Novel strategies for chemical vapor deposition growth and engineering of two-dimensional materials

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**NANYANG
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SINGAPORE

**NOVEL STRATEGIES FOR CHEMICAL VAPOR
DEPOSITION GROWTH AND ENGINEERING OF TWO-
DIMENSIONAL MATERIALS**

Jinjun Lin

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2020

**NOVEL STRATEGIES FOR CHEMICAL VAPOR
DEPOSITION GROWTH AND ENGINEERING OF TWO-
DIMENSIONAL MATERIALS**

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School of Electrical & Electronic Engineering

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

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journal(s) where I was the first author.

Chapter 5 is published as Lin, J.; Tay, R. Y.; Li, H. L.; Jing, L.; Tsang, S. H.; Bolker, A.; Saguy, C.; Teo, E. H. T.*, Concentric Dopant Segregation in CVD-Grown N-doped Graphene Single Crystals. *Appl. Surf. Sci.* **2018**, 454, 121-129.

The contributions of the co-authors are as follows:

- Prof. Edwin Hang Tong Teo provided the initial research direction and guided the project.
- I, Dr. Li Hongling and Dr. Roland Yingjie Tay conceived the idea, synthesized the materials, conducted the characterizations, and drafted the manuscript.
- Dr. Asaf Bolker and Dr. Cecile Saguy conducted the scanning tunneling microscopy (STM) characterizations and help analyzed the STM data.
- Dr. Jing Lin and Dr. Siu Hon Tsang helped with some supporting experiments and manuscript revision.

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The contributions of the co-authors are as follows:

- Prof. Edwin Hang Tong Teo provided the initial research direction and guided the project.
- I, Dr. Roland Yingjie Tay and Dr. Li Hongling conceived the idea, synthesized the materials, conducted the characterizations, and drafted the manuscript.
- Dr. Jing Lin, Dr. Siu Hon Tsang, Dr. Wang Hong, and Dr. Zhu Minmin helped with some supporting experiments and manuscript revision.
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- I, Dr. Wang Hong, Dr. Li Hongling and Dr. Roland Yingjie Tay conceived the idea, synthesized the materials, conducted the characterizations, and drafted the manuscript.
- Dr. Shakerzadeh Maziar helped conducted the XRD characterizations and helped with XRD data analysis.
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Abstract

Two-dimensional (2D) materials are atomically thin materials that possess many superior and outstanding properties as compared to its bulk counterpart. Depending on its elemental composition, 2D materials encompass a full spectrum of electronic properties ranging from semi-metallic to insulating and hold great promise for next-generation nanoelectronics. In order to achieve practical utilization, large-scale fabrication of 2D materials and engineering of their properties are fundamental. In this thesis, chemical vapor deposition (CVD) growth of various types of 2D materials including graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (TMDs) were investigated and new methods were developed to enhance or modify their properties.

Firstly, CVD growth and characterization of hexagonal shaped single-crystal graphene domains on Cu foil was demonstrated. Following this growth strategy, doping of these single crystals was performed by using a nitrogen (N)-containing single-source precursor known as hexamethylenetetramine (HMTA). Importantly, it was discovered for the first time that segregation of dopant concentration exists even in monolayer N-doped graphene (NG) single crystals. This study provides a critical insight into the growth mechanism of CVD-grown NG and enables new opportunities to tailor the properties of graphene toward applications in high-performance 2D electronics.

2D h-BN, an electrical insulator, is a perfect complement to graphene and the best-known substrate material for all 2D materials to date owing to its atomic smoothness and lack of dangling bonds. CVD has been recognized as one of the most pragmatic approach to produce large-area and high-quality h-BN films. However, the strain-induced wrinkles in CVD-grown h-BN films, which cause high surface roughness, still remained a major drawback which severely degrade device performance. Here, by

employing a post-synthesis annealing process, wrinkles on the h-BN film were effectively eliminated. The unwrinkled h-BN film showed significant surface smoothness enhancement and resulted in a much cleaner surface, which has high potential use for scalable fabrication of high-performance 2D heterostructure devices.

Layered TMDs is another important class of 2D materials with exceptional electronic and optoelectronic properties. Particularly, vertically aligned TMDs are highly promising for optoelectronics and electrochemical devices due to the much higher density of exposed active edge compared to their laterally oriented counterparts. In this work, a versatile and scalable CVD growth of vertically aligned MoTe₂ on reusable Mo foil is demonstrated for the first time. Importantly, the as-grown MoTe₂ can be directly dispersed in solvent to produce high-quality MoTe₂ nanosheets. Furthermore, the versatility of this growth strategy was demonstrated by synthesizing other vertically aligned TMDs such as TaTe₂ and MoSe₂. Hence, this work paves the path towards achieving unique TMDs structures to enable high-performance optoelectronic and electrochemical devices.

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List of Abbreviations

2D	Two-dimensional
AB	Ammonia borane
AFM	Atomic force microscopy
AP	Atmospheric pressure
BF	Bright field
BN	Boron nitride
NNNS	Boron nitride nanosheets
CA	Contact angle
CVD	Chemical vapor deposition
CTE	Coefficient of thermal expansion
DF	Dark field
DI	Deionized
DOS	Density of states
DTA	differential thermal analysis
EBS	Electron backscatter diffraction
EDS	Energy dispersive spectroscopy
EELS	Electron energy loss spectroscopy
FT-IR	Fourier-transform infrared spectroscopy
HMTA	Hexamethylenetetramine
h-BN	Hexagonal boron nitride
HR	High resolution
HER	Hydrogen evolution reaction
IPA	Isopropyl alcohol

LP	Low pressure
NG	Nitrogen-doped graphene
OBG	Optical band gap
PMMA	Poly(methyl methacrylate)
RMS	Root-mean-square
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
SF	Sensitivity factor
STM	Scanning tunneling microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TMDs	Transition metal dichalcogenides
UV	Ultraviolet
UV-vis	Ultraviolet-visible
UHV	Ultra-high vacuum
VA	Vertically aligned
vdW	Van der Waals
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1. Introduction

1.1. Backgrounds

Two-dimensional (2D) materials is a class of layered materials where in-plane atoms are connected by strong covalent bonds while individual layers are bonded together by weak van der Waals interaction.¹ Hence, 2D materials can be easily separated from their bulk crystals into few layers or single layer by physical exfoliation. Capable to scale down to one atom thickness, 2D materials exhibit many superior properties as compared to their bulk counterparts. One representative 2D materials is graphene which comprises of sp^2 -hybridized carbon in a honeycomb structure and possesses lots of exceptional properties such as extremely high intrinsic carrier mobility ($20,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),² thermal conductivity ($\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$),³ and mechanical strength ($\sim 1.0 \text{ TPa}^{-1}$).⁴ Spurred by the discovery of graphene, tremendous efforts have been devoted into the exploration of other 2D materials. Hexagonal boron nitride (h-BN) is an isomorph of graphene with alternating boron (B) and nitrogen (N) atoms occupying in honeycomb lattice structure. The close lattice structure of h-BN with graphene ($\sim 2\%$ lattice mismatch) enables it with similarly ultrahigh thermal conductivity and mechanical strength.^{5, 6} Despite their similarities in crystal structure, the different chemical composition between h-BN and graphene results in a large contrast in electronic characteristics. While graphene is semi-metallic with zero bandgap,⁷ h-BN is electrically insulating with a wide bandgap of $\sim 6 \text{ eV}$.⁸ Transition metal dichalcogenides (TMDs) is another emerging group of 2D materials where one transition metal plane is bonded to two chalcogen planes.⁹ Layered TMDs are best known for their semiconducting properties covering a wide range of energy bandgap, which hold great promises for high-performance electronics and optoelectronics.

2D materials to date are mainly fabricated by two types of methods: top-down method and bottom-up method. A typical top-down method is mechanical exfoliation which was first applied to create graphene in 2004 by peeling it off from graphite using an adhesive tape.² Ever since then, this method has been widely used to create all kind of 2D materials because it is easy to be implemented and can produce flakes with high quality. However, mechanical exfoliation method usually produces 2D materials with limited dimension and random yield, which makes it undesirable for large-scale production. Liquid phase exfoliation method by sonicating bulk crystals in solvent is promising for mass production of 2D materials,¹⁰⁻¹² but the as-obtained products inevitably suffer from high level of defect and low quality, which hinder their practical applications. Alternatively, various bottom-up methods have been developed to synthesize 2D materials. Epitaxial graphene can be grown on silicon carbide (SiC) by annealing this substrate under ultra-high vacuum (UHV).^{13, 14} Moreover, graphene was also grown on many single-crystal transition metal substrates including Co (0001),¹⁵ Ni (111),^{16, 17} Pt (111),^{18, 19} Ir (111),^{20, 21} Ru (0001),^{22, 23} and Pd (111)²⁴ by surface segregation of carbon from bulk metals or thermal decomposition hydrocarbon gases on the substrate surface. However, these processes require UHV condition or use of single-crystal substrates, which are costly and limits their utilization for large-scale production. Recently, chemical vapor deposition (CVD) has been recognized as a more pragmatic bottom-up method for large-scale synthesis of high-quality graphene that fits the industry requirements. A breakthrough in CVD growth of graphene was reported by several groups (Li *et al.*, Kim *et al.*, and Reina *et al.*) that achieved large-area growth of monolayer and few layer graphene on polycrystalline Cu or Ni substrates under atmosphere (AP).²⁵⁻²⁷ Subsequently, CVD was extended to grow other 2D materials including hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMDs).

Over years, CVD growth of high-quality 2D materials has progressed dramatically. Centimeter-scale single-crystal graphene has been successfully synthesized on surface-oxidized Cu substrates.²⁸⁻³¹ Wafer-scale single-crystal h-BN monolayer films have been grown on liquid gold (Au) substrates by CVD.³² A universal CVD method has also been developed to grow a wide range of TMDs by using molten salts to reduce the melting point of the reactants and facilitate the forming of intermediate products.³³ Nevertheless, in order to cater for the diverse range of 2D materials, developing new CVD techniques for the growth and engineering of 2D materials is essential.

1.2. Motivation

As mentioned above, large-scale fabrication of high-quality 2D materials is of great importance for their practical application. Among the many methods, CVD has been recognized as the most popular method for the scalable growth of high-quality 2D materials. Although CVD growth of 2D materials has been progressing dramatically, the full realization of the application potentials of 2D materials with over 40 members requires the development of new CVD techniques and in-depth understanding their growth process.

