Optical probing charge density wave and lattice vibration in metallic 2D materials

Chen, Yu

2018

Chen, Y. (2018). Optical probing charge density wave and lattice vibration in metallic 2D materials. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/75862>

<https://doi.org/10.32657/10356/75862>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**OPTICAL PROBING CHARGE DENSITY WAVE AND
LATTICE VIBRATION IN METALLIC 2D MATERIALS**

CHEN YU

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2018

OPTICAL PROBING CHARGE DENSITY WAVE AND LATTICE VIBRATION IN METALLIC 2D MATERIALS

CHEN YU

School of Physical and Mathematical Sciences

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

2018

Acknowledgements

I would like to grab this chance to acknowledge the people who have supported and helped me during the period of my Ph.D. journey. It is their unselfish dedication that assists me to overcome every difficulty in my studies. This thesis could not be completed without their kind help.

First of all, I would like to sincerely express my great appreciation and gratitude to my supervisor, Professor Yu Ting, for his unfailing guidance and fruitful discussions all the way through my Ph.D. study. He showed me the direction as a researcher for the new page of my life, and led me to a research field of the excellent two-dimensional materials. Professor Yu is the best role model for the young scientists, whose abundant research experience and comprehensive knowledge inspired my enthusiasm and critical thinking in the field of research. Although he is a strict mentor, I truly benefited a lot when he ceaselessly pushed and encouraged me to probe and think deeper for my projects. His great passion, active minds and scrupulous attitudes toward scientific research will always be the spiritual pillar in my future research career. Without his patient supports, I could not fulfil the research projects or make it this far in the scientific research.

It is very significant for me to give my special thanks to Nanyang Assistant Professor Liu Zheng and his group members, Dr. Wang Hong, Dr. Fu Wei and Mr. Zhou Jiadong, for providing me the treasured samples and valuable research experiences. They are the genuine scientists, and I am a beneficiary from the pleasant collaboration and discussion with them. I would also thank Professor Xiong Qihua and his student Mr. Liu Sheng

for their kind sharing thermal evaporator system and warm help on the second harmonic generation measurements.

Moreover, I want to convey my cordial gratitude to Professor Cong Chunxiao, whom I regard as my second mentor during the whole Ph.D. career. She taught me patiently the Raman spectroscopy and experimental techniques hand by hand. She always offered me many insightful comments and encouraged me to analyze data very carefully when I discussed with her, which significantly enhanced my understanding of my projects.

My following thank would go to my senior Dr. Shang Jingzhi for his great support and guidance on the experimental design, data analysis and contents organization. I have benefited a lot from his valuable suggestions. I am grateful to all my colleagues from Professor Yu Ting's group, Dr. Shen Xiaonan, Dr. Wang Yanlong, Dr. Yang Weihuang, Dr. Zhang Jing, Mr. Ai Wei, Mr. Cao Bingchen, Mr. Zou Chenji, Mr. Zhang Hongbo, Mr. Feng Shun and Miss Wu Lishu, for their generous help and the good time we enjoyed together. I would give a lot of thanks to my friends who expand my scope of knowledge and provide me a euphoric atmosphere in my life.

Finally yet importantly, I wish to express my heartfelt appreciation to my beloved parents and family. It is their strong faith and unlimited love that help me to get through the toughest time of my Ph.D. life. Specially, I am deeply grateful to Miss Ti Linzhi. She is the one who always encouraged and supported me to regain confidence when I was at the bottom in my lifetime.

Table of contents

Acknowledgements	I
Table of contents	III
Abbreviations	VII
Abstract	IX
Publications	XII
Citations to published work	XV
Chapter 1 Introduction	1
1.1 Introduction to metallic two-dimensional layered materials	1
1.1.1 Crystal structure of 2D TMDs materials	2
1.1.2 Electronic band structure of 2D TMDs materials	6
1.2 Charge density waves in layered materials	10
1.2.1 Formation of CDW in the crystal lattice	11
1.2.2 Kohn anomaly-phonon mode softening	15
1.2.3 CDW orders in metallic TMDs	18
1.3 Detection methods of CDW phase	20
1.4 Motivation and objectives of this thesis	21
1.5 Organization of the thesis	23
Chapter 2 Experimental techniques	25
2.1 Preparation of 2D TMDs	25
2.1.1 Mechanical exfoliation of 2D TMDs	25
2.1.2 Chemical vapor transport growth of 2D TMDs	26

2.1.3 Chemical vapor deposition growth of 2D TMDs.....	27
2.1.4 Dry transfer of exfoliated samples	28
2.2 Raman spectroscopy	30
2.2.1 Basic principles of Raman scattering.....	31
2.2.2 Selection rules of Raman scattering.....	32
2.2.3 Detection of the low frequency Raman modes	35
2.3 Optical characterization	37
2.3.1 Confocal micro Raman spectroscope.....	37
2.3.2 Custom designed magneto-Raman system	38
2.4 Scanning tunneling microscope	40
Chapter 3 Charge density wave phase transitions in CVD synthesized	
atomically thin 1T-TaS₂.....	42
3.1 Introduction.....	42
3.2 Experimental details	43
3.2.1 Sample preparations.....	43
3.2.2 Characterizations.....	44
3.3 Results and discussion	45
3.3.1 Synthesis of ultrathin 1T-TaS ₂ layers by CVD method	45
3.3.2 CDW phase transitions in ultrathin 1T-TaS ₂ layers	51
3.4 Conclusions.....	59
Chapter 4 Thickness dependent charge density wave states in as-	
grown 1T-TiSe₂ layers	60

4.1 Introduction	60
4.2 Experimental details	62
4.2.1 CVD growth of mono- and few-layer 1T-TiSe ₂ crystals	62
4.2.2 CVD growth of large-area few-layer 1T-TiSe ₂ films.....	63
4.2.3 Preparation of STEM sample.....	63
4.2.4 Characterizations.....	63
4.3 Results and discussion	64
4.3.1 Synthesis of ultrathin 1T-TiSe ₂ by salt-assisted CVD method	64
4.3.2 CDW phase transitions in ultrathin 1T-TiSe ₂ layers	72
4.4 Conclusions	76
Chapter 5 Visualizing the suppression of CDW states in graphene/NbSe₂ heterostructures	77
5.1 Introduction	77
5.2 Experimental details	79
5.2.1 Exfoliation of niobium diselenide and graphene	79
5.2.2 Transfer of 2H-NbSe ₂ and graphene	80
5.2.3 Characterizations.....	80
5.3 Results and discussion	81
5.3.1 Raman measurements of graphene/NbSe ₂ heterostructures	81
5.3.2 STM/STS images of graphene/NbSe ₂ heterostructures	90
5.3.3 Discussion.....	93
5.4 Conclusions	95

Chapter 6 In-plane anisotropic thermal conductivity of few-layer transition metal dichalcogenide Td-WTe₂	97
6.1 Introduction	97
6.2 Experimental details	100
6.2.1 Sample preparations	100
6.2.2 Raman spectra measurements	101
6.2.3 Second harmonic generation measurements	101
6.3 Results and discussion	103
6.3.1 Crystal structure of few-layer Td-WTe ₂	103
6.3.2 Anisotropic optical property of few-layer Td-WTe ₂	105
6.3.3 Identifying the crystalline orientations of suspended Td-WTe ₂	111
6.3.4 Anisotropic thermal conductivity of suspended Td-WTe ₂	114
6.4 Conclusions	121
Chapter 7 Conclusions and future work	123
7.1 Conclusions	123
7.2 Future work	127
References	131

Abbreviations

1D	one dimension or one-dimensional
2D	two dimensions or two-dimensional
3D	three dimensions or three-dimensional
AFM	atomic force microscopy
ARPES	angle resolved photoemission spectroscopy
CCD	charge coupled device
CDW	charge density wave
CVD	chemical vapor deposition
CVT	chemical vapor transport
DFT	density functional theory
DI	deionized
DOS	density of state
EDS	energy dispersive X-ray spectra
EELS	electron energy loss spectra
FFT	fast Fourier transformation
FWHM	full width at half-maximum
HAADF	high-angle annular-dark-field
h-BN	hexagonal boron nitride
HF	hydrogen fluoride
IR	infrared
LA	longitudinal acoustic

LWD	long working distance
MBE	molecular beam epitaxy
MFP	mean-free-path
PDMS	polydimethylsiloxane
PMMA	Poly(methyl methacrylate)
PVA	polyvinylalcohol
SAED	selected area electron diffraction
SEM	scanning electron microscopy
SHG	second harmonic generation
SPIP	scanning probe image processor
STEM	scanning transmission electron microscope
STM	scanning tunneling microscopy
STS	scanning tunneling spectroscopy
TE	thermoelectrically
TEM	transmission electron microscopy
TMD	transition metal dichalcogenide
UHTS	ultra-high throughput spectrometer
UHV	ultrahigh vacuum
vdW	van der Waals
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Abstract

Layered metallic transition metal dichalcogenides (TMDs), representing a novel group of two-dimensional (2D) materials, have attracted considerable interest due to its coexistence and competition of collective many-body phenomena, including charge density wave (CDW) and superconductivity. Such van der Waals (vdW) 2D materials are expected to be talented candidates in flexible optoelectronics and thermoelectric applications. In this thesis, we focus on the investigation and manipulation of CDW orders in 2D metallic TMDs (1T-TaS₂, 1T-TiSe₂ and 2H-NbSe₂) through *in situ* Raman measurements. The in-plane anisotropic thermal conductivity, which is related to the lattice vibrations, is also revealed in few-layer Td-WTe₂ films *via* micro Raman spectroscopy.

Metallic 2D TMDs are essential prototypes for the exploration of the collective CDW states. It is believed that reducing the dimensionality of the 2D system greatly affects the instability of CDW orders and is predicted to result in unprecedented properties. Up to now, the atomically thin CDW materials have been mainly fabricated by mechanical exfoliation from their bulk counterparts, which suffers from small sample size and low production yield. The monolayer and large-area 2D CDW conductors can only be achieved by molecular beam epitaxy (MBE) method. Here, we demonstrate the controllable synthesis of atomically thin 1T-TaS₂, as well as large-area films and down to monolayer crystals of 1T-TiSe₂ on SiO₂/Si substrate by ambient-pressure chemical vapor deposition (CVD). With the help of *in situ* temperature-dependent Raman measurements, the spectroscopic signatures of thickness-dependent CDW phase

transitions are observed in our CVD-grown samples.

In addition to the changing of dimensionality, layered metallic TMDs also provide the possibility for electrical control of the CDW orders. It is well known that the atomically thin CDW conductors suffer a severe degradation in the air, and thus are often protected by covering hexagonal boron nitride (h-BN) or graphene layers in most studies. However, the wide range of interactions within these heterostructures may have strong effects on the CDW instabilities. In this research field, we fabricate the graphene/2H-NbSe₂ heterostructures through dry transfer method. The CDW phases of the new system are characterized by using Raman spectroscopy and scanning tunneling microscopy (STM). When covering a single layer graphene, the CDW phase transition temperatures T_{CDW} of 2H-NbSe₂ layers are dramatically decreased. This effect can be understood as the charge transfer between single layer graphene and 2H-NbSe₂ layers. Our research not only enriches our understanding of many-body states of CDW conductors in 2D limit, but also offers a promising approach for designing ultrathin electronic devices.

On the other hand, thermal conductivity plays crucial roles in devices of condensed matters, especially in two-dimensional systems. Among the emerging layered 2D TMDs, Td-WTe₂ has attracted tremendous interest since the discovery of its extremely large non-saturating magnetoresistance. In this work, we report the first experimental evidence of in-plane anisotropic thermal conductivities in suspended Td-WTe₂ layers of different thicknesses, to our best knowledge, which is also the first experimental demonstration of such anisotropy in 2D TMDs. An anisotropy of thermal conductivities

between zigzag and armchair axes are clearly revealed by *in situ* micro Raman spectroscopy, and such discrepancy becomes weaker in thicker layers though the thermal conductivities increase there.

In general, our work on these metallic 2D materials opens up a new window for the controllable synthesis of ultrathin CDW materials and demonstrates effective strategies for tuning these many-body states. The observation of in-plane anisotropic thermal conductivity sheds more light on the design of efficient thermal management schemes in the next-generation thermoelectric devices based on the promising 2D TMDs.

Publications

1. W. Fu,* Y. Chen,* J. Lin,* X. Wang, Q. Zeng, J. Zhou, L. Zheng, H. Wang, Y. He, H. He, Q. Fu, K. Suenaga, T. Yu and Z. Liu, Controlled synthesis of atomically thin 1T-TaS₂ for tunable charge density wave phase transitions, *Chem. Mater.* 2016, 28, 7613-7618 (*Equally contributed)
2. H. Wang,* Y. Chen,* M. Duchamp,* Q. Zeng, X. Wang, S. H. Tsang, H. Li, L. Jing, T. Yu, E. H. T. Teo and Z. Liu, Large-area atomic layers of the charge-density-wave conductor TiSe₂, *Adv. Mater.* accepted (*Equally contributed)
3. H. Wang, X. Huang, J. Lin, J. Cui, Y. Chen, C. Zhu, F. Liu, Q. Zeng, J. Zhou, P. Yu, X. Wang, H. He, S. H. Tsang, W. Gao, K. Suenaga, F. Ma, C. Yang, L. Lu, T. Yu, E. H. T. Teo, G. Liu and Z. Liu, High-quality monolayer superconductor NbSe₂ grown by chemical vapour deposition, *Nat. Commun.* 2017, 8, 394
4. J. Shang, C. Cong, Z. Wang, N. Peimyoo, L. Wu, C. Zou, Y. Chen, X. Y. Chin, J. Wang, C. Soci, W. Huang and T. Yu, Room-temperature 2D semiconductor activated vertical-cavity surface-emitting lasers, *Nat. Commun.* 2017, 8, 543
5. W. L. Chow, P. Yu, F. Liu, J. Hong, X. Wang, Q. Zeng, C. Hsu, C. Zhu, J. Zhou, X. Wang, J. Xia, J. Yan, Y. Chen, D. Wu, T. Yu, Z. Shen, H. Lin, C. Jin, B. K. Tay and Z. Liu, High mobility 2D palladium diselenide field-effect transistors with tunable ambipolar characteristics, *Adv. Mater.* 2017, 29, 1602969-1602977

6. C. Cong, J. Shang, L. Niu, L. Wu, **Y. Chen**, C. Zou, S. Feng, Z. Qiu, L. Hu, P. Tian, Z. Liu, T. Yu and R. Liu, Anti-Stokes photoluminescence of van der Waals layered semiconductor PbI₂, *Adv. Opt. Mater.* 2017, 6, 1700609-1700614
7. S. Feng, C. Cong, N. Peimyoo, **Y. Chen**, J. Shang, C. Zou, B. Cao, L. Wu, J. Zhang, M. Eginligil, X. Wang, Q. Xiong, A. Ananthanarayanan, P. Chen, B. Zhang and T. Yu, Tunable excitonic emission of monolayer WS₂ for the optical detection of DNA nucleobases, *Nano Res.* 2017, <https://doi.org/10.1007/s12274-017-1792-z>
8. W. Yang, J. Shang, J. Wang, X. Shen, B. Cao, N. Peimyoo, C. Zou, **Y. Chen**, Y. Wang, C. Cong, W. Huang and T. Yu, Electrically tunable valley-Light emitting diode (vLED) based on CVD-grown monolayer WS₂, *Nano Lett.* 2016, 16, 1560-1567
9. Y. Wang, C. Cong, R. Fei, W. Yang, **Y. Chen**, B. Cao, L. Yang and T. Yu, Remarkable anisotropic phonon response in uniaxially strained few-layer black phosphorus, *Nano Res.* 2015, 8(12): 3944-3953
10. Y. Wang, C. Cong, W. Yang, J. Shang, N. Peimyoo, **Y. Chen**, J. Kang, J. Wang, W. Huang and T. Yu, Strain-induced direct-indirect bandgap transition and phonon modulation in monolayer WS₂, *Nano Res.* 2015, 8(8): 2562-2572
11. W. Ai, W. Zhou, Z. Du, **Y. Chen**, Z. Sun, C. Wu, C. Zou, C. Li, W. Huang and T. Yu, Nitrogen and phosphorus codoped hierarchically porous carbon as an efficient sulfur host for Li-S batteries, *Energy Storage Materials.* 2017, 6, 112–118

12. W. Ai, W. Zhou, Z. Du, C. Sun, J. Yang, **Y. Chen**, Z. Sun, S. Feng, J. Zhao, X. Dong, W. Huang and T. Yu, Toward high energy organic cathodes for Li-ion batteries: a case study of vat dye/graphene composites, *Adv. Funct. Mater.* 2017, 19, 603-612
13. Z. Du, W. Ai, C. Sun, C. Zou, J. Zhao, **Y. Chen**, X. Dong, J. Liu, G. Sun, T. Yu and W. Huang, Engineering the Li storage properties of graphene anodes: defect evolution and pore structure regulation, *ACS Appl. Mater. Inter.* 2016, 8, 33712–33722
14. **Y. Chen**, C. Cong, J. Shang, L. Wu, W. Yang, J. Zhou, P. Yu, H. Zhang, Y. Wang, C. Zou, J. Zhang, S. Liu, Q. Xiong, Z. Liu, T. Yu and W. Huang, Investigating the anisotropic thermal conductivity of few-layer Td-WTe₂ via micro Raman spectroscopy, to be submitted.
15. **Y. Chen**, C. Cong, L. Wu, H. Xu, H. Zhang, S. Feng, C. Zou, J. Song, K. P. Loh and T. Yu, Visualizing the suppression of CDW states in graphene/NbSe₂ heterostructures, to be submitted.

Citations to published work

1. Majority of Chapter 3 appears in my publication:

W. Fu,* **Y. Chen**,* J. Lin,* X. Wang, Q. Zeng, J. Zhou, L. Zheng, H. Wang, Y. He, H. He, Q. Fu, K. Suenaga, T. Yu and Z. Liu, Controlled synthesis of atomically thin 1T-TaS₂ for tunable charge density wave phase transitions, *Chem. Mater.* 2016, 28, 7613-7618 (*Equally contributed)

2. Majority of Chapter 4 is based on my publication:

H. Wang,* **Y. Chen**,* M. Duchamp,* Q. Zeng, X. Wang, S. H. Tsang, H. Li, L. Jing, T. Yu, E. H. T. Teo and Z. Liu, Large-area atomic layers of the charge-density-wave conductor TiSe₂, *Adv. Mater.* accepted (*Equally contributed)

Chapter 1 Introduction

1.1 Introduction to metallic two-dimensional layered materials

Nanomaterials are generally referred to those materials whose size is limited to the nanoscale (range from 1 to 100 nanometers) at any external dimension. Structures with single unit which is sized in nanoscale along three dimensions (3D), two dimensions (2D) and one dimension (1D) are defined as zero-dimensional, one-dimensional and two-dimensional nanomaterials, respectively [1]. Because the classic Newton's laws are assailable within nanomaterials while quantum mechanics appears and applies, the low-dimensional structures are drawing more interests of modern physicists [2].

Through the ages, two-dimensional nanomaterials have originally been supposed to be not exist due to their thermodynamic instability [3]. However, this belief was not overturned until that Konstantin Novoselov and Andre Geim successfully isolated the atomically thin graphene (single layer carbon sheet) from graphite through mechanical exfoliation method in 2004 [4]. As the first real stable two-dimensional atomic nanomaterial, the monolayer carbon atoms of graphene are arranged into a hexagonal honeycomb crystal structure, its valance band and conduction band are experimentally found to converge at one point (Dirac point in momentum space), which also leads the charge carriers to move like massless Dirac fermions [5,6]. The distinct electronic band structure brings about an abundance of exotic physical properties, and graphene gradually becomes an extraordinarily thin and transparent electrical and thermal conductor [7,8], high mobility electronic device [9], and gas molecule impermeable

membrane [10]. Novoselov and Geim were therefore awarded the 2010 Nobel Prize in physics, and their “*groundbreaking experiments*” established the major position of 2D atomic thin nanostructures for the condensed matter physics research in low-dimensional materials.

Two-dimensional transition metal dichalcogenides, just like the layered graphene, can also be isolated from their bulk crystals. Because of quantum confinement and surface effects, the wide range thickness-dependent optical, electronic and mechanical properties in monolayer and multi-layer structures are much more unique than those in their corresponding bulk counterparts [11]. On the basis of their chemical compositions, transition metal dichalcogenides display a variety of properties and contain true metals (e.g. VSe₂, NbS₂), semimetals (e.g. MoTe₂, WTe₂), semiconductors (e.g. WS₂, WSe₂, MoS₂, MoSe₂) and superconductors (e.g. TaS₂, NbSe₂) [12,13], which almost cover the entire feature. In consequence, these “beyond graphene” 2D TMDs nanostructures have called extensive attention among the researchers.

1.1.1 Crystal structure of 2D TMDs materials

Transition metal dichalcogenides generate a fascinating family of at least 40 layered chemical compounds, which possess the common chemical formula MX₂ [11,13]. M symbolizes the transition metal element of group-IV (e.g. Ti, Zr), group-V (e.g. Ta, Nb) and group-VI (e.g. W, Mo), while X represents the chalcogen in group-VI (S, Se or Te). Every single layer of TMDs compounds has a general hexagonally packed sandwich structure (X-M-X) where the transition metal atom is sandwiched between two layers of chalcogen atoms [12]. The stacking layers by weak van der Waals interactions

compose the layered 2D transition metal dichalcogenides, and bring them another name of “van der Waals materials”.

Figure 1.1 Schematics of the two common polytypes in 2D TMDs: (a) 1T phase has octahedral coordination with tetragonal symmetry, and each layer is a repeat unit. (b) 2H polytype is hexagonal symmetry with trigonal prismatic coordination, and the repeat unit contains two layers. (c) 3R structure is rhombohedral symmetry with trigonal prismatic coordination, and the repeat unit contains three layers. The yellow sphere represents the chalcogen atom (X) while the gray sphere is the metal atom (M).

Adapted from ref. [12], Copyright 2012, Macmillan Publishers Limited.

Depending on the stacking orders between the sandwich layers and the coordination of the transition metal atoms, these layered 2D TMDs exist in various structural polytypes, which are indicated by the prefix before MX_2 . In current 2D TMDs materials, the most representative structural phases are 1T, 2H and 3R. 1T phase displays tetragonal symmetry and belongs to D_{3d} point group. As shown in Figure 1.1(a), the six

stacking in which the chalcogen atoms in the upper layer have an offset from those in the lower plane. On the contrary, the 2H and 3R structures denote an ABA stacking where the adjacent two chalcogen atoms are located in the same position A and the upper layer is exactly arranged on the top of lower one. [17].

Based on the specific elements of transition metal and chalcogen atoms in layered TMDs, either the 1T or 2H structure is thermodynamically stable, while the other one is often regarded as metastable polytype. As illustrated in Figure 1.2, the existing structural phases of current 2D TMDs are classified into a periodic table. For instance, when the chalcogen atoms are combined with the transition metal atom from group-VI, the thermodynamically stable phase in these layered TMDs is usually the 2H polytype while the 1T phase can frequently exist in its metastable form [17].

Figure 1.3 Distorted structures of 2D TMDs in the Td and 1T' polytypes. The blue sphere represents the tungsten atom (W) while the yellow sphere denotes the tellurium atom (Te). Adapted from ref. [18], Copyright 2016, AIP Publishing LLC.

Nevertheless, the periodicity of the structure could be lowered by any possible distortions when numerous individual layers are stacking into few layers or bulk samples. For instance, the in-plane metal-metal bonds will be formed by these distortions in the 1T polytype of group-VI TMDs. As a result, the structure of 2D TMDs can be further defined as Td or 1T' phase shown in Figure 1.3. The monoclinic 1T' structure crystallizes in the $P2_1/m$ space group with metal atoms shifted off-center, which give rise to the zigzag metal chains and warp the chalcogen atom sheets, making a tilted c -axis. Although the orthorhombic Td phase is very analogous to the 1T' structure, it belongs to the $Pmn2_1$ space group with a higher symmetry [19,20]. In some cases, the charge density wave phases could couple with certain weak lattice distortions, which are accompanied by diverse and complex phase diagrams [17].

1.1.2 Electronic band structure of 2D TMDs materials

The electronic properties of 2D TMDs have theoretically and experimentally been found to be highly thickness dependent [21,22]. The general band structures of 2D TMDs are generated from 2H-MoX₂ and WX₂ (X = S or Se) compounds, which are typically semiconductors [21]. Figure 1.4 shows the calculated band structures of 2H-MoS₂ according to the density functional theory (DFT), and their evolution with the thickness decreasing from bulk crystal to monolayer nanosheet [23]. For the bulk 2H-MoS₂, its valence band maximum is located at Γ point while the bottom of conduction band lies between K and Γ points, which result in an indirect bandgap semiconductor. With decreasing the number of layers, it can be seen that the valence band maximum and conduction band minimum change gradually and both of them shift to the K point

in monolayer MoS₂. As a result, the indirect bandgap bulk 2H-MoS₂ becomes to a direct bandgap semiconductor when the thickness is reduced to monolayer [22,23].

Figure 1.4 First principles calculated band structures of bulk, four-layer, bilayer and monolayer 2H-MoS₂. The solid arrows represent the bandgaps (lowest energy transition) from indirect bandgap in bulk to direct bandgap in monolayer. Adapted from ref. [17], Copyright 2017, Macmillan Publishers Limited, part of Springer Nature.

