# Molecular beam epitaxial growth and scanning tunneling microscopy characterization and manipulation of monolayers and heterostructures of two-dimensional ferroelectrics

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# List of Abbreviations

2D	two-dimensional
AL	atomic layer
BL	bilayer
СВМ	conduction band minimum
CVD	chemical vapor deposition
DFT	density functional theory
DOS	density of states
FE	ferroelectric
FFT	fast Fourier transformation
LDOS	local density of states
LHS	lateral heterostructures
LSL	lateral superlattices
LT-STM	low temperature scanning tunneling microscope
MBE	molecular beam epitaxy
ML	monolayer
MOSFET	metal-oxide-semiconductor field-effect transistor
PbTe	lead telluride
PID	proportional-integral-derivative
PVD	physical vapor deposition
RHEED	reflection high-energy electron diffraction
SnSe	tin selenide
SnTe	tin telluride
STM	scanning tunneling microscope
STS	scanning tunneling spectroscopy
TMDC	transition metal dichalcogenide
UHV	ultra high vacuum
VBM	valance valence band maximum

vdW van der Waals

**VT-STM** variable temperature scanning tunneling microscope

## Abstract

Since the experimental realization of monolayer graphene by mechanical exfoliation, the family of 2D materials has rapidly grown. Among them, 2D ferroelectric materials have become an important subset due to their potential for applications in electronic devices, for example, in the form of ferroelectric tunneling junctions. In-plane ferroelectricity was discovered in atomically-thin SnTe grown on graphitized 6H-SiC (0001) substrates. The films were directly deposited using molecular beam epitaxy (MBE) thin film growth methods and the ferroelectricity was observed from band-bending at the ferroelectric domain walls from low-temperature scanning tunneling microscopy (LT-STM) spectroscopy studies. This combination of techniques has provided a new way explore ferroelectricity in high-quality ultrathin materials in an ultra-high vacuum (UHV) environment. In this thesis, I report my work on the realization of high-quality, molecular beam epitaxial synthesis of group-IV monochalcogenide monolayers, and on their lateral heterostructures (LHSs) and lateral superlattices (LSLs), and the characterization and manipulation by scanning tunneling microscopy (STM).

First, I will present the MBE growth of monolayer PbTe/SnTe lateral superlattices on graphene substrates. During the growth of these superlattices, we discovered an asymmetric diffusion at the PbTe/SnTe interfaces. Several factors influence the interdiffusion at such interfaces, including the thickness of the graphene substrate, and the growth sequence of these two materials. Remarkably, ultra-narrow periods in the lateral superlattices with well-defined

interfaces can be realized. By combining experimental data and first principles calculations, we developed a model of the diffusion mechanism that exists in two-dimensional lateral monolayer superlattices.

As a second topic, I introduce the discovery of vortex-oriented ferroelectric domains in PbTe /SnTe monolayer lateral heterostructures. This heterostructure shows a type-II band alignment (a finding supported by the bias-voltage-dependence of the apparent heights of SnTe and PbTe monolayers). Remarkably, we discovered that the ferroelectric domains in SnTe regions that surround a PbTe core form either clockwise or counterclockwise vortex-oriented quadrant configurations are a result of ferroelectricity, charge transfer, and interfacial strain. Our work opens the pathway to potential applications for monochalcogenide monolayer lateral heterostructures and superlattices.

Lastly, I present my work on the defect-free nano-welding of monolayer and bilayer semiconducting SnSe nanoplates. Combining scanning tunneling microscope (STM) manipulation and first-principles calculations, an anisotropic friction is found in SnSe monolayer nanoplates because of the commensuration (or lack thereof) between SnSe and graphene. Taking advantage of *in-situ* annealing in the VT-STM, we observed that nanoplates can merge without any grain boundaries after physically moving the nanoplates together. Our results are a major step towards the controllable manipulation and construction of nanostructures from diverse 2D materials.

# Chapter 1 Introduction

The concept of "*The interface is the device*" was put forward by Herbert Kroemer in his Nobel lecture in 2000 [1]. Even now, physical phenomena created at interfaces within heterostructures are still a central topic in Condensed Matter Physics because of their unconventional properties and their huge potential for technological applications. During the ongoing explosive developments in two-dimensional (2D) materials since the experimental realization of graphene [2]—a monolayer of graphite—2D materials and heterostructures exhibit superior properties in different fields. In this chapter, I will give a brief introduction to 2D materials and heterostructures, 2D ferroelectrics and 2D ferroelectricity discovered in the group-IV monochalcogenide monolayers, and on their van der Waals epitaxial growth.

#### 1.1 Two-dimensional materials and lateral heterostructures

After the groundbreaking experimental realization of graphene [2], the family of twodimensional (2D) materials have been enlarged rapidly, including the graphene family (e.g., graphene and hexagonal boron nitride (hBN)); chalcogenides (e.g., transition metal dichalcogenide (TMDC) and group-IV monochalcogenides) and 2D oxides, and others. Such a variety of 2D materials hugely broadens possibilities for tuning optical, electronic, magnetic, valleytronic, and other physical properties [3][4].

Graphene family	Graphene	hBN 'white graphene'			BCN	Fluorograph	ene	Graphene oxide
2D			Semiconducting dichalcogenides:		Semiconducting dichalcogenides:		Metallic dichalcogenides: NbSe <sub>2</sub> , NbS <sub>2</sub> , TaS <sub>2</sub> , TiS <sub>2</sub> , NiSe <sub>2</sub> and so on	
chalcogenides	1005 <sub>2</sub> , W5 <sub>2</sub>	, 1005e <sub>2</sub> , 105e <sub>2</sub>	MoTe <sub>2</sub> , WTe <sub>2</sub> , ZrS <sub>2</sub> , ZrSe <sub>2</sub> and so on			Layered semiconductors: GaSe, GaTe, InSe, Bi <sub>2</sub> Se <sub>3</sub> and so on		
	Micas, BSCCO	MoO <sub>3</sub> , WC	) <sub>3</sub>		$\begin{array}{c} \text{Perovskite-type:}\\ \text{LaNb}_2\text{O}_7, (\text{Ca},\text{Sr})_2\text{Nb}_3\text{O}_{10},\\ \text{Bi}_4\text{Ti}_3\text{O}_{12}, \text{Ca}_2\text{Ta}_2\text{TiO}_{10} \text{ and so on} \end{array} \begin{array}{c} \text{Hyd}\\ \text{Ni}(\text{OH})_2, \text{Eu} \\ \end{array}$		Hydroxides: H) <sub>2</sub> , Eu(OH) <sub>2</sub> and so on	
2D oxides	Layered Cu oxides	TiO <sub>2</sub> , MnO <sub>2</sub> , M TaO <sub>3</sub> , RuO <sub>2</sub> and	/ <sub>2</sub> O <sub>5</sub> , I so on	Bi <sub>4</sub> T				Others

Figure 1.1: The family of two-dimensional materials, including the graphene family, 2D chalcogenides and 2D oxides, and other materials. Adapted from [4].

Due to the van der Waals force between the interlayers, the common ways to fabricate 2D materials and heterostructures are either mechanical exfoliation or bottom-up growth methods, such as physical epitaxy and chemical vapor deposition (CVD) [3].



Figure 1.2: Three common ways to obtain 2D materials and heterostructures, including the mechanically assembled stacks (top panel), physical epitaxy and chemical vapor deposition (CVD) (bottom panel). Adapted from [3].

Both vertical heterostructures and lateral heterostructures can be formed. These are differentiated by stacking directions whether on top of one another or side by side, as shown schematically in Figure 1.3 [5]. Vertical heterostructures create 2D interfaces, while lateral heterostructures form 1D interfaces.



Figure 1.3: Schematics of lateral and vertical heterostructures. Adapted from [5].

As a fundamental component in metal-oxide-semiconductor field-effect transistors (MOSFETs), lateral heterostructures (LHSs) exhibit great potential for applications. However, compared to vertical heterostructures, lateral heterostructures are less explored due to their complex and limited fabrication methods. One-step or two-step chemical vapor deposition (CVD) has become the most popular method to fabricate lateral heterostructures (LHS) and lateral superlattices (LSL). Experimentally realized lateral heterostructures were first formed by graphene and hexagonal boron nitride (hBN). Afterwards, LHSs composed from a series of transition metal dichalcogenide (TMDC) monolayers such as MoS<sub>2</sub>, MoS<sub>2</sub>, WS<sub>2</sub>, WS<sub>2</sub> and topological insulators (TI) such as Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, or even heterostructures composed from one material but with different thicknesses or with different dielectric environments have been explored [6]-[34]. Figure 1.4 lists examples of reported lateral heterostructures (LHSs) and lateral superlattices (LSLs). These LHSs have been explored by a variety of techniques that includes: electric transport measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), photoluminescence (PL) and Raman spectroscopy. Their electric properties, that includes nonreciprocal diode-like properties, show potential for many forms of electronic, electro-optic and photonic devices [6]-[34].



Figure 1.4: Examples of lateral heterostructures and superlattices: (a) SEM image of graphenehBN lateral heterostructure. Adapted from [6]. (b) Optical image of the WSe<sub>2</sub> -MoS<sub>2</sub> lateral heterostructure. Adapted from [7]. (c) Optical image of a MoS<sub>2</sub>-WS<sub>2</sub> lateral heterostructure. Adapted from [8]. (d) SEM image of a MoSe<sub>2</sub> -WSe<sub>2</sub> lateral heterostructure. Adapted from [9]. (e) SEM image of a WSe<sub>2</sub> -WS<sub>2</sub> lateral superlattice. Adapted from [10]. (f) Optical image of a MoSe<sub>2</sub>-WSe<sub>2</sub> lateral superlattice. Adapted from [11].

#### **1.2 Two-dimensional ferroelectrics**

Research in 2D ferroic materials, such as 2D ferromagnetic (FM) materials and 2D ferroelectric (FE) materials, has expanded rapidly especially due to their high potential for non-volatile memory devices, such as magnetic tunneling junctions and ferroelectric tunneling junctions [35][36][37][38].

I will briefly summarize results on two-dimensional ferroelectrics in the following [39]. The study of 2D ferroelectrics has grown rapidly since the development of exfoliation methods as well as thin film growth techniques such as physical vapor deposition (PVD) and molecular beam epitaxy (MBE). Characterization methods such as piezo-response force microscopy (PFM), second harmonic generation (SHG), Raman spectroscopy, electrical transport experiments, and scanning tunneling microscopy (STM) are used to characterize the ferroelectricity in these 2D ferroelectrics [40]-[44]. The earliest reported ferroelectric

monolayer was that of SnTe with in-plane (IP) ferroelectricity [40], ultrathin CuInP<sub>2</sub>S<sub>6</sub> flakes with in-plane (IP) and out-of-plane (OOP) ferroelectricity [41],  $\alpha$  -In<sub>2</sub>Se<sub>3</sub> with OOP ferroelectricity [42], and TMDCs like WTe<sub>2</sub> and MoTe<sub>2</sub> with OOP ferroelectricity [43][44]. Moreover, unconventional ferroelectricity has been reported in heterostructures such as bilayer graphene on hexagonal boron nitride (BLG)/ h-BN [45] and twisted bilayer h-BN [46], thereby deepening the development of twistronics.

#### 1.3 Two-dimensional ferroelectricity in group-IV monochalcogenides

After introducing 2D ferroelectrics in the previous paragraph, I will focus on 2D ferroelectricity that has been discovered in the group-IV monochalcogenides. Group-IV monochalcogenides are a family of compounds which can be represented as MX, where M is a group-IVA element and X is a group VIA element [39]. Among the group-IV monochalcogenide monolayers, the monolayers SnX (X=S, Se, Te) are all experimentally synthesized and characterized as 2D ferroelectric materials [40][49][50]. Therefore, I will only discuss 2D ferroelectricity in SnX monolayers. The atomic structure of a SnX monolayer is represented in Figure 1.5. Here, SnSe is used as an example. The silver balls and green balls represent Sn atoms and Se atoms, respectively. Top view and side view are in the top panel and bottom panel respectively. The bound charges, marked as the positive charges and negative charges at each edge, determine the in-plane polarization direction, P, which is marked by a solid arrow. The polarization direction P points from the negatively charged edge to the positively charged edge and is always parallel (or antiparallel) to the lattice vector  $a_1$  [49].



Figure 1.5: Atomic structure of group-IV monochalcogenides MX monolayers illustrated with a SnSe monolayer. The silver balls and green balls represent Sn atoms and Se atoms, respectively. Adapted from [49].

Figure 1.6 summarizes the fabrications and characterizations of SnX (X=S, Se, Te) monolayers. The in-plane ferroelectricity in SnS monolayers, grown on a mica substrate by physical vapor deposition (PVD), were characterized by piezoresponse force microscopy (PFM), second harmonic generation (SHG), and electric transport experiments [50]. SnTe and SnSe monolayers, grown on graphitized SiC (0001) substrate by molecular beam epitaxy (MBE), also manifested in-plane ferroelectric domains, which were characterized by a scanning tunneling microscope (STM) [40][49].



