicted by the Equations (4-3) and (4-4) (see the derivation in section 4.4.3) [92, 94]:

$$I_{E'^+} \propto d^2 \cos^2(\varphi + \psi + 3\theta) \quad (4-3)$$

$$I_{E'^-} \propto d^2 \sin^2(\varphi + \psi + 3\theta) \quad (4-4)$$

here ψ is zero because both of the incoming light polarization and the strain axis are fixed along the horizontal direction. The good consistency between the experimental results and the fittings by Equations (4-3) and (4-4) strongly corroborates the theoretical analysis and the value of θ tells the zigzag orientation. For the sample whose optical image is presented in Figure 4.4(b) inset, the zigzag direction is coincidentally very near the strain direction.

To further verify the analysis above, we performed polarization dependent Raman spectroscopy measurements on another piece of single-layer MoS₂ on PET under 2.8% uniaxial strain, which is sufficiently high to make the E' mode split into two sub-modes. As expected, the linear polarizations of the scattered light from E'⁺ and E'⁻ modes are perpendicular (see Figure 4.8(b)). Now, based on the previous analysis, if we change the angle between the strain direction (fixed along the x -axis) and the zigzag direction, different polarization response of splitted E'⁺ and E'⁻ modes should be observed. We re-fixed the same sample including the same flake of monolayer MoS₂ and the PET substrate after it was rotated by an angle of ~90° with respect to the x -axis and strain was fully released, checked by the measured frequency of the E' mode. As anticipated, the splitted E'⁺ and E'⁻ respond differently to the angle

φ and the minima as well as maxima of these two sub-modes shifted, which verifies the previous experimental findings and analysis. The data shown in Figure 4.8(b) and (d) are well fitted by $I_{E^+,+} \propto \cos^2\varphi$, $I_{E^-,+} \propto \sin^2\varphi$, and $I_{E^+,+} \propto \cos^2(\varphi + 80^\circ)$, $I_{E^-,+} \propto \sin^2(\varphi + 80^\circ)$, respectively. Based on Equations (4-3) and (4-4), we can get $\theta=0^\circ$ (before re-mounting) and $\theta=26.7^\circ$ (after re-mounting). This is consistent with the sample rotation angle of $\sim 90^\circ$, which makes the zigzag orientation relative to the x -axis (θ) alter from 0° to $\sim 30^\circ$ (The angle of 26.7 acquired from the polarization dependent Raman measurements is rather close to this value.).

Figure 4.8 (a) and (c) Optical images and schematic diagrams of the same flake of single-layer MoS₂ on PET with uniaxial strain applied along different directions. (b) and (d) show polar plots of the intensities of splitted E⁺ and E⁻ sub-modes as a function of angle φ . It should be noted that for (c) and (d), the sample including both

single-layer MoS₂ and PET was remounted after rotation of around 90° relative to the strain direction after the strain was fully released.

As one might expect, the A'_1 mode follows the same dependence of a $\cos^2\varphi$ perfectly for the sample both before and after rotation, as shown in Figure 4.9.

Figure 4.9 (a) and (b) are the polar plots of the fitted peak intensities of A'_1 bands as a function of angle φ for the identical monolayer MoS₂ flake on PET under uniaxial strain with different strain directions shown in Figure 4.8(a) and (c), respectively.

4.3.2 Probing the lattice vibration and crystallographic orientation in CVD-grown monolayer WS₂ under uniaxial strain by Raman spectroscopy

We next study the phonon properties of single-layer WS₂ under strain. Strain dependent Raman spectra of monolayer WS₂ are displayed in Figure 4.10(a) with the extreme sensitivity of the E' mode to strain observed. The strain-induced redshift and splitting of this mode under high strain can be clearly seen. In contrast, the out-of-plane A'_1 mode is more inert to in-plane strain. As mentioned in the previous

section, the E' mode involves in-plane opposite displacements of tungsten and sulphur atoms, while the A'_1 mode corresponds to vibrations of mere sulphur atoms out of phase perpendicular to the plane [31]. The analysis of different response of these two phonon modes to uniaxial strain in monolayer MoS_2 based on their distinct atomic displacements and symmetry breaking has been discussed in section 4.3.1. To accurately reveal the behaviors of phonon modes under strain, multiple Lorentzian functions were adopted to fit Raman spectra under different strain strength. As clearly seen in fitted phonon frequencies versus strain (Figure 4.10(c)), double degenerate in-plane E' mode linearly softens under small strain and then splits under 1.4% strain, after which both of E'^+ and E'^- peaks have a linear relationship with strain value. The A'_1 mode remains its single Lorentz shape throughout the applied strain range, as expected. It is noticed that a slight redshift of less than 0.4 cm^{-1} happened to the A'_1 mode under high strains, *i.e.* 2% - 3.2%. This is a little surprising because this mode should be insensitive to in-plane strain. We attribute this redshift to laser-induced heating which becomes more remarkable as the laser shining on the sample proceeds instead of the applied strain. Since the A'_1 mode is reported to be more susceptible to the heating induced by laser [55] and temperature [53, 54] than the E' mode for monolayer TMDs, its unexpected redshift under strain is observed in our case.