Such prominent transition of band structure with layer number is mainly induced by the changing in hybridization between the d orbitals of transition metal atom Mo and p_z orbitals from chalcogen atom S [12]. The first principles calculation indicates that the strongly localized d orbitals of the molybdenum atom give rise to the conduction band states at K point, which almost remains unchanged for different numbers of layer. On the contrary, when the d orbitals of the molybdenum atom are combined with the

antibonding p_z orbitals on sulfur atoms, the generated band states near Γ point shift remarkably with MoS_2 thickness owing to the strong interlayer coupling of sulfur atoms [12,23]. Generally, the MoX_2 and WX_2 ($X = \text{S}$ or Se) compounds are predicted to undergo an analogous band structure transition from indirect to direct bandgap semiconductors, covering a wide range of bandgap energy [21,24-28].

Figure 1.5 First principles calculated band structures and partial DOS of two dimensional NbS_2 nanosheets. The band across the Fermi level is primarily due to the d orbitals of niobium atoms, resulting in the metallic behavior of NbS_2 flakes. Adapted from ref. [29], Copyright 2011, Elsevier B.V.

However, the chemical compositions, especially the transition metal atoms also have an effect on the band structures and electronic properties of 2D TMDs. For example,

NbX₂ and TaX₂ nanosheets exhibit metallic properties [29]. The calculated band structure of NbS₂ flakes from first principles is shown in Figure 1.5. It can be clearly seen that there is an electronic band passing through the Fermi level, resulting in the metallic behavior of NbS₂ flakes. By analyzing the partial density of state (DOS), this particular band primarily originates from the *d* orbitals of niobium atoms. Unlike the Mo or W atom, Nb or Ta atom only has one *d* electron, the top of *d* character valence band maximum is hence incompletely occupied which gives rise to the robust metallic character in 2D NbX₂ and TaX₂ nanosheets [29,30].

Figure 1.6 (a) DFT calculated band structure and (b) DOS of bulk and monolayer 2H-TaSe₂. (c) Calculated band structure and (d) DOS of bulk and monolayer 1T-TaSe₂. The black solid lines represent the monolayer while the red dashed lines indicate the bulk counterpart. Adapted from ref. [31], Copyright 2015, Macmillan Publishers Limited, part of Springer Nature.

On the other hand, even though the chemical components of metallic layered TMDs are the same, the diverse crystal structures (2H and 1T polytypes) could display distinct electronic band structures [31]. Figure 1.6 shows the band structures and DOSs of 2H-

and 1T-TaSe₂ in both bulk crystal and monolayer. For the monolayer 2H-TaSe₂, the finite electronic band around Fermi level is mainly due to the *5d* orbitals of the tantalum atom in trigonal prismatic coordination [31]. Conversely, there is no analogous electronic band near Fermi level in the 1T phase, as illustrated in Figure 1.6(c) and (d). The bulk 2H-TaSe₂ has more electronic bands around Fermi level comparing with the monolayer 2H case, and possesses the similar band structure. Nevertheless, the circumstance is dramatically different in the 1T case. It can be seen from Figure 1.6(d) that the monolayer 1T-TaSe₂ exhibits a sharp peak near Fermi level. Such fascinating phenomena in the band structure result from the quantum confinement of electrons in monolayer TaSe₂. The change of Fermi surface denotes the conceivable influence of dimensionality on the CDW phase transitions.

1.2 Charge density waves in layered materials

In condensed matter system, the vigorous equilibrium states always exist in two forms. One is a traditional equilibrium state just like a ball lying on the bottom of a bowl, this stable state is often energetic and can maintain under several slight perturbations. The other one is the unstable equilibrium state just as a ball placed on the top of a cambered roof. One can imagine that it is easily affected by internal and external fluctuations. When the stable state is influenced by certain physical factors in some cases, the system itself would attempt to form a brand-new ground equilibrium state. The charge density wave ground state is a typical instance under spontaneously broken translational symmetry, and primarily takes place in low dimensional materials with highly

anisotropic band structures [32,33]. Generally, the CDW phase transition gives rise to the commensurate or incommensurate periodic lattice distortions, and leads to an opening of energy gaps at Femi level [34]. Comparing to the intrinsic perturbations in low dimensional systems, such phase transition is significantly enhanced by Femi surface nesting and electron-phonon couplings [33].

1.2.1 Formation of CDW in the crystal lattice

In 1930s, Rudolf Peierls first proposed that the periodic charge density modulation is a result of strong electron-phonon coupling, and can be caused by the Femi surface nesting of electrons [35,36].

In the light of linear response theory, an external electric potential $\psi(r)$ can bring about the redistribution of electron charges in the system [34], the induced charge density of the electron gas can be described by

$$\rho(r) = \psi(r)\chi(r), \quad (1.1)$$

where $\chi(r)$ is called the Lindhard response function [37]. As a general rule, the zero energy value of this response function can be used to verify whether the electron response is able to produce the CDW phase transition (Peierls phase transition) [38]. The Lindhard response function is also regarded as Lindhard susceptibility and can be defined as the form of,

$$\chi(\mathbf{q}) = \int \frac{d\mathbf{k}}{(2\pi)^d} \frac{f_{\mathbf{k}} - f_{\mathbf{k}+\mathbf{q}}}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}}, \quad (1.2)$$

where $\mathbf{q}$ and $\mathbf{k}$ are both wave vectors, d represents the number of dimensions, $f_{\mathbf{k}}$ denotes the Fermi-Dirac distribution which has the values of 1 for electrons and 0 for holes at $T = 0$ K, $\epsilon_{\mathbf{k}}$ is the free electron energy of electron gas at the momentum $\mathbf{k}$

[34]. The criteria for Peierls phase transition is that there would be a peak in Lindhard response function at wave vector q where the Fermi surface nesting forms [38].

Figure 1.7 (a) Electron-hole pairing in one-dimensional free electron gas. (b) Lindhard susceptibility as a function of wave vector q for one-, two- and three-dimensional free electron gases. Adapted from ref. [39], Copyright 2016, The Royal Swedish Academy of Sciences.

The Fermi-Dirac distribution f_k in Equation 1.2 demonstrates that the formation of CDW states is only attributed to the exact electron-hole pairs at $k + q$ and q . As shown in Figure 1.7(a) and (b), the two parts of the peak in Lindhard response function get closer and closer with a certain wave vector q which makes the denominator $\epsilon_k - \epsilon_{k+q} \approx 0$ in the k space [33,37]. The nested electron-hole pairs due to such a q bring about comparatively high charge density of states at Fermi level. Therefore, the Lindhard susceptibility of a material significantly relies on the topology of its Fermi surface. As a result, the electronic structure and associated Fermi surface make great contributions to the formation of CDW states.

Figure 1.7(b) describes the calculated Lindhard susceptibility $\chi(\mathbf{q})$ for different dimensions of materials at $T = 0$ K. In a perfect one-dimensional electron gas, the Lindhard response function develops a logarithm-like divergence at a wave vector of $\mathbf{q} = 2\mathbf{k}_f$, whereas there is no such a divergence in two- and three-dimensional systems.

Figure 1.8 Fermi surface nesting with wave vector $\mathbf{q}$ for (a) an ideal one-dimensional Fermi surface (b) an ideal two-dimensional Fermi surface (c) an ideal three-dimensional Fermi surface, and (d) a warped dimensional Fermi surface. Adapted from ref. [33], Copyright 1994, Addison-Wesley Publishing Company.

This circumstance can be caused by taking the topology of specific Femi surfaces for different dimensions into account, as indicated in Figure 1.8. The Femi surface of an ideal 1D free electron gas is composed of two parallel plates located at $-\mathbf{k}_f$ and $+\mathbf{k}_f$. The complete nesting of a great deal of electron-hole pairs between the plates enables the divergence of Lindhard susceptibility $\chi(\mathbf{q})$ at $\mathbf{q} = 2\mathbf{k}_f$ [37]. Between the perfect 1D and 2D systems, there is a warped 1D Femi surface case in one sense, as shown in Figure 1.8(d), which is more likely to develop the charge density nesting at Femi surface and more impressionable to the CDW phase transition than the perfect 2D system. Indeed, the high dimensional materials reduce the Femi surface nesting since fewer states can satisfy the criteria of Lindhard susceptibility divergence. Whereas more charge density of states are able to meet the condition of Femi surface nesting in anisotropic low dimensional systems due to more parallel regions of their Femi surface at $-\mathbf{k}_f$ and $+\mathbf{k}_f$, which consequently makes the CDW phase transition more possible to occur [33,34,37].

Additionally, the wave vector $\mathbf{q}$ dependent Lindhard response function also counts on the temperature. When considering the Femi function for $T \neq 0$ K at the nesting condition $\mathbf{q} = 2\mathbf{k}_f$, the Equation 1.2 then takes the form of

$$\chi(2\mathbf{k}_f, T) = -e^2 n(\epsilon_F) \int_0^{\epsilon_0/2k_B T} \frac{\tan hx}{x} dx, \quad (1.3)$$

where ϵ_0 is the cut-off energy of the integration and can be estimated to the Femi energy, k_B is the Boltzmann constant [40]. In 1D free electron gas system, the calculation changes Equation 1.3 to another form of

$$\chi(2\mathbf{k}_f, T) = -e^2 n(\epsilon_F) \ln \frac{1.14\epsilon_0}{k_B T}, \quad (1.4)$$

which illustrates the logarithmic divergence of $\chi(2\mathbf{k}_f, T)$ peak [34]. Therefore, the idea of CDW transition temperature T_{CDW} is proposed, which makes the $\chi(\mathbf{q})$ sufficient large to meet the criteria of producing a periodic charge density [34].

Figure 1.9 Periodic Peierls transition in one-dimensional atomic chain. (a) A linear chain of metal atoms with equal distance a and electron density $\rho(r)$, the lower part shows its conduction band. (b) The atomic chain is distorted by Peierls transition, opening a bandgap of 2Δ at the Fermi level. The red lines represent the occupied electron states. Adapted from ref. [41], Copyright 1996, American Institute of Physics.

1.2.2 Kohn anomaly-phonon mode softening

The formation of CDW states is typically interpreted by Peierls instability of simple one-dimensional atomic chain model [42]. Imagine that a linear chain of metal atoms with non-interacting free electrons is separated by an equal distance a , which means that each unit cell contains one atom. As shown in Figure 1.9(a), states with energy lower than Fermi level are occupied by electrons, while states with wave vectors larger than $\mathbf{k}_f$ are empty [35]. Now consider the lattice vibrations, the Peierls transition distorts the atomic chain, and makes each atom shift closer to a neighboring one and

further away from another one. Figure 1.9(b) indicates that the lattice distortion doubles its unit cell from a to $2a$, halving the Brillouin zone and opening a bandgap of 2Δ at the Fermi level [37]. The formation of this bandgap lowers the lattice electronic energy, and the generated periodic electron fluctuation is the exactly charge density wave [35]. Since the decrease of energy at the Fermi level is larger than the elastic energy cost of lattice modulation, the CDW transition appears favorable [43,44].

Figure 1.10 Kohn anomaly in the phonon dispersion of different dimensions. Adapted from ref. [37], Copyright 2012, Taylor & Francis Group.

In spite of Peierls instability, the electron-phonon interaction is an alternative trigger of CDW orders through the atomic displacement. Once the electrostatic Coulomb repulsion is conquered by the electron-phonon interaction, the instability emerges in a form of CDW models. As a result, such electron-phonon coupling would change the phonon frequencies and modify the phonon dispersion, leading to a softening of phonon frequency. This effect of phonon renormalization in certain phonon branch is identified

as Kohn anomaly, as shown in Figure 1.10. For instance, the Kohn anomaly is intensely robust in perfect 1D system. The phonon frequency decreases to zero below T_{CDW} at $q = 2k_f$ where the lattice distortion occurs, resulting from the collective oscillations of phonons heavily coupled to the electronic density [37,38].

Figure 1.11 (a) Phonon dispersion of the softened phonon branch of 2H-NbSe₂ at various temperatures. (b) Experimentally obtained phonon damping ratio (Γ/ω_q) in 2H-NbSe₂. Adapted from ref. [45], Copyright 2011, American Physical Society.

In a typical CDW material of 2H-NbSe₂, the phonon dispersion at a variety of q , as

shown in Figure 1.11, exhibits sharp drops at $q = 2k_f$ due to the well-known Kohn anomaly. The renormalization of phonons and the critically damping spread over a range of $0.36 \text{ \AA}^{-1}$ and $0.09 \text{ \AA}^{-1}$, respectively, which may be attributed to the imperfect Fermi surface nesting. However, the various phonon energies can be clearly observed, and suggest that the formation of CDW orders is determined by the strong electron-phonon coupling [45].

Figure 1.12 Resistivity of 1T-TaS₂ crystals as a function of temperature. The upper and lower lines describe the cooling and warming processes, respectively. The right inset represents the normal structure, while the left one denotes the distorted lattice in CCDW phase. Adapted from ref. [46], Copyright 2008, Macmillan Publishers Limited.

1.2.3 CDW orders in metallic TMDs

The CDW phases have been discovered in an abundance of metallic transition metal dichalcogenides for both 1T and 2H structures, such as 1T-TaS₂, 1T-TiSe₂ and 2H-

NbSe₂ [47,48]. These layered metallic TMDs possess a rich and diverse CDW phase diagrams. For instance, 1T-TaS₂ exhibits the metallic nature at high temperature above 550 K, during the cooling process, it transforms into the incommensurate CDW (ICCDW) phase in the temperature range between 350 K and 550 K. With decreasing the temperature, it presents the nearly commensurate CDW (NCCDW) phase and finally becomes the commensurate CDW (CCDW) state below 180 K, where the lattice structure experiences a periodic distortion to a unite cell with $\sqrt{13}a_0 \times \sqrt{13}a_0 \times 13c_0$ [46]. Particularly, thirteen tantalum (Ta) atoms gather together to form a "Star-of-David" superlattice, with a sufficient large displacement up to 0.24 Å [49]. Conversely, there comes out a special trigonal (T) phase during the warming cycle between 220 K and 280K, as shown in Figure 1.12, the resistivity of 1T-TaS₂ at different temperatures perfectly describes the various phase transitions [46,50].

Since the 2D TMDs exhibit intensively thickness-dependent properties, the CDW phase in these van der Waals materials is also found dimension related. Previous studies report that the NCCDW/CCDW phase transitions in 1T-TaS₂ films are suppressed and shift to lower temperatures, as the number of layers decreases [51,52]. In contrast, 1T-TiSe₂ flakes are experimentally revealed to have slightly higher CDW transition temperatures with decreasing the sample thickness [53]. Similarly, a particularly enhanced CDW state is demonstrated in monolayer 2H-NbSe₂ [54]. The transition temperature of 33 K in the bulk 2H-NbSe₂ greatly increases to 145 K when the thickness is reduced to the limit of monolayer. The driven mechanism of CDW formation in layered TMDs is still in dispute, while the theory of Fermi surface nesting has been

well applied in quasi-one-dimensional systems. As the research moves along, more and more scientists believe that the strong electron-phonon coupling plays a vital role in the formation of CDW phases [54-56].

1.3 Detection methods of CDW phase

The formation of CDW states is actually accompanied by a large number of variables and physical phenomena, which take responsibility for the investigation and confirmation of CDW states by using several techniques.

The comparatively straightforward technique to observe the CDW phase transition is the temperature dependent electrical resistivity, as the electronic band structure is particularly sensitive to the CDW formation. This measurement often provides the direct indication of the charge modulation associated with CDW order and gives relatively precise values of CDW transition temperature T_{CDW} [52].

Diffraction probing technique (e.g. electrons, neutrons and X-rays) is frequently employed to detect the CDW related superlattice and lattice distortion. The obtained diffraction patterns can easily identify the wave vector at $\mathbf{q} = 2\mathbf{k}_f$ of the Fermi surface nesting when the temperature is below T_{CDW} . Since the CDW superlattice is weaker than the major structure of the materials to some extent, a high-intensity source, known as the resonant X-ray scattering, is used to enhance the signal and observe the charge modulation directly [53].

Angle resolved photoemission spectroscopy (ARPES) is a powerful experimental tool to observe the band structures and energy gaps linked to the Fermi surface nesting

and lattice distortion [43]. When the material undergoes a CDW phase transition, the newly formed Brillouin zone would modify the distribution of the electrons in the reciprocal space, which can be captured by high-resolution ARPES measurements.

Scanning tunneling microscopy has been successfully used to characterize the electronic properties and crystal structures by imaging the sample surface at the atomic level [57]. The large atomic displacements and the periodic lattice patterns in CDW orders can be straight visualized in real space under the high spatial resolution, meanwhile, the CDW related energy gap could also be detected simultaneously.

Raman spectroscopy is the most common technique for conventional and nondestructive characterization of crystal symmetry and lattice vibrations in 2D materials [58]. Due to the lattice distortion in CDW states, additional phonon modes appear evidently with the folding of the original Brillouin zone, as a result, the high resolution and sensitivity Raman measurements possess the ability to observe these vibrational modes [59]. In addition, the two-phonon scattering generated soft mode is also tightly connected to the CDW formation, making substantial contributions to the change of Raman spectra [60].

1.4 Motivation and objectives of this thesis

The successful fabrication of graphene has evoked extensive investigations in 2D materials. Atomically thin metallic TMDs, standing for a novel set of 2D crystals, have attracted considerable attention due to the coexistence and competition of collective many-body phenomena, including charge density wave and superconductivity. Prior to

becoming the brilliant candidates in flexible optoelectronics and thermoelectric applications, it is of great significance to manipulate and precisely control these electronic collective states in 2D metallic TMDs. Particularly, understanding the alterations of CDW orders and the accompanying periodic lattice distortions is urgently required to reveal the mechanism of coexisting phase diagram in low dimensions.

Reducing the dimensionality is well believed to affect the properties of 2D TMDs as well as the instability of CDW orders. However, atomically thin CDW materials have been so far mainly obtained by mechanical exfoliation method, which leads to the small sample size and low production yield. As a result, developing a controllable synthesis of metallic TMDs with large area and different thicknesses could help investigate the thickness dependent CDW orders in these CDW materials. In addition to the dimensionality, metallic 2D TMDs also provide an ideal platform for electrical control of the CDW orders. It is well known that the atomically thin CDW films suffer a severe degradation in the air, thus they are often protected by covering hexagonal boron nitride or graphene layers in most studies. Nevertheless, these van der Waals heterostructures directly give rise to a large range of interactions at the interface including charge transfer, which may have great effects on the CDW instabilities.

On the other hand, thermal conductivity plays crucial roles in devices of condensed matters, especially in 2D systems. Layered Td-WTe₂ is expected to have anisotropic thermal properties due to the distinct anisotropic Td phase, which should be carefully considered in developing 2D Td-WTe₂ nano-scale magnetic devices.

Motivated by these principal elements, this thesis focuses on investigating the

modulations of CDW phase transition temperatures in CVD-grown 2D TMDs with various thicknesses. The high resolution and nondestructive *in situ* Raman spectroscopy is the main method to determine the T_{CDW} in different layers. With the help of scanning tunneling microscope, the charge transfer induced suppression of CDW states are visualized in graphene/NbSe₂ heterostructures. Furthermore, the anisotropic in-plane thermal conductivities in suspended Td-WTe₂ layers are first experimentally observed. The major objectives of this thesis are to provide effective strategies for tuning CDW states in metallic TMDs and shed more light on the design of next-generation thermoelectric devices based on the promising 2D TMDs.

1.5 Organization of the thesis

This thesis is organized as follows:

Chapter 1 introduces the basic information of 2D materials, the concept of CDW instability and the reviews of current studies about CDW orders in metallic 2D TMDs.

Chapter 2 describes the experimental methods of sample preparation and Raman measurements in exploring the CDW transition temperatures.

Chapter 3 and 4 systematically investigate the thickness dependent CDW phase transitions in atomically thin 1T-TaS₂ and 1T-TiSe₂ films, and both chapters consist of two parts. The first part demonstrates the controllable fabrication of metallic 2D TMD thin films by self-modified chemical vapor deposition method. In the second part, the CDW transition temperatures are obtained by using *in situ* Raman spectroscopy.

Chapter 5 reveals the suppression of CDW states in graphene/NbSe₂ heterostructures.

The CDW transition temperatures and associated periodic superlattice are observed with the help of Raman spectroscopy and scanning tunneling microscope. Moreover, the interactions between single layer graphene and 2H-NbSe₂ films are discussed.

Chapter 6 focuses on the in-plane anisotropic thermal conductivity of suspended few-layer Td-WTe₂ flakes. By utilizing the heat conduction model, the anisotropic thermal conductivities of Td-WTe₂ with different thicknesses are extracted by *in situ* micro Raman spectroscopy.

Chapter 7 includes the summary and future plans in the field of metallic 2D TMDs.

Chapter 2 Experimental techniques

2.1 Preparation of 2D TMDs

The standards and requirements for the preparation of 2D materials demand samples to possess spatial uniformity, wafer scale and high crystalline quality with controllable thickness. The most widespread approaches to prepare 2D materials start from either top-down or bottom-up methods. The former usually contains the mechanical exfoliation and chemical exfoliation [61,62], while the chemical vapor transport (CVT) and chemical vapor deposition are referred to the latter. The metallic 2D TMDs studied in this thesis are mainly fabricated by two techniques: mechanical exfoliation from the bulk crystals (2H-NbSe₂ and Td-WTe₂) and chemical vapor deposition (1T-TaS₂ and 1T-TiSe₂) methods.

2.1.1 Mechanical exfoliation of 2D TMDs

The first discovery of single layer graphene through scotch tape by Novoselov *et al.* has intensively facilitated the top-down mechanical exfoliation method in preparing various 2D materials [4]. Due to the weak van der Waals interactions between the TMD layers, it is possible to utilize such method to peel off mono- and few-layer TMDs [12]. Specifically, the adhesive tape is placed onto the fresh surface of bulk crystals, and then another clean adhesive tape sticks together with the former tape. After that, the peeling process is conducted again and again until the atomically thin flakes appear on the tape. In the end, the scotch tape with thin crystals is uniformly pressed onto the desired substrates. The thin layers with various thicknesses will reserve on the substrates after

peeling off the tape gently in a few minutes. It has suggested that the Si substrates covered with 300 nm-thick SiO₂ layer can offer a high-quality optical contrast [63,64], and the mechanical cleavage from the bulk counterparts can produce high quality films with multiple layers, which are competent to the precise characterizations. In this thesis, the few-layer 2H-NbSe₂ and Td-WTe₂ flakes are obtained on 300 nm SiO₂/Si substrates by mechanical exfoliation method.

2.1.2 Chemical vapor transport growth of 2D TMDs

Chemical vapor transport is one of the most powerful methods to grow pure single crystals *via* the gas phase, and popularized by Harald Schäfer [65]. In the company of a gaseous reactant, which is typically known as the transport agent, the solid can be volatilized in a form of crystal and deposits in another place. The transport agents normally consist of halogens and halogen compounds. To successfully trigger the growth process of CVT, the external conditions for the chemical equilibrium must be different in volatilization and crystallization, such as growth temperature, choice of the transport agent and rate of the mass transport [66].

CVT method has been extensively utilized to synthesize a variety of TMD single crystals. As shown in Figure 2.1, the mixture of source materials and transport agent is sealed in a quartz ampoule under high vacuum, which is subsequently annealed under a temperature gradient [67]. In the high temperature zone, a reversible endothermic reaction of the transport agent generates the volatile intermediates first to carry TMDs into the gas phase. By decomposition of these intermediates, the crystallization of large and high quality TMD single crystals can occur after a long period at the cold end of

the reaction ampule. The bulk crystals of Td-WTe₂ in this thesis are fabricated by a mature CVT approach.

Figure 2.1 Experimental schematic of CVT method for the synthesis of single crystals in a temperature gradient. Adapted from ref. [66]

2.1.3 Chemical vapor deposition growth of 2D TMDs

To overcome the issues of small sample size and low productivity from mechanical cleavage, chemical vapor deposition has been developed to produce large-scale thin films especially the monolayer 2D TMDs, which involves the sulfurization or selenization of transition metal based precursors [68,69]. The basic components of a CVD instrument contain gas supply, quartz tube, pump and furnace. The flowmeter at the upstream region is used to control the flow rate of the carrier gas, which has multiple choices in the lab (e.g. Ar and H₂). During the synthesis, the reaction temperature is maintained by the furnace outside the quartz tube.

The sulfurization or selenization through CVD method is performed in vapor phase under atmospheric pressure and then deposited onto the substrate, as shown in Figure 2.2. The widely used SiO₂/Si substrate is usually loaded face down on the ceramic boat

that contains the precursors. For 2D TMDs, the standard precursors include sulfur (S) and selenium (Se) powder with desired transition metal oxides. Taking the WS₂ for instance, the SiO₂/Si substrates with WO₃ powder are firstly placed at the center of the quartz tube, while a ceramic boat containing S powder is loaded at the upstream region. The argon, which is utilized as both protective and carrier gas, is injected into the quartz tube with a constant flow rate (200 sccm) during the entire synthesis. The furnace controls the temperature with increasing rate of 18 °C/min. After the vaporization of S powder, the temperature increases to 800 °C with a lower rate of 5 °C/min, and keeps for 10 min. The large area monolayer WS₂ triangular flakes are obtained with naturally cooling down the temperature [70]. Therefore, CVD technique is effective in growing ultrathin and large area 2D TMDs, the 1T-TaS₂ and 1T-TiSe₂ films studied in this thesis are synthesized by ambient-pressure CVD technique.