Figure 1.6: Topographic images of (a) SnS monolayer on a mica substrate, adapted from [50]; (b) SnTe monolayer on a graphene substrate, adapted from [40] and (c) SnSe monolayer on graphene substrate, adapted from [49].

In the following, I will introduce four phenomena which can demonstrate the in-plane ferroelectricity by scanning tunneling microscope (STM).

#### (1) Topography and dI/dV mapping images

Ferroelectric domains can be directly observed in topography images and the corresponding dI/dV mapping images. Single domains, 180° domains and zigzag domains exist in monolayer SnSe (Figure 1.7(a)-(c)) [49]. Single domains, 90° domains and zigzag domains are observed in monolayer SnTe (Figure 1.7(d)-(f)) [40]. Studying the topography and dI/dV mapping images at variable temperatures, the ferroelectric transition temperature can be determined, as revealed in Figure 1.8 [49]. The ferroelectric domains vanish above the transition temperature and appear again when the temperature falls below the transition temperature of 270 K and 380 K, respectively [40][49].



Figure 1.7: Three types ferroelectric domains in monolayer SnSe observed by dI/dV mapping images (a-c): (a) single domain, (b) 180° domain, and (c) zigzag domain. Three types ferroelectric domains in monolayer SnTe observed by topography images (d-f): (d) single domain, (e) 90° domain, and (f) zigzag domain. All the polarization directions are marked by solid arrows. Adapted from [40][49].



Figure 1.8: Determination of ferroelectric transition temperature by scanning topography and corresponding dI/dV images on the same SnSe monolayer nanoplate at variable temperatures. Adapted from [49].

#### (2) Band bending

In bulk ferroelectrics with screening, band bending is formed at the edges, as shown in Figure 1.9(a). Moreover, the bandgap at the edges and correspondingly the apparent height measured by STM is different between the negatively-charged edges and positively-charged edges, as illustrated in Figure 1.9(b). The dark blue part between the valance band  $E_v$  and dashed line  $eV_s$ , where  $V_s$  is the bias voltage, presents the density of states contributed for tunneling. The negatively (positively) charged edges have upward (downward) band bending and more (less) density of states (DOS) are contributed for tunneling. Therefore higher (lower) apparent height and bright (dark) edges are formed at the negatively (positively) charged edges. Not only topography, the band bending can also be observed by dI/dV spectra in monolayer SnSe (Figure 1.9(c)) and SnTe (Figure 1.9(d)) [40].



Figure 1.9: Band bending observed from dI/dV spectra for monolayer SnTe and SnSe. Schematic band shift in a bulk ferroelectric (a), the band gap and apparent height shown at the edge (b) and experimentally observed band bending in monolayer SnSe (c) and monolayer SnTe (d) by dI/dV spectra. Adapted from [40][49].

To make a comparison, the dI/dV spectra are also performed on monolayer PbTe, where no band bending is observed, which is consistent with the paraelectric nature of PbTe and also proves that the band bending is formed by the ferroelectricity [40].



Figure 1.10: STM topography image (left panel) and dI/dV spectra (right panel) of monolayer PbTe. Adapted from [40].

By scanning the dI/dV spectra on SnTe monolayers, bilayers, and trilayers, the antiparallel coupling between SnTe interlayers in ultrathin SnTe are determined because of the finite inplane polarizations observed in monolayer (Figure 1.11(b-d)) and trilayer (Figure 1.11(h-j)), and zero total polarizations in bilayer (Figure 1.11(e-g)) [51].



Figure 1.11: Antiparallel coupling between the polarizations of SnTe layers from dI/dV spectra on SnTe monolayer, bilayer, and trilayer [51]. (a) Schematic figure of band bending and antiparallel coupling in monolayer, bilayer, and trilayer SnTe. 2 atomic layers (AL) is 1 monolayer (ML). The topography image and band bending are observed in monolayer (Figure 1.11(b-d)) and trilayer (Figure 1.11(h-j)), while a zero total polarization occurs in the bilayer

(Figure 1.11(e-g)). Adapted from [51].

#### (3) Ferroelectric domain switching by applying a bias voltage pulse

One of the main properties of ferroelectric materials is that their ferroelectric domains can be switched under electric fields. The ferroelectric domain switching in monolayer SnTe and SnSe can be realized in a scanning tunneling microscopy (STM) by applying a bias voltage pulse. The bias voltage pulse can create an instantaneous high electric field to move the domain. At the first trial, a pulse was applied on the monolayer nanoplates which was uncontrollable and destroyed them. Then, the controllable domain switching was realized by applying the electric pulses on the nearby graphene substrate. The domains can be moved by the horizontal component of the electric field created by the bias voltage pulse [40][49].



Figure 1.12: Ferroelectric domain switching realized by electric pluses. (a-g) The controllable switching in SnSe monolayers [49]: (a) Schematics figure of the controllable domain switching by applying the electric pulse on the nearby graphene substrate. (b) Rising magnitude of the

electric pulses. (c-g) A continuous series of ferroelectric domain switching after applying the electric pulse at the same location marked in (c). (h-i) Ferroelectric domain switching in SnTe monolayers. Adapted from [40].

#### (4) Lattice distortion

As indicated in Figure 1.13(a), a lattice distortion appears in ferroelectric phases. When scanning the atom resolved images across a domain boundary, the fast Fourier transformation (FFT) will show a Bragg peak split, which is contributed by two different ferroelectric domains.



Figure 1.13: Schematic of lattice distortion (a) and fast Fourier transformation of atom resolved images across a domain boundary (b). Adapted from [40].

# Chapter 2 Experimental methods

All the sample growth and characterization done in this thesis was accomplished by molecular beam epitaxy (MBE) and scanning tunneling microscopy (STM), including variable temperature scanning tunneling microscopy (VT-STM) and low temperature scanning tunneling microscopy (LT-STM) in ultra high vacuum (UHV) environment. In this chapter, I will introduce these experiment methods separately.

#### 2.1 Ultra High Vacuum (UHV)

A vacuum pressure below  $1 \times 10^{-9}$  mbar is called ultra-high vacuum (UHV). UHV environment is essential for surface science because it can provide an environment to grow the high-quality thin films and to characterize the samples with low energy electron diffraction (LEED) or reflection high-energy electron diffraction (RHEED) [52][53].

In order to reach the ultrahigh vacuum (UHV) environment, a chamber will have a scroll pump or an oil-sealed pump to reach the vacuum around 10<sup>-3</sup> mbar, a turbo pump to reach a vacuum around 10<sup>-8</sup> mbar, and an ion pump, titanium sublimation pump to generate the titanium (Ti) in the chamber and absorb the water and gases. Besides different pumps, ion gauges are used to monitor the vacuum [52].

#### 2.2 Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy (MBE) is a powerful technique for growing high-quality thin films because of its UHV environment, slow and controllable growth rate, and *in-situ* characterization methods [54].



Figure 2.1: Schematic figure of the MBE chamber. Adapted from [54].

A basic MBE chamber will at least have a manipulator, evaporation sources, and an *in-situ* reflection high-energy electron diffraction (RHEED) apparatus. Here, I will introduce these three important parts.

#### (1) Manipulator

The manipulator is used to heat up or cool down and also transfer the sample. In our chamber, there are two ways to heat up the sample: direct heating and resistance heating. Direct heating means the current directly goes through the sample, which needs the sample to be conductive. Through direct heating, samples can reach temperatures above 1000 °C. Normally, direct heating is widely used to anneal conductive substrates, such as graphene or Si substrates. A pyrometer is used to detect the temperature of the sample during the heating process. In the resistance heating process, the power is added on the filament and the heat can be radiated to the sample. Usually, the temperature will not be above 700 °C for a long time to protect the filament. The manipulator can also cool down the sample by using the liquid nitrogen.

#### (2) Evaporator source

Knudsen effusion cells (K-Cell) and electron-beam evaporators (E-beam) are the two kinds of evaporators mostly used in an MBE chamber. The main components of a K-Cell are the crucible, filament, radiation shields, thermocouple, shutter, and cooling water. The temperatures of the evaporators can be precisely controlled by PID (proportional-integral-derivative) with the thermocouple feedback. The maximum temperature of the K-Cell is 2000 °C. Electron-beam evaporators (E-beam) are used for chemical elements or materials with evaporation temperatures above 2000 °C.



Figure 2.2: (a) Knudsen effusion cell (K-Cell, MBE component). Adapted from [55]. (b) electron-beam evaporator (E-beam, SPECS). Adapted from [56].

#### (3) RHEED (reflection high-energy electron diffraction)

Reflection high-energy electron diffraction (RHEED) is a powerful and widely-used *in-situ* characterization method to monitor the surface quality and thickness of the thin film during the growth process [57]. The principle of RHEED is shown in Figure 2.3. High-energy electrons are incident on the sample surface within a very small angle (3~5 degree). Electrons along the intersection between the reciprocal rods and Ewald sphere will reach the fluorescent screen and become the bright spots, therefore the RHEED patterns are formed [57].



Figure 2.3: Principle of the RHEED. Adapted from [57].

Besides from the direct observation of RHEED patterns, RHEED oscillations can also provide information on the quality and thickness of the thin film by RHEED oscillations. When the coverage  $\theta$  ( $\theta = \frac{A_{\text{thin film}}}{A_{\text{substrate}}}$ ,  $A_{\text{thin film}}$  is the area of the thin film on the substrate;  $A_{\text{substrate}}$  is the area of the substrate) is zero, the RHEED intensity reaches its maximum value. When  $\theta$  increases, the intensity decreases, until  $\theta$  reaches a value of 0.5 and the intensity is minimum. Then, the increase of  $\theta$  will lead the increase of the RHEED intensity, until  $\theta$  reaches 1, and the intensity reaches its maximum value again. All the procedures will repeat, forming the oscillation pattern [58].



Figure 2.4: Schematic figure of RHEED oscillation. Adapted from [58].

#### 2.3 Thin film growth

Thin film growth is a dynamic process between thermodynamics and kinetics. After atoms or molecules are absorbed on the substrate's surface, some of them will desorb from the surface, while other will diffuse on the surface and form a nucleus for further growth [59].



Figure 2.5: Typical processes during thin film growth. Adapted from [59].

Three crystal growth modes, (i) layer by layer (or Frank-van der Merwe) (ii) layer plus island (or Stranski-Krastanov), and (iii) island (or Volmer-Weber) mode, which is determined by whether the layer or island are formed on each layer, are represented in Figure 2.6 [60].



Figure 2.6: Three crystal growth modes. (a) layer-by-layer, (b) layer plus island, (c) island. Adapted from [60].

#### 2.3.1 Van der Waals epitaxy

Different from the traditional epitaxy, van der Waals epitaxy can ignore the lattice mismatch between the substrate and a thin film given the weak coupling between them [61]. In this thesis, the SnTe and SnSe monolayers, and the PbTe/SnTe monolayer lateral heterostructures all follow a van der Waals epitaxial growth on the graphene substrate, which will be introduced in the following chapters.



Figure 2.7: Schematic of conventional epitaxy growth (a) and van der Waals epitaxy (b). Adapted from [61].

#### 2.4 Scanning Tunneling Microscopy (STM)

The scanning tunneling microscope (STM) was invented in the 1980s by two scientists from IBM Zürich, Gerd Binnig and Heinrich Rohrer [62][63]. Because of its high resolution at the

atomic scale, STM is widely used in the physics, chemistry and biology fields. Next, I will introduce the principle of STM and STM working at variable-temperature and low temperature (VT-STM/LT-STM).

# 2.4.1 Principle of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS)

The basic principle of STM is the tunneling effect in the quantum mechanics. In the classic mechanics, the particle has no possibility to tunnel if the energy of the particle is less than the energy of the barrier. While, in the quantum mechanics, there is a possibility for a particle to tunnel if the barrier is narrow enough. In the STM, the tip and the sample are separated by a vacuum barrier. However, the electron can tunnel from the tip to the sample if the distance between them is narrow enough. The tunneling current I is

$$I(V) = \frac{4\pi e}{\hbar} \int_{-\infty}^{+\infty} [f(E - eV) - f(E)] \rho_{\rm s}(E - eV) \rho_{\rm t}(E) |M|^2 dE$$
(1)

Where  $\rho_s$ ,  $\rho_t$  are the local density of states (LDOS) of the sample and tip, respectively. f(E) is the fermi distribution function. M is the tunneling matrix element. Assume  $\rho_t$  and M are constant, the tunneling current I can be present as

$$I \propto \int_0^{eV} \rho_{\rm s}(E_f - eV + \varepsilon) \, d\varepsilon \tag{2}$$

Differentiate the tunnel current to the bias voltage,

$$\frac{\mathrm{d}I}{\mathrm{d}V} \propto \rho_{\mathrm{s}}(E_f - eV) \tag{3}$$

dI/dV is proportional to the local density of states (LDOS) of the sample, which is the principle of scanning tunneling spectroscopy (STS).