Figure 4.10 (a) Raman spectra of monolayer CVD WS₂ with increasing strain under 488 nm laser line. (b) Optical image of CVD-grown monolayer WS₂ on PET after transfer process. (c) Fitted phonon frequencies of E' and A₁' modes of single-layer WS₂ under increasing uniaxial strain. (d) and (e) are polar maps of fitted Raman intensities of E'⁺, E'⁻, and A₁' modes as a function of angle φ under 3.2% uniaxial strain.

Polarization dependent Raman spectroscopy under uniaxial strain has been successfully proven to be a unique and efficient way to determine the crystal orientation of mechanically exfoliated monolayer MoS₂ in section 4.3.1. In the present study, we adopted this technique to determine the crystal or edge orientation of our CVD-grown monolayer WS₂. Figure 4.11(a) shows the measured polarization-dependent Raman spectra of the as-transferred CVD-grown monolayer WS₂ under zero strain. In our polarization configuration, the incident light is constantly polarized along the horizontal direction and the scattered light polarization can be chosen with an angle φ corresponding to the horizontal by a linear polarizer.

The fitted results (Figure 4.11(b) and (c)) clearly show that the intensity of the A'_1 mode follows a $\cos^2\varphi$ dependence while that of the E' mode is insensitive to the polarization angle. This has been well explained by their different Raman tensors in section 4.3.1.

Figure 4.11 (a) Raman spectra of the as-transferred CVD monolayer WS₂ as a function of the angle φ . (b) and (c) are polar-dependent Raman scattering intensities of E' and A'_1 modes, respectively.

The schematic diagram of the polarization geometry in our polar-dependent Raman measurements under uniaxial strain is displayed in Figure 4.12(a), which is the same as that adopted to study the crystal orientation of monolayer MoS₂ in section 4.3.1. We fitted the obtained Raman spectra of single-layer WS₂ as a function of angle φ under 3.2% uniaxial strain (see Figure 4.12(b)) and plotted the polar angle dependence of E'^+ , E'^- , and A'_1 peaks in Figure 4.10(d) and (e). The intensity of the

A'_1 mode is proportional to $\cos^2\varphi$ similar to the unstrained case as this out-of-plane mode is seldom affected by in-plane strain. On the contrary, the intensities of E'^+ and E^- modes follow $\cos^2\varphi$ and $\sin^2\varphi$ dependence, respectively. Since the polarization dependent intensities of these two split E'^+ and E^- modes in our configuration are supposed to be proportional to $\cos^2(\varphi+3\theta)$ and $\sin^2(\varphi+3\theta)$, respectively, the θ value is obtained to be zero degree. Thus, the zigzag direction of our CVD-grown monolayer WS_2 is identified to be along the horizontal axis, which happens to overlap with one of the triangle edges as evident from Figure 4.10(b). This confirms the previous observations that the CVD-grown WS_2 edge is zigzag-terminated [76, 114].

Figure 4.12 (a) Schematic diagram of the polarization geometry in our polarization dependent Raman measurements. (b) Raman spectra of monolayer WS_2 as a function of angle φ under 3.2% uniaxial strain.

4.4 Theoretical support

4.4.1 Polarization behaviours of phonon modes for pristine monolayer MS₂

The E' and A₁' modes of monolayer MoS₂ have polarization dependent Raman tensors with the form [47]:

$$R(E') = \begin{bmatrix} 0 & d \\ d & 0 \end{bmatrix}, \quad \begin{bmatrix} d & 0 \\ 0 & -d \end{bmatrix}; \quad R(A_1') = \begin{bmatrix} a & 0 \\ 0 & a \end{bmatrix}. \quad (4-5)$$

The polarization dependent Raman scattering intensity can be calculated by $I_s \propto |e_i \cdot R \cdot e_s^T|^2$, where e_i and e_s denote the unit vectors of the incoming and scattered light polarizations [47]. In this work, the polarization of the incident laser is fixed along the horizontal direction ($e_i = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$) while the scattered light polarization is selected with an angle φ to the horizontal by a polarizer ($e_s = \begin{bmatrix} \cos \varphi \\ \sin \varphi \end{bmatrix}$). Thus, $I_{s(E')} \propto d^2$ and $I_{s(A_1')} \propto a^2(\cos \varphi)^2$ as clearly demonstrated by our fitting results in Figure 4.3(c) and Figure 4.11.

4.4.2 Grüneisen parameter and shear deformation potential for uniaxially strained monolayer MS₂

The Grüneisen parameter of the E' phonon mode, $\gamma_{E'}$, is defined as [156]

$$\gamma_{E'} = - \frac{1}{\omega_{E'}^0} \frac{\partial \omega_{E'}^h}{\partial \varepsilon_h}, \quad (4-6)$$

where $\omega_{E'}^0$ is the E' band position under zero strain, $\varepsilon_h = \varepsilon_{ll} + \varepsilon_{tt}$ signifies the hydrostatic component of the uniaxial strain applied to the sample, l represents the longitudinal direction, parallel to that of the strain, while t denotes the transverse

direction perpendicular to the strain. The shear deformation potential $\beta_{E'}$ can be represented as [157, 158]

$$\beta_{E'} = \frac{1}{\omega_{E'}^0} \frac{\partial \omega_{E'}^s}{\partial \varepsilon_s}, \quad (4-7)$$

in this expression $\varepsilon_h = \varepsilon_{ll} - \varepsilon_{tt}$ is the shear component of the applied uniaxial strain.