First, CVD growth of heteroatom-doped 2D materials holds great potential to fabricate large-area 2D materials with tunable electronic and optoelectronic properties. In particular, doping graphene via CVD methods is especially attracting since it holds great potentials to produced doped graphene with unique properties. However, many of these CVD approaches rely on using separate sources for C and heteroatoms. Moreover, investigation of dopant distribution in graphene mainly focus on polycrystalline films with small grain size, understanding of the dopant segregation in single-crystal graphene is still limited. Therefore, it is important to develop a versatile graphene doping process

using single-source precursor and study the doping characteristics in single-crystal CVD-graphene.

Next, atomically smooth surface is one of the most important features of 2D materials. However, wrinkling in CVD-grown 2D materials has become a common problem across the entire field, restricting their further practical applications. This issue is especially problematic for CVD-grown h-BN which is heavily utilized as an interfacing material in multi-stack 2D structures. The ubiquitous wrinkles in CVD-grown h-BN seriously hinder their utilization in high-performance 2D heterostructure devices. Therefore, to realize the large-scale application of h-BN, an effective method to diminish or smoothen wrinkles in CVD-grown h-BN films would be greatly beneficial.

Finally, the crystallographic orientation of 2D materials plays an important role in their performance. In particular, layered TMDs with vertical orientation with respect to the substrate possess much higher density of exposed edge sites than their laterally oriented counterparts. This in turn enables vertically oriented TMDs with superior optoelectronic and electrochemical properties. However, CVD growth of vertically aligned TMDs is only limited to transition metal sulfides or selenides, no vertically aligned transition telluride has been reported yet. Besides, these approaches rely on using e-beam deposited transition metal films which are not only limited in thickness but also costly. Therefore, it is highly desirable to develop a versatile CVD process for the scalable fabrication of vertically TMDs covering the less explored telluride compounds.

1.3. Objectives and scopes

The aim of this thesis is to develop new CVD techniques for the growth and engineering of various 2D materials (including graphene, h-BN, and TMDs) and to provide critical insights into the growth mechanism and materials characteristics.

With the intention to obtain graphene with tunable properties, a CVD growth of nitrogen-doped graphene (NG) using a novel single-source precursor is explored. Particularly, dopant distribution in the monolayer NG single crystals was investigated in detail. This work focuses on the synthesis process and characterization of the NG single crystals and provides critical insights into the nitrogen atom doping mechanism of CVD-grown graphene.

Wrinkling is a wide-spreading issue in CVD-grown h-BN films on Cu substrate which leads to high surface roughness and has been a major reason why synthetic h-BN films are still much inferior compared to exfoliated flakes. In order to obtain large-area smooth h-BN films, an effective approach was developed to smoothen these wrinkles by thermal annealing as-transferred h-BN films in air. Systematic studies were conducted to identify the critical parameters affecting the unwrinkling process. Detailed insight into the unwrinkling mechanism was also provided in this work.

Finally, a novel CVD process was developed to grow vertically aligned MoTe₂ directly on commercially available Mo foils. Reusability of the Mo foil was also explored. Further discussion of the vertical growth mechanism and extension of this method to grow other vertically aligned TMDs were also demonstrated.

The key objectives are summarized as follows:

- To develop a CVD process for growth of monolayer nitrogen-doped graphene (NG) single crystals.
- To investigate the dopant distribution in the NG single crystals and gain insights into the doping process.
- To develop an effective approach to smoothen wrinkles in CVD-grown h-BN films.

- To gain insight into the unwrinkling mechanism by systematically studying the effect of CVD annealing conditions on surface smoothness of h-BN films.
- To develop a novel and versatile CVD process for the growth of vertically aligned MoTe₂ arrays on reusable Mo foils.
- To extend this method to grow other vertically aligned TMDs arrays on transition metal foils and look into the vertical growth mechanism.

1.4. Major contribution of the Thesis

In this thesis, novel CVD processes were developed for growth and engineering of 2D materials (including graphene, h-BN, and MoTe₂).

A nitrogen doping strategy for graphene was realized by using a new single-source precursor that contains both C and N species. By optimizing the growth parameters, hexagonal shaped monolayer nitrogen-doped graphene (NG) single crystals with a size of ~20 μm were grown on Cu substrates. Investigation of the doping characteristics lead to a discovery of N dopant segregation in the single-crystal NG domains, where separated hexagonal concentric rings comprising lower dopant concentration compared to the region outside the rings were revealed by Raman mapping. Supported by further STM characterization, a hypothesis on the formation of the observed concentric dopant segregation within single crystal NG domains has been proposed. While most previously reported studies focused on the dopant distribution in polycrystalline graphene films, this work provided critical insight into the doping mechanism of CVD-grown single-crystal NG.

Wrinkles in CVD-grown 2D materials could severely impair their surface smoothness, leading to degradation of device performance. This is especially problematic for CVD-grown h-BN since it is widely used as an interfacing materials in construction of 2D heterostructure devices. Therefore, the microstructure of wrinkles in CVD-grown h-BN

was investigated in detail. It was revealed that wrinkles were formed upon the quenching of as-grown h-BN/Cu from high growth temperature (~ 1000 °C) due to the large difference of coefficient of thermal expansion (CTE) between h-BN and Cu. Importantly, it was demonstrated that these wrinkles could be effectively diminished by thermally annealing the as-transferred h-BN films in air. The smoothened h-BN film showed greatly improved surface smoothness with negligible oxidative damage. Detailed insights into the unwrinkling mechanism was provided, which is supported experimentally. The unwrinkling approach proposed in this work would no doubt enhance many of the performance issues plaguing the 2D field which uses h-BN.

Finally, a novel CVD process was developed to grow vertically aligned MoTe_2 directly on commercial Mo foil. The as-grown MoTe_2 arrays can be easily detached from the Mo foil by slightly bending due to the weak interaction between them, which enabled the economic reuse and recycling of Mo foil. High-resolution transmission electron microscopy suggests that the as-grown materials are highly crystalline MoTe_2 layers. Further discussion of the vertical growth mechanism and extension of this method to grow other vertically aligned TMDs such as TaTe_2 and MoSe_2 were also demonstrated.

1.5. Organization of the Thesis

In Chapter 1, the history of 2D materials, including their structure, properties and potential application are first introduced. Following these are the motivation, objective and scope, and major contribution of this thesis. The next chapter will introduce the background knowledge and the challenges faced on CVD growth of 2D materials, as well as the contribution from this thesis in tackling these challenges. Chapter 3 introduces the characterization techniques used in this thesis. Chapter 4 presents the investigation of CVD growth of graphene on Cu substrates. Chapter 5 introduce a CVD

doping strategy for growth of nitrogen-doped graphene. Chapter 6 provides a detailed investigation on the wrinkling issue in CVD-grown h-BN films on Cu substrates. Additionally, a post-synthesis method to smoothen these wrinkles is introduced, and discussion on the unwrinkling mechanism is also presented. Chapter 7 demonstrates a novel CVD growth method to directly synthesize vertically aligned MoTe₂ on Mo foils. Systematic investigation of the effects of key CVD parameters (growth temperature and growth time) on the morphology and crystallinity of the as-grown material was conducted. Discussion on the growth mechanism and extension of this method to grow other vertically aligned TMDs were also presented. Finally, Chapter 8 concludes with a summary of the works accomplished in this thesis and recommendations for further research on the related topics.

2. Literature Review

2.1 Overview

The discovery of graphene in 2004 stimulated an extensively research interest in 2D materials due to the outstanding properties arising from their unique structures and ultrathin thickness.² The layered structures of 2D materials are as depicted in Figure 2-1. In-plane atoms are tied up by strong covalent bonds, whereas the individual layers are held together via weak Van der Waals force. As a representative 2D material, graphene comprises of sp^2 -hybridized carbon in a honeycomb structure as shown in Figure 2-1a. The strong covalent bonds between the in-plane carbon atoms make graphene one of the strongest materials in the world. Besides, graphene also possesses ultrahigh electron mobility and thermal conductivity. These exceptional properties enable graphene with great potential in a wide range of applications such as high-frequency field effect transistors,^{7, 34} ultrathin protective coating,^{35, 36} thermal interfacing materials,³⁷ and space applications.³⁸ An analogue of graphene is h-BN, where alternating boron (B) and nitrogen (N) atoms occupy the honeycomb lattice as shown in Figure 2-1b. Due to its alike structure to graphene, h-BN also has similarly high mechanical strength and high thermal conductivity. H-BN is chemically inert with temperature stability of up to ~ 1000 °C.³⁹ On the other hand, h-BN is an insulator with a wide bandgap of ~ 6 eV.⁸ The electrically insulating nature, atomic smoothness, and low density of dangling bond of h-BN have made it one of the most crucial building blocks of 2D heterostructures devices.⁴⁰⁻⁴² Another important group of 2D materials is TMDs which has a formula of MX_2 , where M stands for a transition metal element (Mo, W, Nb, Pt, Re, Ta *et al*) and X is a chalcogen element (S, Se, and Te).³³ Figure 2-1c shows the structure of single-layer MoS_2 , the most representative TMDs material, is constituted with a Mo plane bonded with two S planes at its top and bottom, respectively. TMDs is a rich family with

over 40 members covering semimetals, semiconductors, and topological insulator. Layered TMDs usually exist in three types of crystal structures (2H, 1T, and 3R).³³

Figure 2-1 Structures of the representative 2D materials: (a) graphene, (b) h-BN, (c) MoS₂.⁴³

Generally, 2D materials can be produced by two type of methods: top-down (mechanical/liquid exfoliation) and bottom-up methods (Figure 2-2).⁴⁴ Although mechanical exfoliation produces high-quality flakes by physically peeling off layers from bulk crystals, the resulting 2D flakes are usually with limited dimension and random yield.^{42, 45} Chemical exfoliation method is promising for mass production of 2D materials, but the obtained products inevitably suffer from severe defects and low quality, which hinder their further practical applications.^{46, 47}

Bottom-up method presents more promising potentials towards manufacturing owing to their capabilities for large-scale production. These approaches include CVD,^{27, 48, 49} ion-beam sputtering,⁵⁰ magnetron sputtering,^{51, 52} pulsed-laser deposition,⁵³⁻⁵⁵ and molecular beam epitaxy.⁵⁶⁻⁵⁸ Among them, CVD is the most commonly used synthesis method to date to fabricate various 2D materials with high quality in controllable way (thickness, phase, orientations *et al.*). In recent years, considerable research efforts have been devoted into CVD growth of 2D materials and exploration of their applications. For examples, Wu *et al.* reported the CVD growth of inch-size single-crystal graphene by locally feeding carbon precursor at desired position

of the substrate.⁵⁹ Ivan *et al.* developed a modified CVD method that delivers hydrocarbon mixture onto Cu foil surface via a small-diameter nozzle and provides constantly flowing Ar and H₂ as buffer gases, which eventually produce foot long monolayer single-crystal graphene film.⁶⁰ Although the development of CVD growth of 2D materials has shown dramatic progress, further up scaling and better quality control in terms of defect level, uniformity and electronic properties are still needed. Therefore, it is vital to explore new methods and optimize the CVD process in order to produce electronic-grade 2D materials in large scale.