Figure 2.8: Tunneling process between the tip and the sample. Adapted from [64].

Two scanning modes, constant current mode and constant height mode, are used during STM measurements, demonstrated in Figure 2.9 [64]. In the constant current mode (Figure 2.9(a)), the tunneling current is set to a fixed value and the feedback loop is on. The tip will approach (retract) when the detected current is lower (higher) than the set point current. Therefore, the apparent height of the surface can be revealed. On the contrary, the constant height mode is working when the feedback loop is closed and the tip stays at a fixed height and the tunneling current is determined by the distance between the tip and the surface. Normally, constant current mode is widely used in topography scanning.



Figure 2.9: Two scanning modes (a) constant current mode and (b) constant height mode. Adapted from [64].

Scanning tunneling microscopes have four main parts: (i) a piezoelectric scanner, (ii) an element to move the tip's position in a coarser fashion, (iii) a vibration isolation setup, and (iv) electronic components, which are used for realizing the tip approach and tip stabilization, reducing the vibration noise, and transferal of electric signals, respectively [65].



Figure 2.10: Schematic figure of STM. Adapted from [65].

#### 2.4.2 Preparation and characterization of STM tip

The STM tip is an essential part in the STM experiments. The most common materials used to make the tip are tungsten (W), platinum-iridium (Pt-Ir) alloy. There are two ways to fabricate the tip, mechanically and electrochemically fabrication. Electrochemical etching is the most common way for the W tip preparation [66]. In our VT-STM system, mechanically sharpened Pt/Ir alloy tips are used. Before each measurement, the tip is calibrated on an Au (111) single crystal. If the tip is not in good conditions and STM images show anomalous artifacts, it can be fixed on the Au (111) single crystal by applying a bias pulse. The atomically flat Au (111) surface used for calibrating the STM tip is prepared by several cycles of Ar<sup>+</sup> ion sputtering and thermal annealing.

## 2.4.3 Variable temperature scanning tunneling microscopy (VT-STM)

The Omicron VT-STM-XT system—with a temperature ranging from 100 K to 500 K—is used in all the work presented in this thesis. Before the measurement, the mechanically sharpened Pt/Ir (80/20) alloy tip has been calibrated on an Au (111) standard sample.



Figure 2.11: Image of VT-STM. Adapted from [67].


Figure 2.12: Schematic of VT-STM. Adapted from [67].

## 2.4.4 Low temperature scanning tunneling microscopy (LT-STM)

Since the ferroelectric transition temperature of SnTe monolayers is 270 K [40], which is below the room temperature, the low temperature scanning tunneling microscope (LT-STM) is a perfect instrument for observing the ferroelectric domains. Figure 2.13 represents the crosssection view of a LT-STM. Compared to the VT-STM, the most important part of the LT-STM is the cryostat system to keep the system stable at ultra-low temperatures. Working at ultra-low temperature makes the LT-STM have a good spatial resolution and less thermal drift compared to the images scanned at room temperature. The low temperature STM measurements in our work are carried out at 2 K.



Figure 2.13: Schematic of LT-STM (USM 1300, UNISOKU Co. Ltd). Adapted from [68].

#### 2.4.5 Scanning tunneling microscopy manipulation

Besides topography and STS, another function of the scanning tunneling microscope—STM manipulation—is widely used for moving atoms or molecules and creating structures at the atomic scale [69]. Figure 2.14 displays the process of moving an atom by the STM tip [69]. Compared to the tunneling condition for scanning the topography images, the distance between the tip and atoms needs to be decreased to enhance the interaction between them. After successfully moving an atom, the STM tip will decrease the tip-atom force and locate the atom on the surface by increasing the tip-atom distance.



Figure 2.14: Schematic depiction of moving an atom using an STM tip. Adapted from [69].

Beyond single atoms, flakes of two dimensional (2D) materials can also be moved controllbly or even folded by an STM tip. This is due to the week (van der Waals) force between the thin film and the substrate [40][49][70][71][72][73]. Figure 2.15 enumerates examples of STM manipulation on van der Waals materials.



Figure 2.15: Examples of STM manipulation on van der Waals materials: (a) MoS<sub>2</sub> flakes on graphite. Adapted from [71]. (b) SnSe monolayer on a graphene substrate. Adapted from [49].
(c) SnTe monolayer on a graphene substrate. Adapted from [40]. (d) Folding and unfolding graphene nanoislands (GNIs) on HOPG. Adapted from [70].

## Chapter 3

## Two-dimensional group IV monochalcogenide monolayers and lateral superlattices

The successful molecular beam epitaxial (MBE) growth of SnTe, PbTe, and SnSe monolayers with a large area and regular shape has been reported [39][47]. In this chapter, I will introduce the molecular beam epitaxial growth of two-dimensional monolayers, monolayer lateral heterostructures, and superlattices of those materials on a graphene substrate. An asymmetric diffusion was found in monolayer PbTe/SnTe lateral heterostructures. The diffusion only exists at PoS (PbTe grown outside SnTe) interfaces, and will be more severe when the nanoplates grow on monolayer graphene, compared to growing on bilayer graphene. However, this diffusion can be suppressed by appropriately decreasing the substrate temperate and the PbTe evaporation time.

### **3.1 Introduction**

Compared to the exfoliation energies of graphite at 11.9-23.3 meV/Å<sup>2</sup> obtained from experiments, group IV monochalcogenides have a higher exfoliation energy at 28.1-55.7 meV/Å<sup>2</sup> provided by calculation [47][74]. Therefore, it is difficult to obtain monolayer monochalcogenides by the exfoliation method, and bottom-up growth techniques are required [47].

Method	Materials	Thickness	Reference
Molecular beam	SnTe on graphene	ML (0.63 nm)	[40]
epitaxy (MBE)	PbTe on graphene	ML	[40]
	SnSe on graphene	ML	[49]
Physical vapor	SnS on mica	ML (0.94 nm)	[50]
deposition (PVD)			

Table 3.1 Examples of forming MX monolayers experimentally [47]

Nitrogen etching	SnSe on SiO <sub>2</sub> /Si	ML (~6.8 Å)	[75]
Laser etching	GeSe on SiO2/Si	ML (1.5nm)	[76] [77]

Table 3.1 lists three most popular methods to create MX monolayers. Among them, molecular beam epitaxy shows its huge capability on stably growing high-quality monolayers without the need of any post-etching [47]. Therefore, molecular beam epitaxy is chosen to grow high-quality monochalcogenide monolayers and the monolayer lateral heterostructures and superlattices. In the next part, I will first introduce the MBE growth of SnTe, SnSe, and PbTe monolayers on the graphene substrate, and will discuss our work on the monolayer lateral heterostructures and superlattices afterwards.

## 3.2 MBE growth of group-IV monochalcogenide monolayers

In this part, I will introduce the MBE growth of monolayer SnTe, SnSe, and PbTe nanoplates on the graphene/SiC (0001) substrate.

The graphene substrates are prepared by the thermal decomposition of SiC (our SiC substrates are  $2 \text{ mm} \times 10 \text{ mm}$  sized n-doped 6H-SiC (0001)). First, the SiC substrate is degassed at 500 °C. Then, we anneal the substrate at 900 °C under Si flux for 15 minutes to form a Si-rich  $3 \times 3$  reconstruction. The final step is to anneal the substrate at 1400 °C for 10 minutes to obtain the graphene/SiC (0001) [40]. The STM topography image is shown in Figure 3.1(a), and an atomically resolved image in Figure 3.1(b). The fast Fourier transform (FFT) image seen as an inset in Figure 3.1(b) is consistent with both the lattice structure and lattice constant of graphene.



Figure 3.1: STM Characterization of the graphene/SiC (0001) substrate. (a) STM image of the graphene substrate. (b) Atom-resolved topography image of graphene, the inset is the Fourier transformed image of (b).

Monolayer SnTe growth and the discovery of a robust in-plane ferroelectricity was experimentally realized by Kai Chang et al. in 2016 [40]. Remarkably, SnTe molecules can be directly evaporated by a SnTe bulk compound, without the need of evaporation from two different sources. The schematics in Figure 3.2 illustrate the MBE growth of SnTe monolayers on a graphene substrate. The SnTe compounds were put in the evaporators, and SnTe molecules can be evaporated out when reaching their evaporation temperature. This method has a huge advantage at controlling stoichiometry, especially when growing SnSe, since excess Se will form SnSe<sub>2</sub> [47]. In this thesis, SnTe, PbTe and SnSe molecules are all evaporated from their compounds.



Figure 3.2: Schematic figure of growing MX monolayers on a graphene substrate by MBE. This figure uses SnTe as the example. Adapted from [47].

SnTe has three phases [78]. SnTe in the rock-salt structure,  $\beta$ -SnTe, is a topological crystalline insulator (TCI) [79]. A slight rhombic distortion along (111) from the rock salt structure will form  $\alpha$ -SnTe phase, which is ferroelectric. Bulk SnTe shows ferroelectricity under the ferroelectric transition temperature at 98 K [40]. Layered (orthorhombic) SnTe ( $\gamma$ -SnTe) is the SnTe phase with the antipolar properties, and it only exists in ultra-thin films [78]. SnTe monolayers show ferroelectricity with a transition temperature at 270 K, almost three times higher than the transition temperature of the bulk [40]. Besides from the different atomistic structures in the three phases, there is another significant difference: Sn vacancies in the  $\beta$ -SnTe are much more than in  $\gamma$ -SnTe (of the order of  $10^2$ - $10^3$  more) [78]. In the  $\gamma$ -SnTe shown in Figure 3.3(e), there are only 4 Sn defects (black spots in crisscross shape) in the 20 nm×20 nm area. This property will be mentioned again in the next part when we discuss the Sn vacancies in the SnTe (inside)/ PbTe (outside) monolayer lateral heterostructures.



Figure 3.3: Lattice structures of SnTe in the  $\gamma$  phase (a) and the  $\beta$  phase (b), and topography images of the  $\gamma$  phase (c) and  $\alpha$  phase (d). Atomically resolved topography images of  $\gamma$  phase (e) and  $\beta$  phase (f). Adapted from [47][78].

In order to grow MX monolayers in a more stable and reproducible way, a two-step growth is put forward. Here, I use monolayer SnSe nanoplate growth as the example. First step is to form the SnSe nucleation on the graphene substrate. To realize it, we deposit SnSe for a very short time, such as 30 s when the substrate is staying at 40-50 °C, or room temperature. The result is presented in Figure 3.4(a). Then, in order to make the shape of SnSe more regular, we will anneal the sample at around 210 °C for 1 h. Figure 3.4(b) manifests the SnSe monolayer in regular shapes after this annealing process. Finally, we will increase the area of the SnSe

nanoplates by continually depositing SnSe when the substrate is staying at the annealing temperature of 210 °C. The deposition time is proportional to the area of the nanoplates shown in Figure 3.4(c) [47]. With this method, we can grow monolayer nanoplates with regular shapes and controllable sizes.



Figure 3.4: Two-step growth of monolayer SnSe. (a) The nucleation of SnSe monolayers by depositing SnSe at room temperature for 30 s. (b) Image after annealing the sample to make the shape more regular. (c) Continually depositing SnSe to increase the area of SnSe monolayers. (d) Apparent height of the SnSe nanoplates in (c). Adapted from [47].

# **3.3 MBE growth of group-IV monochalcogenide monolayer lateral** superlattices

As already discussed in Chapter 1.1, lateral heterostructures are mostly achieved among the van der Waals materials such as graphene, hBN and transition metal dichalcogenides (TMDC) by chemical vapor deposition (CVD) or with lithography assist. Now, I want to introduce the

work on the molecular beam epitaxial growth of high-quality monochalcogenides PbTe/SnTe lateral heterostructure and superlattice monolayers. In this part of work [84], the DFT calculations are provided by Prof. Salvador Barraza-Lopez from University of Arkansas.

Since the very similar lattice structure and lattice parameters, the group-IV monochalcogenides provide a series of materials to fabricate the heterostructures. Therefore, we choose monolayer PbTe and monolayer SnTe as two materials to grow the lateral heterostructures (LHSs) and lateral superlattices (LSLs). The LHSs and LSLs were grown in separate steps.

First, a PbTe monolayer core was deposited on the graphene substrate with the substrate temperature at 180 °C, and a PbTe evaporator temperature at 420 °C for 15 minutes. The STM topography image is shown in Figure 3.5(a). The [10] and [01] edges are marked in the PbTe monolayer. The interfaces are along the [11] edge. The atom-resolved topography image in Figure 3.5(b) reveals the high quality with no defect vacancies in PbTe monolayers.