The secular equation for the E' mode under uniaxial strain can be worked out to be [157-160]:

$$\begin{aligned} \Delta \omega_{E'}^{\pm} &= \Delta \omega_{E'}^h \pm \frac{1}{2} \Delta \omega_{E'}^s, \\ &= -\omega_{E'}^0 \gamma_{E'} (\varepsilon_{ll} + \varepsilon_{tt}) \pm \frac{1}{2} \beta_{E'} \omega_{E'}^0 (\varepsilon_{ll} - \varepsilon_{tt}), \end{aligned} \quad (4-8)$$

where $\Delta \omega_{E'}^h$ is the shift of the E' mode caused by the hydrostatic component of the strain and $\Delta \omega_{E'}^s$ is the mode splitting resulting from the shear component of the strain. $\Delta \omega_{E'}^+$ and $\Delta \omega_{E'}^-$ are the wavenumber shifts of the splitted E^+ and E^- sub-peaks relative to those under zero strain, respectively. The resulting two phonon eigenvectors are orthogonal with the E^+ perpendicular and E^- parallel to the strain direction [157-160].

Under uniaxial strain, due to Poisson effect, $\varepsilon_{ll} = \varepsilon$ and $\varepsilon_{tt} = -\nu \varepsilon$ where ν is the Poisson ratio [156]. If the sample is suspended under strain, then the Poisson ratio of MoS₂ should be used. However, when the sample and PET are in good adhesion in our case, the Poisson ratio value of PET should be chosen. After we substitute ε_{ll} and ε_{tt} with ε and $-\nu \varepsilon$, Equations (4-8) can be rewritten as

$$\Delta \omega_{E'}^{\pm} = -\omega_{E'}^0 \gamma_{E'} (1 - \nu) \varepsilon \pm \frac{1}{2} \beta_{E'} \omega_{E'}^0 (1 + \nu) \varepsilon, \quad (4-9)$$

By solving the equations, we thus can get

$$\gamma_{E'} = -\frac{P_{E'+} + P_{E'-}}{2\omega_{E'}^0(1-\nu)} \quad (4-10)$$

$$\beta_{E'} = \frac{P_{E'+} - P_{E'-}}{\omega_{E'}^0(1+\nu)} \quad (4-11)$$

where $P_{E'-}$ and $P_{E'+}$ are the shift rate of the E^- and E^+ , respectively.

4.4.3 Raman intensities of splitted E^+ and E^- modes of monolayer MS_2 under uniaxial strain

Consider a universal case where the strain is applied with an angle of θ relative to the zigzag direction as shown in Figure 4.6(a). Since the E^+ mode is orthogonal to the strain direction and the E^- mode is parallel to it, the vectors describing their atomic displacements are

$$\vec{v}^+ = \begin{Bmatrix} -\sin \theta \\ \cos \theta \end{Bmatrix} \quad \vec{v}^- = \begin{Bmatrix} \cos \theta \\ \sin \theta \end{Bmatrix} \quad (4-12)$$

Thus, Raman tensors for the E^+ and E^- modes can be obtained by the linear combinations as described below [92]

$$\begin{cases} R^+ = v_x^+ R_x + v_y^+ R_y = \begin{bmatrix} d \cos \theta & -d \sin \theta \\ -d \sin \theta & -d \cos \theta \end{bmatrix} \\ R^- = v_x^- R_x + v_y^- R_y = \begin{bmatrix} d \sin \theta & d \cos \theta \\ d \cos \theta & -d \sin \theta \end{bmatrix} \end{cases} \quad (4-13)$$

For the general case, the polarization vectors of the incoming laser and the scattered lights can be represented by ψ , φ (incoming and scattered light polarizations relative to the strain direction, respectively) and θ :

$$e_i = \begin{Bmatrix} \cos(\theta + \psi) \\ \sin(\theta + \psi) \end{Bmatrix} \quad e_s = \begin{Bmatrix} \cos(\theta + \varphi) \\ \sin(\theta + \varphi) \end{Bmatrix} \quad (4-14)$$

Using the Raman intensity equation $I_s \propto |e_i R e_s|^2$, we can get the intensities of the E'^+ and E'^- modes:

$$\begin{cases} I_{E'^+} \propto d^2 \cos^2(\varphi + \psi + 3\theta) \\ I_{E'^-} \propto d^2 \sin^2(\varphi + \psi + 3\theta) \end{cases} \quad (4-15)$$

4.5 Summary

In summary, we have conducted a micro-Raman spectroscopy investigation of mechanically exfoliated monolayer MoS_2 and CVD-grown monolayer WS_2 flakes on flexible substrate under controllable uniaxial tensile strain. It is found that the doubly degenerate E' mode obviously softens under increasing strain and finally splits into two splitted E'^+ and E'^- modes when the strain is sufficiently high to break the original crystal symmetry. The scattering intensities of these two modes distinctively respond to the angle between the polarizations of the incident and scattered lights. Such polarization dependence can be utilized to efficiently identify the crystal orientation of monolayer MS_2 and confirms the zigzag-type edge of CVD-grown monolayer WS_2 . Our observations could be very significant for investigations of the electronic and mechanical properties of 2D MS_2 and other TMDs under strain.