Figure 2-2 Top-down and bottom-up methods for the fabrication of 2D materials.⁴⁴

2.2 CVD growth of graphene and h-BN

CVD is a process that involves reactants reacting in vapor phase to form solid products on substrates. The properties of CVD-grown 2D materials are largely related to their size, morphology, crystallinity, and defect, which can be controlled by rational design and careful tuning of the CVD process. Therefore, it is of great importance to understand the underlying growth mechanisms and to identify how some critical parameters affect the growth.

CVD growth of graphene and h-BN to date is mostly conducted using Cu, Ni, or their alloy as substrates whose catalytic function can facilitate the decomposition of precursors and formation of products on the metal surface.^{26, 48, 59, 61, 62} Since the CVD set up and growth mechanism of graphene and h-BN on metal substrates are similar, their important growth parameters will be introduced together.

2.2.1. Precursors

In a CVD process, precursors are the compounds participating in a chemical reaction that produce another compound. Therefore, the nature of precursors is one of the key factors that affect the quality or characteristics of the synthesized products. Basically, this is true in the CVD growth of 2D materials. For example, gaseous precursor like methane (CH_4) and hydrogen (H_2) are commonly used in CVD growth of graphene. This is because gaseous precursors allow the precise control over the thickness, size, and morphology of the graphene thin films by changing the flow rate and partial pressure of each precursor. Figure 2-3 shows a typical set up for CVD growth of graphene.⁶³ Generally, CH_4 serves as carbon feedstock during the growth, a higher CH_4 concentration will produce thicker graphene layers. Except for gas sources, liquid precursors such as various liquid alcohols (methanol, ethanol, and propanol),⁶⁴ n-hexane,⁶⁵ and benzene⁶⁶ are also used for the growth graphene, which could allow for low-temperature growth of graphene. Solid C source such as PMMA can also be used for graphene growth. High-quality graphene monolayer can be synthesized by annealing PMMA spin-coated on metal substrates at a temperature of 800 °C under reductive atmosphere of Ar/ H_2 .⁶⁷ Moreover, by introducing a mixture of CH_4 and ammonia (NH_3), the graphene can be doped with N atoms.⁶⁸ H_2 is known to facilitate the decomposition of hydrocarbon and also etch graphene from its edge site at high temperature.⁶⁹ These competing growth and etching processes thus lead to the lateral growth of graphene from

individual nucleation point. Besides, Zhang *et al.* has found that H_2 partial pressure is a crucial factor that affects the ad-layer growth of graphene on Cu.⁶⁹ At low H_2 pressure, graphene edges tend to tightly attach to the Cu surface which prohibits the diffusion of active C species into area beneath top-layer graphene, and therefore the growth of monolayer is favored. In contrast, graphene edges tend to be terminated by H at high H_2 pressure which opens the path for diffusion of active C species into area beneath top-layer graphene, leading to the growth of bilayer or few-layer.⁶⁹

Figure 2-3 Schematic diagram of typical CVD set up for graphene growth.⁶³

For the growth of h-BN, gaseous precursors containing B-species such as boron tribromide, boron trifluoride, boron trichloride and diborane and together with NH_3 as N-species feedstock have been explored.⁷⁰⁻⁷⁹ However, one major drawback of these gaseous sources for h-BN growth is their high toxicity, which brings significant concerns on their storage and usage. One alternative is a solid precursor, ammonia borane (NH_3-BH_3 , AB), which has been proven to be an excellent source as it is much less poisonous and has an intrinsic B/N atomic ratio of 1:1. Therefore, AB as a precursor is much safer to use and more likely to produce h-BN films with high quality. Typically, CVD growth of h-BN is conducted at atmosphere pressure using Cu substrates (Figure 2-4),⁴⁸ AB is evaporated by a heater and carried into reaction zone to start the growth.

The h-BN domain enlarges with increasing precursor evaporation temperature until it reaches the largest size, further increasing the temperature will result in decreasing domain size due to high density of nucleation point. At the evaporation temperature where the largest h-BN domains are grown, further increasing the amount of precursors favors higher density of nucleation, but not larger domain size. Similar to graphene growth, H_2 is also known to etch h-BN under high temperature.⁶²

Figure 2-4 Schematic diagram of typical CVD set up for graphene growth.⁴⁸

2.2.2. Substrates

Substrates in a CVD process refer to where the product is deposited. Apart from that, substrates can also serve as catalysts in the growth of 2D materials. Cu and Ni are the most commonly used substrates in the CVD growth of graphene and h-BN. The growth mechanisms of graphene (h-BN) on Cu and Ni are different. Since Cu has a low solubility of C and N, thus a surface growth mechanism dictates the graphene (h-BN) growth on Cu. As shown in Figure 2-5a,⁸⁰ the decomposed active C sources diffuse on the surface of Cu and assemble to form graphene (or h-BN when a BN source is used).

Since the feedstock cannot access catalysis surface after full-cover film is formed, mainly single-layer film is formed. In contrast, Ni has a relatively high solubility of C, B, and N, the decomposed sources will first dissolve into Ni at high temperature and precipitate onto the metal surface during cooling process to form graphene or h-BN (Figure 2-5b).⁸⁰ Multilayer films are normally produced and the number of layers can be controlled by tuning the amount of feedstock atoms dissolved into Ni and the cooling rate.

Figure 2-5 Graphene growth process on (a) highly carbon soluble metal substrate (e.g., Ni), (b) low carbon soluble metal substrate (e.g., Cu).⁸⁰

Commercially available Cu foils mostly have high surface roughness due to uneven grooves on surface formed at their production, which lead to non-uniform growth and small grain size of graphene and h-BN due to the high density of nucleation sites. Luo *et al.* reported the first usage of electropolished Cu foil with flat surface as substrate, and achieved highly uniform growth of graphene film (over 95% of single layer).⁸¹

Using this smoothened Cu foil, our group first reported the growth of large hexagonal-shaped h-BN domain ($\sim 35 \mu\text{m}^2$).⁸² Furthermore, by using re-solidified Cu as substrates, Wu *et al.* reported the growth of sub-millimeter-size single-crystal graphene and we manage to synthesize single-crystal h-BN domain with aligned orientation over centimeter scale.^{83, 84}

2.2.3. Temperature

The temperature in a CVD system may affect the chemical reaction of the precursors, the transport of chemical species on the substrate surface, and the deposition rate of the product. Therefore, temperature is a critical parameter that affects the composition and uniformity of the as-grown graphene and h-BN.

For the CVD growth of graphene on metal substrate (Cu or Ni) using CH_4 as precursor, a high growth temperature of $\sim 1000^\circ\text{C}$ is normally required for CH_4 to fully decompose. Alternatively, lower deposition temperature is also possible by choosing different sources. Li *et al.* reported the CVD growth of large-area graphene film at a low temperature of $\sim 400^\circ\text{C}$ using PMMA and polystyrene as solid precursors.⁶⁶ Monolayer graphene can be obtained even at temperature as low as 300°C when benzene is used as hydrocarbon source.⁶⁶ Similarly, a high growth temperature at $\sim 1000^\circ\text{C}$ is usually required for the growth of h-BN. A systematic study on atmospheric pressure CVD (APCVD) growth of h-BN by our group revealed that the average domain size, film coverage, and crystallinity of as-grown h-BN can be increased by increasing the growth temperature (950°C to 1050°C).⁶²

2.3 CVD growth of TMDs

2.3.1 Precursors

Depending on the type of precursors used, there are mainly four common routes for CVD synthesis of 2D TMDs to date. (1) The first route is thermal decomposition of

single-source precursors that consist both of the metal and chalcogen elements. Figure 2-6a illustrates a two-step annealing process to synthesis MoS₂ thin films.⁸⁵ After dip-coating of ammonium thiomolybdates ((NH₄)₂MoS₄) solution on substrates, the first annealing process was performed at a low pressure (1 Torr) and a relatively low temperature (500 °C) in an Ar/H₂ atmosphere for 1 hour to remove residual solvent, NH₃ molecules, and other by products. Followed by second annealing process at high temperature (1000 °C) in Ar flow (or Ar+S) to form MoS₂. Additional S vapor introduced into the chamber will greatly improve the crystallinity and electrical performance of the as-grown MoS₂ films. (2) The second route is by sulfurization/selenization/tellurization of pre-deposited transition metal film (Mo, W, Pt, ect.) or transition metal oxides. In a typical process shown in Figure 2-6b, MoO₃ thin film with desired thickness was deposited on substrates by thermal evaporator. The MoO₃ film was first reduced at 500 °C in Ar/H₂ atmosphere, followed by further annealing in S vapor rich atmosphere at 1000 °C to produce MoS₂ thin films.⁸⁶ (3) The third route is to grow high-quality TMDs few layers or monolayer by physical vapor transport process. As illustrated in Figure 2-6c, MoS₂ powder was evaporated at 900 °C to deposit high quality MoS₂ on insulating substrates.⁸⁷ (4) The fourth route is that the transition metal oxides or chlorides react with chalcogen vapor directly at desired temperature to deposit 2D TMDs on substrates (Figure 2-6d).⁴⁹ Many TMDs is difficult to be produced due to the high-melting point of the corresponding metals or metal oxides. Zhou *et al.* proposed a melted-salt-assisted CVD method to synthesize a wide range of 2D TMDs.³³ However, the controllability of TMDs growth using these solid compounds as precursors is still poor since the vapor pressure of the evaporated source is very sensitive to temperature fluctuation. In this regards, gaseous precursor such as Mo(CO)₆ and H₂S has been used to achieve a more uniform growth of TMDs films.⁸⁸⁻⁹⁰