Figure 2.2 *Experimental schematic of CVD method for the synthesis of 2D TMDs. M represents the transition metals. Adapted from ref. [71]*

2.1.4 Dry transfer of exfoliated samples

The precise transfer of 2D materials from one substrate to a target substrate is the

prerequisite for the fabrication of freely suspended flakes and vertical heterostructures by integrating various 2D films, which enables the new phenomena and promotes their performances in complex applications. For instance, the wedging method, chemical etching and polyvinylalcohol (PVA) method have been reported in previous studies [72-74]. However, the wet process and chemical etchant in these transfer techniques may create wrinkles or defects on the sheets and even destroy the samples. Indeed, a rapid and all-dry method is highly demanded for clean and safe transfer of 2D nanostructures.

Figure 2.3 Schematic illustration of transferring 2D materials to a desired area on the acceptor substrate through dry transfer method. Adapted from ref. [75]

Dry transfer is exactly a specific technique to transfer thin films without employing any water or chemicals [75]. Figure 2.3 describes the process of dry transfer method in 2D materials. The stamp adopted in the transfer is a purchasable viscoelastic thin film, which refers to the polydimethylsiloxane (PDMS) in this thesis. To facilitate the operation, the viscoelastic PDMS film is firstly adhered to a glass slide, the atomically

thin structures are then deposited on the PDMS film through the mechanical exfoliation from their bulk counterparts. After identifying and selecting the flake with desired thickness under optical microscope, the glass/stamp with sample is mounted on a homemade three-axis manipulation platform with the sample facing downward. Due to the transparency of glass and PDMS, the optical microscope with long working distance (LWD) objective can be used to align the flake to the preferred area on the acceptor substrate. Eventually, the transfer will success when pressing the stamp against the surface of the acceptor substrate and peeling off very carefully. In this thesis, the graphene/NbSe₂ heterostructures on SiO₂/Si substrate and suspended few-layer Td-WTe₂ are prepared by dry transfer technique in a perfect condition.

2.2 Raman spectroscopy

Raman spectroscopy is a recognized spectroscopic observation to probe vibrations and rotations of atoms or molecules based on Raman scattering. In 1923, A. Smekal theoretically predicted this kind of scattering of light for the first time [76], which was then discovered simultaneously in liquids by C. V. Raman and K. S. Krishnan [77] and in solids by G. S. Landsberg and L. I. Mandelstam [78]. Raman scattering depicts the energy difference of the scattered photons with respect to the incident photons, when the incident laser interacts with crystals. Raman spectroscopy has been commonly utilized in 2D materials to investigate the rich phonon modes and other related phenomena.

2.2.1 Basic principles of Raman scattering

When a material is irradiated under the incident light, besides the reflection, transmission and absorption of light, a fraction of the incident photons is scattered by the molecules or phonons in the material. The most of photon scatterings belong to the elastic scattering, where the energy of scattered photon is the same as that of incident photon. For example, Rayleigh scattering is a representative elastic scattering and originates from the scattering centers whose size is much smaller than the incident light wavelength. Whereas a small portion of the incident light experiences the inelastic scattering, where the incident photons gain or lose energy. Raman scattering is referred to a common inelastic scattering of the photons.

Figure 2.4 Schematic diagram of infrared absorption, elastic scattering and inelastic scattering processes.

In Raman scattering process, the electrons within the materials will be disturbed and

in turn alter the electron clouds, which forms a virtual and short-lived state. Figure 2.4 shows the diagram of two styles of Raman scattering, one is Stokes and another is anti-Stokes Raman scattering. In the case of Stokes Raman scattering, the electron of materials is excited from ground state to a virtual state and then released back to an excited vibrational state, where the energy of the scattered photon is lower than that of the incident photon. The energy loss in Stokes Raman scattering is consistent with the phonon energy, and generally refers to the Raman shift in Raman spectra. The Raman shift is an intrinsic property and does not rely on the incident light. On the contrary, anti-Stokes Raman scattering corresponds to the process of an electron excited from the vibrational state and finally back to the ground electronic state. The scattered photon has higher energy and this energy gain can be also manifested in infrared (IR) absorption. In addition, when the electron is excited to a real state or the incident laser energy is close to the absorption band, the intensity of Raman scattering can be significantly enhanced. This progress is usually defined as resonance Raman scattering.

2.2.2 Selection rules of Raman scattering

The energy and momentum of the concerned photons and phonons should conserve in Raman scattering process. For instance, the first-order Raman scattering process satisfied the formulas of

$$\begin{aligned}\hbar\omega_i &= \hbar\omega_s \pm \hbar\omega_{ph} \\ \hbar k_i &= \hbar k_s \pm \hbar k_{ph},\end{aligned}\tag{2.1}$$

where ω is the angular frequency and k is the wave vector, i , s and ph represent the incident photon, scattered photon and phonon, respectively. The $+$ and $-$ in the

equations indicate the Stokes Raman scattering and anti-Stokes Raman scattering, respectively. Figure 2.5 indicates the momentum conservation of Raman scattering. Generally, the detector has a certain angle θ with respect to the incident light, therefore the phonon wave vector should have

$$k_{ph}^2 = k_i^2 + k_s^2 \pm 2k_i k_s \cos \theta. \quad (2.2)$$

Figure 2.5 Sketch of Raman scattering measurements and the momentum conservation for both Stokes and anti-Stokes scattering.

In Raman measurements, the wavelength of excitation lasers is commonly from near ultraviolet to infrared, whose wave vector is mostly on the order of 10^5 cm^{-1} . According to the energy and momentum conservation, the energy difference between the incident light and scattered light is relatively small, which makes the wave vector of scattered photons maintain the same magnitude. As a result, the phonons involved in Raman scattering have the wave vectors on the order not exceeding 10^5 cm^{-1} . Since the size of Brillouin zone is typically on the order from 10^7 to 10^8 cm^{-1} , only the long-wavelength phonons near the Brillouin zone center (known as the Γ point) actually take part in the Raman scattering.

In addition to the momentum conservation, the phonons involved in Raman

scattering must obey a symmetry selection rule. That is, only the phonon vibration that can change the polarizability is Raman-active. A second-rank tensor $\tilde{R}$ is often used to describe the symmetry of Raman-active vibrational mode, and has the relation with the second-rank electric polarizability tensor $\tilde{\alpha}$

$$\tilde{R} = \frac{\partial \tilde{\alpha}}{\partial Q} Q, \quad (2.3)$$

where Q is the phonon vibration induced vector displacement of a provided atom [79,80]. Particularly, the phonon vibration that changes the electric dipole moment is IR-active [80]. In centrosymmetric crystals, some vibrational modes are both Raman- and IR-active due to the complementation of Raman and IR activities. Whereas the silent or optically inactive modes are neither Raman- nor IR-active.

The experimental observation of Raman-active modes also relies on the polarization vectors of the incident light (e_i) and the scattered light (e_s), and the Raman intensity I of vibrational mode is proportional to $|e_i \cdot \tilde{R} \cdot e_s|^2$. In simple terms, a given phonon mode can be detected by Raman spectroscopy only when the intensity I is non-zero. The Raman tensor $\tilde{R}$ is determined by the crystal symmetry and group theory analysis [81], thus the Raman mode intensity can be expressed by [79],

$$I \propto e_i \cdot \tilde{R} \cdot e_s = \begin{pmatrix} x & y & z \end{pmatrix} \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad (2.4)$$

The most common configuration of Raman measurements is the backscattering geometry, in which the Porto notions of $\bar{A}(BC)A$ is used to represent the polarization configurations [82]. That is, $\bar{A}$ and A denote the directions of the incident and backscattered light, respectively. B is the polarization of the incident light, while C indicates that of scattered light. Specifically, the most often utilized configurations in

2D materials are the parallel-polarized configuration ($\bar{z}(xx)z$) and cross-polarized configuration ($\bar{z}(xy)z$). The Raman intensity therefore can be written as:

$$\begin{aligned} I_{\parallel} &\propto e_i \cdot \tilde{R} \cdot e_s = (x \ 0 \ 0) \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} x \\ 0 \\ 0 \end{pmatrix} \\ I_{\perp} &\propto e_i \cdot \tilde{R} \cdot e_s = (x \ 0 \ 0) \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ y \\ 0 \end{pmatrix}. \end{aligned} \quad (2.5)$$

Concisely, the symmetry selection rule consists of the symmetry of phonon mode and the polarization configurations, which determine the detectability of the vibrational modes in Raman measurements.

2.2.3 Detection of the low frequency Raman modes

The ordinary edge filter used in Raman system can only help detect the phonon modes with frequencies larger than 100 cm^{-1} . However, the frequencies of interlayer shear mode and breathing mode are always located within 50 cm^{-1} , it is of great importance to observe these low frequency Raman modes [83-86]. A triple-grating spectrometer was created to solve this urgent problem, in which the scattered light would travel through three gratings before arriving the detector. The classic triple-grating Raman spectroscopy, as shown in Figure 2.6(a), has two more gratings between the beam splitter and the standard grating comparing to the normal Raman spectroscopy. The polychromatic scattered light is firstly dispersed by the Grating 1 after passing through the slit 0-1. Slit 1-2 is utilized as a bandpass filter to select the scattered light with wavelengths only in a specific region, and all these selected light is then focused by the Grating 2 into the slit 2-3, which generates a new polychromatic light with desired wavelengths. The two more gratings play a role of the tunable bandpass filter in picking

out the required light, and therefore enable the detection of low frequency Raman modes. Recently, a new technique has been developed to observe low frequency Raman spectra with the same principle, but has a much higher collection efficiency. Instead of the triple-grating spectrometer, the BragGrate notch filters are installed between the beam splitter and the conventional monochromator, as illustrated in Figure 2.6(b). Notably, in order to obtain the high signal-to-noise ratio of low frequency Raman spectra, the Rayleigh scattering background should be weakened significantly, which requires that the linewidth of the single-mode excitation laser must be extremely narrow. The low frequency Raman spectra collected in this thesis are dependent on the new technique of BragGrate notch filters.

Figure 2.6 Schematic diagrams of low frequency Raman spectroscopy configurations.

(a) Typical triple-grating spectrometer. (b) BragGrate notch filters with high collection efficiency. Adapted from ref. [86]

2.3 Optical characterization

The Raman measurements conducted in this thesis are dependent on both WITec alpha300 series confocal micro Raman spectroscope and custom designed magneto-Raman system in backscattering configuration.

Figure 2.7 Schematic diagram and the beam paths of the WITec alpha300 series Raman spectroscope. The yellow and green colors represent the beam paths of white light and the excitation laser, respectively. Adapted from ref. [87]

2.3.1 Confocal micro Raman spectroscope

The schematic diagram and the beam paths of the WITec alpha300 series confocal micro Raman spectroscope are shown in Figure 2.7. For lighting system, the Koehler white-light is adopted to illuminate the sample. The video camera collects the reflected light

and records the optical image, which enables the focusing of samples. A XYZ stage is utilized to hold the sample and can be roughly moved along x -, y - and z -axis manually. Moreover, it can be precisely adjusted by piezoelectric control, allowing easily locating the sample position. The excitation laser with wavelength of 532 nm is coupled into a single mode fiber and reflected by the beam splitter to an objective lens, through which it is focused to excite the sample. The diameter of the laser spot can be as small as 0.5 μm after traversing a $100\times$ objective lens with $\text{NA} = 0.95$. The collection system is aligned to the excitation system in a backscattering configuration, which allows the objective lens to collect the scattered light. As a result, the Raman signals are detected by a thermoelectrically (TE) cooled charge coupled device (CCD) after passing through the lens-based ultra-high throughput spectrometer (UHTS) with a 2400 grooves/mm grating. Importantly, the notch filter used in the system facilitates the detection of low frequency Raman modes.

2.3.2 Custom designed magneto-Raman system

The custom designed magneto-Raman system is equipped with a magnet system based on a commercial WITec confocal Raman spectroscope. As shown in the sketch map (Figure 2.8), the main body of the magnet system is a liquid helium based cryostat, which can provide the ultimate stability and keep the temperature down to 4.2 K, and the superconducting magnet is installed inside the cryostat. Samples are fixed on the non-magnetic stage, which is composed of three-axis piezo positioners. The whole stage with samples can be loaded into the cryostat and applied a magnetic field along c -axis from -9 to 9 T when filled with liquid helium.

Figure 2.8 Sketch map of the custom designed magneto-Raman system. (1) Commercial WITec confocal Raman system, (2) liquid helium based cryostat, (3) superconducting magnet to generate magnetic field, and (4) piezo-stage to hold samples. Adapted from ref. [88]

For the optical characterization, a solid-state Nd:YAG laser is utilized to generate the excitation laser with wavelength of 532 nm. The scattered light is selected by the grating monochromator and received by TE-cooled CCD, which are aligned in backscattering

geometry. The optimized laser spot size on the sample can be within about 1 μm . In addition, this system is able to perform electrical measurement when connecting to the semiconductor characterization system. The Raman measurements for graphene/NbSe₂ heterostructures are conducted by the magneto-Raman system.

2.4 Scanning tunneling microscope

In 1982, Gerd Binnig and Heinrich Rohrer invented the scanning tunneling microscope, which has been developed to be a powerful technique for local surface science at atomic scales [89]. Therefore, they received the 1986 Nobel Prize in Physics. STM has been successfully used to characterize the crystal structure and electronic properties of a material. The high spatial resolution makes it achieve an excellent performance on investigating the correlated electronic states, such as charge density wave orders [90].

The basic working principle of STM depends on the quantum mechanical electron tunneling through an energy barrier [91]. As described in Figure 2.9, the probe tip is usually made of W or Pt-Ir alloy, which can be precisely controlled by mutually perpendicular piezoelectric transducers. The distance thus between the tip and the sample is brought into the range of 5 - 10 Å, making the electron wave functions in the tip and the sample surface overlapped. When applying a bias voltage between the tip and sample, the tunneling current will be generated and can flow through the distance due to the sufficient overlap. Typically, such distance between the tip and sample is adjusted by a feedback system to maintain the tunneling current with a constant value. As a result, the topography of the surface is represented by the voltage on the z -piezo.

To achieve the atomic resolution, a vibration isolation is prerequisite, which is offered by springs with a modified resonant frequency. The experiments in the thesis are conducted using the Omicron ultra-high vacuum low-temperature STM.

Figure 2.9 Basic principles of STM in a nutshell. Adapted from ref. [91]

Chapter 3 Charge density wave phase transitions in CVD synthesized atomically thin 1T-TaS₂

3.1 Introduction

Charge density wave materials have attracted a lot attention over the past few years [43,92], and the manipulation of many-body states in these CDW materials becomes a promising approach for designing next-generation electronic devices [93,94]. It is believed that the dimensionality of the CDW materials greatly affects instability of CDW states [54]. With reduction of the dimensionality, Peierls instabilities and electron-phonon interactions are strongly enhanced, which triggers a stronger CDW effect [55]. Thus, two-dimensional (2D) materials, which can be isolated into atomically thin layers, show great potential for CDW applications. For example, the highly unusual enhancement of CDWs was observed in atomically thin 2H-NbSe₂ due to the significantly enhanced electron-phonon interactions [54], and the room-temperature CDWs phase transitions are realized in thin flakes of 1T-TaS₂ and 1T-TiSe₂ through the method of gate-controlled Li⁺ intercalation [52,53,95]. However, to our best knowledge, the fabrication of ultrathin 2D layers mainly relies on the mechanical exfoliation method, which suffers from the low production yield and small sample sizes [96-98].

The chemical vapor deposition method, involving the chemical reactions of gaseous reactants on a heated substrate surface, is regarded as one of the main processing methods for synthesis of 2D materials [99,100]. It can produce large-size and high-

quality 2D materials, such as graphene, MoS₂ [68,101,102], WS₂ [103] and BN [104,105], with controlled thickness. Therefore, the CVD method could be employed as a swift and effective way to synthesize high-quality 2D CDW materials in a controlled manner. In this work, we have demonstrated the controlled synthesis of atomically thin 1T-TaS₂ [46,51,106], via the CVD method. The thicknesses of 1T-TaS₂ can be tuned from two to several hundred nanometers, as revealed by atomic force microscopy (AFM). Their high quality has been confirmed by scanning transmission electron microscope (STEM) and electron energy loss spectra (EELS). With the help of in situ temperature-dependent Raman spectroscopy, we also revealed the thickness-dependent CDW phase transitions in our CVD-grown samples. Briefly, three phases can be found in our CVD-grown 1T-TaS₂: incommensurate CDW (ICCDW), nearly commensurate CDW (NCCDW), and commensurate CDW (CCDW). For a sample of a thickness above 14 nm, a CCDW phase was observed. As its thickness reaches 14 nm, the transition from CCDW to NCCDW phase was identified. As the thickness reaches 6 nm, the transition from the CCDW to NCCDW phase was observed. This controlled synthesis of large-area ultrathin CDW materials via a CVD method shows great potential for the fabrication of next-generation electronic devices.

3.2 Experimental details

3.2.1 Sample preparations

The tantalum pentachloride (Sigma-Aldrich, TaCl₅, >99.5%) and sulfur (Sigma-Aldrich, S, >99.5%) powders were used as solid precursors. A commercial 300 nm-thick SiO₂/Si

wafer was used as a substrate. It is placed in the center of a 4 cm in diameter quartz tube of a CVD tube furnace, and the mixed compounds of 30 mg TaCl₅ and 100 mg S are placed in the crucible (1.5 cm × 5.0 cm) at the entrance of the tube furnace (20 cm upstream from the substrate). The CVD growth occurs at atmospheric pressure in a flow of 90 sccm of Ar gas and 10 sccm of H₂. The furnace temperature is ramped to 1093 K in 18 min. The growing time was changed from 4 to 30 min to controlled synthesize 1T-TaS₂ with different thicknesses. The chemical reaction is shown below:

After a growth period, the furnace is opened, and the sample is rapidly cooled to room temperature in the flowing mixed gases of H₂/Ar.

The high-quality 1T-TaS₂ single crystals were grown using a standard chemical vapour transport method. Thin flakes were obtained by mechanically exfoliating bulk single crystals onto a 300 nm SiO₂/Si wafer by scotch-tape technique.

3.2.2 Characterizations

The X-ray diffraction patterns were obtained from 1T-TaS₂ thin flakes supported on the SiO₂/Si substrates using an X-ray diffractometer (XRD Shimadzu Thin Film), using Cu K α radiation at room temperature in the 2 θ range of 5-80°. The optical images were observed by Olympus BX51. The thickness measurements of 1T-TaS₂ flakes were carried out in AFM (DI-3100). The transmission electron microscopy (TEM) images were taken with a JEM-2100F microscope operated at an acceleration voltage of 200 kV. ADF-STEM imaging was performed on a Nion UltraSTEM-100, equipped with a fifth order aberration corrector, operated at 60 kV. All ADF-STEM images were low-

pass filtered to increase the signal-to-noise ratio.

The Raman spectroscopy measurements were performed by a WITec Alpha300 Series confocal Raman system with 2400 g/mm grating with 532 nm excitation laser. A combination of Bragg notch filter allows the measurements of the low-frequency Raman modes down to approximately $\sim 10\text{ cm}^{-1}$. The beam spot size of excitation laser is focused around $1\text{ }\mu\text{m}$ by a $50\times$ long working distance objective. To avoid the damage of samples by the laser induced heating, the power of the laser was strictly controlled below 1 mW. An integration time of 180 sec was used to obtain the spectra. The temperature dependent Raman measurements were achieved by mounting the Linkam optical DSC600 and LNP95 cooling system. A temperature controllable evacuated chamber was used for preventing the potential oxidation and laser induced local heating of the 1T-TaS₂ samples. The temperature range required during the measurements can be cooled down to 80 K by liquid nitrogen.

3.3 Results and discussion

3.3.1 Synthesis of ultrathin 1T-TaS₂ layers by CVD method

The CVD setup for synthesizing ultrathin 1T-TaS₂ is represented in Figure 3.1(a). The tantalum pentachloride and sulfur powder were used as the precursors of Ta and S, respectively. The SiO₂/Si wafer was chosen as preferred substrate for growth. In a typical process, the mixed powders were placed at an inlet of the tube furnace, while the SiO₂/Si wafer is located at the center of the furnace. Then, under the H₂/Ar mixture (10% H₂) carrier gas, the furnace was heated up to 1093 K to chemically grow 1T-TaS₂

layers on a SiO_2/Si substrate. The introduction of H_2 gas into the reaction region makes a reducing atmosphere, which increases the reducing power during the sulfurization reaction of TaCl_5 .

Figure 3.1 Controlled synthesis of ultrathin 1T- TaS_2 crystals via a CVD method. (a) Schematic of CVD setup for the growth of 1T- TaS_2 on a SiO_2/Si substrate with tantalum pentachloride powder and sulfur powder used as the precursors. (b, c) Crystal structure of distorted 1T- TaS_2 on a SiO_2/Si substrate. (d, e) Optical images of 1T- TaS_2 ultrathin flakes. (f) The controlled thicknesses of 1T- TaS_2 at different growth times. The inset shows an octahedral arrangement of the central Ta atom coordinated with S atoms. (g-l) AFM images and their corresponding height profiles of various 1T- TaS_2 at different growing times. The scale bars are $10\ \mu\text{m}$ in (d) and (e), and $2\ \mu\text{m}$ in (g), (h), and (i).

The side view (Figure 3.1(b)) and top view (Figure 3.1(c)) of the 1T- TaS_2 crystal structure clearly show that 1T- TaS_2 is a typically layered material. Each 1T- TaS_2 layer is composed of the hexagonally arranged Ta atoms sandwiched between two sulfur layers. Sulfur atoms coordinate the central Ta atom in an octahedral arrangement

[107,108]. The weak interlayer van der Waals forces actually help in controlling the number of layers and hence the thickness of 1T-TaS₂. Figure 3.1(d) and (e) show optical images of the 2-nm-thick and 11-nm-thick samples. By controlling the growing time, 1T-TaS₂ samples with different thicknesses were obtained at 1093 K, as shown in Figure 3.1 and Figure 3.2.

Figure 3.2 Optical images of 1T-TaS₂ flakes with thicknesses varying from 5 nm to 220 nm at increased growing time from 4 to 30 mins. (a) 2 nm. (b) 5 nm. (c) 6 nm. (d) 11 nm. (e) 14 nm. (f) 16 nm. (g) 21 nm. (h) 35 nm. (i) 220 nm. The scale bars are 10 μ m.

In fact, one can estimate the thickness of 1T-TaS₂ by its contrast. Thick samples (>10 nm) are in blue while thin films like few-layered 1T-TaS₂ are in purple. In our work,

the thicknesses of 1T-TaS₂ samples were accurately determined by AFM. As can be seen in Figure 3.1(f), the thickness of 1T-TaS₂ is linearly dependent on growing time. As we changed the growing time from 4 to 30 min, the thickness of 1T-TaS₂ increased from 2 nm to above 200 nm. From the AFM images and corresponding height profiles in Figure 3.1(g-l), we can also see that the CVD-grown 1T-TaS₂ samples are uniform for relatively large flakes (>10 μ m). In addition, the X-ray diffraction patterns of a 220 nm-thick sample (in Figure 3.3) confirmed that the structure of our CVD-grown TaS₂ is the 1T phase (JCPDS 73-2201) [109,110].

Figure 3.3 XRD pattern of 220 nm-thick 1T-TaS₂. Insert is the schematic crystal structure of 1T-TaS₂. The XRD result indicated the presence of 1T polytype structure of TaS₂.

The growth time dependence of the sample thickness in our experiments is quite different from MoS₂ layers grown by CVD method [111]. As growth time increases,

the nucleation density of MoS₂ decreases and the grain size becomes larger on the SiO₂/Si substrate. With continuing growth, the MoS₂ flakes start to link together and form a thin film. As a result, the nucleation of MoS₂ is more likely to occur on the SiO₂/Si substrate. However, the analogous growth time dependence we observed has been found in NbS₂ flakes on the same substrate [112]. At the beginning of the synthesis, nucleation sites are first absorbed onto the SiO₂/Si substrate. Once the nucleation occurs, very thin hexagonal 1T-TaS₂ layers start to grow, and the lateral growth dominates in the first few minutes. The active sites including dangling bonds on the crystal edges are responsible for the lateral growth of TaS₂ grains. As the growth proceeds, the vertical growth begins to take over the TaS₂ growth due to the decreased edge/area ratio. After that, more nucleation sites appear on the TaS₂ surface resulting in the thicker TaS₂ flakes.

The quality of the as-grown crystal was further examined by TEM and STEM. Figure 3.4(a) shows a TEM image of the atomically thin 1T-TaS₂ flake, displaying a uniform film with a smooth surface. The selected area electron diffraction (SAED) patterns of the 6-fold rotational symmetric diffraction patterns confirm the hexagonal structure of the CVD-grown 1T-TaS₂ at a large scale. Figure 3.4(b) and (c) show the energy dispersive X-ray spectra (EDS) and EELS of the as-synthesized thin flakes, confirming its chemical composition: Ta and S elements without any other obvious impurities.