Chapter 5 Remarkable anisotropic phonon response in uniaxially strained few-layer BP

5.1 Introduction

Strain serves an effective tool to tune the properties of 2D materials. A lot of investigations have been performed on graphene, with the lattice vibration [90, 92, 94, 96], electronic band structure [95], and magnetism [93] shown to be significantly influenced by strain. In addition to phonon softening and crystallographic-orientation determination [99, 100, 161], strain effects on TMDs have been extended to light emission tuning including linear redshift of bandgap [78, 79, 161], direct-to-indirect bandgap transition [161], enormous valley drift [101], and valley polarization decrease [77] due to their as-born gap. Because of the excellent ability to sustain high strain (around 30% for monolayer BP and 32% for few-layer counterpart) [25], BP is deemed as a good candidate to further study strain effects on 2D materials. More importantly, the unique puckered structure of BP could lead to remarkable anisotropic mechanical response [22-25], in stark contrast to the crystal-orientation-independent effects of uniaxial strain in both graphene and TMD materials [77, 79, 94, 102]. A variety of interesting discoveries of BP under strain have been theoretically demonstrated, such as negative Poisson's ratio [24], direct-indirect bandgap transition [162], rotation of the preferred conducting direction [163], and semiconductor-to-metal transition [164]. However, as far as we know, experimental

studies of strain-dependent phonon properties of BP are still absent. An experimental investigation of how strain can affect the properties of BP should benefit the development of BP-based flexible electronics.

In this project, we report the remarkable dependence of phonon behaviors on crystallographic orientations in uniaxially strained few-layer BP. Because BP with the thickness ranged between 4 to 10 nm may provide the best balance between on-off ratio and mobility [15], we mainly focus on few-layer samples near this thickness range. Anisotropic response of lattice vibrational frequencies to uniaxial strain can be clearly revealed with the help of Raman spectroscopy. It is found that near-armchair direction strain can soften the out-of-plane A_g^1 mode while keep the two in-plane phonon modes nearly unchanged. When the tensile strain is applied approximately along the zigzag direction, B_{2g} and A_g^2 modes linearly redshift with the strain while the A_g^1 mode is inert to it. The observed direction dependent phonon behaviors under uniaxial strain in few-layer BP are explained by anisotropic influence of tensile strain on structural parameters of BP by means of DFT calculations. Our work not only experimentally confirms the anisotropic optical and mechanical properties of BP, but also provides a reference for quantification of strain and estimation of its orientation by Raman spectroscopy.

5.2 Experimental methods

Thin layers of BP were fabricated by mechanical exfoliation onto PET substrate and *in situ* strained Raman measurements were performed after crystal orientation determination. Then, the AFM measurements were performed to determine the sample thicknesses.

Sample preparation: The BP samples were fabricated by mechanical exfoliation [32] of a bulk BP crystal (HQ Graphene, CAS #7803-51-2, Netherlands) and transferred onto PET substrates. Desired flakes were identified by an optical microscope (BX 51).

Characterization: Polarization dependent Raman measurements were performed on the BP samples right after they were pasted on the stage to identify their crystal orientations. In our parallel polar configuration, a half-wave plate was used to tune the linear polarization of incident light and a linear polarizer was employed to collect the scattered light with polarization parallel to that of the incident beam. Then, the samples were stored in the chamber of the E-beam evaporation system to minimize natural degradation. Once the sample firmly adhered to the stage (which generally took around 10 hours), *in situ* strained Raman measurements were conducted by the method as described in section 2.3. All the Raman spectra were taken in the back-scattering configuration by a WITec CRM200 Confocal Raman system with 2400 and 1800 lines/mm grating under 532 nm laser excitation. The laser spot was estimated to be around 500 nm. The laser power on the sample surface was carefully

regulated below 0.2 mW to avoid laser-induced damage. The Raman measurements were conducted under the same condition for different strain strength. AFM (Veeco, Nanoscope V) in tapping mode was adopted to determine the thickness. When shipped to different systems for characterization, BP sample were kept in a container (Circular Bottom Desi-Vac, Fisher Scientific) with vacuum pump to achieve vacuum preservation. All the measurements were conducted at room temperature.

5.3 Results and discussion

Figure 5.1(a) shows the typical Raman spectrum of BP on PET substrate (corresponding optical image can be found in Figure 5.1(c)) and it reveals three distinct bands at 361 cm^{-1} , 438 cm^{-1} , and 467 cm^{-1} , which are attributed to A_g^1 , B_{2g} , and A_g^2 modes, respectively [18]. The symmetry classification of Raman modes and corresponding Raman tensors apply to BP with any thickness, because thin layers (whether odd or even numbers) share the identical point group (D_{2h}) with the bulk [66]. The atomic displacements of three phonon modes are plotted in Figure 5.1(b) [18, 19, 67]. A_g^1 is an out-of-plane mode, with the phosphorus atoms in top and bottom sub layers vibrating in opposite directions. In contrast, B_{2g} and A_g^2 modes involve in-plane zigzag and armchair oscillations, respectively, with adjacent atoms vibrating out of phase. Figure 5.1(c) and (d) demonstrate optical images of few-layer BP flake 1 and flake 2 studied in this work. According to their height profiles from

AFM images shown in Figure 5.1(e) and (f), the thicknesses are obtained to be 5.5 nm for flake 1 and 10.4 nm for flake 2, corresponding to 9- and 17-layer BP, respectively.

Figure 5.1 (a) Typical Raman spectrum of BP on PET. (b) Schematic diagram of atomic displacements of observed phonon modes. (c) and (d) show optical images of BP flake 1 and flake 2 on PET, respectively. (e) and (f) are the corresponding AFM images of BP flake 1 and flake 2, respectively.