Figure 2-6 Four common routes for CVD growth of TMDs. (a) Two-step thermolysis of $(\text{NH}_4)_2\text{MoS}_4$ to synthesize MoS_2 thin layers on insulating substrates.⁸⁵ (b) Synthesis of MoS_2 thin films by sulfurization of pre-deposited MoO_3 .⁸⁶ (c) Physical vapor transport growth process by using MoS_2 powder as source.⁸⁷ (d) Schematic of controlled growth of monolayer MoSe_2 . MoO_3 powder and Se pellets are used as metal and chalcogen sources, respectively.⁴⁹

2.3.2 Substrates

TMDs are commonly grown on dielectric substrates such as SiO_2/Si , sapphire, and mica. For SiO_2/Si substrates, modification of their wettability has been shown to be effective in control the growth of TMDs on top. For example, Jaeho *et al.* reported that large-area MoS_2 films with uniform thickness can be grown on SiO_2/Si substrates by changing its surface to hydrophilic using oxygen plasma (Figure 2-7a).⁹¹ Besides, various seed promoters including perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS), 3,4,9,10-perylene-tetracarboxylicacid-dianhydride (PTCDA), reduced graphene oxide (r-GO), and aromatic molecules have been shown to be able to facilitate the nucleate and growth of large-area continuous MoS_2 film on SiO_2/Si substrate (Figure 2-7b).⁹² Mica is an excellent substrate with flat and inert surface which can facilitate the epitaxial

growth of TMDs.⁹³ For example, ReS₂ has been known to favor out-of-plane growth on SiO₂/Si substrates, which lead to thick flake, dendritic, and flower-like structures of ReS₂.^{94, 95} By utilizing mica as substrate, which has flat surface and weak van der Waals interaction with ReS₂, large-area and continuous ReS₂ thin film can be produced.^{96, 97} Moreover, the lattice structure of substrate also significantly affects the growth of TMDs. Owing to the specific lattice orientation of c-plane and atomically smooth surface of sapphire substrates, TMDs grown on this kind of substrate show a specific orientation preference.⁹⁸ Except for dielectric substrates, gold with catalytic function has also been used as substrates in the CVD growth of TMDs.^{99, 100}

Figure 2-7 (a) Schematic of layer-controlled growth of MoS₂ film by oxygen plasma treatment of substrate surface.⁹¹ (b) Growth of large-area and high-quality MoS₂ single layers using aromatic molecule as seeding promoter.⁹² (c) Schematic illustration of epitaxial growth of MoS₂ single crystals on mica substrates.⁹³ (d) Orientation control of MoS₂ on sapphire substrates by tuning the precursor's ratio (S/MoO₃).⁹⁸

2.3.3 Temperature

Temperature plays an important role in the CVD growth of TMDs in the following two aspects. First, solid precursors are commonly used in the CVD growth of TMDs,

therefore, temperature of the CVD system will affect the evaporation rate of the sources, including chalcogen sources (S, Se, and Te) and transition metal source (transition metal oxides or chlorides). Generally, a higher temperature leads to a higher concentration of sources in the reaction zone, thus results in thicker TMDs crystals or films. Secondly, the growth temperature also has a huge impact on the crystalline structure of the as-grown TMDs. For example, in the CVD growth of MoTe_2 , a growth temperature below 670°C mainly leads to MoTe_2 crystalizing in hexagonal or triangular facets, corresponding the 2H MoTe_2 , while a growth temperature above 710°C results in 1T' MoTe_2 with distorted octahedral coordination.¹⁰¹

Figure 2-8 (a) Temperature profile for CVD growth of MoTe_2 with mixture of 1T'/2H phases. (b) The relative ratio of 1T'/2H phases at different growth temperature. Only 1T' MoTe_2 is grown at high temperature of 710°C , while the ratio of 2H phase increases at lower growth temperature.¹⁰¹

2.4 Challenges faced and contributions of this thesis

Although substantial progresses have been made on large-area CVD growth of single-crystal 2D materials (graphene and h-BN films, and TMDs) in recent years, the realization of their promising potential applications is still challenging. Further development of new CVD processes or engineering methods for growth of 2D materials and modification of their physical and chemical properties are still required. In this section, literatures regarding the challenges faced in synthesis and applications of graphene, h-BN, and MoTe₂ will be reviewed and the contribution of this thesis in tackling these challenges will be summarized.

2.4.1 Heteroatom-doped graphene

The exceptional properties of graphene, including atomic thickness, ultrahigh carrier mobility, high thermal conductivity, and high mechanical strength, make it an ideal candidate material for next-generate nanoscale devices, such as high-speed 2D FET, photodiodes, and laser application. However, since graphene is a semimetal with zero bandgap, FET using graphene as channel material suffers from low on/off ratio due to large leakage current, which severely restricts its application in logic circuit.

To address this issue, considerable efforts have been devoted to open the bandgap and modulate the electronic and optical properties of graphene. In particular, nitrogen doping of graphene via CVD is one of the most viable approaches. Typically, CVD synthesis of nitrogen-doped graphene (NG) can be achieved by thermal decomposition of gaseous hydrocarbon and ammonia gases.^{68, 102} For example, large-area few-layer NG films have been synthesized via CVD using methane (CH₄) and ammonia (NH₃) as carbon and nitrogen sources, respectively. Due to the substitutional doping effect, the NG exhibited an n-type semiconductor behavior that led to an increased on/off ratio.⁶⁸ Additionally, single-source precursors that contain both carbon and nitrogen

species have also been explored for more controllable synthesis process. For example, pyridine has been shown to be an effective precursor for CVD growth of monolayer single-crystal NG at temperature as low as 300 °C.¹⁰³

Meanwhile, dopant distribution in NG have also attracted much research attention given its potential influence on the electronic properties of as-grown NG. It has been revealed that N dopants could avoid the grain boundaries/edges of NG films during CVD growth, resulting in an inhomogeneous N dopant distribution in the polycrystalline NG films.¹⁰⁴ Besides, atomic scale study on CVD-grown NG shows that N dopants will reside at different sublattices during the growth process, forming well-separated sublattice domains.¹⁰⁵

It can be noted from the aforementioned literatures that various precursors have been explored in the CVD growth of NG. Besides, understanding of the dopant distribution in CVD-grown NG has been progressing recently. However, there are still several issues regarding the scalability of the growth process and the understanding of the growth mechanism. Firstly, most of the precursors used are either flammable or toxic, causing safety concerns on the growth process. Looking for more reliable and environmentally friendly precursors is still in demand. In addition, it is still unknown if dopant concentrations segregation exists in monolayer single-crystal NG domains. Understanding this fundamentally important growth mechanism would be key for future utilization of CVD-grown NG and facilitates a perspective for better and novel growth procedures.

In this thesis, large hexagonal-shaped monolayer NG single crystals were grown on Cu substrates via CVD using an environmentally friendly single-source precursor. Detailed investigations on the dopant distribution within the single crystals performed on the monolayer NG single crystals reveals that the distribution of N dopants in the

monolayer NG single crystals is not homogenous, where concentric hexagonal rings comprising N depleted regions are observed within the single crystal as determined by Raman spectroscopy. This phenomenon occurred in all our sampled monolayer NG single crystals, independent of their growth rate and crystal size. Supported by scanning tunneling microscopy (STM) measurements, we proposed that these alternating high and low doping concentration are formed as a consequence of sublattice segregation as dictated by the different types of edge attachments during growth (i.e., zigzag and Klein edges). This study provides new insights into the growth mechanism of NG crystals and enables new opportunities for tailoring the optical and electronic properties of graphene single crystals.

2.4.2 The h-BN as interfacing materials

The atomically smooth and dangling-bond-free surface, and electrical insulation of h-BN have made it an ideal interfacing material in many 2D heterostructures. Recently, CVD-grown h-BN films are becoming increasingly popular in this perspective due to its potential for large-scale production. CVD-grown h-BN has been used as an effective substrate of graphene-based FET for improved carrier mobility.^{106, 107}

Nevertheless, the use of CVD-grown h-BN in building various 2D stacks requires polymer-assisted transfer step which will inevitably cause contamination of the h-BN film, limiting the performance of the 2D heterostructure devices.¹⁰⁷⁻¹⁰⁹ Moreover, h-BN films grown on metal substrates (Cu, Ni, and Fe) often suffer from a relatively rough surface due to the formation of wrinkles,^{6, 110, 111} which degrading its material performance. Therefore, large-area production of smooth and interface-clean CVD-grown h-BN films is in great demand.

In this thesis, detailed characterization was performed to determine the microstructure of wrinkles in CVD-grown h-BN films and demonstrate a simple and effective method

that can significantly smoothen them. Briefly, wrinkles are formed upon thermal quenching at high growth temperature of ~ 1000 °C due to the large difference in coefficient of thermal expansion between the h-BN film and metal substrate. It is showed that by thermally annealing in air after transferring the h-BN film onto SiO₂/Si substrate, the height and width of the wrinkles became diminished. The smoothened h-BN film showed improved surface smoothness by up to 60 % and resulted in a much cleaner surface due to the elimination of polymer residues with no substantial oxidative damage to the film. A detailed explanation of the unwrinkling mechanism is presented in this thesis. Now, finally, this simple yet effective post-synthesis treatment for h-BN films would enable future utilizations of grown h-BN films which are urgently needed for the fabrication of high-performance scalable heterostructure devices.

2.4.3 Orientation control of TMDs

As an emerging group of 2D materials, TMDs have attracted extensive attention owing to their unique structure and diverse composition that enable them with fascinating applications potential in high-performance 2D electronics and optoelectronics.

Particularly, layered TMDs with vertical orientation could exhibit intriguing electrical properties and outstanding performance in various energy-related applications due to their high density of exposed chemically active edge sites. For example, vertically aligned (VA) MoS₂ has been fabricated by sulfidation of pre-deposited Mo film. The VA MoS₂ exhibits an excellent catalytic performance in hydrogen evolution reaction due to the high density of exposed edges.¹¹² Following this study, several other TMDs with vertical orientation (including WS₂, WSe₂, MoSe₂, and PtSe₂) were reported using similar processes, arousing tremendous research interests in synthesis of VA TMDs.¹¹³⁻

Recently, an increasing research interest has been focused on MoTe₂ due to its exceptional properties. For example, 2H MoTe₂ exhibits a narrow bandgap that is close to Si (~1.1 eV), making it a highly attractive materials in Si-based optoelectronics and photovoltaic devices.¹¹⁸ 1T' MoTe₂ has been reported to have Hall mobility of 4000cm² V⁻¹ s⁻¹, which is among the highest in 2D TMDs.¹¹⁹ The strong spin-orbit couple in MoTe₂ also make it desirable in valleytronics and spintronics.¹²⁰ The small ground-state energy difference per formula unite (~40 meV) between its semiconducting 2H phase and metallic 1T' phase also promises MoTe₂ in phase-changing-related applications such as phase-change memory device and creation of ohmic heterophase homojunction.¹²¹⁻¹²³ However, CVD growth of VA transition metal tellurides has remained unexplored. Hence, the CVD growth VA MoTe₂ layers is highly desirable in order to explore its unique properties and realize its application promises.