Figure 3.4(d) shows a high-resolution Z-contrast STEM image of a monolayer region near the edge of the thin flakes. Ta (bright spots) and S atoms can be easily identified by their contrast. However, S atoms are nearly invisible due to the large difference of the atomic number between Ta and S. In order to reveal the position of the S atoms, a

fast Fourier transformation (FFT) filtered image is provided in Figure 3.4(e) and (f). Figure 3.4(e) shows clearly the displaced S2 columns surrounding the Ta atoms, which is consistent with the 1T structural model as overlaid in the same image. These high-resolution STEM images assured the high quality of our CVD-grown TaS₂ flakes in the intrinsic 1T phase.

Figure 3.4 TEM/STEM characterization of a 1T-TaS₂ atomically thin flake. (a) Low-resolution TEM image. Inset is the corresponding SAED patterns of the marked flake with 6-fold rotational symmetry. EDX (b) and EELS (c) spectra of the thin flakes. The occurrence of the Au signal comes from the nearby gold TEM grid bars. (d) High-resolution STEM image along the [001] direction of a monolayer region near the edge of a thin TaS₂ flake. (e) FFT filtered image of (d) with enhanced visibility, showing the positions of Ta and S atoms inside the hexagonal 1T lattice. The atomic structural model is overlaid on the image. (f) FFT pattern of the region shown in (d).

Moreover, the X-ray photoelectron spectroscopy (XPS) was used to identify the chemical binding in the CVD-grown 1T-TaS₂ flake. The XPS results are shown in Figure 3.5. In the high-resolution Ta 4f spectrum, the Ta 4f_{5/2} and Ta 4f_{7/2} peaks are located at 24.7 and 22.7 eV, respectively, corresponding to Ta⁴⁺ from TaS₂ [113]. In the high-resolution S 2p spectrum, peaks at 161 and 160 eV are from the S 2p_{1/2} and S 2p_{3/2}, respectively [114]. The small amounts of Ta₂O₅ species, caused by surface oxidation of 1T-TaS₂, were also detected on the flake.

Figure 3.5 XPS spectra of CVD-grown 1T-TaS₂ flake. (a) Survey spectrum, (b) High resolution Ta 4f spectrum, (c) High resolution S 2p spectrum.

3.3.2 CDW phase transitions in ultrathin 1T-TaS₂ layers

Our CVD-grown 1T-TaS₂ shows rich CDW phases. As seen in Figure 3.6, 1T-TaS₂

undergoes a series of CDW transitions from metallic ICCDW, to textured NCCDW, to insulated CCDW, on lowering the temperature. The low-temperature CCDW phase is characterized by $\sqrt{13} \times \sqrt{13}$ superlattice of David stars formed by 12 Ta atoms clustered around a 13th Ta atom [115]. The periodic lattice distortion creates energy gaps in the 1T-TaS₂ band structure and leaves exactly one conduction electron per David star [116]. The on-site Coulomb repulsion further localizes this conduction electron and produces a Mott insulator state [46].

Figure 3.6 Raman characterization of as-grown 1T-TaS₂ samples. (a) Schematic of CDW phase transitions measured by Raman spectroscopy. (b) AFM topography of the 16-nm-thick flake. (c) Raman spectra at points A-F collected at 80 K. (d, e) The thickness-dependent Raman spectra and plotted Raman map at 110 K. The presence of two broad modes of 60.5 and 71.2 cm⁻¹ and the splitting of 61 and 77 cm⁻¹ modes revealed the transitions of ICCDW to NCCDW and NCCDW to CCDW, respectively.

It is believed that the phonons could couple strongly to the collective modes of CDW states. Raman spectroscopy has been a powerful tool to investigate the CDW phase transitions due to the high resolution and high sensitivity. Many additional Raman modes appear in the commensurate CDW state due to the folding of the original Brillouin zone [117]. Here, we conducted the temperature dependent *in situ* Raman measurements on our 1T-TaS₂ samples to understand the thickness-dependent CDW phase transitions.

Figure 3.7 The plotted Raman intensity map from Raman spectra of 16 nm-thick sample at a temperature of 80 K.

The 16 nm-thick sample was used in this experiment as shown in Figure 3.6(b). First, we investigated its structural homogeneity. We selected six locations, labeled as A-F (as seen in Figure 3.6(b)), to collect the Raman spectra. The Raman spectra and plotted

intensity mapping collected at 80 K are shown in Figure 3.6(c) and Figure 3.7, respectively. It can be seen that the pronounced out-of-plane A_{1g} modes of 70, 78, and 112 cm^{-1} and in-plane E_g modes of 60 and 99 cm^{-1} are clearly detected in the Raman spectra, indicating the existence of the CCDW state [118,119]. The homogeneous Raman spectra in Figure 3.6(c) further confirms the good quality of our CVD-grown 1T-TaS₂. Figure 3.6(d) shows the Raman spectra collected at 110 K from samples with various thicknesses from 2 to 21 nm. It can be seen that, as the thickness increased, the appearance of two broad modes at 60.5 and 71.2 cm^{-1} was first observed on a 6 nm-thick sample which can be attributed to the presence of the NCCDW phase. Also, their subsequent splitting into many well-resolved peaks was detected on a 16 nm-thick sample, which corresponds to the presence of the CCDW phase. These results revealed the thickness-dependent CDW transitions [118]. It can be clearly seen from thickness-dependent Raman mapping in Figure 3.6(e). Moreover, this result further proved the high quality of our as-grown 1T-TaS₂.

To understand the CDW phase transitions of as-grown 1T-TaS₂ samples, we conducted the *in situ* temperature-dependent Raman measurements. For a 21 nm-thick sample, Figure 3.8(c) and (f) show the plotted Raman intensity map and Raman spectra at 270, 200, 140, and 80 K, respectively. As the temperature decreases, the Raman peaks corresponding to NCCDW state become significantly intense. The A_g mode at 77 cm^{-1} is the strongest peak and shows a large temperature-dependent Raman shift. According to the previous reports [117,119,120], the modes below 140 cm^{-1} are derived from the acoustic phonon branches which resulted from the vibrations of the tantalum atoms.

When the temperature decreased to 170 K, the Raman modes at 61 and 77 cm^{-1} split into a few more peaks. These new modes can contribute to the increase in the number of zone center (Γ -point) phonon modes when the original Brillouin zone folds [52]. The results evidenced the phase transition from NCCDW to CCDW at 170 K, which agrees with various retrospective studies [106,117,121].

Figure 3.8 Thickness-dependent CDW phase transitions in CVD-grown 1T-TaS₂ thin flakes. (a-f) The Raman intensity counter maps and Raman spectra for 1T-TaS₂ flakes with different thicknesses. The transition from NCCDW to CCDW in the 21 nm-thick sample was not observed in 5 and 12 nm-thick samples. (g) The thickness-temperature phase diagram for CVD-grown samples. As the sample thickness reduced, both transitions of ICCDW/NCCDW and NCCDW/CCDW were shifted to lower temperatures, and then vanished at critical thicknesses of 6 and 14 nm, respectively.

For a 12 nm-thick sample, Figure 3.8(b) and (e) only show the characteristic phonon modes of the NCCDW phase at frequencies of 60, 71, 77, and 97 cm^{-1} without splitting. This result dictates the suppression of a phase transition from NCCDW to CCDW at a 12 nm-thick 1T-TaS₂ flake. A similar phenomenon was also observed in ultrathin flakes at thicknesses of 11 and 13 nm, which can be concluded from their Raman analysis in Figures 3.9 and 3.10. When we focused on the 5 nm-thick 1T-TaS₂ flake, no characteristic phonon modes of NCCDW were detected in Raman spectra (Figure 3.8(a) and (d)), revealing the suppression of a phase transition from ICCDW to NCCDW at the 5 nm-thick 1T-TaS₂ flake.

Figure 3.9 The Raman intensity evolution maps and characteristic Raman spectra of a 11 nm-thick flake of 1T-TaS₂.

Moreover, in order to clarify the thickness-dependent CDW phase transitions, we examined the thinner sample down to 2 nm. The thickness-temperature phase diagram is shown in Figure 3.8(g). As the sample thickness was reduced, the phase transitions of ICCDW to NCCDW and NCCDW to CCDW were shifted to lower temperatures,

and vanished at a critical thickness of 6 and 14 nm, respectively, demonstrating that the phase-transition temperature can be tuned by the thickness of the as-grown 1T-TaS₂.

Figure 3.10 *Temperature-dependent Raman spectra of a 13 nm-thick flake of 1T-TaS₂.*

In order to compare the property of CDW phase transitions between CVD-grown 1T-TaS₂ flakes and mechanical exfoliated samples, we also carried out in situ temperature-dependent Raman measurements on the mechanically exfoliated thin flake. The Raman

spectra of CVD-grown and mechanically exfoliated samples are shown in Figure 3.11.

Figure 3.11 Phase-transition comparison between CVD-grown 1T-TaS₂ flakes and mechanically exfoliated ones. (a, b) Temperature-dependent Raman spectra and intensity maps of CVD-grown samples. (c, d) The temperature-dependent Raman spectra and intensity maps of mechanically exfoliated samples. The Raman vibration modes and transition feature from NCCDW to CCDW matches quite well for both samples, confirming the high quality of the CVD-grown samples.

Although both samples exhibit the similar temperature-dependent CDW phase transitions, the slight broadening of peak line width of the CVD-grown sample was observed as compared to that of the mechanically exfoliated one, which might be due to the increased lattice defects in CVD-grown samples. Moreover, the suppression of

the CCDW transition from 170 to 160 K was also detected in the CVD-grown sample. The reason can be that lattice defects might have disordered the positions of Ta atoms in a superlattice of David stars, which subsequently results in the suppression of a Mott insulating state or CCDW phase [110].

3.4 Conclusions

To summarize, we have developed a CVD method to synthesize metallic 1T-TaS₂ atomically thin crystals on a SiO₂/Si substrate with controlled thickness. The high quality of CVD-grown 1T-TaS₂ is confirmed by complementary characterizations like XPS, AFM, and STEM. We also identified the thickness-dependent CDW phase transitions using Raman spectroscopy. This work provides a promising way to produce high-quality 2D CDW materials and related electronics devices.

Chapter 4 Thickness dependent charge density wave states in as-grown 1T-TiSe₂ layers

4.1 Introduction

Layered transition metal dichalcogenides possess a whole spectrum of electronic properties covering insulators, semiconductors, semimetals and metals [122]. Semiconducting TMDs members (MoS₂, WSe₂, etc.) have been widely investigated and show great potentials for high-performance electronic and optoelectronic devices, due to their high mobility and wide band gap coverage [12,123,124]. The Ti-, Ta- and Nb-based TMDs are another fascinating material category because of the coexistence and interplay of competing ordered phases including charge density waves and superconductivity [54,92,125]. Among them, 1T-TiSe₂ provides an ideal opportunity to investigate the quantum phase transition between CDW and superconducting orders [92,95,126]. A CDW is a periodic modulation of both the electron density and the crystal lattice arising from an instability of the coupled electron-lattice system. In bulk 1T-TiSe₂, superconductivity emerges when CDW is suppressed by pressure or by intercalation of Cu atoms [127,128]. Reducing the system dimensionality is expected to lead to unprecedented and novel properties and phenomena. For instance, the CDW and superconducting order as well as their phase transitions could be tuned in 2D ultrathin TiSe₂ by an electric field [95]. On the other side, CDW can move and carry electric current when it is depinned by the application of a sufficient electric field [129]. 2D ultrathin CDW conductors with high transition temperatures (1T-TiSe₂, 1T-TaS₂ and

1T-TaSe₂) are potentially suitable for applications in ultrafast memories [130,131], oscillators [132] and logic circuits [133,134].

A central issue in any thin-film application of 1T-TiSe₂ is the synthesis of large-area ultrathin films. 1T-TiSe₂ prepared by mechanically exfoliating bulk crystals are small flakes with uncontrolled thickness [135-137]. Currently, large-area 1T-TiSe₂ films can only be grown by molecular beam epitaxy under ultrahigh vacuum (UHV) [53,138-140]. The development of a facile growth routine of 1T-TiSe₂ is desirable. In the past few years, ambient-pressure CVD has been developed for growing semiconducting TMDs thin layers such as MoS₂ and WSe₂ [98,141-146]. However, the CVD synthesis of 1T-TiSe₂ has not been realized experimentally as conventional CVD routine is not applicable. Recently, Wang *et al.* reported the growth of small 1T-TiSe₂ flakes down to 4.5 nm by reaction of titanium and selenium in a sealed ampoule [147]. However, the synthesis of large-area 1T-TiSe₂ by CVD remains elusive. In addition, facile synthesis of monolayer 1T-TiSe₂ is another outstanding issue that limits the exploration of correlated phenomena such as CDW and superconductivity of 1T-TiSe₂ in 2D limit. For example, the spectroscopic signatures of CDW phase in monolayer 1T-TiSe₂ remains to be clarified [137]. Here we demonstrate the synthesis of monolayer crystals and large-area films of 1T-TiSe₂ by salt-assisted ambient-pressure CVD. High-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM) characterization indicates that the as-grown films are highly crystalline 1T-TiSe₂. With low-temperature Raman spectroscopy technique, we investigated the spectroscopic signatures of CDW phase in CVD grown 1T-TiSe₂ with thickness down to 1.4 nm.

4.2 Experimental details

4.2.1 CVD growth of mono- and few-layer 1T-TiSe₂ crystals

Titanium oxide (TiO_x) precursor was prepared by heating titanium powder (Alfa Aesa, 325 mesh, 99.5%) at a temperature of ~820 °C for 15 min in air. The bottom dark grey powder was used as the TiO_x precursor. The synthesis of 1T-TiSe₂ was conducted in a 1 inch OD fused quartz tube heated by a Lindberg/Blue M (TF55035C-1) split-hinge furnace. The TiO_x (60 mg) and LiCl (2.5 mg, Sigma-Aldrich, 99.99%) precursors were mixed in an alumina boat and then positioned in the center of the furnace. 300 nm SiO₂/Si substrate was placed just above the powder mixture with the polished side face down. Selenium powder was placed at the upstream of the quartz tube where the temperature is ~260 °C during the reaction. 80 sccm (cubic centimeters per minute) Ar and 15 sccm H₂ were used as carrier gases. The furnace was heated to 600 °C in 14 min and maintained at that temperature for 13 min to allow the synthesis of 1T-TiSe₂ layers. After growth, hydrogen was turned off and the furnace was rapidly cooled to room temperature under 180 sccm Ar. The above growth condition allows the deposition of high-density monolayer 1T-TiSe₂ crystals, plus a small proportion of few-layer and even thicker 1T-TiSe₂ layers on the nearby SiO₂/Si substrates. All the Raman spectra in this work were collected on 1T-TiSe₂ layers grown under the same CVD condition as that described above.

4.2.2 CVD growth of large-area few-layer 1T-TiSe₂ films

Large-area 1T-TiSe₂ films were synthesized by increasing the amount of the precursors (TiO_x: 80 mg, LiCl: 3.5 mg) and setting the heating temperature of selenium at ~300 °C during growth period, while keeping all other growth parameters identical to the value mentioned above.

4.2.3 Preparation of STEM sample

A thin Poly(methyl methacrylate) PMMA film was spin-coated on top of 1T-TiSe₂ layers grown on 300 nm SiO₂/Si and cured at 130 °C for 6 min in an Ar glove box. The PMMA/TiSe₂ film was detached from the substrate by etching SiO₂ layer in hydrogen fluoride (HF). After rinsed in deionized (DI) water, it was scooped up by a TEM grid and dried in an Ar glove box. Finally, PMMA was removed by acetone.

4.2.4 Characterizations

AFM images were taken using the Asylum Research Cypher AFM in tapping mode. HAADF-STEM images were recorded using a probe corrected Jeol ARM200F using an inner collection angle of 68 mrad and a convergence angle of 30 mrad at 80 keV. Raman measurements were conducted in vacuum by a WITec system with 50 × objective lens and a 2400 lines/mm grating under 532 nm laser excitation. The laser power is kept below 0.6 mW. For low temperature Raman measurements, a temperature-controlled evacuated chamber cooled by liquid nitrogen is used for preventing the potential oxidation and local heating of the 1T-TiSe₂ samples under laser irradiation.

Figure 4.1 XRD pattern of the partially oxidized Ti powder TiO_x ($x \leq 2$). After oxidation, the powder contains Ti_2O , TiO and Ti .

4.3 Results and discussion

4.3.1 Synthesis of ultrathin 1T- TiSe_2 by salt-assisted CVD method

As described in the Experimental Section, we grew atomically-thin 1T- TiSe_2 layers on SiO_2/Si substrates by salt-assisted CVD under atmospheric pressure. Partially oxidized Ti powder (TiO_x , $x \leq 2$) was firstly prepared and used as the Ti precursor for 1T- TiSe_2 growth. X-ray diffraction (XRD) analysis suggested the obtained power consisted mainly of Ti_2O , TiO and Ti (Figure 4.1). The TiO_x and LiCl powder mixture was loaded into the center of a tube furnace. Selenium powder was positioned at upstream and the heating temperature was $\sim 260^\circ\text{C}$ during the reaction. A mixture of argon and hydrogen was used as the carrier gas and provided reducing atmosphere to support the reaction.

Previous studies suggested that a relatively low temperature near or below 600 °C should be used for synthesizing high-quality bulk 1T-TiSe₂ crystals [95,119,148]. For the melting salt-assisted CVD growth of ultrathin 1T-TiSe₂, LiCl was chosen because its melting point (~605 °C) is very close to the suitable growth temperature (~600 °C).

Figure 4.2 Atomic structure and characterization of atomic-thin 1T-TiSe₂ crystals.

(a) Top-down and side views of the atomic structure of 1T-TiSe₂. (b) Optical image of monolayer 1T-TiSe₂ crystals grown on a SiO₂/Si substrate. AFM measurement (inset) indicates the thickness of 1T-TiSe₂ is ~ 1.4 nm. (c) SEM image showing the 1T-TiSe₂ crystals with different shapes. (d) Raman spectra of the deposited 1T-TiSe₂ crystals with different thickness from 1.4 nm to 22 nm. (e) Illustration of the E_g and A_{1g} crystal lattice vibrations in 1T-TiSe₂. (f) The thickness dependence of Raman intensity of A_{1g} and E_g modes.

As shown by the optical image (Figure 4.2(b)), uniform ultrathin 1T-TiSe₂ crystals with triangular shape were deposited on a SiO₂/Si substrate. Atomic force microscope (AFM) height measurements (inset of Figure 4.2(b)) indicate the deposited 1T-TiSe₂

crystals have a typical thickness of ~ 1.4 nm. Given the fact that ultrathin 1T-TiSe₂ is unstable under ambient conditions and the AFM was measured in air, small oxidized particles may form on the surface of 1T-TiSe₂, which makes the measured thickness slightly larger than that of air-stable TMDs such as MoS₂ and WS₂. Therefore, the measured thickness of 1.4 nm could be assigned to a monolayer [136]. 1T-TiSe₂ typically crystallizes in a layered 1T CdI₂-type structure (Figure 4.2(a)). Ti atoms form a hexagonal sheet and are sandwiched by two layers of hexagonally packed Se atoms. In our experiment, we find that 1T-TiSe₂ layers usually crystallize in triangular and hexagonal configurations on SiO₂/Si substrates (Figure 4.2(c)).

Figure 4.3 Full Raman spectrum of CVD grown (a) monolayer and (b) 22 nm 1T-TiSe₂, showing the intensity comparison with silicon peak located at 520 cm⁻¹.

Raman spectroscopy was used to examine the lattice vibrational modes and to confirm the identity of the as-grown materials (Figure 4.2(d) and Figure 4.3). According to previous theoretical and experimental studies [148,149], there are two Raman-active modes in bulk 1T-TiSe₂, corresponding to A_{1g} and E_g symmetries with measured

frequencies centered at 195-203 cm^{-1} and $\sim 134 \text{ cm}^{-1}$, respectively. The E_g mode corresponds to in-plane vibration of Se atoms, while the A_{1g} mode corresponds to out-of-plane vibration, as indicated in Figure 4.2(e). Our Raman measurements were performed in vacuum to avoid the oxidation of samples in ambient conditions. The as-grown layers show two Raman peaks located at $\sim 134 \text{ cm}^{-1}$ and $\sim 198 \text{ cm}^{-1}$ (Figure 4.2(d)) which match very well with the E_g and A_{1g} optical phonon modes of 1T-TiSe₂. The weak peak at around 300 cm^{-1} might be attributed to the overlap of the two phonon processes of 1T-TiSe₂ and the overtone of acoustic phonons of the silicon substrate [119,148,150].

Figure 4.4 (a) Raman map of intensity of A_{1g} mode and (b) typical Raman spectrum of a few-layer triangular 1T-TiSe₂ crystal.

Moreover, Raman intensity map of a few-layer triangular 1T-TiSe₂ (Figure 4.4) indicates the Raman intensity is nearly uniform in each crystal. With the new developed synthesis technology, we were able to study the thickness-dependence of Raman spectra of CVD grown 1T-TiSe₂ down to monolayer. As plotted in Figure 4.2(f), the

intensities of A_{1g} and E_g modes of few-layer (7.9 nm) 1T-TiSe₂ are higher than those of monolayer and thick (22 nm) 1T-TiSe₂, similar to the case of MoS₂, which is attributed to the optical interference effect between thin layers and SiO₂/Si substrates [151].

Figure 4.5 Large area atomic-thin 1T-TiSe₂ films. (a) High-density 1T-TiSe₂ nucleation with triangular shape. (b) Optical (b) and SEM (c) images of the near-continuous 1T-TiSe₂ film. The inset of panel b and c indicates the film is made of approximately triangular 1T-TiSe₂ crystals. AFM height profile (lower inset in panel (b)) suggests that the film is ~4.5 nm thick. (d) Optical image of a large-area 1T-TiSe₂ films covering $\sim 5 \times 10^5 \mu\text{m}^2$.

In addition to individual 1T-TiSe₂ crystals, large-area 1T-TiSe₂ films can also be produced by adjusting the CVD parameters. By increasing the amount of precursors

and the heating temperature of Se, high-density 1T-TiSe₂ few-layers (Figure 4.5(a)) and nearly continuous film (Figure 4.5(b)) were deposited on SiO₂/Si substrates. AFM height measurement (inset of Figure 4.5(b)) indicates the film is about 4.5 nm thick. Uniformly compact and approximately triangular crystals are observed by optical and scanning electron microscopy (SEM) (inset of Figure 4.5(b) and (c)), which suggests that the large film is made of high crystalline 1T-TiSe₂ crystals.

Figure 4.6 SEM images of 1T-TiSe₂ nucleation with (a) and without (b) LiCl. The black dots in (a) are identified as 1T-TiSe₂ nuclei. No 1T-TiSe₂ nucleation can be observed for CVD growth without LiCl.

Figure 4.5(d) shows a $\sim 5 \times 10^5 \mu\text{m}^2$ large-area 1T-TiSe₂ film grown on a SiO₂/Si substrate. Meanwhile, it was noted that no nucleation of 1T-TiSe₂ on substrates could be observed without the addition of LiCl salt (Figure 4.6). The reason is that titanium oxide alone is not a suitable CVD precursor due to its very high melting point ($>1500^\circ\text{C}$). Previous studies indicate that salts (LiCl, NaCl, CaCl₂, etc.) react with molybdenum/tungsten oxides to give volatile oxychlorides [152-154]. Therefore, it is suggested that titanium oxychlorides may form as intermediates in our CVD reaction, and further react with selenium to produce 1T-TiSe₂. Due to the highly volatile property of titanium oxychlorides, the vapor pressure of titanium precursor is greatly enhanced, therefore making the synthesis of large-area 1T-TiSe₂ films on substrates possible.

The crystallographic structure and the chemical composition of the ultrathin 1T-TiSe₂ layers were further characterized by atomic resolution HAADF-STEM imaging and energy-dispersive X-ray spectrometry (EDX). The as-grown few-layer 1T-TiSe₂ on SiO₂/Si substrate was coated with a thin layer of PMMA, and then transferred onto a TEM grid by etching SiO₂ in HF. Figure 4.7(a) shows a lower magnification STEM image of the 1T-TiSe₂ film. Figure 4.7(b) shows an atomically resolved HAADF-STEM image of the dark area (as indicated by the yellow circle in Figure 4.7(a)). HAADF-STEM is sensitive to average atomic number of the elements, a bright contrast is associated to an element with a larger atomic number. The overall empty hexagonal structure is formed by the Se ($Z=34$) atoms. The lighter Ti ($Z=22$) atoms are just seen in the middle of the hexagon. The STEM image can be perfectly overlaid with the 1T-TiSe₂ atomic model (Figure 4.7(c)), which confirms the 1T structure of the as-grown

material. In addition, EDX-STEM mapping (Figure 4.7(d) and (e)) and spectrum (Figure 4.7(f)) of the area indicated by the red square frame in Figure 4.7(a) confirms the thin film is composed of Se and Ti atoms. The EDX maps show an excess of Se atoms which aggregate on the surface of the film, forming some rod-like structures, while Ti atoms are evenly distributed in the layer.

Figure 4.7 HAADF-STEM and EDX characterizations of the as-grown 1T-TiSe₂ layers. (a) A low magnified HAADF-STEM image showing a large region of 1T-TiSe₂. (b-c) Atomic resolution HAADF-STEM images and the associated structural model of the 1T-TiSe₂. (d) Se, and (e) Ti elemental EDX map and (f) averaged EDX spectrum of the region shown in (a). The Cu signal in the EDX spectra comes from the Cu TEM grid.