Then, SnTe was deposited at the same substrate temperature (180 °C) with a SnTe evaporator temperature of 400 °C for 10 min. The topography image in Figure 3.5(c) manifests the formation of PbTe/SnTe monolayer LHSs. The inner (darker) part is PbTe while the outer (brighter) part is SnTe. The different apparent heights between PbTe and SnTe are caused by the bias-voltage dependence, which will be discussed in section 3.4. The atom-resolved topography image acquired at the interface– (Figure 3.5(d)) represents a clean interface at SoP (SnTe outside PbTe) with no defects in the PbTe and SnTe monolayer constituents.

The substrate temperature during the second material deposition is crucial for lateral heterostructures. In the PbTe/SnTe heterostructures, the lateral heterostructure monolayers can only be formed when the substrate temperature was between 120 °C to 300 °C during the second deposition. If the substrate temperature was lower than 120 °C and higher than 300 °C, the coverage of PbTe/SnTe lateral heterostructure monolayers decreases dramatically and

bilayers appear.

Next, PbTe was deposited at the same substrate temperature of 180 °C with the evaporator temperature 420 °C, and a growth time of 10 minutes. The topography image of three-layer LHS is shown in Figure 3.5(e). The atom-resolved topography image obtained at PbTe-1, SnTe-1 interface and SnTe-1, PbTe-2 interface are represented in Figures 3.5(g) and (f), respectively.

When scanning at the negative bias voltage, -0.6 V, the dark spots in the SnTe compound are the Sn vacancies and the bright spots in the PbTe part are the Sn atoms diffused into the PbTe film. Figure 3.5(f) shows that the amount of Sn vacancies in SnTe and Sn atoms diffused into PbTe is far larger than the intrinsic vacancies in  $\gamma$ -SnTe (Figure 3.3(e)) and PbTe monolayers (Figure 3.5(b)). Combining Figures 3.5(g) and (h), we can clearly confirm that the diffusion only appears in the PbTe and SnTe sections at the PoS (PbTe grown outside SnTe) interface.

Finally, SnTe was deposited at the same substrate temperature 180 °C, with an evaporator temperature of 400 °C and a growth time of 10 minutes. Figure 3.5(i) is the topography image of a four-layer LHS. The atom-resolved topography image of SoP (SnTe grown outside PbTe) interface with few defect vacancies in the SnTe part are represented in Figure 3.5(j).

From the topography images and atomic resolved images at interface after each step, we can see that an asymmetric diffusion appears in the PbTe/SnTe monolayer LHSs. Importantly, the growth order determines the diffusion at the interface: the diffusion only appears in the PbTe and SnTe part at the PoS (PbTe grown outside SnTe) interface.



Figure 3.5: Growth process of a PbTe-SnTe-PbTe-SnTe lateral heterostructure (LHSs) monolayer. (a) Topography image of a PbTe monolayer core. ( $V_s = -0.7 \text{ V}$ ,  $I_t = 2 \text{ pA}$ ). (b) Atomresolved topography image of a PbTe monolayer. The inset is a FFT image ( $V_s = -0.3 \text{ V}$ ,  $I_t = 10 \text{ pA}$ ). (c) Topography image of a PbTe/SnTe LHS monolayer ( $V_s = -0.4 \text{ V}$ ,  $I_t = 2 \text{ pA}$ ). (d) Atom-resolved topography image at SoP interface ( $V_s = -0.7 \text{ V}$ ,  $I_t = 1 \text{ nA}$ ). (e) Topography image of a PbTe/SnTe/PbTe LHS monolayer ( $V_s = -0.7 \text{ V}$ ,  $I_t = 1 \text{ nA}$ ). (e) Topography image of a PbTe-2) interface and SoP (PbTe-1 and SnTe-1) interface ( $V_s = -0.7 \text{ V}$ ,  $I_t = 2 \text{ nA}$ ). (h) Topography image ( $V_s = -0.7 \text{ V}$ ,  $I_t = 2 \text{ nA}$ ). (i) Topography image of a PbTe/SnTe/PbTe/SnTe monolayer heterostructure ( $V_s = -0.3 \text{ V}$ ,  $I_t = 2 \text{ pA}$ ). (j) Atom-resolved topography image at SoP (SnTe-2 and PbTe-2) interface ( $V_s = -0.3 \text{ V}$ ,  $I_t = 2 \text{ pA}$ ). (j) Atom-resolved topography image at SoP (SnTe-2 and PbTe-2) interface ( $V_s = -0.7 \text{ V}$ ,  $I_t = 2 \text{ pA}$ ). (j) Atom-resolved topography image at SoP (SnTe-2 and PbTe-2) interface ( $V_s = -0.7 \text{ V}$ ,  $I_t = 700 \text{ pA}$ ). (k) Topography image at SoP (SnTe-2 and PbTe-2) interface ( $V_s = -0.7 \text{ V}$ ,  $I_t = 700 \text{ pA}$ ).

## 3.4 STM characterization on monolayer lateral heterostructures and lateral superlattices

Figure 3.5 shows the growth of monolayer PbTe/SnTe lateral superlattices. The lattice structure and topography images are displayed in Figures 3.6(a) and (b), respectively. The structure in Figure 3.6(b) was scanned under a 3.0 V bias voltage. At this bias voltage, PbTe (SnTe) has a higher (lower) apparent height and shows a brighter (darker) area. The bias-voltage dependency has been found in PbTe/SnTe lateral heterostructures and superlattices scanned under the different bias voltages, which will be discussed in Figure 3.7. The bias-voltage dependency is consistent with the type-II band alignment in this heterostructures and superlattices, which is shown in Figure 3.7(a).



Figure 3.6: Monolayer PbTe/SnTe lateral superlattice. (a) lattice structure, (b) topography image ( $V_s = 3.0 \text{ V}$ ,  $I_t = 10 \text{ pA}$ ).

As discussed in Section 2.3.1, the apparent height of the sample is influenced by the integral of the local density of states (LDOS) from 0 to  $eV_s$  of the sample. Figure 3.7(a) illustrates the principle of the bias-voltage dependency. The darker part represents the LDOS that contributed to the tunneling current.  $V_s$  is the bias voltage during scanning. The left (right) panel represents the situation scanned under the positive (negative) bias voltages. The valence band maximum (VBM) and conduction band minimum (CBM) of PbTe (red curve) and SnTe (blue curve) are determined by dI/dV spectra from Figure 3.7(b).

When  $V_s < -1.2$  V, the apparent heights of monolayer PbTe ( $z_p$ ) and SnTe ( $z_s$ ) have similar values, so,  $\Delta z = z_p - z_s = 0$ . When increasing the bias voltages while still in the negative bias voltages, the SnTe (PbTe) monolayer has more (less) density of states in the valence band and shows a brighter (darker) area from the topography images. This trend will exist until scanning at -0.1 V, and the difference between  $z_p$  and  $z_s$ ,  $\Delta z$  reaches the minimum value of -2.6 Å. When scanning under a positive bias voltage, the PbTe (SnTe) monolayer has more (less) density of states in the conduction band contributing for tunneling and the difference between  $z_p$  and  $z_s$  increases and reaches the maximum value of 1.6 Å when scanned under 1.2 V. When continually increasing the bias voltages, the  $\Delta z$  will decrease until reaching a magnitude around 0 when scanned under a 1.8 V bias. This trend has been revealed in Figure 3.7(c), which shows a nonmonotonic relation between the bias voltage and  $\Delta z$ . Figure 3.7(d) contains a series of topography images scanned under different bias voltages. When scanning at -1.2 V, the difference between the PbTe and SnTe monolayers is almost unnoticeable. When increasing the bias voltage to -0.8 V and -0.4 V,  $\Delta z$  decreases and the PbTe becomes darker ( $z_p < z_s$ ). When increasing the voltage to 1.6 V and 1.8 V,  $\Delta z$  decreases until reaching a value close to 0 and the height among PbTe and SnTe is almost the same again.



Figure 3.7: Bias-voltage dependency of monolayer PbTe/SnTe lateral heterostructures. (a) The schematic figure of type-II band alignment in PbTe/SnTe lateral heterostructures. The blue bars above (below) the fermi level ( $E_F$ ) represent the conduction (valence) band. (b) dI/dV spectra of PbTe (red curve) and SnTe (blue curve) monolayers. (c) Bias voltage dependence of apparent height difference between SnTe and PbTe ( $\Delta z=z_p-z_s$ ). (d) Topography images of a heterostructure scanned under different bias voltages ( $I_t = 30$  pA). Adapted from [84].

#### **3.5** Asymmetric diffusion in PbTe/SnTe monolayer lateral heterostructures

As indicated before, an asymmetric diffusion had been discovered in PbTe/SnTe lateral interfaces. The SoP (SnTe grown outside PbTe) interface showed a clean and sharp interface and almost no vacancies in both PbTe and SnTe regions, while a rather severe diffusion happened at the PoS (PbTe grown outside SnTe) interface. In the latter case, the Pb atoms substitute in the SnTe part and form the Sn vacancies. At the same time, the Sn atoms diffuse

into PbTe, as emphasized in Figures 3.8(b) and (c). This asymmetric diffusion is consistent with the topography image in the PbTe-SnTe-PbTe-SnTe lateral superlattice monolayer in Figure 3.8(a).



Figure 3.8: Asymmetric diffusion at the monolayer SoP (SnTe grown outside PbTe) and monolayer PoS (PbTe grown outside SnTe) interfaces. (a) STM image for a lateral superlattice  $(V_s = -0.7 \text{ V}, I_t = 500 \text{ pA})$ . (b) Atomic resolved image of SoP interface. ( $V_s = -0.7 \text{ V}, I_t = 1 \text{ nA}$ ). (c) Atomically resolved image of PoS interface ( $V_s = -0.7 \text{ V}, I_t = 1 \text{ nA}$ ).

We performed a systematic study discoveroffing the asymmetric diffusion in the monolayer PbTe/SnTe lateral heterostructures. Since the diffusion only appeared in the PoS (PbTe grown outside SnTe) interfaces, a series of SnTe (core)/ PbTe (surrounding) LHSs with fixed SnTe growth parameters, with different PbTe growth parameters were grown and statistical studies of vacancies concentrations were performed. The method used to calculate the vacancy concentration is presented in Appendix A.

We found that the thickness of the graphene substrate influences the vacancy density, as revealed in Figure 3.9. The lateral superlattices grown on monolayer graphene (MLG) show more severe diffusion (Figure 3.9(d,e)) than those grown on bilayer graphene (BLG) (Figure 3.9(b,c)). This comparison is clearly seen within a same SnTe area covered on both MLG and BLG in Figure 3.9(f).



Figure 3.9: Comparison of the diffusion between the LHSs grown on monolayer and bilayer graphene. (a) Atomically resolved images of monolayer graphene (MLG) and bilayer graphene (BLG) ( $V_s$ = -20 mV,  $I_t$ = 100 pA). (b, c) Topography images of a same LSL grown on the BLG scanning under the positive bias voltage and negative bias voltage ( $I_t$ = 10 pA). (d, e) Topography images of a same LSL grown on the MLG scanning under positive bias voltage and negative bias voltage ( $I_t$ = 10 pA). (d, e) Topography images of a same LSL grown on the MLG scanning under positive bias voltage and negative bias voltage ( $I_t$ = 10 pA). (f) Topography image of a SnTe part covered on both MLG and BLG ( $V_s$ = 1.5 V,  $I_t$ = 10 pA).

In the next parts, we only choose the lateral heterostructures grown on the bilayer graphene for statistical studies. A series of LHSs were grown with same PbTe evaporation temperature (420 °C, which means the same PbTe flux) and PbTe growth time (10 minutes), but with different substrate temperatures (from 180 °C to 270 °C). The 20 nm× 20 nm atomically resolved images that resulted from those experiments are shown in Figure 3.10(a-d). The vacancy concentration of Sn atoms substituted in the PbTe part,  $n_{Sn:PbTe}$ , was found to be proportional to the substrate temperature. In the optimized range of substrate temperatures for the monolayer lateral heterostructures, the lower (higher) the substrate temperature is, the lower (higher) the vacancy concentrations of Sn atoms diffused in the PbTe part,  $n_{Sn:PbTe}$ , are, which

is shown in Figure 3.10(h). The vacancy concentration of Sn atoms substituted in the PbTe part,  $n_{\text{Sn:PbTe}}$ , decreases from  $5.5 \times 10^{13} \text{ cm}^{-2}$  to  $1.1 \times 10^{13} \text{ cm}^{-2}$  when only decreasing the substrate from 270 °C to 180 °C.

Besides the substrate temperature, the flux of PbTe (which is controlled by the evaporation temperature) and growth time both influence the diffusion. The higher (lower) evaporation temperature, which corresponds to the higher (lower) PbTe flux and lower (higher) PbTe growth time, will lead to the lower (higher) vacancy concentration in the PbTe section.