In this thesis, a scalable CVD growth of vertically aligned MoTe₂ layers on commercial Mo foil was presented. Due to the weak interaction, the as-grown MoTe₂ arrays can be easily detached from the Mo foil by slightly bending, which enables the economic reuse and recycling of Mo foil. High-resolution transmission electron microscopy suggests that the as-grown materials are highly crystalline MoTe₂ layers. Further discussion on the growth mechanism and extension of the growth method to other TMDs such as TaTe₂ and MoSe₂ were demonstrated. This study offers a versatile strategy for scalable fabrication of vertically aligned TMDs via CVD, which paves the way for their future utilization in high-performance optoelectronics and electrochemical devices.

3. Characterization Techniques

After the synthesis of 2D materials, various characterization techniques are adopted to investigate their structural properties, morphologies, elemental composition, and the growth mechanism. Understanding the working principles of these techniques are essential for the analysis of obtained data. Therefore, the following part introduces the characterization techniques used in this thesis.

Figure 3-1 (a) Schematic of transferring as-grown graphene on Cu to glass substrate.¹²⁴
 (b) Schematic of transferring as-grown MoS₂ on FTO substrate.¹²⁵

As graphene and h-BN are primarily grown on metal substrates and TMDs are mainly synthesized on dielectric substrates, the as-grown 2D materials need to be detached onto other substrates such as glass, Cu grid, and a clean SiO₂/Si substrate for further characterizations and device fabrication. Figure 3-1 illustrates a typical lift-off process that is commonly used for the transfer of graphene, h-BN and TMDs. Generally, the surface of as-grown 2D films was first spin-coated with a layer of thin PMMA. Subsequently, the as-grown films coated with PMMA can be detached by etching away the underlying substrates using a wet method. For graphene or h-BN grown on Cu,

etchant such as iron chloride (FeCl_3) solution or ammonium persulfate solution is commonly used, while potassium hydroxide (KOH) solution is often used to etch away SiO_2 in the transfer of TMDs. After extracting the PMMA-coated 2D materials onto a desired substrate, the PMMA is removed by soaking the films into acetone. However, this method may introduce contamination such as PMMA residue, etchants, or metal residues on the surface of the film. Therefore, improved or new methods such as electrochemical delamination and all-dry transfer method have been developed to produce cleaner and smoother films.

3.1. Scanning electron microscopy

Figure 3-2 Schematic of an SEM set up.¹²⁶

Scanning electron microscopy (SEM) is an equipment that can provide detailed characterization of samples topography by collecting signals from the interaction

between electron beam and the sample. As shown in the typical SEM set up in Figure 3-2, a focused electron beam emits from the electron gun sealed under vacuum and further accelerated to strike on the surface of samples. Secondary electrons emit from the sample when the electron beam collide with the shell electrons of the sample atoms. The intensity of the emitted secondary electrons is then converted into an image that can reflects the morphology and topography of the sample.

In this thesis, SEM is used to the characterize the morphologies and microstructures of 2D materials. Figure 3-3a,b presents representative SEM images of single-crystal h-BN domain with triangular shape and full-cover h-BN film with surface wrinkling, respectively.⁶² Therefore, SEM is an essential instrument to identify the morphologies details of 2D materials.

Figure 3-3 SEM images of h-BN on Cu (a) single crystals, (b) full-cover films.⁶²

3.2. Transmission electron microscopy

Figure 3-4 Schematic of a TEM set up.¹²⁶

Another electron microscopy technique is transmission electron microscopy (TEM). As shown in Figure 3-4, an electron beam is accelerated to strike on and transmitted through the sample. The objective lens focus the transmitted electrons to form an image that can be further zoomed in by the projector and intermediate lens. Due to the small de Broglie wavelength of electrons, TEM can capture fine details of the sample even as small as a single atom.

Over recent years, TEM has been widely used to analyze the microstructure and atomic characteristics of various 2D materials. Figure 3-5a show a raw TEM image of h-BN films taken by an aberration-corrected TEM with a monochromator, B and N

atoms can be clear distinguished in the atom intensity profile below.¹²⁷ The atomic resolution TEM image of the h-BN film is shown in Figure 3-5b. The hexagonal configuration of the h-BN plane and a triangle defect created by electron beam striking during TEM measurement can be identified.¹²⁷

Dark-field (DF) TEM imaging is able to show image of samples in specific crystal orientation, while selected area electron diffraction (SAED) is a crystallographic technique that can be used to identify the crystal structures and defect of materials. Combining these two techniques provides an effective way to determine the orientations of each single-crystalline domains within a polycrystalline 2D material. As shown in Figure 3-5c, a false color DF-TEM image of a polycrystalline h-BN film, where each crystal orientation as determine by SAED was represented by one color, clearly reveals the size and boundaries of each single crystal domains.⁸⁴ TEM equipped with electron energy loss spectroscopy (EELS) is capable of determining the elemental composition of a material with ultrahigh resolution. As shown in the EELS spectrum of h-BN film (Figure 3-5d), the characteristic K-shell ionization edges of B and N are indicated.⁶

Figure 3-5 (a) Raw TEM image of h-BN film, below is the atoms intensity profile along the trace.¹²⁷ (b) An atomic resolution TEM image showing a triangle hole in h-BN film.¹²⁷ (c) False color DF-TEM image of polycrystalline h-BN film comprising two orientations. The inset shows the SAED pattern with colored circles on the corresponding diffraction spots.⁸⁴ (d) EELS spectrum of the h-BN film.⁶

3.3. Atomic force microscopy

Atomic force microscopy (AFM) is capable of providing surface characterization of 2D materials such as morphologies, thickness, and lateral dimension in high resolution on the order of nanometers. As shown in Figure 3-6, AFM consists a photodiode and a cantilever tip that is attached with an ultra-fine needle. The cantilever tip deflects when the needle scans after brought into proximity of the sample surface. The deflection is monitored in real-time using a beam-deflection method, where a laser used to track the angular displacement of the cantilever, producing a topography image of the sample surface.¹²⁸

Figure 3-6 Schematic of an AFM set up.¹²⁸

Figure 3-7 show a representative AFM image and the corresponding height profile of graphene single crystals on SiO_2/Si substrate. The contrast variation in the topography image well presents the height and surface roughness of the graphene domains, and the thickness and roughness can be extracted across the selected area and line.¹²⁹ Therefore, the number of layers, size, and smoothness of 2D materials can be determined using AFM characterization technique.

Figure 3-7 AFM image of single-crystal graphene domains on h-BN flakes.¹²⁹

3.4. Raman spectroscopy

Raman spectroscopy is a powerful characterization technique capable of identifying a material based on the unique lattice vibrational frequency of specific chemical bonds within the materials. Figure 3-8 shows a schematic set up of a Raman spectrometer, a source of monochromatic light (laser) in visible, near infrared, or near ultraviolet range is shined on the surface of specimen.¹³⁰ The incident laser (light) interacts with the phonons, molecular vibration, or other excitements, resulted inelastic radiation with energy level of the laser phonons shifted up or down is referred as Raman scattering. This shift in energy contains the information about the vibrational modes of the specimen, thus is collected and processed for the identification of the lattice structure of the specimen.

In this thesis, Raman measurement was conducted at room temperature by a Witec system with a 532 nm laser excitation to determine the crystalline structures of various 2D materials.

Figure 3-8 Schematic of a Raman spectrometer.¹³⁰

As shown in Figure 3-9, two strong and intense characteristic peaks near $\sim 1583\text{ cm}^{-1}$ and $\sim 2676\text{ cm}^{-1}$ are assigned to the primary in-plane vibration mode (G band) and the second-order overtone of a different in-plane vibration mode (2D) of graphene, respectively. It is observed that the relative intensity of G band and 2D band are associated with the number of layers. For monolayer graphene, the intensity ratio of I_{2D}/I_G is ~ 2 , while bilayer graphene corresponds to a value of ~ 1 .¹³¹ Therefore, Raman spectroscopy is also used as a convenient tool to identify the layer number of graphene.

Figure 3-9 Raman spectra of mono-, bi-, tri-, and four-layer graphene and corresponding Raman intensity ratio of 2D band over G band.¹³¹

For the Raman spectrum of h-BN, peaks between 1365 cm^{-1} and 1370 cm^{-1} are assigned to the E_{2g} vibrational mode (Figure 3-10).¹³² Since the Raman signals of atomically thin h-BN is relatively weak, they are normally only used for indicating the presence of h-BN, while other information such as number of layers and defects require additional characterization techniques.

Figure 3-10 Raman spectra of 2D h-BN film.¹³²

Layered TMDs mainly exhibit four Raman active modes. A typical Raman spectra of MoS₂ is presented in Figure 3-11, where its A_{1g} , E_{2g}^1 , E_{1g} and E_{2g}^2 vibrational modes can be observed. A_{1g} mode is an interlayer mode due to the out-of-plane vibration of S atoms along c axis while E_{2g}^1 mode is an interlayer mode due to the in-plane vibration of S atoms with respect to Mo atoms.¹³³ E_{1g} mode resulted from the in-plane vibration of S atoms is negligible in backscattering geometry due to the forbidden selection rule of from the symmetry point of view.¹³³ E_{2g}^2 mode, which is also known as shear mode, originates from the rigid in-plane vibration against adjacent layers.¹³³ Apart from identifying molecules including the doping, the layer numbers of TMDs can be determined by the layer-number evolution of phonons in the Raman spectra.¹³³ In

addition, Raman spectroscopy is also extensively used to investigate the doping, interlayer coupling, spin-orbit splitting, and external perturbations in TMDs.¹³³

Figure 3-11 Raman spectra of layered MoS₂.¹³³

3.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique used to determine the elemental compositions, chemical valence state and the ratio of the elements of a material. As shown in Figure 3-12, the electron from the inner shell of the specimen atom is excited by the incident X-ray beam and move to a high energy

Figure 3-12 Schematic of an XPS set up.

level, when it returns to a lower energy level, a photon with wavelength that is characteristic for the specific element will be emitted. Thus, analysis of the XPS spectrum can produce qualitative results of the elemental composition of a specimen.