Figure 4.8 Raman spectra showing the CDW transition in the as-grown 1T-TiSe₂ for different thickness. (a, c, d) Raman intensity maps as a function of wavelength (horizontal axis) and temperature (vertical axis) for (a) 22 nm, (c) 3.7 nm and (e) 1.4 nm thick 1T-TiSe₂ crystals. (b, d, f) Representative Raman spectra of (b) 22 nm, (d) 3.7 nm and (f) 1.4 nm thick 1T-TiSe₂ samples at selected temperatures.

4.3.2 CDW phase transitions in ultrathin 1T-TiSe₂ layers

Understanding the dependence of CDW transition properties on film thickness is essential for any thin-film application. Therefore, we use low-temperature Raman spectroscopy to investigate the CDW transition in the as-grown 1T-TiSe₂. To avoid oxidation, the 1T-TiSe₂ samples were sealed within a chamber in an Ar glove box

immediately after CVD growth and then transferred for Raman test under vacuum. The total sample exposure time in air is less than 1 min.

Figure 4.9 CDW transition as a function of thicknesses. (a) Temperature-dependent scattering intensities of the A_{1g} -CDW mode showing that the mode vanishes around 187.5 K and 212.5 K for 22 nm and 3.7 nm thick 1T-TiSe₂, respectively. (b) Thickness–temperature phase diagram for 1T-TiSe₂ grown by CVD.

The variable-temperature Raman spectra of 1T-TiSe₂ with the thicknesses of 22 nm, 3.7 nm and 1.4 nm are displayed in the bottom panels in Figure 4.8. For ease of comparison, the results are further plotted as contour maps of Raman intensity versus temperature and frequency (top panels in Figure 4.8). For 1T-TiSe₂ samples at 80 K, in addition to the original A_{1g} and E_g peaks, two new modes including a clear and strong peak near 110 cm⁻¹ and a broad one near 75 cm⁻¹ emerge in the Raman spectrum (Figure 4.8(a) and (b)). According to the previous studies of bulk 1T-TiSe₂, these two modes were attributed to CDW amplitude modes (A_{1g} -CDW and E_g -CDW) which resulted from the folding of transverse acoustic phonons from the L point at the Brillouin zone

surface to zone center due to CDW superlattice formation [148,149]. Notably, for the monolayer (1.4 nm thick) 1T-TiSe₂, the A_{1g}-CDW Raman mode is still clearly visible, although slightly broader compared to thicker samples (Figure 4.8(e) and (f)). When temperature increases to higher than 80 K, the broad E_g-CDW peak at 75 cm⁻¹ becomes too broad to be discernible, while the A_{1g}-CDW mode remains detectable. Therefore, we use the A_{1g}-CDW mode as an indicator for the presence of CDW in CVD-grown 1T-TiSe₂.

The integrated intensities of the A_{1g}-CDW mode are displayed as a function of temperature in Figure 4.9(a). One can see that for a given sample, the intensity of CDW mode decreases with increasing temperature, and finally drops to zero, indicating the transition from CDW to normal phase. The CDW onset temperature is around 187.5 K for 22 nm thick 1T-TiSe₂, and increases to around 212.5 K for a 3.7 nm thick sample. The thickness–temperature phase diagram for CVD-grown 1T-TiSe₂ is summarized in Figure 4.9(b). It is noted that the CDW order is enhanced in few-layer 1T-TiSe₂ as compared with a much thicker (22 nm) sample.

The previous work on pressure dependent CDW phase transitions in 1T-TiSe₂ indicated a decreasing CDW transition temperature by applying a pressure [155]. The results strongly demonstrate that the improved interlayer coupling is unfavorable to the formation of CDW phase in 2D 1T-TiSe₂ layers. Indeed, the decreased CDW transition temperatures with the increasing sample thickness are comparable to the pressure induced CDW phase transitions. Moreover, it has been recently found a dramatically enhanced CDW transition temperature in atomically thin 2H-NbSe₂, which can be also

indicated by a much larger reduction of energy due to the CDW transition in monolayer 2H-NbSe₂ as compared to that in the bulk crystal [54]. The increased transition temperature with decreasing thickness is consistent with our experimental findings of 1T-TiSe₂, and it can be attributed to the enhanced electron-phonon interaction.

The slightly lower onset temperature (around 202.5 K, Figure 4.10) in 1.4 nm thick sample might result from the higher instability of monolayer 1T-TiSe₂ compared with few-layers. The short air exposure before Raman measurement as well as the weak laser irradiation during the measurement could induce disorders and suppress the CDW order in monolayer 1T-TiSe₂ [148]. To our knowledge, this is the first Raman spectroscopic observation of CDW phase transition in monolayer 1T-TiSe₂.

Figure 4.10 Temperature-dependent scattering intensity of the A_{1g} -CDW mode for a 1.4 nm thick 1T-TiSe₂. The mode vanishes around 202.5 K.

The as-grown few-layer 1T-TiSe₂ shows a transition temperature (~212.5 K) close to the reported value of MBE-grown 3-6 layer samples (~205 K) revealed by angle-

resolved photoemission spectroscopy and XRD [139,140]. Therefore, the crystalline quality of few-layer CVD-TiSe₂ is comparable with that prepared by MBE. Additionally, ARPES and XRD experiments suggest an enhanced transition temperature (~232 K) in MBE-grown monolayer 1T-TiSe₂, which is significantly higher than that of CVD monolayer 1T-TiSe₂ (~202.5 K) deduced from Raman spectroscopy. The main reason is probably that ARPES and XRD experiments were measured *in situ* after MBE growth under UHV, while Raman test was conducted *ex situ* after CVD growth in non-UHV environment. As discussed earlier, disorders might be easily induced in CVD monolayer 1T-TiSe₂ before and during Raman measurement, resulting in a lower CDW transition temperature.

4.4 Conclusions

In conclusion, we demonstrated the synthesis of mono- and few-layer 1T-TiSe₂ crystals and large-area ($\sim 5 \times 10^5 \mu\text{m}^2$) films on insulating SiO₂/Si substrates. HAADF-STEM imaging confirms the as-grown samples are highly crystallized 1T-phase TiSe₂. Low-temperature Raman measurement reveals the thickness-dependent CDW phase transition in the as-grown samples. The transition temperature of 212.5 K in few layers suggests the CVD 1T-TiSe₂ films crystallize in high quality. Our work has implications for the synthesis and development of other fascinating 2D charge ordering and superconducting materials (TaS₂, NbSe₂, TaSe₂, etc.).

Chapter 5 Visualizing the suppression of CDW states in graphene/NbSe₂ heterostructures

5.1 Introduction

The successful isolation of graphene from graphite has intrigued extensive exploration of the analogous layered transition metal dichalcogenides in solid-state physics because of their flexible properties and feasible revolution in modern technology [12,13]. Apart from the well-studied two-dimensional semiconducting MX₂ (e.g., M=Mo, W; X=S, Se), atomically thin metallic TMDs have a variety of prevailing collective many-body phenomena, including the competing charge density wave orders and superconductivity [17,43]. Understanding the electronic modulations of CDW states and the associated spontaneous periodic lattice distortions is significantly required to unveil the mechanism of coexisting phase diagram in low dimensions [54].

The layered TMD niobium diselenide (2H-NbSe₂), which is a hole metal at room temperature [156], has recently gathered tremendous attention as it provides an essential prototype for the exploration of the collective many-body electronic phases. Bulk 2H-NbSe₂ undergoes a second-order phase transition from metal state into incommensurate CDW state at 33 K, and superconductivity state appears when further decreasing the temperature below 7.2 K [47]. The successful fabrication of monolayer and few-layer 2H-NbSe₂ by mechanical exfoliation [54], molecular beam epitaxy [56] and chemical vapor deposition [157] methods has unraveled the extraordinary changes in these electronic states with the layer thickness. It is believed that the CDW instability

in 2H-NbSe₂ originates from the strong electron-phonon coupling [45,158,159]. As the number of layers approaches the single layer limit, the superconductivity is significantly suppressed and Ising pairing of spins emerges in monolayer NbSe₂ [160]. However, there arises the discrepancy of changes in CDW phase transition temperature. Specifically, Xi *et al.* reported a dramatically enhanced CDW transition temperature up to 145 K in mechanical exfoliated monolayer 2H-NbSe₂ [54]. Ugeda *et al.* successfully synthesized monolayer 2H-NbSe₂ films on epitaxial bilayer graphene *via* MBE, but observed a lower CDW phase transition temperature [56]. Furthermore, it is well known that the atomically thin 2H-NbSe₂ films suffer a severe degradation when exposed to the air. The ultrathin 2H-NbSe₂ sheets are often protected by covering hexagonal boron nitride, graphene or selenium layers in most studies [161-164], as the exotic layered structure enables the stacking of different 2D materials into heterostructures. Conversely, these van der Waals coupled heterostructures could straight give rise to a wide range of interactions at the interface including charge transfer [165] and band structure modulation [166,167], which may have great effects on the electronic instabilities. For instance, Li *et al.* discovered an increased CDW phase transition temperature in 1T-TiSe₂ flakes by encapsulation with h-BN films [135]. Unlike the insulator h-BN, graphene is a semimetal with abundant electronic properties, although the single layer graphene is believed to play a role, the study on CDW orders in metallic 2D TMDs with graphene protective layer is still lacking.

Direct characterization by *in situ* Raman spectroscopy and scanning tunneling microscopy/spectroscopy (STM/STS) can deliver a precise presence of the complex

CDW orders and facilitate a better investigation of the interplay between graphene and CDW materials. In this work, the heterostructures of stacking single layer graphene on 2H-NbSe₂ layers have been systematically investigated by using diverse techniques. Firstly, the CDW phase transition temperatures are clearly identified through *in situ* temperature dependent Raman spectroscopy. By comparison, the T_{CDW} of 2H-NbSe₂ is significantly lowered when covering a single layer graphene. Then, STM/STS is employed to identify the CDW orders and provides evidence of interlayer charge transfer within graphene/NbSe₂ heterostructures. To our best knowledge, this is the first visualizing of the interplay that graphene protective layer strongly affects the CDW states in 2D TMDs. Our discoveries remind us that we should carefully take into account the protective materials when we investigate the electronic instabilities of 2D TMDs. These observations in graphene/NbSe₂ heterostructures develop a direct and non-destructive routine to explore the proximity effect-induced tuning of CDW order transition, and further enrich the basic understanding of CDW formation mechanism in 2H-NbSe₂.

5.2 Experimental details

5.2.1 Exfoliation of niobium diselenide and graphene

The niobium diselenide (2H-NbSe₂) bulk crystals and macro-crystalline graphite used in this project are purchased from HQ graphene (a 2D material supplier company registered in the Netherlands, Europe) and NGS Naturgraphit GmbH (specialized as a graphite producer in Germany), respectively. With our modified mechanical exfoliation

method, the 2H-NbSe₂ and graphene flakes were firstly dropped onto Scotch tape, followed by further thinned down with several times tape folding. Secondly, the crystals on the tapes with suitable thickness were gently placed on the PDMS, which is pre-deposited on the glasses, hence few-layer 2H-NbSe₂ and monolayer graphene with relatively large sizes were obtained on the PDMS.

5.2.2 Transfer of 2H-NbSe₂ and graphene

To artificially deposit graphene on 2H-NbSe₂, we first transferred few-layer 2H-NbSe₂ with a large size onto SiO₂ (300 nm)/Si substrate by a facile method, which is to directly place sample/PDMS/glass on the SiO₂/Si substrate, followed by peeling off the PDMS/glass. Furthermore, using the optical microscope equipped with long working distance lens (10 × and 20 ×) and the micromanipulators, the monolayer graphene was transferred onto few-layer 2H-NbSe₂ with high fidelity. Different from those reported heterostructure transfer method, none of thermal heating was applied in the overall graphene/NbSe₂ heterostructures fabrication process, which aims to reduce the oxidation and etching of the crystals.

5.2.3 Characterizations

The temperature dependent Raman measurements were conducted using a WITec confocal magneto-Raman mapping system equipped with liquid helium cryostat (Attocube). An 532 nm Nd:YAG laser was used to excite the samples through 50 × objective lens with a laser spot size of around 1 μm. A thermal-meter was used to manipulate the temperature and a grating of 1800g/mm was utilized to integrate the

Raman signals.

The graphene/NbSe₂ heterostructures were also characterized using Omicron ultra-high vacuum low-temperature STM. The sample was transferred into the UHV analysis chamber to outgas at 120 °C for a few hours. The STM imaging and STS measurements were performed at $T = 77.8$ K. The dI/dV spectrum on Au (111) substrate was used as an STS reference for tip calibration. The STM and STS data were analyzed and rendered using Scanning Probe Image Processor (SPIP) software.

5.3 Results and discussion

5.3.1 Raman measurements of graphene/NbSe₂ heterostructures

2H-NbSe₂ is one of the most representative metallic TMDs with both CDW and superconductivity orders. It consists of hexagonal layers of niobium (Nb) atoms that are sandwiched between selenium (Se) layers in a trigonal prismatic crystal structure. Particularly, the hexagonal Nb plane plays a vital part in the formation of CDW as the atomic displacements create a $3a_0 \times 3a_0$ incommensurate CDW supercell with clusters of Nb atoms [168]. Figure 5.1(a) illustrates the schematic of fabricating the graphene/NbSe₂ heterostructures *via* our modified exfoliation and transfer method. The 2H-NbSe₂ flakes with different layers and monolayer graphene were pre-exfoliated onto PDMS. With the help of optical microscope and micromanipulators, we first transferred few-layer NbSe₂ film with large size onto SiO₂/Si substrate, followed by the stacking of monolayer graphene onto it.

Figure 5.1 Graphene/NbSe₂ heterostructures on SiO₂/Si substrate. (a) Schematic of fabricating the graphene/NbSe₂ heterostructures. (b) Optical images of prior 2H-NbSe₂ films and subsequent graphene/NbSe₂ heterostructures. The pristine 2H-NbSe₂ and heterostructures with different thicknesses are labelled as N and GN, respectively. (c) Non-polarized Raman spectra from graphene, pristine 2H-NbSe₂, and graphene/NbSe₂ heterostructures at room temperature.

Figure 5.1(b) shows the optical images of prior 2H-NbSe₂ films and subsequent graphene/NbSe₂ heterostructures. It is clear that no bubbles and wrinkles were left during this process. The intrinsic 2H-NbSe₂ (N), single layer graphene (G) and the corresponding graphene/NbSe₂ heterostructures (GN) are labelled in the optical image. The thickness and uniformity of the 2H-NbSe₂ flake were characterized by topological atomic force microscope scans. The height profile shows that a thickness of the thinnest part, which is indicated as N1 in Figure 5.1(b), is approximately 6.9 nm (see Figure 5.2).

Figure 5.2 AFM height profiles of few-layer 2H-NbSe₂ flake. (a), (b) and (c) AFM images of N1, N2 and N3 on the 2H-NbSe₂ flake. (d), (e) and (f) Cross section profiles of the areas indicated by the red lines. The obtained thicknesses of N1, N2 and N3 are 6.9 nm, 9.6 nm and 23.2 nm, respectively.

The non-polarized Raman spectra measured on graphene/NbSe₂ heterostructures at room temperature are shown in Figure 5.1(c). The two major Raman features centered at around 1580 cm⁻¹ and 2670 cm⁻¹ are distinctly observed in the Raman spectra of pure graphene layer, which can be easily assigned to the so-called G band and 2D band, respectively. The sharp and symmetric 2D band combined with a large intensity ratio of the 2D and G peaks make us certainly identify that our graphene sheet is single layer [169]. The Raman spectra of 2H-NbSe₂ film are dominated by sharp peaks of A_{1g} mode (out-of-plane vibrations) at about 230 cm⁻¹ and E_{2g} mode (in-plane vibrations) at 250 cm⁻¹ [170]. Below 200 cm⁻¹, there is a broad soft mode centered at 180 cm⁻¹ with the full width at half-maximum (FWHM) of approximate 50 cm⁻¹, which is associated with a second-order scattering process [54]. Surprisingly, we also found a wide hump emerging at higher frequencies (above 1000 cm⁻¹), according to the previous report, such broad band may be attributed to the absorption of atomically thin 2H-NbSe₂ film at the same range [54]. The coexisting Raman features of both 2H-NbSe₂ and graphene reveal the successful fabricated heterostructures.

To determine the precise CDW transition temperatures in our graphene/NbSe₂ system, the temperature dependent changes in Raman spectra were utilized due to the strong optical signatures of CDW phase transitions. Figure 5.3(a) shows the temperature dependent Raman spectra from the thinnest part of N1. The room temperature soft mode at around 180 cm⁻¹ undergoes a significant softening and becomes broader and broader as the temperature decreases. When the temperature approaches the CDW transition point (~150 K), this broad phonon mode starts freezing

and maintains in lower temperatures.

Figure 5.3 Temperature dependent Raman spectra obtained from graphene/NbSe₂ heterostructures. (a), (c) and (e) Temperature dependent Raman spectra of pristine 2H-NbSe₂. (b), (d) and (f) Temperature dependent Raman spectra of graphene/NbSe₂ heterostructures. The red dashed lines represent the evolution of soft mode at various temperatures, and indicate the CDW phase transition temperatures.

The perceptible features from room temperature down to 6 K were also observed in previous studies [54,170,171]. It is suggested that the broad soft mode is linked to the double resonant scattering of two longitudinal acoustic (LA) soft modes with opposite momentums, which involve the formation of CDW superlattice. As a result, such remarkable evolution could serve as a criterion to determine the CDW transition temperature. Interestingly, we discover a lower CDW phase transition temperature at about 120 K when the single layer graphene is introduced onto the thinnest 2H-NbSe₂ film indicated as GN1, although the similar Raman feature appears in Figure 5.3(b). It seems that the CDW order in 2H-NbSe₂ film is considerably suppressed by the single layer graphene.

In order to dig out the truth of this phenomenon, we further fitted the prominent Raman peaks of both 2H-NbSe₂ and graphene by Lorentz function. As apparent from Figure 5.4(a), the FWHM of A_{1g} mode from N1 initially increases upon cooling and reaches its maximum when the temperature comes close to 150 K. However, the linewidth in reverse decreases with the continuative cooling. Notably, the critical temperature of 150 K coincides with the CDW transition temperature determined by the soft mode. From the FWHM of A_{1g} mode collected on GN1, as shown in Figure 5.4(b), the maximum linewidth takes place at the temperature of 120 K, which is also in agreement with the CDW transition temperature of GN1. It is well known that the electron-phonon coupling plays a significant role in contribution to the phonon linewidth [172]. Our results reveal that the A_{1g} mode of 2H-NbSe₂ couples more tightly with electrons, and the alteration in the A_{1g} linewidth is a consequence of the CDW

states related electron-phonon coupling. Indeed, a straightforward and accurate approach is established to experimentally determine the T_{CDW} of 2H-NbSe₂.

Figure 5.4 The linewidth of A_{1g} mode as a function of temperature. Temperature dependent A_{1g} mode linewidth of pristine 2H-NbSe₂ (N1-N3) and graphene/NbSe₂ heterostructures (GN1-GN3). The temperatures where the kinks occur coincide with the CDW phase transition temperatures. The single layer graphene definitely suppresses the intrinsic CDW orders of the 2H-NbSe₂ layers. Error bars are evaluated from the standard deviation of the Raman fitting.

Moreover, the CDW transition temperatures for other parts with different thicknesses in our graphene/NbSe₂ heterostructures were identified in the same manner (see Figure 5.3(c-f) and 5.4(c-d)). The uncovered 2H-NbSe₂ layers always have the higher T_{CDW} than those of their corresponding heterostructures, even though all the CDW phase transition temperatures shift towards lower values upon increasing the thickness of 2H-NbSe₂ layers. The thickness dependent T_{CDW} realizes that the major mechanism for CDW states in atomically thin 2H-NbSe₂ is most likely attributed to the strong electron-phonon coupling [54].

Figure 5.5 CDW transition temperatures of graphene/NbSe₂ heterostructures. (a) The positions of 2D band collected from graphene/NbSe₂ heterostructures as a function of temperature, showing obvious kinks at around 120 K, 110 K and 80 K for GN1, GN2 and GN3, respectively. (b) The CDW transition temperatures from the pristine and covered 2H-NbSe₂ films. Error bars are evaluated from the standard deviation of the Raman fitting.

For the single layer graphene, the fitting results of 2D band are summarized in Figure

5.5(a) due to the weak features of G band. The frequencies of 2D band follow a drastically redshift with the increasing temperature, arising from the anharmonic terms in the lattice potential energy [173]. Importantly, we found that the evolution of peak frequency as a function of temperature was not a linear progress, exhibiting evident kinks at around 120 K, 110 K and 80 K for GN1, GN2 and GN3, respectively. All of these temperatures at which the kinks occur are well coincident with the CDW transition temperatures. Since the positions of 2D Raman peak can be modified through electrical doping by means of electron-phonon coupling [174], in turn, the formation of CDW orders in 2H-NbSe₂ film may modulate the carrier density of single layer graphene. The CDW transition temperatures from the various areas of heterostructures extracted using different criteria are listed in Table 5.1 and presented in Figure 5.5(b). The disparity of T_{CDW} between the intrinsic and covered 2H-NbSe₂ films becomes smaller and smaller with increasing the thickness of 2H-NbSe₂ layers, and almost vanishes in thick samples.

Table 5.1 The CDW transition temperatures (K) extracted using different criteria.

	N1	GN1	N2	GN2	N3	GN3
Soft mode	150	120	130	110	80	70
Kink of A _{1g} linewidth	150	120	130	110	80	80
Kink of 2D band		120		110		80

5.3.2 STM/STS images of graphene/NbSe₂ heterostructures

Figure 5.6 STM images of pristine 2H-NbSe₂ samples at the temperature of 77.8 K. The STM images (a) and the corresponding 2D-FT transform image (b) at the bulk 2H-NbSe₂ sample. The STM images (c) and the corresponding 2D-FT transform image (d) at the thick 2H-NbSe₂ sample indicated as N3 area in Figure 5.1(b).

The low temperature STM measurements were also carried out to analyze the CDW orders and interlayer coupling in the graphene/NbSe₂ systems. Figure 5.6 shows the STM images with resolution of atomic level taken on the 2H-NbSe₂ layers without

covering graphene at a temperature of 77.8 K. Figure 5.6(a) and (b) show a standard STM and corresponding 2D-Fourier transform (FT) images at the bulk 2H-NbSe₂. It exhibits a typical metal phase at low temperature, in which the surface selenium atoms form a hexagonal lattice to display a 1×1 surface with lattice spacing of 3.44 Å. Although some Se defects or interstitials are visible, the density of such defects is very low, which indicates a best crystal preparation. When we move STM tip to image the thick area of 2H-NbSe₂ on the heterostructures (N3 labeled in Figure 5.1(b)), there appears a perfect long-range incommensurate (3×3) charge-ordered CDW phase, as shown in Figure 5.6(c) and (d). Here, it is clearly confirmed that a CDW phase transition happened depending on the flake thickness. That is in a good agreement with the previous observation that CDW phase transition temperatures shift towards lower values upon increasing the thickness of 2H-NbSe₂ layers.

Furthermore, in order to explore the effect of single layer graphene, we have imaged the combined junction between the pure graphene layer and the graphene/NbSe₂ heterostructure (marked as G and GN3 areas in Figure 5.1(b)). After stacking a single layer graphene on the 2H-NbSe₂ flake, the atom-resolved STM images were taken at GN3 area, where the thickness of 2H-NbSe₂ is same as N3 area. Figure 5.7(a) is a topographic image of graphene/NbSe₂ heterostructure, the graphene domain and graphene/NbSe₂ heterostructure domain are separated by an obvious grain boundary, which indicates that the fabricated graphene/NbSe₂ heterostructure is of very high quality. In Figure 5.7(b), the underneath 2H-NbSe₂ flake was imaged unambiguously after changing the tunneling condition.

Figure 5.7 STM/STS images of pure graphene and heterostructure boundary area.

(a) STM image from the interface between graphene and GN3 area. (b) Close examination of STM image from GN3 area. The 2H-NbSe₂ layer covered by graphene shows the random CDW superlattice, indicating the distinct suppression of CDW state due to the upper graphene layer. STM (c) and STS (d) images of the top layer graphene. The arrow represents the position of Dirac point E_D . Tunneling parameters: $V = 0.8$ V, $I = 500$ pA, $P = 3.3 \times 10^{-11}$ mbar, $T = 77.8$ K.