As a nondestructive and effective tool for investigations of the layer number [52, 117, 118], stacking influence [30, 120, 121, 165], edge chirality [148, 149, 166], optical conductivity [167], and thermal effects [53, 122] in graphene and TMD materials, Raman spectroscopy has also been employed for the study of 2D BP since 2014 [14, 18, 19, 40, 66, 67, 70, 82, 168]. Here, we identified crystal orientations of our BP samples by the polarization dependent Raman spectroscopy before applying strain [18, 19, 66]. The parallel polar configuration for the polarization dependent

Raman measurements is schematically illustrated in Figure 5.2. The polarizations of incident and scattered lights were kept parallel and rotated simultaneously with a step size of 30 °.

Figure 5.2 The polar configuration for the polarization dependent Raman measurements.

Assuming that the zigzag direction of the BP sample has an angle of θ relative to the horizontal direction and the polarizations of both incoming and scattered lights are rotated to a position where they have ϕ angle compared with the horizontal direction, we can obtain the following expressions for the intensities of three phonon modes based on their Raman tensors and the polarization vectors (see detailed discussion in section 5.4.1) [19]:

$$I_{A_g^1} \propto [|a_1| \cos^2(\phi - \theta) + |c_1| \sin^2(\phi - \theta)]^2 \quad (5-1)$$

$$I_{B_{2g}} \propto [|e| \sin(2\phi - 2\theta)]^2 \quad (5-2)$$

$$I_{A_g^2} \propto [|a_2|^2 \cos^4(\phi - \theta) + |c_2|^2 \sin^4(\phi - \theta)] \quad (5-3)$$

Because the crystal orientation of the sample may change during the mounting process on the strain stage, polarization dependent Raman spectroscopy was employed after mounting of the sample to accurately determine the relative angle between its crystal orientation and the strain direction (fixed along the horizontal direction). Figure 5.3(a) presents the Raman spectra as a function of polar angle for flake 1. Lorentzian functions are chosen to fit the obtained Raman spectra and the polarization dependent phonon intensities plotted in Figure 5.3(b-d) can be well fitted by Equations (5-1), (5-2), and (5-3), respectively. All of the three fitted curves simultaneously give a θ value of 75 degree, which indicates that the armchair direction has an angle of 15 degree respect to the strain orientation.

Figure 5.3 (a) Raman spectra and polar maps of fitted Raman intensities of (b) A_g^1 , (c) B_{2g} , and (d) A_g^2 modes as a function of polarization angle ϕ for flake 1.

Following that, the *in situ* strained Raman measurements were performed. Figure 5.4(a) presents the evolution of Raman spectra in flake 1 as a function of uniaxial strain. With increasing strain ranged from 0 to 2.2%, there is an obvious redshift of the A_g^1 mode while the two in-plane modes are insensitive to strain. As can be seen in fitted lattice vibrational frequencies versus strain (Figure 5.4(b)), the A_g^1 mode is linearly redshifted at a rate of $-1.3 \text{ cm}^{-1}/\%$ while the shift rates of B_{2g} and A_g^2 modes are negligible with tensile strain applied near the armchair direction.

Figure 5.4 (a) Raman spectra and (b) fitted phonon frequencies as a function of uniaxial strain for flake 1. The relationship between the armchair orientation and uniaxial strain direction is shown in (c). The red point indicates the position where strain dependent Raman spectra were taken.

To further probe the crystal-orientation-dependent effects of uniaxial strain in BP, next we study the evolution of lattice vibrations under zigzag direction strain. The same method was applied to determine the crystal orientation of fake 2 after its fixation on the strain stage and polarization dependent Raman spectra were plotted in Figure 5.5(a). By fitting the phonon intensities as a function of ϕ (Figure 5.5(b), (c), and (d)), θ value is extracted to be 10 degree for fake 2, which shows that the zigzag direction of fake 2 is very close to the strain direction as indicated in Figure 5.6(c).

Figure 5.5 (a) Raman spectra and polar maps of fitted Raman intensities of (b) A_g^1 , (c) B_{2g} , and (d) A_g^2 modes as a function of polarization angle ϕ for fake 2.

The strain dependent Raman spectra of fake 2 are shown in Figure 5.6(a). To precisely demonstrate the evolution of phonon frequencies under strain, the frequencies of three phonon peaks as a function of strain are read from Lorentzian line

shape fitting and plotted in Figure 5.6(b). Contrary to the observations under the armchair direction condition, B_{2g} and A_g^2 modes linearly redshift with the tensile zigzag strain (with the shift rates of $-2.3 \text{ cm}^{-1}/\%$ and $-1.1 \text{ cm}^{-1}/\%$, respectively) while the A_g^1 mode is inert to it.

Figure 5.6 (a) Raman spectra and (b) fitted phonon frequencies as a function of uniaxial strain for flake 2. The relationship between the zigzag orientation and uniaxial strain direction is shown in (c). The red point indicates the position where strain dependent Raman spectra were taken.