For XPS spectrum of pristine h-BN in Figure 3-13, the B 1s and N 1s core levels with a binding energy of 190.7 eV and 398.3 eV are observed, respectively, assigning to B–N bond.¹³⁴ Since XPS is a surface characterization technique with analysis depth of ~1–10 nm, it is important to avoid surface oxidation on the sample surface to obtain accurate results.

Figure 3-13 (a) B 1s (b) N 1s XPS spectra of h-BN.¹³⁴

3.6. Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FT-IR) is an effective instrument particularly for identifying chemical bonds in a sample. As shown in Figure 3-14, when IR radiation with different frequency is struck onto a sample, IR light with certain frequencies will be absorbed by molecules. The absorbed IR radiation then excites molecules into higher vibrational state. The wavelength of IR light absorbed by a molecule is determined by the energy difference between its ground state and excited state. Therefore, the raw absorption data contain detailed information of the chemical bonds in the sample. The FTIR uses an interferometer to modulate the wavelength from a broadband infrared source. The intensity of the transmitted light is measured by a detector. Since the

obtained signals is an interferogram, Fourier transformation is required to convert the acquired data into actual FTIR spectra.

Figure 3-14 Schematic of a FT-IR set up.¹³⁵

3.7. Ultraviolet-visible (UV-vis) spectroscopy

Ultraviolet-visible (UV-vis) spectroscopy studies the absorption or reflectance of a material near UV and in full visible spectral regions. This technique is widely used to determine the concentration of analytes in solution and optical bandgap of a material. Figure 3-15 shows a diagram of the components of a typical UV-vis spectrometer, the main components include a light source, a monochromator, a sample holder, and a detector. A beam of light from a visible and/or UV light source is separated into two beams. One of the two beams, the reference, transmits through the solvent or bare substrate, while the other beam passes through the solution to be studied or the materials on transparent substrate. The intensities of these two beams are then measured by corresponding detectors and compared to acquire the final spectrum.

Figure 3-15 Schematic of a UV-vis spectrometer set up.¹³⁶

In order to obtain the absorption spectrum of the h-BN film, it needs to be transferred onto a highly transparent substrate such as a quartz, which allows the light transmit through the film and reach the detector. As shown in Figure 3-16a, absorbance spectrum of the as-transferred h-BN exhibits a peak at ~202 nm.⁷⁹ The optical bandgap (OBG) of h-BN film is then calculated by converting the absorption spectrum to Tauc's plot by

Figure 3-16 (a) UV-vis absorbance spectrum and corresponding (b) Tauc's plot of as-transferred monolayer h-BN.¹³⁷

using the derived formula for a direct band gap semiconductor,¹³⁸

$$\alpha = C(E - E_g)^{1/2}/E \quad (1-4)$$

As shown in Figure 3-16b, by plotting $(\alpha E)^2$ against E , a straight line can be extrapolated and the intersection against the x-axis (E) is the extracted OBG. For monolayer h-BN film, the theoretical value is 6.0 eV.¹³⁹

3.8. X-ray diffraction

X-ray diffraction (XRD) is a technique used to identify the crystalline structure of materials. The three-dimensional structure of a crystalline materials is defined by regular and repeating atomic planes that form a crystal lattice. When monochromatic X-rays are struck onto the material and diffracted by the atomic planes, the distance between adjacent atom planes (d-spacing) can be measured by interpreting the diffracted X-rays data. Therefore, the crystalline structure of the material can be determined by comparing the characteristic set of d-spacing with standard reference patterns. As shown in Figure 3-17, an X-ray diffractometer consists of three main components: X-ray source, sample holder and detector. X-rays are generated when an accelerating electron beam emitted from a heated filament hits the target materials (Cu, Fe, Mo, Cr). By further filtering the X-rays using foils or crystal monochrometers, monochromatic X-rays are produced and directed toward samples. The diffracted X-ray data detected by the detector is processed by computer to acquire XRD spectrum. XRD characterization of bulk and thin film materials is typically operated in θ - 2θ scan mode, where the sample rotates with an angle of θ to receive the incident X-rays and the detector rotates 2θ to detect the corresponding diffracted X-ray.¹⁴⁰

Figure 3-17 Schematic diagram of XRD set up.¹³⁶

4. Graphene Single Crystals on Cu Foils

4.1 Introduction

Graphene is a 2D material comprising sp^2 -hybridized carbon in a honeycomb structure with extraordinary properties such as extremely high intrinsic carrier mobility,² thermal conductivity,³ and mechanical strength⁴. To date, graphene has been mainly fabricated by top-down (mechanical/chemical exfoliation) and bottom-up (CVD and molecular beam epitaxy) methods. Although mechanical exfoliation produces high-quality graphene by physically peeling off layers from graphite, the resulting flakes are usually with limited dimension and random yield.^{42,45} Chemical exfoliation method is promising for mass production of graphene nanosheets, but the obtained products inevitably suffer from relatively high defect level and low quality, which hinder their further practical applications.^{46, 47} Alternatively, CVD offers more pragmatic approaches to scalable fabricate high-quality graphene with controllable thickness.^{27, 48, 49} Therefore, this chapter focuses on APCVD growth and of monolayer graphene single crystals. Additionally, detailed characterizations were performed to evaluate the crystalline structure and quality of the graphene domains.

4.2 Experimental section

The CVD growth of graphene was conducted in a 1-inch quartz tube under atmosphere pressure using a 25- μ m-thick Cu foil (Nilaco) as substrates. Firstly, the surface coating of Cu foil was removed using dilute hydrochloric acid and the foil was further cleaned by rinsing in deionized (DI) water. As shown in the experimental setup in Figure 4-1, the loaded Cu foil was put in the middle of the furnace at constant Ar/H₂ flow. The furnace was ramped up to 1035 °C at a rate of 25 °C/min and remained constant for another 30 min for Cu annealing. Subsequently, 19 sccm CH₄ was flown into the quartz

tube to start the growth. After keeping the furnace at 1035 °C to finish the growth, the CH₄ and H₂ flow were stopped and the sample was cooled down rapidly under the protection of Ar flow.

Figure 4-1 Schematic layout of CVD set up for graphene growth.

4.3 Results and discussion

Figure 4-2 shows the SEM image of as-grown graphene on Cu foil. Some of the domains have complete hexagon shape that are referred as graphene single crystals, whereas the others are comprised of some hexagons merged together because of the closely situated nucleation sites. The as-grown graphene was then transferred on to SiO₂/Si substrates for further characterization. The slightly blue appearance on SiO₂/Si substrate (Figure 4-3a) indicates the presence of as-transferred graphene on top. The

Figure 4-2 SEM image of CVD-grown graphene single crystals on Cu. Inset is a magnified SEM image of a graphene single crystal.

hexagonal shape of a graphene can be clearly seen in the optical image (Figure 4-3b) of as-transferred graphene, showing that the morphologies of the domains were well preserved after transfer. Raman spectroscopy was performed to determine the structure of graphene. As shown in Figure 4-3c, the Raman spectrum of the monolayer graphene single crystal exhibits two strong and intense characteristic peaks corresponding to G band at $\sim 1583\text{ cm}^{-1}$ and 2D band at $\sim 2676\text{ cm}^{-1}$, with a negligible D band.¹⁴¹ This indicates an almost perfect crystal structure with very little defects, similar to that of mechanically exfoliated graphene. The intensity ratio of 2D over G bands (I_{2D}/I_G) is ~ 2 , signaling it was a single layer.¹³¹ The Raman intensity ratio map (I_{2D}/I_G) was performed over the domain (Figure 4-3d). The uniform color contrast indicates the high uniformity

Figure 4-3 (a) Optical image of the as-transferred graphene on SiO₂/Si substrate. (b) Optical image of the graphene domains on SiO₂/Si substrate. The hexagon shape of a graphene domain is outlined. (c) Raman spectrum of monolayer single-crystal graphene on SiO₂/Si substrate. (d) Raman intensity ratio (I_{2D}/I_G) map of a graphene domain.

of the synthesized monolayer graphene single crystals.

TEM was further utilized to examine the crystallinity of the graphene domains. Figure 3-4a shows a typical low-magnification TEM image of a suspended graphene membrane over the Cu grid. The corresponding SAED pattern (inset of Figure 3-4a) shows only one set of hexagonal diffraction spots, which indicates the single crystalline and high quality of the graphene domain.¹⁴² The atomically resolved TEM image (Figure 3-4b) shows atomic structure of the single-crystal graphene, which further verifies the high quality of the synthesized graphene sample.

Figure 3-4 (a) Low-magnified TEM image of as-transferred graphene film on Cu grip. Inset shows the FFT image. (b) The corresponding high-magnified TEM image.

4.4 Summary

In summary, an APCVD growth of monolayer graphene single crystals on Cu foil was demonstrated. Raman spectroscopy revealed that they are monolayer and high-quality graphene domains. TEM imaging showed that the graphene single crystals are highly crystalline and with perfect atomic structure. This work presented the CVD growth strategy and characterization techniques of graphene, which paves the way for the further engineering of its properties.

5. Nitrogen-doped Graphene Single Crystals

5.1 Introduction

Although graphene possesses exceptional electronic properties, there are substantial limitations for its practical utilization in many electronic and optical applications since it is considered a semi-metal with zero bandgap.⁷ The ability to modulate the electrical properties of graphene is hence important for the integration of graphene-based electronics. To date, one of the most controllable methods to open the bandgap in graphene is by substitutional doping with foreign atoms such as nitrogen (N) or boron (B); thereby enabling either an n-type or p-type semiconductor.^{68, 143, 144}

Doping of graphene can be obtained through: (i) direct synthesis processes such as CVD,⁶⁸ arc-discharge,^{145, 146} and solvothermal,¹⁴⁷ and (ii) post-synthesis processes such as thermal annealing,¹⁴⁸ plasma exposure,^{149, 150} and ion bombardment¹⁰⁵ with N-containing gases. Among these synthesis methods, CVD is considered as a more pragmatic approach to fabricate large-scale doped graphene with relatively high quality. In particular, most studies have been allocated to nitrogen-doped graphene (NG) because of the availability of N- and C-containing precursors such as using a mixture of gaseous sources including methane and ammonia,^{68, 102, 151} bubbling of liquid sources including acetonitrile¹⁵² and pyridine^{103, 153}, or by sublimation of solid sources such as melamine¹⁵⁴ and pentachloropyridine¹⁵⁵. Differing from post-synthesis doping processes where the dopants are randomly distributed, CVD-grown NG films have well-segregated regions comprising higher and lower doping concentration.¹⁰⁴ In addition, sublattice segregation is also known to occur for N dopants in NG, where the N atoms reside in the same sublattice within regions extending beyond 100 nm.^{105, 156}

To this end, investigations on the variations in N doping concentration are mainly conducted on highly polycrystalline films with small grain sizes.^{103, 104, 157} It is still

unknown whether dopant segregation occurs within a NG single crystal. Understanding this fundamentally important growth mechanism would be key for future utilization of CVD-grown NG and facilitates a perspective for better and novel growth procedures.