In contrast to the 2H-NbSe₂ flake of N3 area, the long-range ordered CDW state of 2H-NbSe₂ was broken into many short-range ordered patches after introducing the graphene top layer. The random CDW domains very resemble the phenomena that were observed in 2H-NbSe₂ crystals intercalated with metal atoms [175]. The results of STM measurements confirm that the CDW phase transition temperature T_{CDW} was lowered

and the CDW phase coherence was suppressed after covering a graphene layer. Figure 5.7(c) shows a perfect hexagonal atomic structure of the top layer graphene. The STS dI/dV spectrum taken on the top graphene layer is shown in Figure 5.7(d). A gap-like feature was observed in the tunneling conductance spectrum, leading to the asymmetry of spectrum about the Fermi energy (E_F). This local conductance minimum can be attributed to the inelastic tunneling to the Dirac point (E_D) of graphene, which is also a minimum in the density of states, and has been identified as the Dirac point [176-179]. Remarkably, the dI/dV spectrum exhibits the Dirac point of top graphene layer shifted to a positive value, which agrees well with the previous reports of single layer graphene on negative gate voltage [176,177]. Such Dirac point located at $\sim +0.4\text{V}$ unambiguously manifests a strong p-type doping by the bottom 2H-NbSe₂ layer. In consequence, it seems that the interplay of charge transfer occurred between the single layer graphene and 2H-NbSe₂ layers, which has a significant impact on the CDW instabilities.

5.3.3 Discussion

The prominent suppression of CDW orders observed in our experiments is very likely a result of screening effect in the heterostructure system, whereby the dimensionless electron-phonon interaction strength (i.e. electron phonon coupling constant or density of states effect) is being modified downwards by charge transfer between the single layer graphene and the 2D 2H-NbSe₂.

Work function is quite significant to describe the surface properties of a material. It plays a vital role in charge transfer at the interfaces when different two materials are

contacting together. In 2D system, charge transfer is the most common interlayer coupling since the layered structure of 2D materials makes it possible to fabricate various heterostructures. The work function of 2H-NbSe₂ crystals has been estimated as 5.9 eV experimentally [180], while the single layer graphene was reported to have the work function in a range of 4.6 eV by previous studies [181-183]. Hence, the electrons are more likely to transfer from graphene to 2H-NbSe₂ layers when covered by a proximal graphene.

Figure 5.8 2D band frequencies from both pure graphene and heterostructures at various temperatures.

To verify the direction of charge transfer in our heterostructures, the frequencies of graphene Raman peaks were analyzed by Lorentz fitting. It has been well identified in top-gated graphene transistor that the positions of both G band and 2D band are highly

sensitive to the electron or hole doping [184,185]. Specifically, the behavior of G band position exhibits blue-shift when the single layer graphene is doped by either holes or electrons, whereas the 2D band softens for electron doping and shows distinct stiffening for hole doping. As a result, the frequencies of 2D band take the responsibility to confirm the charge transfer direction. Figure 5.8 summarizes the 2D band positions from both pure graphene and heterostructures at various temperatures. Surprisingly, the 2D bands of all the heterostructures display a remarkable blue shift compared to that of pure single layer graphene, which clearly demonstrates the p-type doping of graphene when stacked on the 2H-NbSe₂ layers.

The experimental results presented above provide a strong evidence that the electrons were transferred from the top layer graphene to the bottom 2H-NbSe₂ layer. As a canonical hole metal, the electron doping could dramatically decrease the hole density of 2H-NbSe₂, the carrier density and the electronic density of state near the Fermi surface as a consequence modulate the electron-phonon coupling [156], resulting in the suppression of CDW transitions.

5.4 Conclusions

We investigated the CDW phase transitions of 2H-NbSe₂ layers in graphene/NbSe₂ heterostructures, to our best knowledge, which is the first visualization of the negative effect on CDW orders by covering a top layer graphene. We firstly employed the *in situ* low temperature Raman spectroscopy to determine the CDW phase transition temperatures of both pristine 2H-NbSe₂ and heterostructures. All the evidences,

including the evolution of soft mode, the kink of A_{1g} linewidth, even the peak positions of 2D band, demonstrate that the top layer graphene lowers the transition temperature T_{CDW} . Following, the STM images exhibit the perfect long-range CDW order in pristine 2H-NbSe₂, which is broken by the single layer graphene. In addition, the STS dI/dV spectrum reveals a strong p-type doping of the top graphene layer. The Raman and STM/STS studies of the CDW orders in graphene/NbSe₂ heterostructures indicate that the CDW states suppression can be likely attributed to the interlayer charge transfer between the single layer graphene and 2H-NbSe₂ layers. The results suggest that the protective materials should be chosen very carefully in the future research, and also open up a new area to explore collective electronic phases such as CDW and superconductivity by creating multiple heterostructures.

Chapter 6 In-plane anisotropic thermal conductivity of few-layer transition metal dichalcogenide Td-WTe₂

6.1 Introduction

Layered transition metal dichalcogenides, whose transition metal atoms are sandwiched between two chalcogen layers, have drawn widespread attention in the field of condensed matter physics [12]. These van der Waals materials exhibit fascinating optical, electronic and thermal properties when they are thinned down from bulk crystal to atomic-thin layer [13,17,27,186,187]. In particular, the trigonally coordinated 2H-MX₂ (M=Mo, W; X=S, Se) displays semiconducting nature and undergoes a transition from indirect band gap to direct band gap as the number of layers decreases to monolayer [22,23,70,188]. On the other hand, one of the extraordinary electronic properties in octahedrally coordinated 1T phase is charge density wave. For example, the CDW phase transition points of 1T-TaS₂ move to lower temperatures while decreasing the thickness [52,59].

In contrast to these familiar TMDs, naturally formed tungsten ditelluride (WTe₂) proves to have its lowest energy in a Td-polytype, which is the distorted 1T phase and exhibits semimetallic properties [189-191]. Excitingly, the nonmagnetic Td-WTe₂ has been brought into the sight of researchers since the recent experiments discovered its extremely large and non-saturating positive magnetoresistance at low temperature, and the magnetoresistance even increased to $1.3 \times 10^7\%$ at 60 T without any sign of saturation [192]. The size of the electron pocket in Td-WTe₂ is verified to be

fundamentally same as that of hole pocket by angle-resolved photoemission spectroscopy [193,194] and Hall effect [195] measurements. In addition, Zhou *et al.* observed that Td-WTe₂ could be completely transformed into monoclinic 1T' phase under high pressure [18], and the superconductivity was found in 1T' phase when the pressure was higher than 15.5 GPa [18,196]. Very recent studies recognized that Td-WTe₂ is an ideal contact for two-dimensional semiconductors to effectively tune the Schottky barrier due to its comparatively low work function [197]. All these intriguing physical properties show the most promising applications of Td-WTe₂ in nano-scale magnetic devices. It is known that the thermal transport properties are of great significance in design and operation of these ultra-thin nanodevices [198]. For instance, thermal conductivity plays a vital part in adjusting the heat dissipation and thermoelectric efficiency. One effective approach to improve the performance of thermoelectric and thermal insulating materials is to lower the thermal conductivity with no impact on electronic properties [199,200]. Specifically, ultralow thermal conductivity is central to avoid the hot reflux from the cool end to the heat source, which is crucial to make an enormous improvement in energy conversion efficiency [201]. Semimetal Td-WTe₂ is theoretically predicted to have low thermal conductivity because of its heavy atom mass and low Debye temperature, which makes it a predominant candidate in thermoelectric materials [202,203]. Nonetheless, the studies on the in-plane thermal conductivity of Td-WTe₂ are still at the initial stage. The recent first-principles calculations predicted that the anisotropy existed in the in-plane thermal conductivity of bulk Td-WTe₂ along different lattice directions, with the maximum

value along [010] direction (*a*-axis) whereas the minimum one in [100] direction (*b*-axis) [204]. On the contrary, Ma *et al* revealed that the calculated anisotropic thermal conductivity of monolayer Td-WTe₂ had its maximum value along *b*-axis [205]. The only experimental results to date indicated that the lateral thermal conductivity of Td-WTe₂ thin flake was smaller than 2 Wm⁻¹K⁻¹ at room temperature without any anisotropy [206,207]. Although, the distinct crystal structure of Td-WTe₂ implied notable anisotropic properties [208-210], experimental demonstration of such in-plane anisotropic thermal conductivity is still lacking, even in layered 2D TMDs. Moreover, the large discrepancy in both theoretical calculations and experiments also requires further investigation urgently.

The up-to-date Raman spectroscopy has been the most conventional and nondestructive technique for characterization of thermal conductivity in 2D materials, such as graphene [8,211,212], MoS₂ [186,213,214], WS₂ [187] and so on. The focused laser enables the anharmonic lattice vibrations and thermal expansion due to the temperature rising [173,215]. The thermal conductivity can be then extracted by combining the temperature and laser induced phonon softening. In this work, suspended Td-WTe₂ layers with different thicknesses have been systematically investigated by using various types of optical probes. Firstly, the crystal orientation (zigzag and armchair directions) is clearly identified by linear polarization dependent Raman spectroscopy and second harmonic generation (SHG). Then, *in situ* micro Raman spectroscopy is employed to reveal the thermal conductivities of the layers. To our best knowledge, the remarkable in-plane anisotropic thermal conductivities and layer

dependency of such 2D systems are experimentally explored for the first time. Our findings remind us that we should carefully consider the anisotropic thermal effects when we develop 2D Td-WTe₂ nano-scale magnetic devices. The observation of the in-plane anisotropic thermal conductivities in Td-WTe₂ layers is also the first demonstration of such interesting anisotropy in 2D TMDs, which will open up numerous opportunities for further studies and applications of the next-generation thermoelectric devices based on the promising 2D TMDs.

6.2 Experimental details

6.2.1 Sample preparations

Bulk Td-WTe₂ crystals were synthesized by chemical vapor transport technique. The W powder and Te lumps were sealed in the quartz tube together with iodide, which was used as transporting agency. The whole growth process was kept in vacuum with 10^{-6} Torr. To avoid the transportation of the samples, the grown zone and reaction zone were set at 850 and 750 °C for 24 hours, respectively. After that, the temperature gradient was achieved by programing the reaction zone and the growth zone at 950 and 850 °C for 7 days, respectively. Indeed, the single crystals were obtained after naturally cooling the furnace to the room temperature.

The few-layer Td-WTe₂ flakes were mechanically exfoliated from the bulk crystals onto the PDMS first. After locating the samples by optical microscope, the selected films were then transferred on the holes chemically etched on the 300 nm SiO₂/Si substrate through dry transfer method.

6.2.2 Raman spectra measurements

A WITec Alpha300 Series confocal Raman system with 2400 g/m grating was used to perform the Raman measurements. The spectral resolution is 0.9 cm^{-1} . All the Raman spectra were collected under backscattering configuration with a 532 nm excitation laser.

In the polarized dependent Raman measurements, a $100\times$ objective lens of NA = 0.95 was used, and the laser spot size is around $0.5 \mu\text{m}$ in diameter. The linear polarized configurations were achieved by placing two polarization analyzers in front of the input laser fiber and the output fiber, respectively. To obtain the angle dependent Raman spectra, the incident laser polarization was fixed with rotating the samples.

For *in situ* temperature dependent Raman measurements, a $50\times$ long working distance objective lens of NA = 0.55 was used. The temperature from 80 K to 300 K were controlled by a Linkam optical DSC600 system. The sample was sealed in a vacuum chamber and cooled by liquid nitrogen.

6.2.3 Second harmonic generation measurements

The SHG measurements were carried out using micro-Raman spectrometer (Horiba-HR800) in reflection geometry with laser excitation perpendicular to the substrate. A mode-locked Ti/Sapphire oscillator was used as the pumping source at 800 nm wavelength (Spectra-Physics, 80 MHz, 100 fs). With a $100\times$ objective, the pumping light was focused to a spot size of $\sim 3 \mu\text{m}$ in diameter on the sample. For SHG polarization measurement, polarizations of excitation and detection were consistent and fixed, while the sample stage was rotated to achieve the angle-resolved SHG spectra.

Figure 6.1 *Crystal structure and Raman vibrational modes of Td-WTe₂. (a) Top and side views of Td-WTe₂ crystal structure. The side view indicates that Td structure is a distorted octahedral 1T phase. The adjacent layers are rotated 180° with each other, forming AB stacking. The Wigner-Seitz cell is highlighted by red rectangle. (b) Atomic displacements and irreducible representations of observed Raman-active modes in our experiments. The arrows display the motions of W and Te atoms.*

6.3 Results and discussion

6.3.1 Crystal structure of few-layer Td-WTe₂

As shown in Figure 6.1(a), tungsten ditelluride normally crystallizes into an orthorhombic Td structure with the point group C_{2v}^7 , which is a distorted octahedral 1T phase [189]. The side views of Td-WTe₂ crystal indicate that the Td-WTe₂ layers are AB stacking. Within the single Td-WTe₂ layer, the bottom tellurium (Te) atomic layer is rotated 180° with regard to the upper tellurium layer, which significantly lowers the lattice symmetry in comparison with the original 1T structure [190]. However, the tungsten (W) atoms shift off-centered from their ideal positions both in *ab* plane and along *c*-axis, and shape W-W zigzag chains along *a*-axis, exhibiting analogous metallic bonding in the tungsten metal [216]. Whereas, the vertical shift of Te atoms along *c*-axis also results in the noncoplanar layers and forms the puckering of both W and Te atomic layers, as demonstrated in Figure 6.1(a).

Bulk Td-WTe₂ belongs to the space group $Pmn2_1$ with 12 atoms in the unit cell [217]. The symmetry analysis denotes that there are 33 Raman-active modes at the center of the Brillion zone due to the low symmetry structure, and their irreducible representations can be expressed as:

$$\Gamma_{\text{bulk}}=11A_1+5B_1+6A_2+11B_2. \quad (6.1)$$

Since the Raman measurements in our experimental configurations are conducted on the *ab* plane, the Td structure symmetry only allows 17 Raman-active modes of (11A₁+6A₂). While the incident laser beam is parallel to the *a*- or *b*-axis, the rest 16 Raman-active modes of (5B₁+11B₂) can become detectable [208]. Figure 6.1(b) reveals

the atomic displacements of observed Raman-active modes in the unit cell of the bulk Td-WTe₂ crystal. Unlike the usual 2H or 1T phase 2D TMDs (e.g. 2H-MoS₂) whose Raman-active modes vibrate uniformly either in the plane (E_{2g} mode) or out of the plane (A_{1g} mode) [218], it can be clearly seen that the directions of most lattice vibrations in Td-WTe₂ include a certain angle relative to the atomic layers.

Figure 6.2 Crystal orientations and unpolarized Raman spectrum of few-layer Td-WTe₂. (a) The optical image of few-layer Td-WTe₂ flake with well-defined edges. The red point presents the laser spot. (b) Schematics of laser polarization and Td-WTe₂ crystal directions in polarized Raman measurements. The W-W zigzag chains are emphasized by pink lines. The green arrows indicate the laser polarization. (c) The non-polarized Raman spectrum measured at room temperature.

6.3.2 Anisotropic optical property of few-layer Td-WTe₂

Figure 6.2(a) illustrates the optical microscope image of mechanical exfoliated Td-WTe₂ flakes on 300 nm SiO₂/Si substrate. The purple film (indicated as A) can be classified as few-layer Td-WTe₂ by optical contrast, and shares the same crystalline orientation with that of adjacent thicker part (indicated as B). We choose this piece of sample because it has two near-perfect perpendicular sides, which are labelled by x - and y -axes. Figure 6.2(b) shows the schematics of laser polarization and Td-WTe₂ crystal directions in polarized Raman measurements, where the a -axis, which contains the W-W zigzag chains, can be defined as zigzag direction, while the vertical b -axis is expressed as armchair direction. In this work, we fixed the polarization of incident laser, and set θ as the angle between the polarization of incident laser and the crystal principal a -axis that could be constantly altered by rotating the sample. The non-polarized Raman spectrum of Td-WTe₂ flakes measured on part A at room temperature is shown in Figure 6.2(c). The seven prominent Raman peaks centered at 83.5 cm⁻¹, 90.6 cm⁻¹, 109 cm⁻¹, 119 cm⁻¹, 133 cm⁻¹, 164 cm⁻¹ and 214 cm⁻¹ are observed and assigned to ²A₁, ²A₂, ³A₂, ³A₁, ⁴A₁, ⁸A₁ and ¹⁰A₁ symmetries, respectively [208].

The effective Raman tensors of observed A₁ and A₂ modes in Td-WTe₂ crystal have the form of [208]

$$R(A_1) = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}, \quad R(A_2) = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (6.2)$$

In our experimental configuration, the Raman measurements were conducted on the ab plane, and the sample rotated with an angle θ relative to x -axis. As a result, the rotation matrix and its inverse matrix can be written as [219]

$$r = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad r^T = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (6.3)$$

Figure 6.3 Angle dependent Raman spectra of few-layer Td-WTe₂. The evolutions of Raman spectra with rotating the few-layer Td-WTe₂ flake (as shown in Figure 6.2) from 0° to 360° under parallel polarization configuration (a) and perpendicular polarization configuration (b).

Then the transformation of the effective Raman tensors to the rotation coordination can be derived as [220]

$$\begin{aligned}\tilde{R}(A_1) &= rR(A_1)r^T = \begin{pmatrix} a \cos^2 \theta + b \sin^2 \theta & \frac{(a-b)}{2} \sin 2\theta & 0 \\ \frac{(a-b)}{2} \sin 2\theta & a \cos^2 \theta + b \sin^2 \theta & 0 \\ 0 & 0 & c \end{pmatrix} \\ \tilde{R}(A_2) &= rR(A_2)r^T = \begin{pmatrix} -d \sin 2\theta & d(1 - 2 \sin^2 \theta) & 0 \\ d(1 - 2 \sin^2 \theta) & d \sin 2\theta & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (6.4)\end{aligned}$$

Owing to the Placzek approximation, the intensity of Raman modes under linear polarized configuration is described by [221]

$$I \propto |e_i \cdot \tilde{R} \cdot e_s|^2. \quad (6.5)$$

Among them, the electric polarization vector of the incident laser beam is given by $e_i = (\cos \alpha \quad \sin \alpha \quad 0)$, where α is the polarization angle of the incident laser. While the polarizations of scattered light are $e_s = \begin{pmatrix} \cos \alpha \\ \sin \alpha \\ 0 \end{pmatrix}$ and $\begin{pmatrix} -\sin \alpha \\ \cos \alpha \\ 0 \end{pmatrix}$ under parallel and cross polarization configurations, respectively. Consequently, the angle dependent Raman intensities of A_1 and A_2 modes can be obtained.

For parallel configuration ($e_i \parallel e_s$):

$$I_{A_1} \propto [b + (a - b) \cos^2(\alpha - \theta)]^2, \quad (6.6)$$

$$I_{A_2} \propto [d \sin 2(\alpha - \theta)]^2. \quad (6.7)$$

For perpendicular configuration ($e_i \perp e_s$):

$$I_{A_1} \propto \left[\frac{(b-a)}{2} \sin 2(\alpha - \theta) \right]^2, \quad (6.8)$$

$$I_{A_2} \propto [d \cos 2(\alpha - \theta)]^2. \quad (6.9)$$

In this work, the polarization angle of the incident laser is parallel to the x -axis ($\alpha = 0^\circ$). Indeed, the above Raman intensities can be revised as follows:

$$\begin{aligned}
I_{A_1}^{\parallel} &\propto [b + (a - b) \cos^2 \theta]^2, \\
I_{A_2}^{\parallel} &\propto [d \sin 2\theta]^2, \\
I_{A_1}^{\perp} &\propto \left[\frac{(b-a)}{2} \sin 2\theta \right]^2, \\
I_{A_2}^{\perp} &\propto [d \cos 2\theta]^2.
\end{aligned} \tag{6.10}$$

Figure 6.4 Angle dependent Raman contour maps and polar plots of few-layer WTe₂.

The contour maps of angle dependent Raman intensity of Td-WTe₂ flake under parallel-polarized configuration (a) and cross-polarized configuration (c). (b) and (d) The polar plots and fitted curves of ⁸A₁ and ³A₂ peak intensities in two configurations. In $e_i \parallel e_s$, the intensity of ⁸A₁ mode exhibits two-fold symmetry, while the intensity of ³A₂ peak displays four-fold symmetry. In $e_i \perp e_s$, the angular dependences of both ⁸A₁ and ³A₂ modes show four-fold symmetric patterns.

From the derived formulas, it can be clearly seen that the Raman intensity of A₁

modes exhibits a 180° variation period in $e_i \parallel e_s$ configuration, and reaches the maximum values when the incident laser polarization is parallel to the zigzag direction (a -axis) [222]. Conversely, the A_2 modes show a 90° variation period with maximum values at 45° , 135° , 225° and 315° . In $e_i \perp e_s$ configuration, the Raman intensities of both A_1 and A_2 modes display the 90° variation period. However, the four-lobed shape of A_1 mode rotates 45° with respect to that of A_2 mode.

The angle dependent polarized Raman spectra are shown in Figure 6.3, and their Raman peak intensities as a function of the rotation angle θ are shown in Figure 6.4 and Figure 6.5. It is found that the intensities of nearly all the Raman peaks demonstrate a periodical change as rotating the sample. Figure 6.4(a) displays the contour map of angle dependent Raman intensity under parallel-polarized configuration, where the incident light polarization (e_i) is parallel to the scattered light polarization (e_s). With the sample rotated from 0° to 360° , the intensities of A_1 modes exhibit two-fold symmetry, while the intensities of A_2 modes display four-fold symmetry. For example, the polar plots and fitted curves of 8A_1 peak intensities clearly demonstrate that its intensity reaches the maximum value at $\theta=0^\circ$ and 180° , as illustrated in Figure 6.4(b), the intensity of 3A_2 mode has four maximums at 45° , 135° , 225° and 315° . In cross-polarized configuration ($e_i \perp e_s$), the angular dependences of both A_1 and A_2 modes show four-fold symmetric patterns (Figure 6.4(c-d) and Figure 6.5). Nevertheless, the polar plots and fitted curves in Figure 6.4(d) reveal that the four-lobed shape of 8A_1 mode is rotated by 45° with respect to that of 3A_2 mode. Our experimental results are in strict accordance with the relationship between Raman tensors and laser polarizations,

and imply the noteworthy anisotropic structure of Td-WTe₂, which could be used to conveniently and rapidly identify the zigzag and armchair directions of Td-WTe₂.

Figure 6.5 Polar plots of few-layer Td-WTe₂ Raman peak intensities. Polar plots and fitted curves of Raman intensities for observed A₁ and A₂ modes as a function of sample rotation angle in both parallel and perpendicular polarization configurations.

6.3.3 Identifying the crystalline orientations of suspended Td-WTe₂

Considering the obvious anisotropy of lattice vibrational strength (phonon mode intensity) revealed by the angle dependent polarized Raman measurements, we hypothesize that thermal conductivity of Td-WTe₂ may also exhibit the anisotropy. To further investigate the anisotropic thermal conductivities of few-layer Td-WTe₂, it is of great significance to identify the crystalline orientation of the samples first.

Figure 6.6 Schematic of experimental setup on suspended Td-WTe₂. (a) The optical microscope image of suspended few-layer Td-WTe₂ flake on array of holes. The angle between the laser polarization and the sample edge is defined as θ . (b) Schematic diagram of experimental setup for thermal conductivity measurements. The black arrow represents the incident laser polarization.

The exfoliated few-layer Td-WTe₂ flake was transferred onto the holes of 2.8 μm in radius etched on SiO₂/Si substrate, as shown in Figure 6.6(a). The thickness and uniformity of the Td-WTe₂ flake were characterized by topological atomic force microscope scans. The height profile shows that a thickness of the thinnest part is approximately 11.2 nm (see Figure 6.7). Figure 6.6(b) depicts the schematic diagram

of our experimental setup. The thermal conductivities were obtained by Raman measurements on the suspended few-layer Td-WTe₂ samples with the polarization of incident laser beam along both zigzag and armchair axes.

Figure 6.7 *AFM height profiles of suspended few-layer Td-WTe₂. (a) The optical microscope images of suspended Td-WTe₂ flakes with different thicknesses. The red rectangles represent the AFM measurement areas. (b) The height profiles obtained from AFM measurements indicate that the thicknesses of the suspended H1, H2, H3 and H4 are 11.2 nm, 21.1 nm, 27.0 nm and 12.6 nm, respectively.*

To determine the crystalline orientations, we observed the variations of Raman peaks and SHG intensities in parallel-polarized configuration when rotating the Td-WTe₂ flake with respect to the sample edge (defined as x -axis). The contour map and polar plots of angle dependent Raman intensity under parallel-polarized configuration for the thinnest flake are shown in Figure 6.8(a) and (b), respectively.

Figure 6.8 Angle dependent Raman peaks and SHG intensities of suspended few-layer Td-WTe₂. (a) The contour map of angle dependent Raman intensity of the 11.2 nm-thick Td-WTe₂ flake under parallel-polarized configuration. (b) The polar plots and fitted curves of the Raman intensities for four dominating peaks. The variation periods and the maximum value angles of Raman intensities clearly manifest that the x-axis of the sample edge is the zigzag direction. (c) The polar plots of the parallel polarization dependent SHG intensity for the thinnest Td-WTe₂ flake.

The 2A_2 mode reaches its maximum values at 45° and 135°, showing the four-fold symmetry, while the 2A_1 , 8A_1 and ${}^{10}A_1$ modes exhibit two-fold symmetric patterns. However, both 2A_1 and ${}^{10}A_1$ modes achieve their maximum values at 90°, the highest values of 8A_1 mode appear at 0° and 180°. The variation periods and the maximum

value angles of Raman intensities are strongly consistent with the previous experiments starting initially along the a -axis [208]. To further verify the crystalline orientation, we also conducted the polarization dependence of second harmonic generation. The initial excitation angle was also aligned with the x -axis of the sample. In Figure 6.8(c), the polar plots of SHG angular dependence for the 11.2 nm-thick Td-WTe₂ flake were obtained under parallel polarization. The SHG intensity has a well-defined two-fold symmetric pattern with its zero value at 0° and 180°, which evidently implies that the zigzag direction is exactly along the x -axis [223]. The periodic results clearly manifest that the x -axis along the sample edge is the zigzag direction. Here, we identified the crystalline orientations of few-layer Td-WTe₂ by combining the angle dependent Raman spectroscopy and SHG measurements, and this method could have a great application prospect to other 2D materials.