This way, lateral heterostructures or lateral superlattices with the sharper and cleaner interfaces can be grown by increasing the PbTe evaporation temperature (decrease the PbTe growth time), while appropriately decreasing the substrate temperature (not below 120 °C) in order to make sure the high coverage of the monolayers lateral superlattices.



Figure 3.10: Dependency of Sn substitution concentration on substrate temperature and PbTe evaporation temperature for the PbTe region. (a-d) Atomically resolved images acquired at the PoS interface [(a)  $V_s = -1.0$  V,  $I_t = 200$  pA; (b)  $V_s = -0.7$  V,  $I_t = 2$  nA; (c)  $V_s = -0.7$  V,  $I_t = 1$  nA; (d)  $V_s = -0.7$  V,  $I_t = 2$  nA]. (e-g) Atomic resolved images acquired at the PoS interface with

different flux of PbTe and growth time [(e)  $V_s = -0.6$  V,  $I_t = 10$  pA; (f) and (g)  $V_s = -0.5$  V,  $I_t = 100$  pA]. (h) The substrate temperature dependence of the Sn substitutions concentrations in the PbTe part,  $n_{\text{Sn:PbTe.}}$  (i) The PbTe flux dependence of the Sn substitution concentration in the PbTe section.

Even though Pb substitutions in the SnTe part and Sn substitution in PbTe part exist at the same interface, the distributions are different. The uniform Pb doping is observed in a 100-nm wide SnTe core with a 10-nm wide PbTe surrounding lateral heterostructure, which is shown in Figure 3.11.



Figure 3.11: Uniform distribution of Pb substitution in the SnTe region. (a) The STM image of PoS (PbTe grown outside SnTe) interface. (b) Atomically resolved image in the dashed square area in (a). ( $V_s = -0.6$  V,  $I_t = 10$  pA). A uniform Pb doping in the SnTe part is observed.

However, Figure 3.12 shows that the Sn substitution has a spatial distribution in the PbTe region. The concentration of SnTe drops quickly from 95 % to 5 % in a short distance and keeps a long "tail" at a long distance. This phenomenon leads a different diffusion mechanism for the one that existed in the PbTe/SnTe lateral heterostructures, which will be discussed in section 3.6.



Figure 3.12: Spatial distribution of Sn substitution in the PbTe region: (a) Topography image of 4-layer lateral heterostructure (PbTe/SnTe/PbTe/SnTe). (b) The SnTe percentage in (a): the Sn substitution in the PbTe part shows a marked spatial distribution.

### **3.6 Diffusion mechanism in PbTe/SnTe lateral heterostructures**

We discovered interdiffusion in the previously studied lateral heterostructures. Figure 3.13 contains examples of diffusion in heterostructures reported in the literatures. Unlike the diffusion caused by the substrate temperature [82], we will focus on the intrinsic interdiffusion here. Pb atoms diffused into SnTe part when SnTe (001) was grown on Pb (111), and formed Sn<sub>1-x</sub>Pb<sub>x</sub>Te-Pb heterostructures [81]. Asymmetric diffusion had also been revealed in WSe<sub>2</sub>-MoSe<sub>2</sub> lateral heterostructures. The MoW (MoSe<sub>2</sub> grown outside WSe<sub>2</sub>) interface is clean and sharp, while the diffusion happened at the WoM (WSe<sub>2</sub> grown outside MoSe<sub>2</sub>) interface; this is shown in Figure 3.13(d, e) and it is consistent with Figure 3.13(f). W vacancies existed in the WoM (WSe<sub>2</sub> grown outside MoSe<sub>2</sub>) interfaces (Figure 3.13(g)) and RoM (ReSe<sub>2</sub> grown outside MoSe<sub>2</sub>) interfaces (Figure 3.13(h)), the diffusion still existed.



Figure 3.13: Examples of diffusion in existing lateral heterostructures. (a-c) The diffusion in Sn<sub>1-x</sub>Pb<sub>x</sub>Te- Pb lateral heterostructures. Adapted from [81]. (a) STM topography images of lateral heterostructure. (b) Atomic resolved images of Sn<sub>1-x</sub>Pb<sub>x</sub>Te (001). (c) Atomically resolved image of Pb (111). The bright spots in (b) are the Pb atoms diffused in SnTe part and form Sn<sub>1-x</sub>Pb<sub>x</sub>Te. (d, e). The asymmetric diffusion at the MoSe<sub>2</sub>/WSe<sub>2</sub> interface. The diffusion happened at the WoM (WSe<sub>2</sub> grown outside MoSe<sub>2</sub>) interface (d), while a clean and sharp interface existed at the MoW (MoSe<sub>2</sub> grown outside WSe<sub>2</sub>) interface (e). Adapted from [11]. (f) Scanning transmission electron microscopy (STEM) image of the interface between MoSe<sub>2</sub> (darker) and WSe<sub>2</sub> (brighter contrast). Adapted from [9]. (g) The scanning transmission electron microscopy (STEM) image of a monolayer heterostructures between 1T'-ReSe<sub>2</sub> and 2H-MoSe<sub>2</sub>. Adapted from [83].

In the PbTe/SnTe system, the asymmetric diffusion existed because of the huge difference of the formation energy between the Pb:SnTe defects and Sn:PbTe defects,  $E_{Pb:SnTe} = 11$  meV per substitution and  $E_{Sn:PbTe} = 35$  meV per substitution. The energy of forming a Pb vacancy in SnTe region is less than forming a Sn vacancy in PbTe part, thus the diffusion only exists in the PoS (PbTe grown outside SnTe) interface.

However, the diffusion mechanism is still unclear. First, we assume the diffusion process is dominated by inter-layer hopping, as depicted in Figure 3.14(a). The PbTe diffused into the SnTe part by inter-layer hopping. The spatial distribution of SnTe in the lateral heterostructure described by the Boltzmann-Matano (BM) model imply a 100 % concentration in the middle area of SnTe and a smooth, symmetric reduction of the SnTe concentration at the interface, which is totally different from the experimental data in Figures 3.11 and 3.12.

The uniform distribution of Pb doping in the SnTe part and the spatial distribution of Sn substitution in the PbTe part call for another diffusion mechanism for the PbTe/SnTe lateral heterostructures.

Thus, the surficial diffusion mechanism illustrated in Figure 3.14(b) was put forward. The replacement of PbTe molecules with SnTe molecules happened during the deposition of PbTe. The substitute SnTe desorbed from the surface or diffused into the PbTe part along the surface and formed bonds with PbTe when reaching the edge of the nanoplate. This mechanism caused a uniform distribution of Pb doping in the SnTe part, which is consistent with our observation in Figure 3.11 and the observation that SnTe concentration in the SnTe part are less than 100 %. At the interface, the concentration of SnTe at the interface dropped suddenly and decreased as a function of 1/|x| according to the surficial diffusion model, which was fitted to the experimental data from Figure 3.12. Figure 3.14(c-e) is an analysis of data extracted from Figure 3.12: Figure 3.14(c) is the STM topography image of the PbTe part by adding the coordinate. The analyses in (d) and (e) mark the diffusion of Sn atoms in the PbTe area, and show the number of Sn defects in PbTe,  $n_{Sn:PbTe}$  fits the function  $a/|x-x_0|$  along the *x* axis (Sn defects distributed randomly along the *y* axis).



Figure 3.14: Diffusion mechanism in the PbTe/SnTe lateral heterostructure monolayers. (a) Schematic figure of a diffusion process dominated by inter-layer hopping and a curve of SnTe spatial concentration based on the Boltzmann-Matano (BM) analysis. (b) Schematic figure of the surficial diffusion mechanism and a curve of SnTe spatial concentration based on the surficial diffusion mechanism. (c-e) Analysis of the data extracted from Figure 3.13(a). The Sn atoms diffused in the PbTe area were fitted using a function of  $a/|x-x_0|$  along the *x* axis, and a random distribution along the *y* axis.

## **Chapter 4**

## Vortex-Oriented Ferroelectric domains in PbTe/SnTe monolayer lateral heterostructures

In this chapter, I will introduce the STM characterization of monolayer PbTe/SnTe lateral heterostructures grown on a graphitic substrate. Besides the bias-voltage dependence of apparent height found in the heterostructures, which is consistent with a type-II band alignment, vortex-oriented quadrant ferroelectric domains in either clockwise or counterclockwise directions are also found. Supported by first principles calculations, the quadrant configurations are induced by the interaction between ferroelectricity, charge transfer and interfacial strain effects [84].

### 4.1 Introduction

Different from other existing lateral heterostructures, which are mostly composed by graphene, hBN and transition metal dichalcogenides (TMDC), the PbTe/SnTe lateral heterostructures will display unconventional properties including diode-like current rectification [6]-[34] due to the ferroelectricity in SnTe monolayers. Ferroelectric materials with switchable spontaneous polarizations may have a huge potential in applications, such as ferroelectric tunneling junctions [48] and field electric transistors (FET). However, experiments focused on lateral heterostructures formed by two-dimensional ferroelectric and paraelectric materials are still rare because of difficulties in obtaining the monolayer heterostructures by exfoliation, and due to the complexities involved in the growth of heterostructures. With the successful molecular beam epitaxial growth of PbTe/SnTe lateral heterostructure monolayers, we provide a platform for further research. In the next part, I will introduce the STM characterization of the monolayer PbTe/SnTe lateral heterostructures. The DFT calculations in this chapter [84] are provided by Prof. Salvador Barraza-Lopez from University of Arkansas.

## 4.2 MBE growth of monolayer PbTe/SnTe lateral heterostructures

The monolayer PbTe/SnTe lateral heterostructures are grown on a graphene substrate by molecular beam epitaxy. Schematics, lattice structure, STM topography image and atomic resolved image are shown in Figure 4.1. Since SnTe monolayers show ferroelectricity at temperatures below the transition temperature of 270 K, a lattice distortion and spontaneous polarization take place in the SnTe part, shown in Figure 4.1(b). The polarization direction of the SnTe monolayer is parallel or anti parallel to the [10] edge. On the other hand, the PbTe monolayer always shows paraelectricity. As mentioned in section 3.3, the apparent heights of this heterostructure are determined by the STM bias voltage. When scanning at -0.4 V, PbTe (SnTe) has less (more) density of state contributed, therefore, PbTe (SnTe) has less (more) apparent height and show darker (brighter), which is consistent with Figure 4.1(d), is clean and sharp without any diffusion happening.



Figure 4.1: Characterization of monolayer PbTe/SnTe lateral heterostructures (LHSs). (a) Schematic figure of PbTe/SnTe lateral heterostructures on the graphene/SiC (0001) substrate. (b) Lattice structure at a LHS interface. (c) Topography image of monolayer LHS ( $V_s = -0.4$  V,  $I_t = 30$  pA). (d) Atom-resolved topography image at the PbTe (core)/SnTe (outside) interface ( $V_s = -0.7$  V,  $I_t = 100$  pA). The images were taken at 1.9 K. Adapted from [84].

## 4.3 Vortex-oriented ferroelectric domains in lateral heterostructure monolayers

Characterized by the LT-STM at 1.9 K, except when the bias voltage dependence of the apparent height of SnTe and PbTe are found as already been discussed in Figure 3.7, vortexoriented ferroelectric domains either in clockwise or in counterclockwise directions are found in the SnTe monolayer sections. When scanning at 1.6 V, PbTe (SnTe) shows a brighter (darker) contrast, which is consistent with the topography images in Figure 4.2.

The SnTe part had been separated into four regions based on the different moiré pattern periods created between SnTe and graphene, marked by dashed lines. The solid arrows mark the polarization direction in each area. In the whole SnTe region, the ferroelectric polarization directions form clockwise or counterclockwise vortex orientations, revealed in Figure 4.2, which is also consistent with the 90° ferroelectric domain observed earlier in monolayer SnTe. The existence of vortex-oriented ferroelectric domains in Figure 4.2(a) is further confirmed by the spatially resolved dI/dV spectra measured on the same lateral heterostructure, and presented in Figure 4.3.



Figure 4.2: Vortex-oriented ferroelectric domain in clockwise (a) and counterclockwise (b) directions ( $V_s = 1.6 \text{ V}$ ,  $I_t = 30 \text{ pA}$ ). The SnTe part had been separated into four regions by dashed

lines based on their different moiré patterns. The polarization direction in each area was marked by a solid arrow. The images were taken at 1.9 K. Adapted from [84].