This chapter focuses on the synthesis of hexagonal-shaped monolayer NG single crystals with sizes of $\sim 20\ \mu\text{m}$ on Cu substrates using hexamethylenetetramine (HMTA, $(\text{CH}_2)_6\text{N}_4$) as a single-source solid precursor. Importantly, it is discovered that dopant segregation can exist in monolayer NG single crystals. Specifically, discrete segregation of concentric hexagonal rings within a single crystal comprising N depleted regions with widths spanning from ~ 0.5 to $1\ \mu\text{m}$ was revealed by Raman spectroscopy. The number of concentric rings that are parallel to the domain edges may vary between individual crystals. We gain further insights into the different dopant sublattice distributions by performing scanning tunneling microscopy (STM)

5.2 Experimental section

The growth of NG was conducted in a 1-inch quartz tube heated by a thermal CVD system. The schematic layout of the CVD set up is shown in Figure 5-1a. Firstly, the Cu foil surface was cleaned by dipping it into dilute hydrochloric acid and rinsing in deionized (DI) water. The Cu foil was then loaded into the quartz tube and 3 mg of hexamethylenetetramine (HMTA, VWR, product no. 24560, 99%) in a ceramic boat was put outside of the heating zone. The system was then purged with an Ar/H₂ flow of 200:20 sccm to remove the oxygen inside. The furnace was heated to 1050 °C at a rate of 25 °C/min and maintained at this temperature for 1h for Cu annealing. Subsequently, the HMTA powder was sublimated at 80 °C to commence film growth. After keeping the furnace at 1050 °C for another 30min to finish the growth, the sample was cooled down rapidly without changing the gases flow.

Figure 5-1. (a) Schematic diagram of CVD growth NG films. (b) TGA (black) and DTA (blue) curves of HMTA under an inert condition. (c) Possible reaction routes for the synthesis of NG by using HMTA as a sole precursor.

5.3 Results and discussion

Figure 5-1b shows the thermogravimetric analysis (TGA) and its corresponding differential thermal analysis (DTA) spectra of HMTA under an inert environment. A gradual weight loss of 0.8% can be observed at 100 °C, indicating that HMTA starts to sublime even at lower temperature and it fully decomposes with one endothermic peak at 200 °C. Figure 5-1c depicts the possible thermal decomposition paths for HMTA. When HMTA sublimates at an elevated temperature, it decomposes into various compounds such as trimethylamine ((CH₃)₃N), dimethylamine ((CH₃)₂NH), methylamine (CH₃NH₂), ethylene imine ((CH₂)₂NH), propionitrile (CH₃CH₂CN), and acetonitrile (CH₃CN).¹⁰²⁻¹⁰³ These heavier compounds (or HMTA itself) can be further (directly) broken down into lighter gases such as methane (CH₄), ammonia (NH₃),

Figure 5-2. (a–e) SEM images of NG/Cu grown at (a) 800 °C, (b) 900 °C, (c) 950 °C, (d) 1000 °C, and (e) 1050 °C. The insets show their corresponding magnified SEM images.

hydrogen (H_2), and nitrogen (N_2),^{158, 159} which are essentially the sources needed to fabricate NG films.⁶⁸ Since the release of the precursor gases can be controlled by using an appropriate sublimation temperature, the use of this single-source solid precursor can thus enable a relatively uniform growth of NG single crystals. We determined that the optimal sublimation temperature is 80 °C which resulted in well-defined hexagonal-shaped NG domains with sizes of up to $\sim 20 \mu m$, whereas a higher sublimation temperature will introduce more precursor vapor into the reaction zone, leading to higher density of nucleation and multilayer growth of NG.

The growth temperature is known to change the quality (thickness, uniformity, crystallinity et al.) of graphene. Thus, controlled experiments were conducted to investigate the effect of growth temperature on NG. SEM image (Figure 5-2a) and optical image (Figure 5-3a) show that mainly particles are deposited on Cu surface at 800 °C, which is amorphous carbon as indicated by the broadening of D peak ($\sim 1350 \text{ cm}^{-1}$) and G peak ($\sim 1588 \text{ cm}^{-1}$) (I_D/I_G), as well as their high intensity ratio (I_D/I_G) (Figure 5-3f).¹⁶⁰ Increasing the growth temperature (up to 1050 °C) was found to improve the quality of NG domains as indicated by their enlarging size, narrowing Raman peaks and

increasing I_D/I_G (Figure 5-3f),^{68, 161, 162} and decreasing thickness (Figure 5-4). Further increasing of the growth temperature is not applicable as it will lead to melting of the Cu substrate. Wrinkles are observed in the AFM images of transferred NG domains on SiO₂/Si, which was formed due to the large different of coefficient of thermal expansion between graphene and Cu.

Because of the impermeable nature of graphene,¹⁶³ the underlying Cu has temporal resistance to oxidation.^{36, 164} Hence, a quick method to determine the presence of graphene is to oxidize the Cu surface by heating the as-grown sample in air.¹⁶⁴ Figure 4-5a shows an optical image of an air-oxidized NG/Cu sample which clearly reveals the

Figure 5-3. (a–e) Optical images of transferred NG on SiO₂/Si substrates grown at (a) 800 °C, (b) 900 °C, (c) 950 °C, (d) 1000 °C, and (e) 1050 °C. (f) Corresponding Raman spectra of the NG in (a–e).

Figure 5-4. AFM images of NG on SiO₂/Si substrates which were grown at (a) 900 °C, (b) 950 °C, (c) 1000 °C, and (d) 1050 °C.

hexagonal edges of the NG domains. The regions that are covered by the NG domains retained the same optical contrast as non-oxidized Cu (bright contrast), whereas the regions that are exposed became oxidized (dark contrast). Figure 5-5b shows a typical SEM image of NG domains on Cu. Some of the observed domains have a complete hexagonal shape, which is referred to as a single crystal, whereas others comprise merged domains because of closely situated nucleation sites. Figure 5-5c shows an optical image of the transferred NG domains on the SiO₂/Si substrate. The hexagonal shape of a NG single crystal is outlined, showing that the morphologies of the NG domains are well preserved after transfer. Figure 5-5d shows an AFM image of a NG

Figure 5-5. (a) Optical image of an oxidized NG/Cu sample. The NG single crystals are in pink color while the oxidized Cu surface is in orange color, respectively. (b) SEM image of the as-synthesized hexagonal-shaped NG single crystals on Cu substrate. The inset shows the corresponding magnified SEM image. (c) Optical image of the as-transferred NG on SiO₂/Si with an NG domain outlined by a black frame. (d) AFM image of an edge of a hexagonal-shaped NG single crystal on SiO₂/Si substrate. The inset shows the height profile along the blue line. (e) Typical low-magnification TEM image of a suspended NG film over a TEM grid hole. High-resolution TEM images taken at the (f) edge and (g) interior of the NG film. The inset in (g) shows its corresponding SAED.

domain with a thickness of ~ 0.8 nm corresponding to a single layer. Transmission electron microscopy (TEM) was used to determine the microstructure of the NG crystals. Figure 5-5e shows a typical bright-field TEM image of a suspended NG film covering over a grid hole. Folding and tears in some regions of the transferred film can be readily observed because of the rough handling procedures of transfer process. The monolayer nature and crystalline structure of the NG film were further determined by the high-magnification TEM images which were taken at the edge and the interior of the suspended NG film, as shown in Figure 5-5f,g, respectively. The corresponding SAED pattern showed one set of hexagonal diffraction spots, which confirms the hexagonal lattice structure of the NG single crystal.

The chemical composition and bonding structures of the transferred NG were investigated using XPS. Figure 5-6a,b shows the deconvoluted high-resolution C 1s and N 1s XPS spectra, respectively. There are four components in the C 1s spectrum; the main peak at 284.7 eV corresponds to the graphitic sp^2 C,⁶⁸ indicating that most of the C atoms in the NG are arranged in a conjugated honeycomb lattice, whereas the peaks centering at 285.9 eV, 287.1 eV, and 289.1 eV are attributed to the N- sp^2 C, N- sp^3 C bonds, and oxidized C, respectively.^{68, 165} For the N 1s spectrum, two components can be distinguished. The peak located at 399.7 eV corresponds to graphitic N which means that N atoms are substitutionally doped into the graphene lattice, while a less intense peak at 402.2 eV corresponds to oxidized N.^{103, 148, 165-167} The extracted N doping concentration based on the integral intensities of C 1s and N 1s peaks is $\sim 0.6\%$. The relatively low doping concentration is attributed to the high growth temperature that favors the formation of C–C bonds while suppressing N–C bonds.^{151, 168} Raman spectroscopy was further carried out to investigate the crystallography and doping

Figure 5-6. Deconvoluted high-resolution (a) C 1s and (b) N 1s XPS spectra of transferred NG on SiO₂/Si substrate (c) Raman spectrum of monolayer single-crystal NG on SiO₂/Si substrate.

characteristics of the as-prepared NG (Figure 5-6c). Besides two typical peaks of graphene at $\sim 1588\text{ cm}^{-1}$ (G band) and $\sim 2676\text{ cm}^{-1}$ (2D band), the NG single crystal showed two additional peaks at $\sim 1343\text{ cm}^{-1}$ (D band) and $\sim 1623\text{ cm}^{-1}$ (D' band) which are activated by defects or lattice distortion and are characteristic of NG.^{141, 168-171}