6.3.4 Anisotropic thermal conductivity of suspended Td-WTe₂

Taking into account the anisotropy in thermal conductivity, the temperature dependent Raman spectra were collected along both pre-determined zigzag and armchair directions, where the excitation laser polarizations are aligned to zigzag and armchair axes, respectively. Here, we only focused on the two pronounced Raman peaks at around 164 cm⁻¹ and 214 cm⁻¹. Figure 6.9(a) shows the Raman spectra along the zigzag-axis of the 11.2 nm-thick Td-WTe₂ flake with the temperature range from liquid nitrogen to room temperature. Both the ⁸A₁ and ¹⁰A₁ peaks follow a drastically redshift with the increasing temperature, resulting from the anharmonic lattice vibrations and the thermal expansion [217].

Figure 6.9 Temperature and laser power dependent Raman spectra of 11.2 nm-thick suspended Td-WTe₂. Temperature dependent (a) and excitation laser power dependent Raman spectra (c) of the 11.2 nm-thick suspended Td-WTe₂ with incident laser polarization fixed along zigzag direction. The linear fitting of the ¹⁰A₁ peak frequency as a function of temperature (b) and excitation laser power (d) along both zigzag and armchair directions.

The Lorentz fitting of these two Raman modes indicates that the ¹⁰A₁ mode at around 214 cm⁻¹ is more sensitive to the temperature change comparing to the ⁸A₁ mode. This effect could be attributed to the high sensitivity of ¹⁰A₁ mode to the decrease of the interlayer coupling with increasing temperature [217]. Thus, the ¹⁰A₁ mode was chosen for the further thermal conductivity study. The evolution of peak frequency ω as a

function of temperature was linearly fitted by the equation of $\omega = \omega_0 + \chi T$, where ω_0 is the Raman peak position at 0 K and the slope $\chi = \delta\omega / \delta T$ is the first-order temperature coefficient. The linearly fitted results of $^{10}A_1$ mode along both zigzag and armchair directions are illustrated in Figure 6.9(b). The extracted first-order temperature coefficients are $\chi_{\text{zigzag}} = -0.01231 \text{ cm}^{-1}/\text{K}$ and $\chi_{\text{armchair}} = -0.00889 \text{ cm}^{-1}/\text{K}$, which are in the same order of magnitude as those in the previous work [217]. The larger absolute value of χ_{zigzag} may result from the anisotropic thermal expansion along different crystalline orientations.

To reduce the heat dissipation of the substrate, the excitation laser power dependent Raman spectra were studied on suspended Td-WTe₂ films. The prerequisite to extract high accurate thermal conductivity is that the hole under the sample must be adequately large. The size of the smallest hole in our measurements is 2.2 μm in diameter, which is sufficiently larger than the diameter of the laser spot (0.5 μm). The laser power dependent Raman spectra of suspended 11.2 nm-thick sample are shown in Figure 6.9(c). The excitation laser power is lower than 0.2 mW to avoid the laser-induced damage. As the laser power increases, the local temperature rise in suspended film results in the phonon softening of Raman peaks. Figure 6.9(d) illustrates the fitted frequencies of $^{10}A_1$ mode shifting with the laser power, where the $^{10}A_1$ mode also exhibits the linear redshifts along both crystalline orientations. The slopes ($\delta\omega / \delta P$) are $-0.02637 \text{ cm}^{-1}/\mu\text{W}$ and $-0.02202 \text{ cm}^{-1}/\mu\text{W}$ for zigzag and armchair directions, respectively.

The precise reply of phonon frequency to the local temperature increase makes the

Raman spectroscopy possible to estimate the thermal conductivity of few-layer Td-WTe₂. The heat dissipation equations within the suspended region and outside the hole can be described as follows [186]:

$$\kappa \frac{1}{r} \frac{d}{dr} \left[r \frac{dT(r)}{dr} \right] + q(r) = 0 \quad (r < R) \quad (6.11)$$

$$\kappa' \frac{1}{r} \frac{d}{dr} \left[r \frac{dT'(r)}{dr} \right] - \frac{G}{h} [T'(r) - T_0] = 0 \quad (r > R), \quad (6.12)$$

where κ and κ' are the thermal conductivities of suspended and supported films, respectively. r is the distance between the position and the hole center. $T(r)$ and $T'(r)$ are the temperature distribution inside and outside the hole, respectively. The radius of the hole for 11.2 nm-thick film is $R = 2.8 \mu\text{m}$. $q(r)$ indicates the volumetric optical heating. G is the interfacial thermal conductance between Td-WTe₂ and the substrate, its typical value is $50 \text{ MWm}^{-2}\text{K}^{-1}$ for van der Waals materials [186]. T_0 is the room temperature (300 K).

By solving the heat dissipation equations, we can get the temperature profiles for both inside and outside hole:

$$T(r) = c_1 - 2c_2 \ln r + c_2 Ei \left[1, \left(\frac{r}{r_0} \right)^2 \right], \quad (6.13)$$

$$T'(r) = c_3 K_0 \left[0, r \sqrt{\frac{G}{\kappa' h}} \right] + T_0, \quad (6.14)$$

where K_0 is the Bessel function of the second kind [186], Ei is the exponential integral, and r_0 is the half of the Gaussian beam width of $0.5 \mu\text{m}$. Taking into consideration the boundary conditions:

$$\begin{aligned} T(R) &= T'(R) \\ T'(r) &= T_0 \quad (r \rightarrow \infty), \end{aligned} \quad (6.15)$$

the temperature profile $T(r)$ within the hole range can be expressed as a function of thermal conductivity under different laser powers.

Figure 6.10 Anisotropic in-plane thermal conductivities of few-layer Td-WTe₂. (a)

The weighted average temperature of suspended 11.2 nm-thick Td-WTe₂ flake versus the thermal conductivity under different laser powers. (b) The calculated curve of $\delta T_m / \delta P$ as a function of the thermal conductivity. The thermal conductivities along zigzag and armchair directions are extracted by plugging the experimentally obtained $\delta T_m / \delta P$ into the theoretical curve. (c) The extracted thermal conductivities along zigzag and armchair directions of Td-WTe₂ with different thicknesses. (d) The anisotropic difference of thermal conductivities as a function of sample thickness. Error bars are evaluated from the standard deviation of the Raman peak position.

The volumetric optical heating is described as:

$$q(r) = \frac{I\tau}{h} \exp\left[-\left(\frac{r}{r_0}\right)^2\right], \quad (6.16)$$

where I is peak absorbed laser power per unit area at the center of the laser spot, h is the thickness of suspended sample in nanometer and τ is the optical absorption. Therefore, the average temperature T_m inside the laser spot can be easily calculated by above equations.

In our Raman experiments, the laser-induced weighted average temperature inside the laser spot is expressed as:

$$T_m \approx \frac{\int_0^R T(r)q(r)rdr}{\int_0^R q(r)rdr}. \quad (6.17)$$

Figure 6.10(a) shows the average temperature of suspended 11.2 nm-thick Td-WTe₂ flake as a function of the thermal conductivity under different excitation laser powers. Accordingly, the theoretical curve of $\delta T_m / \delta P$ related to the value of thermal conductivity can be then obtained, as illustrated in Figure 6.10(b). The experimental value of $\delta T_m / \delta P$ is easily determined by the slopes of both temperature and laser power dependent redshifts of ¹⁰A₁ mode. Thus, we can extract the thermal conductivity of suspended Td-WTe₂ by comparing the experimental value with the calculated curve of $\delta T_m / \delta P$. From the above measurements, the $\delta T_m / \delta P$ of 11.2 nm-thick Td-WTe₂ along zigzag and armchair directions are 2.142×10^6 K/W and 2.477×10^6 K/W, respectively. As a result, the extracted thermal conductivity $\kappa_{zigzag} = 0.743$ Wm⁻¹K⁻¹ is 16.3 % larger than the $\kappa_{armchair} = 0.639$ Wm⁻¹K⁻¹, showing a strong anisotropy in thermal conductivity. The obtained thermal conductivities in our work are comparable with the previous results determined by the beam-offset-TDTR technique [206].

Figure 6.11 The thermal conductivities of suspended few-layer WTe₂ with different thicknesses. The weighted average temperature versus the thermal conductivity under different excitation lasers for Td-WTe₂ samples with thickness of 12.6 nm (a), 21.1 nm (c) and 27.0 nm (e). (b), (d) and (f) The corresponding $\delta T_m / \delta P$ curves and their extracted thermal conductivities along zigzag and armchair directions.

The anisotropic group velocities of phonons in Td-WTe₂ have been calculated by earlier first-principles study, from which the larger group velocity of phonons along

zigzag direction results in a relatively greater thermal conductivity [204]. Furthermore, we also extracted the thermal conductivities from other suspended samples of 12.6 nm, 21.1 nm and 27.0 nm in thickness (see details in Figure 6.11), as summarized in Figure 6.10(c). With increasing the thickness, κ_{zigzag} rises to $1.697 \text{ Wm}^{-1}\text{K}^{-1}$ for the thickest film, analogous tendency also appears in the armchair direction, where $\kappa_{armchair}$ increases to the value of $1.539 \text{ Wm}^{-1}\text{K}^{-1}$. The significant thickness dependence of the thermal conductivity may result from the surface scattering of acoustic phonons, where the decreasing thickness enhances the surface phonon scattering, leading to the suppression of the thermal conductivity. Similar results have been verified in few-layer Bi_2Te_3 and black phosphorus (BP) [224,225]. Figure 6.10(d) shows that the in-plane anisotropy of thermal conductivity becomes less remarkable as the thickness increases, reflected by a decreasing rate of thermal conductivity increment from 16.3 % to 10.3 % ($(\kappa_{zigzag} - \kappa_{armchair}) / \kappa_{armchair}$), which is slightly different from the experimental results of anisotropic thermal conductivities from few-layer black phosphorus [225]. The precise mechanism requires further theoretical calculations.

6.4 Conclusions

We explored the anisotropic in-plane thermal conductivities of suspended few-layer Td-WTe₂ flakes by Raman spectroscopy for the first time. This is also the first experimental demonstration of such anisotropy in 2D TMDs. Considering the strong angular dependence in an anisotropic system, we firstly employed the linear polarization dependent Raman spectroscopy and SHG to identify the crystalline

orientations (zigzag and armchair axes) of the Td-WTe₂ flakes. Following, we investigated the thermal conductivities of Td-WTe₂ layers by *in situ* micro Raman spectroscopy and found the thermal conductivities of 0.743 and 0.639 Wm⁻¹K⁻¹ in 11.2 nm-thick layer along the zigzag and the armchair axes, respectively. The larger group velocity of phonons along zigzag direction is responsible for the greater thermal conductivity of zigzag direction. The studies of thickness dependent thermal conductivity further reveal that the increment of thickness could weaken such anisotropy though the thermal conductivities along both directions increase, which may arise from the less surface phonon scattering. The results shed more light on the applications of Td-WTe₂ and the designs of efficient thermal management schemes in the next-generation thermoelectric devices.

Chapter 7 Conclusions and future work

7.1 Conclusions

In this thesis, the charge density wave instabilities, phonon vibrations and thermal conductivities of the layered metallic transition metal dichalcogenides have been optically investigated by *in situ* Raman spectroscopy and scanning tunneling microscope. This thesis essentially contains four parts. In the first two parts, we have synthesized the atomically thin charge density wave conductors of 1T-TaS₂ and 1T-TiSe₂ crystals through chemical vapor deposition method, and the thickness dependent CDW phase transitions have been studied *via* Raman spectroscopy. Furthermore, the effects of interlayer coupling on the CDW states have been explored in graphene/NbSe₂ heterostructures. Finally, the in-plane anisotropic thermal conductivities of suspended few-layer Td-WTe₂ have been experimentally demonstrated and extracted by both temperature and excitation laser power dependent Raman measurements.

Part I: CDW phase transitions in atomically thin 1T-TaS₂

Two-dimensional 1T-TaS₂ layers have been successfully synthesized on SiO₂/Si substrates through the typical CVD method. The mixed sulfur and tantalum pentachloride powder was used as the precursor, and placed at the entrance of quartz tube. The thickness of as-grown TaS₂ flakes can be controlled by tuning the growing time, and thinnest layer was revealed to be two nanometers. The 1T structure of the samples has been confirmed by the X-ray diffraction patterns. In addition, the high quality of 1T-TaS₂ has been demonstrated by using several techniques, such as TEM,

EDS, EELS and XPS.

Due to the high sensitivity and resolution, the temperature dependent Raman spectroscopy was utilized to investigate the CDW instabilities of as-grown 1T-TaS₂ layers. Practically, the emergence of two broad peaks at around 60 and 71 cm⁻¹ can be used to indicate the appearance of NCCDW phase, while the splitting of Raman peaks at 60 and 77 cm⁻¹ can be attributed to the transition from NCCDW to CCDW phase. The thickness dependent CDW phase transitions have been systematically studied in this work. With decreasing the thickness of layers, both the ICCDW to NCCDW and NCCDW to CCDW phase transitions shifted to lower temperatures, and vanished in the critical thicknesses of 6 and 14 nm, respectively.

Part II: Thickness dependent CDW phase transitions in as-grown 1T-TiSe₂

The synthesis of atomically thin 1T-TiSe₂ crystals has been experimentally realized through the salt-assisted CVD method for the first time. The mixed partially oxidized Ti and LiCl powder was placed at the center of the tube furnace, as the melting point of LiCl is very similar to the proper growing temperature of 1T-TiSe₂. The 1.4 nm-thick flake was confirmed by AFM and assigned to the monolayer 1T-TiSe₂. Additionally, the large-area thin film of 1T-TiSe₂ has been successfully achieved by increasing the growing temperature and the amount of precursors, since the vapor pressure of titanium oxychlorides is strongly enhanced. The structure and high crystallinity of CVD-grown samples have also been characterized and verified by HAADF-STEM and EDX techniques.

With the help of low temperature Raman spectroscopy, the thickness dependent

CDW phase transition properties have been extensively explored. The obvious and strong peak at approximately 110 cm^{-1} is ascribed to the CDW amplitude mode and can be used as indicator for the CDW phase transition. When the thickness of 1T-TiSe₂ decreased, the CDW orders were enhanced as the transition temperatures increased. However, the slightly decreased transition temperature in monolayer sample might be due to the instability of monolayer 1T-TiSe₂. Importantly, it is the first Raman spectroscopic realization of CDW state in monolayer 1T-TiSe₂.

Part III: Suppressing the CDW orders in graphene/NbSe₂ heterostructures

The interlayer coupling between the single layer graphene and 2H-NbSe₂ layers has been discovered to significantly influence the CDW orders in 2H-NbSe₂. Firstly, the graphene/NbSe₂ heterostructures were successfully fabricated through dry transfer method. The *in situ* temperature dependent Raman spectroscopy was employed to determine the CDW phase transition temperatures of different parts on the heterostructures. The soft mode at around 180 cm^{-1} underwent a significant softening as the temperature decreased, and became freezing when the temperature reached the CDW transition point. In addition, both the linewidth of A_{1g} mode and the frequency of 2D band as a function of temperature exhibited kinks at the temperature of transition point. By contrast, the T_{CDW} of 2H-NbSe₂ was significantly lowered when covered by a single layer graphene.

Then the heterostructures were characterized by scanning tunneling microscope/spectroscopy. The perfect long-range periodic atomic patterns on 2H-NbSe₂ layers identified the incommensurate CDW orders. While such patterns were broken into

short-range ordered patches when covered by the graphene, which indicated that the graphene layer significantly suppressed CDW states of 2H-NbSe₂ films. The STS of graphene provided evidence of interlayer charge transfer between the single layer graphene and 2H-NbSe₂ layers.

Part IV: In-plane anisotropic thermal conductivity of few-layer Td-WTe₂

Due to the distinct orthorhombic Td structure, two-dimensional WTe₂ layers have unique anisotropic properties. The optical anisotropic characterizations have been investigated by angle dependent polarized Raman spectroscopy. In parallel-polarized configuration, the intensities of A₁ modes exhibit two-fold symmetry, while those of A₂ modes display four-fold symmetry. Conversely, the angle dependent intensities of both A₁ and A₂ modes show four-fold symmetric patterns under cross-polarized configuration. Therefore, the crystalline orientations (zigzag and armchair directions) of suspended few-layer Td-WTe₂ have been identified by Raman characterizations and verified by second harmonic generation measurements under a parallel-polarized configuration.

Moreover, the anisotropic in-plane thermal conductivities have been explored by *in situ* Raman spectroscopy. To our best knowledge, this is the first demonstration of such anisotropy in 2D TMDs. The thermal conductivities of 0.743 and 0.639 Wm⁻¹K⁻¹ in 11.2 nm-thick layer were found along the zigzag and the armchair axes, respectively, showing a strong anisotropy. With increasing the thickness, the thermal conductivities of both two directions rose up, which results from the less surface scattering of acoustic phonons in thicker flakes. However, the increment of sample thickness could weaken

the thermal anisotropy, and the precise mechanism requires further theoretical calculations

7.2 Future work

(1) Intrinsic CDW phase transition in monolayer 1T-TiSe₂

Figure 7.1 Energy gap evolution as a function of temperature. The red dashed line represents the linear approximation near the transition point of 232 K. Adapted from ref. [53]

As revealed in Chapter 4, the CDW transition temperature decreased to 202.5 K in monolayer 1T-TiSe₂ crystal, which might be attributed to the instability of the samples since the monolayer 1T-TiSe₂ was exposed to the air shortly before Raman

measurements. However, Chen *et al.* demonstrated a definitely high CDW transition temperature of 232 K in monolayer 1T-TiSe₂ grown by molecular beam epitaxy method [53], as shown in Figure 7.1. The monolayer samples were measured by ARPES and XRD under ultrahigh vacuum, suggesting a strongly enhanced CDW state in monolayer 1T-TiSe₂. As a result, investigating the intrinsic CDW order of monolayer 1T-TiSe₂ is of great significance for the understanding of ultra-thin electronic systems. The further meaningful work will be focused on the low temperature Raman measurements of monolayer 1T-TiSe₂. We will find out a protection method to prevent the sample from oxidation after CVD growth. It is believed that the monolayer should have higher CDW transition temperature.

(2) Enhancing the CDW states by fabricating heterostructures

The charge-density-wave layered TMD materials often suffer a severe degradation when exposed to the air, therefore such atomically thin films are protected by h-BN or graphene layers in a majority of studies. These protective layers are capable to enhance or suppress the intrinsic CDW properties of the materials. For example, Li *et al.* realized an enhanced CDW transition temperature in 1T-TiSe₂ layers when encapsulated by h-BN films [135]. While the single layer graphene obviously decreased the CDW transition points of 2H-NbSe₂ in our experiments, which can be due to the electron transfer from graphene to the 2H-NbSe₂ layer. As enhancing the CDW states in 2D materials is much more meaningful for electronic device applications, the next step is to figure out another material that can obtain electrons from 2H-NbSe₂ layer when stacking together, leading to the enhancement of CDW transition temperatures.

Furthermore, investigating the CDW instabilities of the heterostructures by stacking the different CDW conductors together will open up a new window for the understanding of many-body electronic instabilities and the application of CDW based two-dimensional devices.

Figure 7.2 In-plane anisotropic thermal conductivities of few-layer black phosphorus.

(a) Extracted thermal conductivities along zigzag and armchair directions in BP with different thicknesses. (b) The thickness dependent anisotropic ratio $k_{\text{zigzag}}/k_{\text{armchair}}$.

Adapted from ref. [225]

(3) Exploring the mechanism of thickness dependent in-plane anisotropic thermal conductivity of 2D Td-WTe₂ crystals

Recently, the anisotropic in-plane thermal conductivity of few-layer black phosphorus has been reported by Raman spectroscopy [225]. As illustrated in Figure 7.2, it is found that the thickness dependent anisotropy in thermal conductivity results from the thickness dependences of surface acoustic phonon scattering, particularly the long mean-free-path (MFP) phonons. In our experiments, the similar thickness dependence

of thermal conductivities in Td-WTe₂ was also observed, but the anisotropy exhibited a completely opposite evolution with increasing the sample thickness. It is well known that black phosphorus is a semiconductor, while Td-WTe₂ is a semimetal whose electrons play a vital role in thermal conductivity as well [226]. The theoretical explanation of BP is entirely not applicable in the case of Td-WTe₂. Since this is the first time to demonstrate the anisotropic in-plane thermal conductivity in 2D TMDs experimentally, understanding the precise mechanism by theoretical calculations will facilitate the fundamental exploration on such atomically thin semimetals.

References

- [1] C. Buzea, I. I. Pacheco, and K. Robbie, *Biointerphases* **2**, MR17 (2007).
- [2] J. H. Davies, *The physics of low-dimensional semiconductors: an introduction* (Cambridge University Press, 1997), 1-44.
- [3] N. D. Mermin, *Physical Review* **176**, 250 (1968).
- [4] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004).
- [5] A. Bostwick, T. Ohta, T. Seyller, K. Horn, and E. Rotenberg, *Nature Physics* **3**, 36 (2007).
- [6] M. Sprinkle *et al.*, *Physical Review Letters* **103**, 226803 (2009).
- [7] K. S. Kim *et al.*, *Nature* **457**, 706 (2009).
- [8] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, *Nano Letters* **8**, 902 (2008).
- [9] A. S. Mayorov *et al.*, *Nano Letters* **11**, 2396 (2011).
- [10] J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. Van Der Zande, J. M. Parpia, H. G. Craighead, and P. L. McEuen, *Nano Letters* **8**, 2458 (2008).
- [11] J. Wilson and A. Yoffe, *Advances in Physics* **18**, 193 (1969).
- [12] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nature Nanotechnology* **7**, 699 (2012).
- [13] M. Chhowalla, H. S. Shin, G. Eda, L. J. Li, K. P. Loh, and H. Zhang, *Nature Chemistry* **5**, 263 (2013).
- [14] H. Katzke, P. Tolédano, and W. Depmeier, *Physical Review B* **69**, 134111 (2004).
- [15] G. Eda, T. Fujita, H. Yamaguchi, D. Voiry, M. Chen, and M. Chhowalla, *ACS Nano* **6**, 7311 (2012).
- [16] J. Shi *et al.*, *Advanced Materials* **29**, 1701486 (2017).
- [17] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, *Nature Reviews Materials* **2**, 17033 (2017).
- [18] Y. Zhou *et al.*, *AIP Advances* **6**, 075008 (2016).

- [19] Y. Qi *et al.*, Nature Communications **7**, 11038 (2016).
- [20] J. Yang, J. Colen, J. Liu, M. C. Nguyen, G. W. Chern, and D. Louca, Science Advances **3**, 4949 (2017).
- [21] A. Kuc, N. Zibouche, and T. Heine, Physical Review B **83**, 245213 (2011).
- [22] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Physical Review Letters **105**, 136805 (2010).
- [23] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli, and F. Wang, Nano Letters **10**, 1271 (2010).
- [24] A. Klein, S. Tiefenbacher, V. Eyert, C. Pettenkofer, and W. Jaegermann, Physical Review B **64**, 205416 (2001).
- [25] A. Ramasubramaniam, Physical Review B **86**, 115409 (2012).
- [26] L. Liu, S. B. Kumar, Y. Ouyang, and J. Guo, IEEE Transactions on Electron Devices **58**, 3042 (2011).
- [27] C. Ataca, H. Sahin, and S. Ciraci, The Journal of Physical Chemistry C **116**, 8983 (2012).
- [28] T. Böker, R. Severin, A. Müller, C. Janowitz, R. Manzke, D. Voß, P. Krüger, A. Mazur, and J. Pollmann, Physical Review B **64**, 235305 (2001).
- [29] Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi, and W. Tang, Physica B: Condensed Matter **406**, 2254 (2011).
- [30] A. Ayari, E. Cobas, O. Ogundadegbe, and M. S. Fuhrer, Journal of Applied Physics **101**, 014507 (2007).
- [31] J. Yan, M. A. D. Cruz, B. Cook, and K. Varga, Scientific Reports **5** (2015).
- [32] S. Smaalen, Acta Crystallographica Section A: Foundations of Crystallography **61**, 51 (2005).
- [33] G. Gruner, Frontiers in Physics **89**, 259 (1994).
- [34] G. Grüner, Reviews of Modern Physics **60**, 1129 (1988).
- [35] R. E. Thorne, Physics Today **49**, 42 (1996).
- [36] H. Frohlich, Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences **223**, 296 (1954).
- [37] P. Monceau, Advances in Physics **61**, 325 (2012).