The apparent height along the dashed line (c) and (d) in Figure 4.3 confirmed the existence of in-plane polarization. For ferroelectric materials, the apparent height of the positively charged edge is higher (lower) than the negatively charged edge when  $eV_S > E_{CBM}$  ( $eV_S < E_{VBM}$ ) (see Figure 4.3(a) middle and bottom panel, where positive (negative) charged edge is on the right (left) side). When scanning under +1.6 V,  $eV_S > E_{CBM}$ , the apparent height is higher when the edge is positively charged. So, the apparent height is higher when across the bright edge, where the positive bound charges existed. Figure 4.3(b) is the dI/dV image acquired simultaneously with Figure 4.2(a).



Figure 4.3: Apparent height measured along two dashed lines in (b): (a) Schematic figure of the apparent height across the band bending area. (b) dI/dV image of lateral heterostructure simultaneously recorded with Figure 4.2(a) ( $V_s = 1.6 \text{ V}$ ,  $I_t = 30 \text{ pA}$ ). (c, d) The apparent height measured across the dashed lines marked in (b). Adapted from [84].

The vortex-oriented ferroelectric domains are confirmed by spatially resolved dI/dV spectra along the three dashed line in the same lateral heterostructure in Figure 4.2(a), which is shown in Figure 4.4. When scanning dI/dV spectra perpendicular to the edges, the path (a) and (b), the clear band bending can be observed stemming from the bound charges at the SnTe outer edge and the PbTe/SnTe interface. On the other hand, there is no bend bending observed along the diagonal of the heterostructure, when the positive charges and negative charges appear at the two adjacent edges of the diagonal, for example the path (c).



Figure 4.4: Spatially resolved dI/dV spectra along three dashed lines (a), (b), (c) in the same lateral heterostructure in Figure 4.2(a) ( $V_s = 3.0 \text{ V}$ ,  $I_t = 100 \text{ pA}$ ). The dI/dV spectra were taken at 1.9 K. Adapted from [84].

Multiple potential domain configurations schematically shown in Figure 4.5 can be considered. After investigating multiple lateral heterostructures, only the clockwise and counterclockwise vortex-oriented quadrant configurations had been observed, the same schematic figure in Figure 4.5A and B and there is no favorable orientation between clockwise and counterclockwise since the similar amount of these two orientations existed on one sample. Compared to all the forbidden situations, in both allowed situations, the bound charges at PbTe/SnTe interface are always positive and the perpendicular components of polarizations (which is perpendicular to the interface) always point from SnTe to PbTe.The reasons behind these configurations are that the SnTe and PbTe has different work functions, and the strain at the interfaces. Here I will elaborate them.



Figure 4.5: Schematic figure of two types of allowed domain configurations (A, B) and four types of forbidden domain configurations (D-F). Adapted from [84].

The work function of graphene, SnTe and PbTe are  $W_G = 4.16 \text{ eV}$ ,  $W_S = 4.17 \text{ eV}$ ,  $W_P = 4.25 \text{ eV}$  obtained from the first-principles calculations. Due to the very similar work function of graphene and SnTe, there is no charge transfer between them (top panel in Figure 4.6). However, there is charge transfer between graphene and PbTe and electrons flow from graphene to PbTe (bottom panel in Figure 4.6). The work function of SnTe  $W'_S$  and PbTe  $W'_P$  after charge balance are obtained from Gundlach oscillations [86] of the dz/dV spectra.



Figure 4.6: Schematic figure of charge transfer between graphene and SnTe (top panel) and between bilayer graphene and PbTe (bottom panel). Adapted from [84].

In order to compare the work function of SnTe  $W'_{S}$  and PbTe  $W'_{P}$  after charge balance, dz/dV spectra were obtained from lateral heterostructures. The local probe scanning tunneling microscopy (STM) and spectroscopy (STS) provide a method to measure the work function of the thin film. Gundlach oscillations are the field emission resonance formed by the electrons interference within the gap between the tip and sample [87]. From the inset of dz/dV spectra in Figure 4.7(b), which is the energy of the first-order peak, we can obtain the  $\Delta W = W'_{P} - W'_{S} = 90 \pm 28$  meV. The zeroth order peak is ignored since it cannot reflect  $\Delta W$  well. All the results confirm that the work function of PbTe is larger than SnTe.



Figure 4.7: Work function of SnTe  $W'_S$  and PbTe  $W'_P$  after charge balance calculated by dz/dV spectra measured on the lateral heterostructure. The inset in (b) is the energy of the first-order peak. The dz/dV spectra were taken at 77 K. Adapted from [84].

The optimized substrate temperature during the growth is 120-300°C, which is higher than the ferroelectric transition temperature of SnTe at 270 K. Therefore, the SnTe remains paraelectric after the growth. There is only interfacial electric field  $E_{int}$  pointing from SnTe to the negatively charged PbTe. When the sample cooling down below the transition temperature ( $T < T_c$ ), SnTe become ferroelectric. Therefore, the dipole energy in the electric field U, which is proportional to  $-P \cdot E_{int}$ ,  $U \propto -P \cdot E_{int}$ , is more energetically stable when the small angle exists between P and  $E_{int}$ . Thus, P and  $E_{int}$  have the same direction pointing from SnTe to PbTe and the polarization direction leads to the positive charges existing at PbTe/SnTe interface, since the polarization C and D in Figure 4.5 are forbidden since the negative charges exist at the PbTe/SnTe interface.



Figure 4.8: Schematic figure of the reason that from the side view the ferroelectric polarization direction always points from SnTe to PbTe. The top panel shows the lateral heterostructure from the side view when SnTe is paraelectric ( $T > T_c$ ) and SnTe is ferroelectric ( $T < T_c$ ). Adapted from [84].

The reason that configuration E is not energy favorable is the lattice mismatch between SnTe and PbTe. The lattice constants of SnTe are  $a_1 = 4.58$  Å,  $a_2 = 4.44$  Å. And the lattice constants of PbTe are square lattice with a = 4.60 Å. The lattice mismatch is -3.5 % when  $a_1$  of SnTe perpendicular to [10] edge of PbTe ( $a_2$  // PbTe [10] edge) and -0.4 % when  $a_1$  parallel to PbTe [10] edge. Since  $a_1$  is parallel to the polarization direction, the polarization direction at the corner is also parallel to the interface in order to avoid the larger lattice elastic energy. For configuration F, the more ferroelectric domains will also introduce more electrostatic energy. Thus, compared to the configuration C-F, configuration A and B most likely exist.

## **Chapter 5**

# Defect-free nano-welding of monolayer and bilayer semiconducting SnSe nanoplates

In this chapter, I will introduce the work based on the STM manipulation on the SnSe nanoplates. Since the van der Waals force between the SnSe nanoplate and graphene substrate, SnSe can be controllably moved by STM tip. Supported by the density functional theory calculations, the anisotropic friction, which is caused by the commensurate orientation between the nanoplates and graphene substrate, leads the controllable movement of SnSe nanoplate. Combining the *in-situ* annealing at the VT-STM, the defect-free nano-welding between nanoplates can be experimentally realized.

### 5.1 Introduction

Nano-welding, a bottom-up technique used for realizing the nano-structures, is explored in order to reach the high-quality designed structures under the quantum limit [88]. In the previous researches, the nano-welding can be achieved in various methods, such as thermal annealing, cold welding, electron beam exposure, laser annealing, near-field effects, mostly on the carbon nanotubes, metallic nanowire, ceramic nanowire and semiconductor nanoparticles [89]-[99]. Table 5.1 and Figure 5.1 represent examples of the existing methods to realize the nano-welding.

Table 5.1	Examp	les of	existing	methods	to realize	nano-welding.
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Methods	Materials	References
Thermal annealing	Ge nanowire	[89]
	Ag nanowire	[90][91]
	PbSe quantum dots	[92]
Cold welding	Au nanowire	[93]
Electron beam exposure	Carbon nanotubes	[94]

	Ceramic nanowire	[95]
Laser annealing	Au nanoparticles	[96]
	Ag	[96][97]
	nanowires/nanoparticles	
Near-field effects	Carbon nanotubes	[98][99]
Near-field with laser	Carbon nanotubes with	[100]
	Ag solder	



Figure 5.1: Examples of methods to realize nano-welding. (a). TEM images of linking Ge nanowires by annealing at 850 °C. Adapted from [89]. (b). Molecular connection between carbon nanotubes induced by electron beam irradiation. Adapted from [94]. (c). Scanning probe microscope nano-welding on single-walled carbon nanotubes (SWNT). Adapted from [98]. (d). Cold welding between Au nanowires. Adapted from [93]. (e). Nano-welding between Au nanoparticles by femtosecond laser irradiation. Adapted from [96].

The existing nano-welding methods are mostly achieved between metallic materials, seldom between the semiconductors and ceramic materials. Here, I want to highlight the result of fusion between PbSe quantum dots by *in-situ* transmission electron microscopy (TEM) [92].

Figure 5.2 shows the images and schematic figures of the whole fusion process between PbSe quantum dots. The fusion process between quantum dots had realized the defect-free interface. However, the controllable manipulation on the PbSe quantum dots was still missing. In the next part, I will introduce our work on the realization of nano-welding between SnSe nanoplates with assistance of anisotropic friction, which can controllably move the nanoplates. The DFT calculations in this chapter are provided by Prof. Salvador Barraza-Lopez from University of Arkansas.



Figure 5.2: Images and schematic figure of the fusion process between PbSe quantum dots. Adapted from [92].

### 5.2 Characterization of SnSe monolayers

Monolayer SnSe nanoplates are grown on graphene substrate by molecular beam epitaxy, which had been discussed in Figure 3.4. In order to control the stoichiometry, SnSe molecules are evaporated from SnSe compound. Monolayer SnSe ( $a_1 = 4.35 \pm 0.02$  Å and  $a_2 = 4.26 \pm 0.02$  Å) has a highly oriented growth because the lattice parameter  $a_2$  fits the  $\sqrt{3}$  times of the graphene lattice constant (2.46 Å) along the armchair direction ( $\sqrt{3} \times 2.46$  Å = 4.26 Å), which is also can be proved by RHEED pattern [49].



Figure 5.3: Lattice structure (a) and highly existed orientations of monolayer SnSe on graphene substrate (b). (a) The lattice structure of monolayer SnSe. The Sn and Se atoms are represented by gray and green balls. The in-plane ferroelectric polarization direction is marked with solid arrows, which is parallel with  $a_1$ . (b) Three orientations highly existed in monolayer SnSe on graphene substrate, in which  $a_2$  fits the  $\sqrt{3}$  times of the graphene lattice constant (2.46 Å) along the armchair direction. Adapted from [49].

With the ferroelectric transition temperature at 380 K in SnSe monolayers, it is feasible to observe and manipulate the ferroelectric domains at room temperature [49]. Figure 5.4 represent the topography, dI/dV mapping and atomic resolved image of monolayer SnSe, which reveals the single ferroelectric domain with polarization direction P and commensurate orientation between SnSe monolayer and graphene substrate.


Figure 5.4: Characterization of SnSe monolayer on graphene substrate. (a) STM Topography image. The polarization direction is marked in solid arrow. ( $V_s = -0.2$  V,  $I_t = 2$  pA.) (b). simultaneously recorded dI/dV mapping. (c). Atomic resolved images of SnSe obtained from the solid square area in (b). Inset is the fast Fourier transform image of (c) ( $V_s = -20$  mV,  $I_t = 500$  pA).

#### 5.3 Anisotropic friction in SnSe monolayers on graphene substrate

Anisotropic friction had been discovered since the early 1990s. The most of the reported work were characterized by force microscopy, such as friction force microscopy (FFM), on the van der Waals materials such as mica [101], graphite [102][103], graphene [104][105], black phosphorus [106], MoO<sub>3</sub> [107] etc. In these systems, the anisotropic friction exists since the friction enhanced at certain orientations or in commensurate orientations. On the contrary, if the system is in the incommensurate orientation, the friction tends to be canceled and the friction will be reduced. This anisotropic friction is also found in the SnSe/Graphene system.

In SnSe/Graphene system, the commensurate and incommensurate orientation are represented in Figure 5.5(a) and (c) respectively. In the commensurate orientation, since the periodicity between the lattice constant of  $a_2$  (4.26 Å) in SnSe monolayers and lattice constant of graphene along the armchair direction (2.46 Å), the  $a_2$  is highly commensurate with graphene along the armchair direction and  $a_1$  is still incommensurate with zigzag direction, which is shown in Figure 5.5(a). Figure 5.5(b) is the energy corrugation landscape of moving SnSe laterally ( $\Delta x$ ,  $\Delta y$ ) away from the configuration in (a) provided by density functional theory (DFT) calculations.  $\Delta E$  is defined as the energy difference between the energy minimum configuration in (a).

When moving along x axis, the fluctuation of  $\Delta E$  is around 0.1 meV/Å<sup>2</sup>, while along y axis, the fluctuation of  $\Delta E$  is larger than 0.5 meV/Å<sup>2</sup>, which means that in the commensurate orientation, there is a large energy barrier when moving SnSe monolayers along y axis, the armchair direction or perpendicular to the polarization direction.