To better guide our understanding of the observed remarkable dependence of phonon behaviors on the crystallographic orientation in uniaxially strained few-layer BP, we calculated the evolution of geometric properties under both armchair and zigzag strain (0-3%) in bi-layer (2L), tri-layer (3L), quadruple-layer (4L), and

quinary-layer (5L) BP. Important physical parameters are marked in top (Figure 5.7(a)) and side (Figure 5.7(b)) views of BP, such as two inequivalent bond lengths (in-plane r_1 and out-of-plane r_2) and the inter-distance which defines the shortest length between two phosphorous atoms in the neighbouring layers (L). We present the response of the structural parameters to both armchair (ε_z) and zigzag (ε_x) strain for 5L BP in Figure 5.7(c) and those for 2L to 4L BP in section 5.4.2. Linear dependence is observed in all cases within the range of 0 to 3% strain. Because the variations of structural parameters are qualitatively similar for 2L to 5L BP, we will use those of 5L BP (which are closer to thickness of our measured samples) to explain the strained Raman results. From the schematic diagram of atomic displacements of the A_g^1 mode in the Figure 5.1(b), it can be seen that the restoring force acted on a certain atom mainly comes from its nearest neighbours in both adjacent sublayer and neighbouring layer, which vibrate out of phase with it. Taking atom 1 for example, its interactions with atoms 4 and 7 force it back to the equilibrium position during the out-of-plane oscillation and therefore r_2 and L have significant influence on the vibrational frequency of the A_g^1 mode. Under the armchair direction strain both r_2 and L increase, which lowers the restoring force and results in the redshift of the A_g^1 mode. In contrast, strain along the zigzag direction extends L while shrinks r_2 with similar rates of change. In consequence, the overall restoring force does not vary much and the A_g^1 mode is inert to zigzag strain. As to the B_{2g} and A_g^2 phonon modes, all of the three nearby atoms exert influence on the in-plane vibrational frequencies of a certain atom

based on their schematic representation and thereby three aforementioned parameters need to be considered altogether when analyzing the trends of these two modes under strain. When the armchair strain is applied, decrease of r_1 accompanied by increase of r_2 and L is observed. Though the shift rate of L is more significant than those of the other two parameters, given its larger value in pristine BP, the change percentage of L is in fact similar to that of r_1 . As a result, the effects of these three changing parameters on lattice vibrations under armchair strain are offset so that no obvious shift of B_{2g} and A_g^2 modes is observed under armchair strain. On the other hand, r_1 and L enlarge while r_2 reduces slightly under tensile zigzag strain according to our calculation results. On account of the more prominent change rate of r_1 compared with those of the two bond lengths, the overall restoring force is weakened by zigzag strain and leads to the softening of B_{2g} and A_g^2 modes. As can be seen from Figure 5.7(a), the orientation of the bond linking atoms 1 and 4 is vertical to the zigzag direction in unstrained structure of BP and therefore the corresponding covalent force has trivial contribution to the restoring force in the B_{2g} mode. Accordingly, the decrease of this bond length r_2 barely exerts influence on the frequency of B_{2g} as it does on the A_g^2 mode, which well explains the observation that the shift rate of the former with strain is apparently larger than that of the latter.

Figure 5.7 (a) Top and (b) side view of 2L BP. r_1 and r_2 are in-plane and out-of-plane P-P bond lengths, respectively. L is the inter-distance. The unit cell is indicated with the blue dashed rectangle. (c) Calculated bond lengths (r_1 , r_2) and inter-distance (L) as a function of uniaxial strain applied along armchair and zigzag directions for 5L BP.

In order to give readers a comprehensive picture of the anisotropic response of the lattice vibrations to uniaxial strain in BP, finally we explored the effects of uniaxial strain in between the aforementioned two extreme conditions. Using the method described above, we obtain the θ angle to be -56 degree for flake 3 from 2D polar maps (data not shown). Thus, in this case, strain was applied along the direction with 34 degree compared with the armchair direction (Figure 5.8(c)). Under this strained condition, detectable softening occurs to all the three phonon modes (see Figure 5.8(a)). As shown in Figure 5.8(b), the linear redshift rates are extrapolated to be -1.1, -1.4, and -0.5 $\text{cm}^{-1}/\%$ for A_g^1 , B_{2g} , and A_g^2 modes, respectively.

Figure 5.8 (a) Raman spectra and (b) fitted phonon frequencies as a function of uniaxial strain for flake 3. The relationship between the armchair orientation and uniaxial strain direction is shown in (c). The red point indicates the position where Raman spectra were taken.

5.4 Theoretical support

5.4.1 Polarization behaviours of phonon modes for few-layer BP

The Raman tensors of A_g and B_{2g} modes for BP are shown as follows [169]:

$$R(A_g) = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix}; \quad R(B_{2g}) = \begin{bmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{bmatrix}. \quad (5-4)$$

Based on these matrix elements and the polarization scattering geometry, the Raman scattering intensity can be calculated by [47]:

$$I_s \propto |e_i \cdot R \cdot e_s^T|^2 \quad (5-5)$$

In our parallel polar configuration as shown in Figure 5.2, the zigzag direction of the BP sample has an angle of θ compared with the horizontal direction and the polarizations of incident and scattered lights are parallel to each other with a tunable ϕ angle relative to the horizontal direction. Thus, the electric polarization vectors of incoming and scattered lights can be expressed as: $e_i = e_s = (\cos(\phi - \theta), 0, \sin(\phi - \theta))$. We can deduce the following expressions for the intensities of A_g and B_{2g} phonon modes under the parallel configuration using Equation (5-5):