- [38] X. Zhu, Y. Cao, J. Zhang, E. Plummer, and J. Guo, Proceedings of the National Academy of Sciences **112**, 2367 (2015).
- [39] S. Dugdale, Physica Scripta **91**, 053009 (2016).
- [40] E. Sola, A. Polls, and F. Mazzanti, Journal of Low Temperature Physics **127**, 29 (2002).
- [41] R. E. Thorne, Physics Today **49**, 42 (1996).
- [42] R. E. Peierls, *Quantum theory of solids* (Oxford University Press, 1955), 23.
- [43] K. Rossnagel, Journal of Physics: Condensed Matter **23**, 213001 (2011).
- [44] S. Kagoshima, H. Nagasawa, and T. Sambongi, *What Are One-Dimensional Conductors?* (Springer, 1988), 1-3.
- [45] F. Weber *et al.*, Physical Review Letters **107**, 107403 (2011).
- [46] B. Sipos, A. F. Kusmartseva, A. Akrap, H. Berger, L. Forró, and E. Tutiš, Nature Materials **7**, 960 (2008).
- [47] J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Advances in Physics **50**, 1171 (2001).
- [48] S. Sugai, K. Murase, S. Uchida, and S. Tanaka, Solid State Communications **35**, 433 (1980).
- [49] N. Dean, J. C. Petersen, D. Fausti, R. a. I. Tobey, S. Kaiser, L. Gasparov, H. Berger, and A. Cavalleri, Physical Review Letters **106**, 016401 (2011).
- [50] R. Manzke, T. Buslaps, B. Pfalzgraf, M. Skibowski, and O. Anderson, Europhysics Letters **8**, 195 (1989).
- [51] M. Yoshida, Y. Zhang, J. Ye, R. Suzuki, Y. Imai, S. Kimura, A. Fujiwara, and Y. Iwasa, Scientific Reports **4**, 7302 (2014).
- [52] Y. Yu *et al.*, Nature Nanotechnology **10**, 270 (2015).
- [53] P. Chen, Y. H. Chan, X. Y. Fang, Y. Zhang, M. Y. Chou, S. K. Mo, Z. Hussain, A. V. Fedorov, and T. C. Chiang, Nature Communications **6**, 8943 (2015).
- [54] X. Xi, L. Zhao, Z. Wang, H. Berger, L. Forró, J. Shan, and K. F. Mak, Nature Nanotechnology **10**, 765 (2015).
- [55] M. Calandra, I. Mazin, and F. Mauri, Physical Review B **80**, 241108 (2009).
- [56] M. M. Ugeda *et al.*, Nature Physics **12**, 92 (2016).

- [57] G. Binnig and H. Rohrer, *Surface Science* **126**, 236 (1983).
- [58] P. Graves and D. Gardiner, *Practical Raman Spectroscopy* (Springer, 1989), 55-76.
- [59] W. Fu *et al.*, *Chemistry of Materials* **28**, 7613 (2016).
- [60] S. Sugai, *Physica Status Solidi (B)* **129**, 13 (1985).
- [61] J. N. Coleman *et al.*, *Science* **331**, 568 (2011).
- [62] E. Varrla, C. Backes, K. R. Paton, A. Harvey, Z. Gholamvand, J. McCauley, and J. N. Coleman, *Chemistry of Materials* **27**, 1129 (2015).
- [63] D. Abergel, A. Russell, and V. I. Fal'ko, *Applied Physics Letters* **91**, 063125 (2007).
- [64] P. Blake, E. Hill, A. Castro Neto, K. Novoselov, D. Jiang, R. Yang, T. Booth, and A. Geim, *Applied Physics Letters* **91**, 063124 (2007).
- [65] M. Binnewies, R. Glaum, M. Schmidt, and P. Schmidt, *Zeitschrift für Anorganische und Allgemeine Chemie* **639**, 219 (2013).
- [66] P. Schmidt, M. Binnewies, R. Glaum, and M. Schmidt, in *Advanced Topics on Crystal Growth* (InTech, 2013), 227.
- [67] D. Hu *et al.*, *Angewandte Chemie International Edition* **56**, 3611 (2017).
- [68] S. Najmaei *et al.*, *Nature Materials* **12**, 754 (2013).
- [69] A. M. Van Der Zande *et al.*, *Nature Materials* **12**, 554 (2013).
- [70] N. Peimyoo, J. Shang, C. Cong, X. Shen, X. Wu, E. K. Yeow, and T. Yu, *ACS Nano* **7**, 10985 (2013).
- [71] N. Peimyoo, Doctoral thesis, Nanyang Technological University, 2015.
- [72] G. F. Schneider, V. E. Calado, H. Zandbergen, L. M. Vandersypen, and C. Dekker, *Nano Letters* **10**, 1912 (2010).
- [73] X. Li *et al.*, *Science* **324**, 1312 (2009).
- [74] C. R. Dean *et al.*, *Nature Nanotechnology* **5**, 722 (2010).
- [75] A. Castellanos-Gomez, M. Buscema, R. Molenaar, V. Singh, L. Janssen, H. S. van der Zant, and G. A. Steele, *2D Materials* **1**, 011002 (2014).
- [76] A. Smekal, *Naturwissenschaften* **11**, 873 (1923).
- [77] C. V. Raman and K. S. Krishnan, *Nature* **121**, 501 (1928).

- [78] G. Landsberg and L. Mandelstam, *Naturwissenschaften* **16**, 557 (1928).
- [79] P. Y. Yu and M. Cardona, *Fundamentals of semiconductors: physics and materials properties* (Springer, 2010), 378.
- [80] J. R. Ferraro, *Introductory raman spectroscopy* (Academic Press, 2003), 15.
- [81] R. Loudon, *Advances in Physics* **50**, 813 (2001).
- [82] T. C. Damen, S. Porto, and B. Tell, *Physical Review* **142**, 570 (1966).
- [83] C. Cong and T. Yu, *Nature Communications* **5**, 4709 (2014).
- [84] C. H. Lui, Z. Ye, C. Keiser, E. B. Barros, and R. He, *Applied Physics Letters* **106**, 041904 (2015).
- [85] C. H. Lui, Z. Ye, C. Keiser, X. Xiao, and R. He, *Nano Letters* **14**, 4615 (2014).
- [86] P. Tan *et al.*, *Nature Materials* **11**, 294 (2012).
- [87] C. Cong, Doctoral thesis, Nanyang Technological University, 2011.
- [88] C. Qiu, X. Shen, B. Cao, C. Cong, R. Saito, J. Yu, M. S. Dresselhaus, and T. Yu, *Physical Review B* **88**, 165407 (2013).
- [89] G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, *Physical Review Letters* **49**, 57 (1982).
- [90] C. Arguello *et al.*, *Physical Review B* **89**, 235115 (2014).
- [91] C. J. Chen, *Introduction to scanning tunneling microscopy* (Oxford University Press, 2008), 2.
- [92] Y. I. Joe *et al.*, *Nature Physics* **10**, 421 (2014).
- [93] I. Vaskivskiy, J. Gospodaric, S. Brazovskii, D. Svetin, P. Sutar, E. Goreshnik, I. A. Mihailovic, T. Mertelj, and D. Mihailovic, *Science Advances* **1**, e1500168 (2015).
- [94] Y. Cai, Q. Wei, F. Huang, S. Lin, F. Chen, and W. Gao, *Renewable Energy* **34**, 2117 (2009).
- [95] L. Li, E. O'Farrell, K. Loh, G. Eda, B. Özyilmaz, and A. C. Neto, *Nature* **529**, 185 (2016).
- [96] C. Zhi, Y. Bando, C. Tang, H. Kuwahara, and D. Golberg, *Advanced Materials* **21**, 2889 (2009).

- [97] S. H. Aboutalebi, M. M. Gudarzi, Q. B. Zheng, and J. K. Kim, *Advanced Functional Materials* **21**, 2978 (2011).
- [98] C. Cong, J. Shang, X. Wu, B. Cao, N. Peimyoo, C. Qiu, L. Sun, and T. Yu, *Advanced Optical Materials* **2**, 131 (2014).
- [99] K. Choy, *Progress in Materials Science* **48**, 57 (2003).
- [100] X. Hou and K. L. Choy, *Chemical Vapor Deposition* **12**, 583 (2006).
- [101] Y. H. Lee *et al.*, *Advanced Materials* **24**, 2320 (2012).
- [102] Y. Gong *et al.*, *Nature Materials* **13**, 1135 (2014).
- [103] Y. Zhang *et al.*, *ACS Nano* **7**, 8963 (2013).
- [104] Z. Liu *et al.*, *Nature Nanotechnology* **8**, 119 (2013).
- [105] Z. Liu *et al.*, *Nature Communications* **4**, 2541 (2013).
- [106] A. W. Tsen *et al.*, *Proceedings of the National Academy of Sciences* **112**, 15054 (2015).
- [107] D. Cho, S. Cheon, K.-S. Kim, S. H. Lee, Y. H. Cho, S. W. Cheong, and H. W. Yeom, *Nature Communications* **7**, 10453 (2016).
- [108] T. Pillo, J. Hayoz, H. Berger, M. Grioni, L. Schlapbach, and P. Aebi, *Physical Review Letters* **83**, 3494 (1999).
- [109] X. C. Wu, Y. R. Tao, and Q. X. Gao, *Chemical Communications* **0**, 6008 (2009).
- [110] L. Li, W. Lu, Y. Liu, Z. Qu, L. Ling, and Y. Sun, *Physica C: Superconductivity* **492**, 64 (2013).
- [111] B. Zheng and Y. Chen, in *IOP Conference Series: Materials Science and Engineering* (IOP Publishing, 2017), 012085.
- [112] T. Yanase, S. Watanabe, M. Weng, M. Wakeshima, Y. Hinatsu, T. Nagahama, and T. Shimada, *Crystal Growth & Design* **16**, 4467 (2016).
- [113] E. S. Peters, C. J. Carmalt, I. P. Parkin, and D. A. Tocher, *European Journal of Inorganic Chemistry* **2005**, 4179 (2005).
- [114] Z. Zeng, C. Tan, X. Huang, S. Bao, and H. Zhang, *Energy & Environmental Science* **7**, 797 (2014).
- [115] L. Perfetti, P. Loukakos, M. Lisowski, U. Bovensiepen, H. Berger, S.

- Biermann, P. Cornaglia, A. Georges, and M. Wolf, *Physical Review Letters* **97**, 067402 (2006).
- [116] J. Tersoff, *Physical Review Letters* **57**, 440 (1986).
- [117] J. Duffey, R. Kirby, and R. Coleman, *Solid State Communications* **20**, 617 (1976).
- [118] S. Sugai, K. Murase, S. Uchida, and S. Tanaka, *Physica B+ C* **105**, 405 (1981).
- [119] S. Uchida and S. Sugai, *Physica B+ C* **105**, 393 (1981).
- [120] L. Gasparov, K. Brown, A. Wint, D. Tanner, H. Berger, G. Margaritondo, R. Gaal, and L. Forró, *Physical Review B* **66**, 094301 (2002).
- [121] M. Yoshida, R. Suzuki, Y. Zhang, M. Nakano, and Y. Iwasa, *Science Advances* **1**, e1500606 (2015).
- [122] P. Miró, M. Audiffred, and T. Heine, *Chemical Society Reviews* **43**, 6537 (2014).
- [123] M. Buscema, J. O. Island, D. J. Groenendijk, S. I. Blanter, G. A. Steele, H. S. van der Zant, and A. Castellanos-Gomez, *Chemical Society Reviews* **44**, 3691 (2015).
- [124] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, and M. C. Hersam, *ACS Nano* **8**, 1102 (2014).
- [125] M. Calandra, *Nature Nanotechnology* **10**, 737 (2015).
- [126] M. Calandra and F. Mauri, *Physical Review Letters* **106**, 196406 (2011).
- [127] A. F. Kusmartseva, B. Sipos, H. Berger, L. Forro, and E. Tutiš, *Physical Review Letters* **103**, 236401 (2009).
- [128] E. Morosan, H. Zandbergen, B. Dennis, J. Bos, Y. Onose, T. Klimczuk, A. Ramirez, N. Ong, and R. Cava, *Nature Physics* **2**, 544 (2006).
- [129] T. Adelman, S. Zaitsev-Zotov, and R. Thorne, *Physical Review Letters* **74**, 5264 (1995).
- [130] I. Vaskivskiy, I. Mihailovic, S. Brazovskii, J. Gospodaric, T. Mertelj, D. Svetin, P. Sutar, and D. Mihailovic, *Nature Communications* **7**, 11442 (2016).
- [131] D. Mihailovic, D. Dvorsek, V. Kabanov, J. Demsar, L. Forro, and H. Berger,

- Applied Physics Letters **80**, 871 (2002).
- [132] G. Liu, B. Debnath, T. R. Pope, T. T. Salguero, R. K. Lake, and A. A. Balandin, Nature Nanotechnology **11**, 845 (2016).
- [133] J. Renteria *et al.*, Journal of Applied Physics **115**, 034305 (2014).
- [134] R. Samnakay, D. Wickramaratne, T. Pope, R. Lake, T. Salguero, and A. Balandin, Nano Letters **15**, 2965 (2015).
- [135] L. Li, W. Zhao, B. Liu, T. Ren, G. Eda, and K. Loh, Applied Physics Letters **109**, 141902 (2016).
- [136] D. L. Duong, G. Ryu, A. Hoyer, C. Lin, M. Burghard, and K. Kern, ACS Nano **11**, 1034 (2017).
- [137] P. Goli, J. Khan, D. Wickramaratne, R. K. Lake, and A. A. Balandin, Nano Letters **12**, 5941 (2012).
- [138] K. Sugawara, Y. Nakata, R. Shimizu, P. Han, T. Hitosugi, T. Sato, and T. Takahashi, ACS Nano **10**, 1341 (2015).
- [139] P. Chen, Y. H. Chan, M. H. Wong, X. Y. Fang, M. Y. Chou, S. K. Mo, Z. Hussain, A. V. Fedorov, and T. C. Chiang, Nano Letters **16**, 6331 (2016).
- [140] X. Y. Fang, H. Hong, P. Chen, and T. C. Chiang, Physical Review B **95**, 201409 (2017).
- [141] J. K. Huang *et al.*, ACS Nano **8**, 923 (2013).
- [142] J. H. Ahn, M. J. Lee, H. Heo, J. H. Sung, K. Kim, H. Hwang, and M. H. Jo, Nano Letters **15**, 3703 (2015).
- [143] M. Hafeez, L. Gan, H. Li, Y. Ma, and T. Zhai, Advanced Materials **28**, 8296 (2016).
- [144] X. Duan *et al.*, Nature Nanotechnology **9**, 1024 (2014).
- [145] Y. Zhou *et al.*, ACS Nano **8**, 1485 (2014).
- [146] Y. Kim, B. Kang, Y. Choi, J. H. Cho, and C. Lee, 2D Materials **4**, 025057 (2017).
- [147] J. Wang *et al.*, Journal of the American Chemical Society **138**, 16216 (2016).
- [148] J. Holy, K. Woo, M. Klein, and F. Brown, Physical Review B **16**, 3628 (1977).

- [149] C. Snow, J. Karpus, S. Cooper, T. Kidd, and T. C. Chiang, *Physical Review Letters* **91**, 136402 (2003).
- [150] P. A. Temple and C. Hathaway, *Physical Review B* **7**, 3685 (1973).
- [151] S. L. Li, H. Miyazaki, H. Song, H. Kuramochi, S. Nakaharai, and K. Tsukagoshi, *ACS Nano* **6**, 7381 (2012).
- [152] S. Li, S. Wang, D.-M. Tang, W. Zhao, H. Xu, L. Chu, Y. Bando, D. Golberg, and G. Eda, *Applied Materials Today* **1**, 60 (2015).
- [153] K. V. Manukyan, K. G. Kirakosyan, Y. G. Grigoryan, O. M. Niazryan, A. V. Yeghishyan, A. G. Kirakosyan, and S. L. Kharatyan, *Industrial & Engineering Chemistry Research* **50**, 10982 (2011).
- [154] M. Erdoğan and İ. Karakaya, *Metallurgical and Materials Transactions B* **41**, 798 (2010).
- [155] A. F. Kusmartseva, B. Sipos, H. Berger, L. Forro, and E. Tutiš, *Physical Review Letters* **103**, 236401 (2009).
- [156] X. Xi, H. Berger, L. Forró, J. Shan, and K. F. Mak, *Physical Review Letters* **117**, 106801 (2016).
- [157] H. Wang *et al.*, *Nature Communications* **8**, 394 (2017).
- [158] C. Arguello *et al.*, *Physical Review Letters* **114**, 037001 (2015).
- [159] T. Valla, A. Fedorov, P. Johnson, P. Glans, C. McGuinness, K. Smith, E. Andrei, and H. Berger, *Physical Review Letters* **92**, 086401 (2004).
- [160] X. Xi, Z. Wang, W. Zhao, J.-H. Park, K. T. Law, H. Berger, L. Forró, J. Shan, and K. F. Mak, *Nature Physics* **12**, 139 (2016).
- [161] R. He, J. van Baren, J. A. Yan, X. Xi, Z. Ye, G. Ye, I. H. Lu, S. Leong, and C. Lui, *2D Materials* **3**, 031008 (2016).
- [162] A. Tsen *et al.*, *Nature Physics* **12**, 208 (2016).
- [163] L. Nguyen *et al.*, *ACS Nano* **11**, 2894 (2017).
- [164] S. Onishi *et al.*, *Physica Status Solidi (B)* **253**, 2396 (2016).
- [165] C. H. Lee *et al.*, *Nature Nanotechnology* **9**, 676 (2014).
- [166] B. Hunt *et al.*, *Science* **340**, 1427 (2013).
- [167] C. Dean *et al.*, *Nature* **497**, 598 (2013).

- [168] C. D. Malliakas and M. G. Kanatzidis, *Journal of the American Chemical Society* **135**, 1719 (2013).
- [169] Z. Ni, Y. Wang, T. Yu, and Z. Shen, *Nano Research* **1**, 273 (2008).
- [170] Y. Wu, M. An, R. Xiong, J. Shi, and Q. Zhang, *Journal of Physics D: Applied Physics* **41**, 175408 (2008).
- [171] J. Tsang, J. Smith Jr, and M. Shafer, *Physical Review Letters* **37**, 1407 (1976).
- [172] B. Chakraborty, A. Bera, D. Muthu, S. Bhowmick, U. V. Waghmare, and A. Sood, *Physical Review B* **85**, 161403 (2012).
- [173] I. Calizo, A. Balandin, W. Bao, F. Miao, and C. Lau, *Nano Letters* **7**, 2645 (2007).
- [174] J. Yan, Y. Zhang, P. Kim, and A. Pinczuk, *Physical Review Letters* **98**, 166802 (2007).
- [175] U. Chatterjee *et al.*, *Nature Communications* **6**, 6313 (2015).
- [176] Y. Zhang, V. W. Brar, F. Wang, C. Girit, Y. Yayon, M. Panlasigui, A. Zettl, and M. F. Crommie, *Nature Physics* **4**, 627 (2008).
- [177] S. Wickenburg *et al.*, *Nature Communications* **7**, 13553 (2016).
- [178] J. Chae *et al.*, *International Journal of High Speed Electronics and Systems* **20**, 205 (2011).
- [179] P. Dabrowski, M. Rogala, I. Wlasny, Z. Klusek, M. Kopciuszynski, M. Jalochowski, W. Strupinski, and J. Baranowski, *Carbon* **94**, 214 (2015).
- [180] T. Shimada, F. S. Ohuchi, and B. A. Parkinson, *Japanese Journal of Applied Physics* **33**, 2696 (1994).
- [181] T. Filleter, K. Emtsev, T. Seyller, and R. Bennewitz, *Applied Physics Letters* **93**, 133117 (2008).
- [182] Y. Shi, X. Dong, P. Chen, J. Wang, and L.-J. Li, *Physical Review B* **79**, 115402 (2009).
- [183] Y. J. Yu, Y. Zhao, S. Ryu, L. E. Brus, K. S. Kim, and P. Kim, *Nano Letters* **9**, 3430 (2009).
- [184] A. Das *et al.*, *Nature Nanotechnology* **3**, 210 (2008).
- [185] M. Kalbac, A. Reina-Cecco, H. Farhat, J. Kong, L. Kavan, and M. S.

- Dresselhaus, ACS Nano **4**, 6055 (2010).
- [186] R. Yan *et al.*, ACS Nano **8**, 986 (2014).
- [187] N. Peimyoo, J. Shang, W. Yang, Y. Wang, C. Cong, and T. Yu, Nano Research **8**, 1210 (2015).
- [188] Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi, and W. Tang, Physica B: Condensed Matter **406**, 2254 (2011).
- [189] B. E. Brown, Acta Crystallographica **20**, 268 (1966).
- [190] C. H. Lee, E. C. Silva, L. Calderin, M. A. T. Nguyen, M. J. Hollander, B. Bersch, T. E. Mallouk, and J. A. Robinson, Scientific Reports **5**, 10013 (2015).
- [191] J. Augustin, V. Eyert, T. Böker, W. Frentrop, H. Dwelk, C. Janowitz, and R. Manzke, Physical Review B **62**, 10812 (2000).
- [192] M. N. Ali *et al.*, Nature **514**, 205 (2014).
- [193] I. Pletikosić, M. N. Ali, A. Fedorov, R. Cava, and T. Valla, Physical Review Letters **113**, 216601 (2014).
- [194] J. Jiang *et al.*, Physical Review Letters **115**, 166601 (2015).
- [195] Y. Luo *et al.*, Applied Physics Letters **107**, 182411 (2015).
- [196] X. C. Pan *et al.*, Nature Communications **6**, 7805 (2015).
- [197] Y. Liu, P. Stradins, and S. H. Wei, Science Advances **2**, 1600069 (2016).
- [198] A. Taube, J. Judek, A. Łapińska, and M. Zdrojek, ACS Applied Materials & Interfaces **7**, 5061 (2015).
- [199] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'quinn, Nature **413**, 597 (2001).
- [200] A. Majumdar, Science **303**, 777 (2004).
- [201] Y. Ma, M. Liu, A. Jaber, and R. Y. Wang, Journal of Materials Chemistry A **3**, 13483 (2015).
- [202] G. A. Slack, Journal of Physics and Chemistry of Solids **34**, 321 (1973).
- [203] G. A. Slack, Solid State Physics **34**, 1 (1979).
- [204] G. Liu, H. Y. Sun, J. Zhou, Q. F. Li, and X.-G. Wan, New Journal of Physics **18**, 033017 (2016).
- [205] J. Ma, Y. Chen, Z. Han, and W. Li, 2D Materials **3**, 045010 (2016).

- [206] Y. Zhou *et al.*, *Advanced Functional Materials* **27**, 1605928 (2017).
- [207] M. J. Mleczko, R. L. Xu, K. Okabe, H.-H. Kuo, I. R. Fisher, H.-S. P. Wong, Y. Nishi, and E. Pop, *ACS Nano* **10**, 7507 (2016).
- [208] X. Ma *et al.*, *Physical Review B* **94**, 214105 (2016).
- [209] W. D. Kong, S. F. Wu, P. Richard, C. S. Lian, J. T. Wang, C. L. Yang, Y. G. Shi, and H. Ding, *Applied Physics Letters* **106**, 081906 (2015).
- [210] E. Zhang *et al.*, *Nano Letters* **17**, 878 (2017).
- [211] H. Malekpour and A. A. Balandin, *Journal of Raman Spectroscopy* **10**, 5230 (2017).
- [212] J. D. Renteria, S. Ramirez, H. Malekpour, B. Alonso, A. Centeno, A. Zurutuza, A. I. Cocemasov, D. L. Nika, and A. A. Balandin, *Advanced Functional Materials* **25**, 4664 (2015).
- [213] X. Zhang, D. Sun, Y. Li, G.-H. Lee, X. Cui, D. Chenet, Y. You, T. F. Heinz, and J. C. Hone, *ACS Applied Materials & Interfaces* **7**, 25923 (2015).
- [214] E. Yalon *et al.*, *ACS Applied Materials & Interfaces* **9**, 43013 (2017).
- [215] N. Bonini, M. Lazzeri, N. Marzari, and F. Mauri, *Physical Review Letters* **99**, 176802 (2007).
- [216] A. Mar, S. Jobic, and J. A. Ibers, *Journal of the American Chemical Society* **114**, 8963 (1992).
- [217] M. K. Jana, A. Singh, D. J. Late, C. R. Rajamathi, K. Biswas, C. Felser, U. V. Waghmare, and C. Rao, *Journal of Physics: Condensed Matter* **27**, 285401 (2015).
- [218] Y. Wang, C. Cong, C. Qiu, and T. Yu, *Small* **9**, 2857 (2013).
- [219] J. C. Familton, Doctoral thesis, Columbia University, 2015.
- [220] J. B. Bates and A. S. Quist, *The Journal of Chemical Physics* **56**, 1528 (1972).
- [221] R. Loudon, *Advances in Physics* **13**, 423 (1964).
- [222] Q. Song *et al.*, *Scientific Reports* **6**, 29254 (2016).
- [223] R. Beams *et al.*, *ACS Nano* **10**, 9626 (2016).
- [224] M. T. Pettes, J. Maassen, I. Jo, M. S. Lundstrom, and L. Shi, *Nano Letters* **13**, 5316 (2013).

- [225] Z. Luo, J. Maassen, Y. Deng, Y. Du, R. P. Garrelts, M. S. Lundstrom, D. Y. Peide, and X. Xu, *Nature Communications* **6**, 8572 (2015).
- [226] J. P. Issi and J. Heremans, *Thermal Conductivity 15* (Springer, 1978), 63-72.