When rotating SnSe monolayers by 90°,  $a_1$  parallel to the armchair direction, the incommensurate orientation appears in (c). The energy corrugation landscape in (d) reveals that the fluctuations of  $\Delta E$  are always lower than 0.1 meV/Å<sup>2</sup> both moving along the *x* axis and *y* axis, which means there is no significant barrier in the incommensurate orientation. Combining (b) and (d), we can conclude that there is a significant anisotropic in the commensurate orientation direction. This conclusion is consistent with the experimental data, which will be discussed in Figure 5.7.



Figure 5.5: Structure and energy corrugation landscape of SnSe/Gra system in commensurate orientation and incommensurate orientation. The lattice structure in commensurate orientation (a) and incommensurate orientation (c). The grey and green atoms are Sn and Se atoms respectively. The brown atoms, which form a honeycomb structure, represent the carbon atoms. (b,d) The energy corrugation landscape when SnSe moving laterally ( $\Delta x$ ,  $\Delta y$ ) away from the original configuration in commensurate orientation and incommensurate orientation. There is

a significant energy barrier in commensurate orientation.

Owing to the relatively weak van der Waals force between the nanoplates and graphene substrate, it is feasible to manipulate the nanoplates by STM tip [40][49]. Figure 5.6 showcases the schematic figure of the standard moving process in order to ensure the repeatability of all the experiments. In each moving process, the start point is on the nearby graphene substrate rather than on the nanoplates to avoid possible damage on the nanoplates. Then we decrease the distance between the tip and substrate by increasing the value of tunneling current,  $I_i$ , and decreasing the absolute value of the bias voltage,  $|V_s|$ , to increase the force between the tip and nanoplates, which is marked as (1) in the figure. After setting the appropriate bias voltage and tunneling current, the STM tip will move from start point to end along the straight path, represented as (2) in the figure. During this process, the friction between the tip and nanoplate,  $f_T$ , and between nanoplate and graphene substrate,  $f_B$ , existed. Only when  $|f_T| > |f_B|$ , the nanoplate can be moved along the tip.



Figure 5.6: Schematic figure of the controllable moving of SnSe nanoplates by STM tip. Step (1): Decrease the distance between the tip and substrate. Step (2): Tip moves from the start point to end point along the straight path. The friction between the tip and nanoplate,  $f_{\rm T}$ , and between the nanoplate and graphene substrate,  $f_{\rm B}$ , are marked in the solid arrows and have the opposite directions. Only when  $|f_{\rm T}| > |f_{\rm B}|$ , the nanoplate can be moved along the tip.

Figure 5.7 lists three attempts on a SnSe monolayer. The polarization direction is parallel to  $a_1$ . The tip moves in the following three conditions: (a) perpendicular to the polarization direction under the parameter of  $V_s = -2$  mV,  $I_t = 7.5$  nA, v = 5 nm/s; (b) parallel to the polarization direction under the parameter of  $V_s = -2$  mV,  $I_t = 2.5$  nA, v = 5 nm/s; (c) with a random angle with the polarization direction under the parameter of  $V_s = -2$  mV,  $I_t = 2.5$  nA, v = 5 nm/s; (c) with a random angle with the polarization direction under the parameter of  $V_s = -2$  mV,  $I_t = 2.5$  nA, v = 5 nm/s; (c) with a random angle with the polarization direction under the parameter of  $V_s = -2$  mV,  $I_t = 2.5$  nA, v = 5 nm/s. The original position and current position are represented in red dashed area and blue solid area, respectively. The magenta dashed arrows represent the STM tip moving direction. In all of three attempts, the nanoplate cannot be moved only when tip moving perpendicular to the polarization direction in Figure 5.7(a). When tip moving along the parallel (Figure 5.7(b)) and random angle to the polarization direction. This anisotropy friction is consistent with the density functional theory (DFT) calculations in Figure 5.5.



Figure 5.7: Three types of moving processes when STM tip moves perpendicular to the

polarization direction (a), parallel to the polarization direction (b) and with an acute angle between the polarization direction (c) ( $V_s = -0.2$  V,  $I_t = 2$  pA). Only when the tip moving perpendicular to the polarization direction, the nanoplate cannot moved.

The SnSe monolayer cannot be moved when the tip moved perpendicular to the polarization direction under the parameter of  $V_s = -2 \text{ mV}$ ,  $I_t = 7.5 \text{ nA}$ , v = 5 nm/s in Figure 5.7(a). The SnSe monolayer was broken finally when the tip moved along the same direction under the parameter of  $V_s = -1 \text{ mV}$ ,  $I_t = 15 \text{ nA}$ , v = 5 nm/s shown in Figure 5.8.



Figure 5.8: Breakdown of SnSe monolayer. (a) Topography image of SnSe monolayer when tip moved along the magenta dashed arrow, perpendicular to the polarization direction. (b) The breakdown of the SnSe monolayer.

Because of the anisotropic friction existed in the monolayer SnSe, the nanoplates always moved along the polarization direction, without any rotation movement found in the monolayers. However, when the thickness of nanoplates increases, the anisotropic friction decreases. A bilayer SnSe had been found to rotate when the tip moved parallel to one side, as shown in Figure 5.9.



Figure 5.9: Rotation found in the bilayer SnSe nanoplate. (a) Translating the SnSe bilayer nanoplate on the graphene substrate. The moving direction is parallel to one side, marked in the blue solid arrow and the tunneling condition during moving process are marked above the arrow. (b) The bilayer nanoplate rotates on the substrate and contacts a stationary bilayer flake to come to rest. (c) Zoom-in of (b) ( $V_s = -0.4$  V,  $I_t = 2$  pA).

#### 5.4 Defect-free nano-welding of SnSe nanoplates

Combining the controllable moving of the nanoplate and *in-situ* annealing in VT-STM, the nano-welding without any defect between the semiconducting SnSe nanoplates is experimentally realized.

The experimental realization of nano-welding between two SnSe naonplates with the assistance of anisotropic friction are represented in Figure 5.10 and 5.11. The experiment started from two bilayer SnSe nanoplates with same crystalline orientation in Figure 5.10 (a). STM tip moved under the parameter  $V_s = -1$  mV,  $I_t = 2$  nA, v = 5 nm/s along the magenta dashed arrow until two nanoplates had the contact area shown in (b). The original position and current position are marked with red dashed area and blue solid area. Two separated nanoplates merged after in-situ annealing in VT-STM at 450 K for 1 hour shown in (c). The atomic resolved images scanning at the black area marked in (c) reveals the continuous and defect-free area.



Figure 5.10: Nano-welding realized in two bilayer nanoplates by in-situ annealing in the VT-STM. (a). Initial state. The SnSe nanoplate had been moved along the magenta dashed arrow  $(V_s = -0.4 \text{ V}, I_t = 2 \text{ pA})$ . (b). After moving. Two nanoplates had the contacted area  $(V_s = -0.4 \text{ V}, I_t = 2 \text{ pA})$ . (c). After *in-situ* annealing at 450 K for 1h. The original two nanoplates merged into one  $(V_s = -0.4 \text{ V}, I_t = 2 \text{ pA})$ . (d) Atomic resolved image scanned at the contact area, the same area with the blue rectangular in (c)  $(V_s = -40 \text{ mV}, I_t = 400 \text{ pA})$ .

The temperature-dependence of *in-situ* annealing between two bilayer SnSe nanoplates reveals the details existed in the process of nano-welding. A bilayer SnSe nanoplate moved along the magenta dashed arrow. STM tip moved under the parameter of  $V_s = -1$  mV,  $I_t = 1$  nA, v = 5nm/s. Topography images and corresponding differential images of the two bilayer SnSe naonplates were scanned at 300 K, 320 K, 340 K, 360 K, 380 K, 400 K, 420 K, 450 K respectively. The grain boundary disappeared gradually and vanished at 420 K. The atomic resolved image scanned at the original contacted area revealed the defect-free area.



Figure 5.11: Temperature dependence of *in-situ* annealing and nano-welding between two SnSe bilayer islands. (a) Initial state. The SnSe nanoplate had been moved in the direction of magenta dashed arrow. ( $V_s = -0.35$  V,  $I_t = 2$  pA) (b) After moving the nanoplate. Two nanoplates had the contact area. ( $V_s = -0.4$  V,  $I_t = 2$  pA) (c-j) Topography images and corresponding differential images of the two contacted nanoislands scanned at 300 K, 320 K, 340 K, 360 K, 380 K, 400 K, 420 K, and 450 K. ( $V_s = -0.4$  V,  $I_t = 2$  pA) (k) Atomic resolved image scanning at the contact area, marked in the blue square in (k) ( $V_s = -30$  mV,  $I_t = 800$  pA).

# Chapter 6 Conclusion

The family of two-dimensional ferroelectric materials has developed rapidly over the past decade. Amongst these materials the family of the group-IV monochalcogenides is very interesting since the monolayers can exhibit, on the one hand, extremely high ferroelectric ordering temperatures compared to bulk materials and, on the other hand noble antiferroelectric ordering. This thesis is devoted to this family of ferroelectrics and two advanced techniques were employed to fabricate ultra thin layers and to explore their ferroelectric properties. The first technique is that of molecular beam epitaxy (MBE) that was shown to provide an excellent means of preparing high-quality monolayers of SnTe, SnSe and PbTe, as well as PbTe/SnTe lateral heterostructures (LHSs) and lateral superlattices (LSLs) each formed from components just one monolayer thick. In all cases these monolayer materials were deposited on high quality graphene layers prepared on SIC substrates. The second experimental technique is that of characterize ferroelectrics. The second experimental technique is that of characterize these following results.

(1) Monolayer PbTe/SnTe lateral heterostructures (LHSs) and lateral superlattices (LSLs) on graphene substrates are experimentally fabricated by molecular beam epitaxy (MBE). Characterized by scanning tunneling microscopy (STM) at room and low temperatures, an asymmetric diffusion takes place in the monolayer LHSs. The PoS (PbTe grown outside SnTe) interfaces show severe diffusion, while the SoP (SnTe grown outside PbTe) interfaces are sharp and clean. Besides the growth sequence, the asymmetric diffusion is also influenced by the thickness of the graphene substrate. The monolayer heterostructures or superlattices grown on monolayer graphene (MLG) substrates exhibit more severe diffusion as compared to the monolayers grown on bilayer graphene (BLG). Remarkably, we found that lower substrate temperatures and higher PbTe fluxes (less deposition time) in certain ranges suppress the diffusion (defect concentrations decreasing from 10<sup>13</sup> cm<sup>-2</sup> order) so that one can realize lateral superlattices with ultra-narrow

periods and nearly-clean interfaces. Moreover, a surface diffusion mechanism for twodimensional superlattices was proposed.

- (2) A bias-voltage dependence of the apparent height, as determined from low temperature scanning tunneling microscopy (LT-STM), allowed for the discovery of clockwise and counterclockwise vortex-oriented ferroelectric domains in monolayer PbTe (inside)/SnTe (outside) lateral heterostructures grown on graphene substrates. Supported by first principles calculation, the vortex-oriented ferroelectric domain structures are induced by the difference in the work functions of the SnTe and PbTe monolayers, their polarization, and interfacial strain.
- (3) Due to very weak van der Waals forces between the SnSe nanoplates and the graphene substrate, nanoplates can be controllably manipulated by an STM tip and moved only along the polarization direction. This anisotropic friction is only found when the nanoplates and graphene substrate are in a commensurate orientation. Moreover, the nano-welding of nanoplates can be realized by *in-situ* annealing in the VT-STM with the assistance of the anisotropic friction. Remarkably the welded boundaries between the nanoplates show no defects.

The extensive work on the group IV monochalcogenide two-dimensional ferroelectric materials, based on molecular beam epitaxial growth, scanning tunneling microscopy characterization and manipulation, and the exploration of 2D ferroelectric monolayers, heterostructures, and superlattices at the atomic level, show the huge potential of 2D ferroelectrics for applications, such as ferroelectric tunneling junctions.

# Appendix A. Method of calculating vacancy concentrations in SnTe and PbTe

The total number of Pb (Sn) substitutions in SnTe (PbTe) area  $N_{Pb:SnTe} / N_{Sn:PbTe}$  are calculated by following formula.

$$N_{\rm Pb:SnTe} = n_{\rm Pb:SnTe} \times A_{\rm SnTe} \tag{4}$$

$$N_{\rm Sn:PbTe} = n_{\rm Sn:PbTe} \times A_{\rm PbTe} \tag{5}$$

Where  $n_{Pb:SnTe}$  is the vacancies density concentration of Pb substitutions in SnTe area and  $n_{Sn:PbTe}$  is the concentration of Sn substitutions in PbTe area.  $A_{SnTe}$  and  $A_{PbTe}$  are the total area of SnTe and PbTe in the lateral heterostructure or superlattices.