$$I_{A_g} \propto [a \cos^2(\phi - \theta) + c \sin^2(\phi - \theta)]^2 \quad (5-6)$$

$$I_{B_{2g}} \propto [e \sin(2\phi - 2\theta)]^2 \quad (5-7)$$

It should be noted that the expressions above are obtained when only real parts of Raman tensor elements are considered. One recent work has reported that imaginary parts should also be taken into consideration when calculating the polarization dependent Raman scattering intensities of anisotropic BP [19]. Specifically speaking, after the complex values of the Raman tensor elements are taken into account, the expressions for two A_g modes will differ from Equation (5-6) while that for the B_{2g} mode will remain the same as Equation (5-7) [19]. According to the updated polarization dependence of the A_g modes and the phase difference between a and c [19], the revised expressions for the intensities of the A_g modes under 532 nm excitation laser should be:

$$I_{A_g^1} \propto [|a_1| \cos^2(\phi - \theta) + |c_1| \sin^2(\phi - \theta)]^2 \quad (5-8)$$

$$I_{A_g^2} \propto [|a_2|^2 \cos^4(\phi - \theta) + |c_2|^2 \sin^4(\phi - \theta)] \quad (5-9)$$

5.4.2 Evolution of structural properties under uniaxial strain

The atomic structures of few-layer BP were fully relaxed according to the force and stress calculated by the DFT method within the LDA. All atoms in it were allowed to be relaxed until the residual force per atom was converged to be less than $0.001 \text{ eV } \text{\AA}^{-1}$. The electronic structures were obtained by solving the Kohn-Sham equation with normal-conserving pseudopotentials. A $14 \times 10 \times 1$ k-point sampling grid was chosen and 35 Ry was used as the plane-wave cutoff energy for converged calculations.

The calculated parameters of unstrained few-layer BP, including the inter-distance, bond lengths, and bond angles (results not shown here) are in excellent agreement with previous theoretical calculation results [16, 23, 164]. We present the response of the structural parameters to both armchair (ϵ_z) and zigzag (ϵ_x) strain for 2L to 4L BP in Figure 5.9. Structural parameters are linearly dependent on uniaxial strain in all cases, similar to the findings in 5L BP (see Figure 5.7(c)).

Figure 5.9 Calculated bond lengths and inter-distance as a function of uniaxial strain applied along armchair and zigzag directions for (a) 2L, (b) 3L, and (c) 4L BP.

Table 5.1 summarizes the slopes of r_1 , r_2 , and L versus armchair and zigzag strain for 2L to 5L BP by linear fitting.

Table 5.1 Linearly fitted slopes of r_1 , r_2 , and L ($\text{\AA}/\%$) versus armchair and zigzag strain for 2L to 5L BP.

Strain	2L			3L			4L			5L		
direction	r_1 ($\text{\AA}/\%$)	r_2 ($\text{\AA}/\%$)	L ($\text{\AA}/\%$)	r_1 ($\text{\AA}/\%$)	r_2 ($\text{\AA}/\%$)	L ($\text{\AA}/\%$)	r_1 ($\text{\AA}/\%$)	r_2 ($\text{\AA}/\%$)	L ($\text{\AA}/\%$)	r_1 ($\text{\AA}/\%$)	r_2 ($\text{\AA}/\%$)	L ($\text{\AA}/\%$)
Armchair	-0.0005	0.0013	0.0085	-0.0022	0.0020	0.0044	-0.0015	0.0018	0.0056	-0.0025	0.0014	0.0043
Zigzag	0.0087	-0.0020	0.0013	0.0090	-0.0026	0.0026	0.0091	-0.0027	0.0041	0.0096	-0.0026	0.0035

5.5 Summary

In summary, we have identified different crystal orientations of few-layer BP flakes on flexible substrate and investigated their distinct responses of the lattice vibrations to adjustable uniaxial tensile strain. We demonstrate that the out-of-plane A_g^1 mode is sensitive to uniaxial strain along the near-armchair direction while the in-plane B_{2g} and A_g^2 modes are susceptible to near-zigzag direction strain. When the uniaxial strain is applied along the direction roughly intermediate between the two edge orientations, all of the three phonon modes linearly redshift. Our DFT calculations clearly demonstrate the anisotropic mechanical response to uniaxial strain in BP as a consequence of its unique puckered crystal structure and could be used to elucidate the striking dependence of strained phonon frequencies on crystal orientations. Our findings extend previous explorations of strained atomically thin layered materials, offering better understanding of rich strain-engineered phonon

modifications in 2D materials. The special anisotropic response of the lattice vibration to strain makes BP hold promise for diverse applications such as detection of the strain orientation.

Chapter 6 Conclusions and future work

6.1 Conclusions

In this thesis, the band structure evolutions and lattice vibrational responses in 2D WS₂, MoS₂, and BP crystals under uniaxial tensile strain have been systematically investigated by *in situ* PL and Raman spectroscopy, supported by the DFT calculations. This dissertation mainly contains three parts. Firstly, we employed PL spectroscopy and DFT calculations to demonstrate the sensitivity of the light emission to uniaxial strain in atomically thin WS₂. In addition, phonon response and crystallographic orientation determination in uniaxially strained monolayer WS₂ and MoS₂ were investigated by Raman spectroscopy. Lastly, Raman spectroscopy and DFT calculations were used to study the remarkable anisotropic response of lattice vibrations to uniaxial strain in BP.