The topography images and the atomic resolved images at the interface can provide the value of  $A_{\text{SnTe}}$ ,  $A_{\text{PbTe}}$ ,  $n_{\text{Pb:SnTe}}$  and  $n_{\text{Sn:PbTe}}$ .

Figure A.1 and A.2 are two examples to calculate the total number of Pb (Sn) substitution in SnTe (PbTe) area in two different 3-layer LHSs. All the atomic resolved images at the interface are scanned in 20 nm  $\times$  20 nm. If scanning at the straight rim, the area of SnTe and PbTe part can vary from 160 nm<sup>2</sup> to 240 nm<sup>2</sup>, which means the width of SnTe and PbTe regions in the atomic resolved images can vary from 8 nm to 12 nm.



Figure A.1: Example of calculating the vacancies in SnTe and PbTe region in a 3-layer (PbTe-SnTe-PbTe) LHS. (a) The topography image of 3-layer LHS. ( $V_s$ = -0.2 V,  $I_t$  = 2 pA) (b)-(m) Atom-resolved topography images obtained from SoP (SnTe grown outside PbTe) and PoS (PbTe grown outside SnTe) interface. ( $V_s$ = -0.7 V,  $I_t$  = 2 nA)

Table A.1: Statistics of the data from Figure A.1, including the number of vacancies, the areaand the vacancy concentration in SnTe and PbTe regions.

Figure	b	с	d	e	f	g
The number of	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:
vacancies in SnTe area	36	33	42	33	29	29
$N_{ m Pb:SnTe}$						
Area of SnTe A <sub>SnTe</sub>	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:
(nm <sup>2</sup> )	180	200	220	180	170	160
Vacancies concentration	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:
in SnTe area <i>n</i> <sub>Pb:SnTe</sub>	2.00	1.65	1.91	1.83	1.71	1.81
$(10^{13} \text{cm}^{-2})$						
The number of	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:
vacancies in PbTe area	0	24	0	18	0	26
$N_{\mathrm{Sn:PbTe}}$						
Area of PbTe A <sub>PbTe</sub>	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:
(nm <sup>2</sup> )	220	200	180	220	230	240
Vacancies concentration	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:

in PbTe area <i>n</i> <sub>Sn:PbTe</sub>	0.00	1.20	0.00	0.82	0.00	1.08
$(10^{13} \text{cm}^{-2})$						
Figure	h	i	j	k	1	m
The number of	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:
vacancies in SnTe area	64	16	84	19	78	13
$N_{ m Pb:SnTe}$						
Area of SnTe $A_{SnTe}$	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:
(nm <sup>2</sup> )	268	135	274	80	280	100
Vacancies concentration	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:
in SnTe area <i>n</i> <sub>Pb:SnTe</sub>	2.39	1.18	3.07	2.38	2.79	1.30
$(10^{13} \text{cm}^{-2})$						
The number of	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:
vacancies in PbTe area	0	34	0	45	0	45
$N_{\mathrm{Sn:PbTe}}$						
Area of PbTe $A_{PbTe}$	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:
(nm <sup>2</sup> )	132	265	126	320	120	300
Vacancies concentration	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:
in PbTe area <i>n</i> <sub>Sn:PbTe</sub>	0.00	1.28	0.00	1.41	0.00	1.50
$(10^{13} \text{cm}^{-2})$						
Average vacancies	SnTe-1: 2.00					
concentration in SnTe						
area $n_{\rm Pb:SnTe} (10^{13} {\rm cm}^{-2})$						
Average vacancies	PbTe-1: 0.00					
concentration in PbTe	PbTe-2: 1.22					
area $n_{\text{Sn:PbTe}} (10^{13} \text{cm}^{-2})$						

From topography image Fig A.1 (a), we can obtain the total area of PbTe-1, SnTe-1, PbTe-2 are

$$A_{PbTe-1} = 75nm \times 55nm = 4125 nm^2 = 4.13 \times 10^{-11} cm^2.$$
$$A_{SnTe-1} = 107nm \times 82nm - 75nm \times 55nm = 4649 nm^2 = 4.65 \times 10^{-11} cm^2.$$
$$A_{PbTe-2} = 138nm \times 110nm - 107nm \times 82nm = 6406 nm^2 = 6.41 \times 10^{-11} cm^2.$$

The average vacancies concentration in SnTe area  $n_{\text{Pb:SnTe}}$  is 2.00 × 10<sup>13</sup> cm<sup>-2</sup>. So, the total number of Pb substitution in the SnTe part is 930.

$$N_{\text{Pb:SnTe-1}} = n_{\text{Pb:SnTe}} \times A_{\text{SnTe-1}} = 2.00 \times 10^{13} \text{ cm}^{-2} \times 4.65 \times 10^{-11} \text{ cm}^{2} = 930.$$

The average vacancies concentration in PbTe-2 area  $n_{\text{Sn:PbTe}}$  is  $1.22 \times 10^{13}$  cm<sup>-2</sup>. So, the total

number of Sn substitution in the PbTe part is 782 since there is no diffusion in PbTe-1.

$$N_{\text{Sn:PbTe-2}} = n_{\text{Sn:PbTe-2}} \times A_{\text{PbTe-2}} = 1.22 \times 10^{13} \text{ cm}^{-2} \times 6.41 \times 10^{-11} \text{ cm}^{-2} = 782.$$

(a) (d) (b) (C) SnTe-1 PbTe-1 SnTe-1 SnTe-1 PbTe-1 SnTe-1 h z (nn z(A) z(A) (h) (f) (i) (e) (g) PbTe-2 SnTe-1 SnTe-1 PbTe-1 PbTe-2 SnTe-1 5 nm 4 z(A) 4 z(A) z (A) ×(A)

The result shows that the Pb substitution in SnTe area is more than Sn substitution in PbTe area.

Figure A.2: Example of calculating the vacancies in SnTe and PbTe regions in a 3-layer (PbTe-SnTe-PbTe) LHS. (a) The topography image of 3-layer LHS. (V = -0.2 V, I = 2 pA) (b)- (i) Atom-resolved topography images obtained from SoP and PoS interface. (V = -0.7 V, I = 2 nA)

Table A.2. Statistics of the data from Figure A.2, including the number of vacancies, the areaand the vacancy concentration in SnTe and PbTe regions.

Figure	b	с	d	e
The number of	SnTe-1: 40	SnTe-1: 35	SnTe-1: 28	SnTe-1: 28
vacancies in SnTe area				
$N_{ m Pb:SnTe}$				
Area of SnTe $A_{SnTe}$	SnTe-1: 225	SnTe-1: 180	SnTe-1: 170	SnTe-1: 170
(nm <sup>2</sup> )				
Vacancies concentration	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:
in SnTe area <i>n</i> <sub>Pb:SnTe</sub>	1.78	1.94	1.64	1.64
$(10^{13} \text{cm}^{-2})$				
The number of	PbTe-1: 0	PbTe-2: 29	PbTe-1: 0	PbTe-2: 19
vacancies in PbTe area				
$N_{\mathrm{Sn:PbTe}}$				
Area of PbTe A <sub>PbTe</sub>	PbTe-1: 175	PbTe-2: 220	PbTe-1: 0	PbTe-2: 230

(nm <sup>2</sup> )					
Vacancies concentration	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:	
in PbTe area <i>n</i> <sub>Sn:PbTe</sub>	0.00	1.31	0.00	0.83	
$(10^{13} \text{cm}^{-2})$					
Figure	f	g	h	i	
The number of	SnTe-1: 39	SnTe-1: 24	SnTe-1: 75	SnTe-1: 35	
vacancies in SnTe area					
NPb:SnTe					
Area of SnTe $A_{SnTe}$	SnTe-1: 160	SnTe-1: 160	SnTe-1: 283	SnTe-1: 140	
(nm <sup>2</sup> )					
Vacancies concentration	SnTe-1:	SnTe-1:	SnTe-1:	SnTe-1:	
in SnTe area <i>n</i> <sub>Pb:SnTe</sub>	2.43	1.50	2.65	2.50	
$(10^{13} \text{cm}^{-2})$					
The number of	PbTe-1: 0	PbTe-2: 28	PbTe-1: 0	PbTe-2: 36	
vacancies in PbTe area					
N <sub>Sn:PbTe</sub>					
Area of PbTe A <sub>PbTe</sub>	PbTe-1: 240	PbTe-2: 240	PbTe-1: 117	PbTe-2: 260	
(nm <sup>2</sup> )					
Vacancies concentration	PbTe-1:	PbTe-2:	PbTe-1:	PbTe-2:	
in PbTe area <i>n</i> <sub>Sn:PbTe</sub>	0.00	1.17	0.00	1.38	
$(10^{13} \text{cm}^{-2})$					
Average vacancies	SnTe-1: 2.01				
concentration in SnTe					
area $n_{\rm Pb:SnTe} (10^{13} {\rm cm}^{-2})$					
Average vacancies	PbTe-1: 0.00				
concentration in PbTe	PbTe-2: 1.17				
area $n_{\text{Sn:PbTe}}(10^{13} \text{cm}^{-2})$					

From topography image Figure A.2 (a), we can obtain the total area of PbTe-1, SnTe-1, PbTe-2 are

$$A_{PbTe-1} = 111nm \times 80nm = 8880 nm^2 = 8.88 \times 10^{-11} cm^2.$$
$$A_{SnTe-1} = 143nm \times 111nm - 111nm \times 80nm = 6993 nm^2 = 6.99 \times 10^{-11} cm^2.$$
$$A_{PbTe-2} = 183nm \times 145nm - 143nm \times 111nm = 10662 nm^2 = 1.07 \times 10^{-10} cm^2.$$

The average vacancies concentration in SnTe area  $n_{\text{Pb:SnTe}}$  is 2.01 × 10<sup>13</sup> cm<sup>-2</sup>. So, the total number of Pb substitution in the SnTe part is 1405.

$$N_{\text{Pb:SnTe-1}} = n_{\text{Pb:SnTe}} \times A_{\text{SnTe-1}} = 2.01 \times 10^{13} \text{ cm}^{-2} \times 6.99 \times 10^{-11} \text{ cm}^{2} = 1405.$$

The average vacancies concentration in PbTe-2 area  $n_{\text{Sn:PbTe}}$  is  $1.17 \times 10^{13}$  cm<sup>-2</sup>. So, the total number of Sn substitution in the PbTe part is 1252.

$$N_{\text{Sn:PbTe-2}} = n_{\text{Sn:PbTe-2}} \times A_{\text{PbTe-2}} = 1.17 \times 10^{13} \text{ cm}^{-2} \times 1.07 \times 10^{-10} \text{ cm}^{2} = 1252.$$

The result shows that the Pb substitution in SnTe area is more than Sn substitution in PbTe area.

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### **Publications**

- Jing-Rong Ji, John W. Villanova, Salvador Barraza-Lopez, Stuart S. P. Parkin, Kai Chang, Defect-free nano-welding of monolayer and bilayer semiconducting SnSe nanoplates. (Submitted)
- Amilcar Bedoya-Pinto<sup>#</sup>, Jing-Rong Ji<sup>#</sup>, Avanindra K. Pandeya *et al.*, Intrinsic 2D-XY ferromagnetism in a van der Waals monolayer. *Science* 374, 616 (2021). <u>doi:10.1126/science.abd5146</u>
- Kai Chang<sup>#</sup>, John W. D. Villanova<sup>#</sup>, Jing-Rong Ji<sup>#</sup> et al.
   Vortex-Oriented Ferroelectric Domains in SnTe/PbTe Monolayer Lateral Heterostructures. Advanced Materials 33, 2102267 (2021). doi:10.1002/adma.202102267
- Kai Chang, Felix Küster, Brandon J. Miller, Jing-Rong Ji et al. Microscopic manipulation of ferroelectric domains in SnSe monolayers at room temperature.

Nano letters 20, 6590 (2020). doi:10.1021/acs.nanolett.0c02357

 Paolo Sessi, Feng-Ren Fan, Felix Küster, Kaustuv Manna, Niels B. M. Schröter, Jing-Rong Ji, et al.

Handedness-dependent quasiparticle interference in the two enantiomers of the topological chiral semimetal PdGa.

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# Curriculum Vitae

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#### Eidesstattliche Erklärung

Hiermit erkläre ich, **Jingrong Ji**, dass ich die vorliegende Arbeit mit dem Titel: **Molecular beam epitaxial growth and scanning tunneling microscopy characterization and manipulation of monolayers and heterostructures of two-dimensional ferroelectrics** in allen Teilen selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe. Alle wörtlich oder sinngemäß übernommenen Textstellen habe ich als solche kenntlich gemacht.

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Des Weiteren erkläre ich hiermit, dass ich bisher keine andere Arbeit zur Promotion eingereicht noch mit einer anderen Arbeit den Versuch zur Promotion unternommen habe.