(1) Electronic band structure engineering of 2D WS₂ via uniaxial strain

We have systematically investigated the strain-dependent light-emission properties of CVD-grown single-layer and mechanically exfoliated bi-layer WS₂. For monolayer WS₂, both the bandgap-energy tuning and direct-indirect transition achieved by strain can be revealed from strained PL spectra and confirmed by the DFT calculations. Decrease of the trion dissociation energy under increasing strain has been observed in monolayer WS₂. In bi-layer WS₂, both direct and indirect bandgap energies linearly redshift with uniaxial strain. The observed sensitivity of the

light emission to strain in 2D WS₂ indicates that this atomically thin semiconducting TMD material holds promise for various applications such as strain detection and optoelectronics. Our results also show that special care might also be needed to pay when one designs and studies stretchable electrical or optoelectrical devices based on monolayer WS₂ due to its strain-dependent response.

(2) Raman spectroscopy study of the lattice vibration and crystallographic orientation of monolayer MS₂ (M=Mo, W) under uniaxial strain

We have carried out a Raman spectroscopy investigation of monolayer mechanically exfoliated monolayer MoS₂ and CVD-grown monolayer WS₂ flakes on flexible PET substrate under controllable uniaxial tensile strain. It is found that uniaxial tensile strain can soften the in-plane E' phonon mode followed by lifting its two-fold degeneracy, which makes the frequency of the E' mode a good choice for quantifying the amount of strain. The scattering intensities of the two splitted sub-peaks, E'⁺ and E'⁻, orthogonally respond to the angle between the polarizations of the incoming and scattered lights. Such polarization dependence can be utilized to efficiently determine the crystal orientation of monolayer MS₂.

(3) Remarkable dependence of phonon behaviors on crystal orientations in uniaxially strained few-layer BP

The remarkable dependence of phonon behaviors on crystallographic orientations in uniaxially strained few-layer BP has been studied. Anisotropic response of lattice vibrational frequencies to uniaxial strain can be clearly revealed with the help of

Raman spectroscopy. It has been demonstrated that the out-of-plane A_g^1 mode is sensitive to uniaxial strain along the near-armchair direction while the in-plane B_{2g} and A_g^2 modes are susceptible to near-zigzag direction strain. When the uniaxial strain is applied along the direction roughly intermediate between the two edge orientations, all of the three phonon modes linearly redshift. The observed direction dependent phonon behaviors under uniaxial strain in few-layer BP are explained by its anisotropic mechanical response to uniaxial strain by means of DFT calculations. Our findings extend previous explorations of strained atomically thin layered materials, offering better understanding of rich strain-engineered phonon modifications in 2D materials. The special anisotropic response of the lattice vibration to strain in BP provides a perfect platform for the implementations of conceptually new ideas.

6.2 Future work

(1) Strain effects on other 2D materials and 2D-crystal-based heterostructures by optical probes

The study of strain effects on atomically thin materials is still at an early stage. Up to now, the experimental investigations of strain engineering in 2D crystals have mainly focused on graphene and MS_2 ($M=Mo, W$) [77-79, 90, 92, 94, 96, 99, 100, 161]. Actually, other families of 2D materials provide a good platform for further studying strain control of various properties in atomically thin materials. For example, the vanishing interlayer coupling has been recently reported in ReS_2 and makes it

possible to probe the response of different sublayers to strain [170]. In addition, vertical heterostructures composed of different 2D crystals have been shown to hold promise for solar energy conversion and optoelectronic devices [108, 171]. We will probe the strain dependent properties of both unexplored homogeneous 2D materials and heterostructures by Raman and PL spectroscopy. This part of investigations will lay a foundation for developing various applications of these materials based on their strain dependent properties.

(2) Gated Raman study of BP

As is known to all, the carrier mobility is primarily limited by phonon scattering and the largest current is normally controlled by hot phonons in a FET [64]. These two issues are largely dependent on the electron-phonon coupling (EPC). Raman spectroscopy has been reported to be a powerful technique to investigate the EPC in graphene [8, 172-176] and TMD materials [64]. Future work will focus on the Raman study of gated FET devices based on thin layers of BP. It is aimed at exploring the dependence of phonon behaviors on doping level and gaining a better understanding of the EPC in BP.

(3) Tuning the interlayer coupling in BP/MS₂ (M=Mo, W) heterostructures by changing the orientation relationship between individual domains

A variety of interesting discoveries of BP-based heterostacks have been experimentally demonstrated, such as the BP/MoS₂ heterostructure with strong gate-tunable current-rectifying I-V characteristics [177], strong PL quenching in

BP/WS₂ heterostack [178], and heterobilayers of BP-hexagonal boron nitride (h-BN) with a mobility up to 4000 cm²V⁻¹s⁻¹ [179]. Tuning the significant interlayer couplings in these heterostructures could offer a route to control the properties of these artificial stacks [180]. BP possesses intriguing anisotropic properties [17] and its crystal orientation could be conveniently identified by Raman spectroscopy [18, 66]. Besides, the CVD-grown monolayer MS₂ has a zigzag-oriented edge, which makes it easy to know the crystal orientation of one component with respect to the other in BP-MoS₂ heterostack. Therefore, we will tune the interlayer coupling in the BP/MS₂ heterostructure by changing the orientation relationship between individual domains. This study may enrich our understanding of the interlayer coupling in modulating the properties of heterostructures.

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