Figure 5-7a,b shows an optical image of NG domains transferred onto a SiO₂/Si substrate and its corresponding Raman spectra collected at various positions within a single-crystal domain. The Raman spectra are consistent which comprise all the characteristic peaks (D, G, D' and 2D peaks), indicating that N dopants are present throughout the entire domain.^{68, 161, 162} To investigate the dopant distribution, we performed Raman mapping over the domain within the black boxed region in Figure 5-7a. Figure 5-7c–e shows the intensity maps of the D, G and 2D bands, respectively. Remarkably, concentric hexagonal rings with widths of ~ 0.5 to $1\text{ }\mu\text{m}$, parallel to the edges of the domain, can be readily observed in the D and 2D intensity maps, whereas the G band intensity remained almost consistent throughout the domain. These rings comprise Raman spectra with a slight attenuation in the D band and a more intense 2D band (Figure 5-7f), indicating that these regions have a relatively lower doping concentration.¹⁰⁴

Raman intensity ratios of I_D/I_G and I_{2D}/I_G have been previously used to monitor the

Figure 5-7. (a) Optical image of the transferred NG single crystals on SiO₂/Si substrate. (b) Raman spectra acquired at different positions over a NG single crystal in (a). (c–e) Raman intensity maps of the (c) D, (d) G, and (e) 2D bands over the black boxed region in (a). (f) Comparison of the Raman spectra acquired at the black and red spots as indicated in (e).

doping level in graphene, it is found that I_D/I_G increases while I_{2D}/I_G decreases for increasing doping.¹⁷²⁻¹⁷⁴ Thus, to further verify the inhomogeneous distribution of N dopants within the single crystal, we mapped out the intensity ratios of I_G/I_D and I_{2D}/I_G in Figure 5-8a,b respectively. Note that I_G/I_D instead of I_D/I_G is mapped to enhance the contrast. As can be seen in the corresponding plots below each Raman maps extracted across the black lines, the concentric rings (indicated by blue arrows) exhibit a decreased

I_D/I_G ratio of $\sim 0.107 \pm 0.022$ and a increased I_{2D}/I_G ratio of $\sim 0.146 \pm 0.047$ compared to regions outside the concentric rings. Hence, we can reasonably conclude that there are well-segregated regions comprising lower concentration of N dopants within the single crystal which extends up to $\sim 1 \mu\text{m}$.¹⁷² Because of the opposing trends in I_D/I_G and I_{2D}/I_G , the I_{2D}/I_D ratio amplifies the doping variations within the NG single crystals and can be used as a quick method for doping homogeneity characterization.¹⁰⁴ Figure 5-9a–d shows four representative I_{2D}/I_D Raman maps collected within one transferred sample under the same CVD growth. It is observed that the number of concentric rings may vary between individual single crystals, and even for adjacent merged grains as shown in Figure 5-9c. From our 15 randomly selected samples of single crystals, we observed that these rings can range from 1 to 4, and none of them is without any concentric ring. Furthermore, by increasing (decreasing) the H_2 flow to reduce (increase) the growth rate of the single crystal, the presence of concentric ring(s) is consistently observed (Figure 5-10).

Figure 5-8. Raman maps of the intensity ratios, (a) I_G/I_D and (b) I_{2D}/I_G , of the NG single crystal. The corresponding plots below are extracted across the black line.

Atomic resolution STM measurements were performed on the NG/Cu samples to obtain direct visualization of the N dopants and their atomic configurations. Figure 5-11a shows an atomically resolved topography of the NG sample. In agreement with previous reports,^{104, 144, 175-177} graphitic N dopant in graphene appears dark in the STM image, while the three surrounding C atoms are bright, forming a triangle, due to an increased local density of states (DOS). The line profile across the dopant (inset of Figure 5-11a) yielded atomic corrugation with an apparent maximum out-of-plane height of ~50 pm. STM measurement of the differential conductance, dI/dV , was performed on the N dopant indicated in Figure 5-11a. The dI/dV curve in Figure 5-11b shows distinct gap-like features centered at zero bias and a local conductance minimum at ~230 meV. The gap-like feature arises from phonon-mediated inelastic tunneling

Figure 5-9. (a–d) Raman maps of I_{2D}/I_D of various NG single crystals which exhibit different number of concentric hexagonal rings for different individual domains.

Figure 5-10. Raman maps of I_{2D}/I_D of the NG single crystals grown using (a) 10 sccm, (b) 20 sccm and (c) 40 sccm of H_2 flow rate.

electrons into graphene, and the -230 meV feature results from inelastic tunneling to the Dirac point of an electron-doped graphene layer. Given that the geometry, the height of the N atoms and the distinct features in the dI/dV curve are all in correspondence to graphitic N doping,^{104, 156, 177, 178} we use this to further analyze the occupancy of the N dopants within the graphene sublattice.

Recently, there have been several groups that reported heterogeneity and segregation of N dopants in CVD-grown NG films.^{104, 105, 156} For example, Zhao *et al.* evidenced heterogeneity of N doping concentration in polycrystalline NG films where N dopants are depleted along the grain boundaries and edges for over micron length scales.¹⁰⁴ Zabet-Khosousi *et al.* reported the segregation of N dopants where the N atoms preferentially occupy the same sublattice which extends to over 100 nm.¹⁰⁵ In our STM measurement on NG sample, we observed similar phenomenon where N dopants can occupy two different sublattices of graphene, as can be seen within the mirroring blue and red triangles in Figure 5-11c. However, segregation in the distribution of the N dopants can be observed where clusters of N atoms often occupy the same sublattice.^{105,}
¹⁵⁶ Figure 5-11d shows an STM image of the NG sample, where N dopants occupying

two different sublattices are indicated by the blue and red triangles, respectively. Importantly, Figure 5-11d also shows a phenomenon of sublattice segregation of N dopants, that is, the two clusters of N dopants located at different sublattices are obviously segregated from each other.

From our aforementioned analysis on relatively large hexagonal-shaped single-crystal NG, we denote three important observations that provide further insights into the growth mechanism: (i) the concentric rings comprising depleted N dopants have parallel edges to the single-crystal NG domain with widths spanning up to $\sim 1\ \mu\text{m}$, (ii) the number of concentric rings is not uniform and can vary between adjacent domains, and (iii) there is a segregation of N dopants that occupy two different sublattices of graphene. Because the hexagonal concentric rings shown in the Raman maps of our NG sample have parallel edges to the single-crystal domain, which are very similar to the isotope-labeled Raman maps of graphene,¹⁷⁹ they must form along the growth fronts of the NG domain by edge attachment in a surface-mediated growth process.^{26, 105, 156, 179, 180} The variation in concentration of N-containing precursor gas (i.e., NH_3) during growth is unlikely the reason for dopant depletion because the number of concentric rings may vary between similar-sized single-crystal domains where the distances between each successive rings are different. Furthermore, the decomposition of HMTA cannot yield such intermittent trend comprising alternating high and low concentration of N when using a constant sublimation temperature. The depletion of N dopants along grain boundaries also cannot explain our observation because the segregation occurs within a single crystal with no grain boundary. Hence, based on our STM measurements, we propose that the observed heterogeneity is the consequence of sublattice selectivity of N dopants.

For CVD growth of NG, two types of N edge attachments are considered where energy is at minima: zigzag and Klein edges.¹⁰⁵ These edges thus dictate the corresponding sublattices the substitutional N atoms occupied within the graphene

Figure 5-11. (a) An atomically resolved STM image of an N dopant. The inset shows the height profile across the dopant. (b) dI/dV curve obtained at the N dopant. (c) STM images of individual N dopants occupying different graphene sublattices indicated by blue and red triangle. (d) Large-area STM image showing discrete segregation of the N dopants occupying different sublattices.

lattice. Although N attachment to either edges are considered to be energetically stable, as evidenced by the N atoms occupying different sublattices, the zigzag edge is slightly more favorable than the Klein edge (< 0.04 eV).¹⁰⁵ Therefore, we expect that edge

attachment of N to the zigzag edges should be more dominant and these regions should comprise slightly higher N concentration as compared to Klein edges. However, because the difference in energy between zigzag and Klein edges is relatively small, the occurrence of N attachment to Klein edges is viable as well. The discrete segregated regions with N dopants in different sublattices that extend to over micrometer length scales imply that the same edge attachment of N (to either zigzag or Klein) replicates itself in successive rows as a consequence of energy minimization;¹⁰⁵ thereby resulting in the formation of concentric segregated hexagons in the Raman maps of hexagonal-shaped NG domains.

The transition of N attachment via zigzag edges to Klein edges is more complex and not fully understood. Zabet-Khosousi *et al.* suggested that this could arise from either merged NG grains or an abrupt change on the Cu surface such as transient terrace steps.¹⁰⁵ However, both these explanations are not applicable in our hypothesis. The segregation of N dopants is observed in a single crystalline structure and the concentric hexagonal rings that have parallel edges to the NG domain cannot be caused by the underlying Cu structure. The transition from high to low N concentration and vice-versa must have happened during the growth of the single crystal and their occurrences may differ between individual crystals as observed by the non-uniformity in the number of concentric rings.

5.4 Summary

In summary, large hexagonal-shaped monolayer NG single crystals were grown on Cu substrates by CVD using HMTA as a single-source solid precursor. Importantly, Raman characterization evidenced that dopant segregation exists in monolayer NG single crystals. Concentric hexagonal rings with edges parallel to the NG crystal and widths of

~0.5 to 1 μm comprising N depleted regions are readily observed as determined by the attenuation in D band and more intense 2D band. We observed that the number of concentric rings is not dependent on the size of the NG crystal and may vary between adjacent single crystals. STM measurements confirmed that N atoms are introduced into different sublattices of graphene in substitutional sites. The doping inhomogeneity is attributed to sublattice selectivity of the N dopants by attachment via zigzag or Klein edges, where the former resulted in higher doping concentration and the latter are N depleted regions. Given that NG with uniform dopant distribution and large grain size is more favored in electronics application, further effort to achieve a uniform dopant distribution in NG single-crystal and to improve the grain size of NG is still required for their practical application. This work provides important insights into the growth mechanism of CVD-grown NG single crystals and enables new opportunities for tailoring the electronic and optical properties in graphene.

6. Unwrinkling of CVD-grown h-BN Films

6.1. Introduction

Atomically thin hexagonal boron nitride (h-BN) is a 2D material comprises of alternating boron and nitrogen atoms arranged in a sp^2 -bonded honeycomb network.¹⁸¹ The h-BN is an insulator and has an atomically smooth and dangling-bond-free surface, which make it one of the crucial building blocks for two-dimensional (2D) heterostructure devices.⁴⁰⁻⁴² To date, the most utilized synthesis technique to fabricate large-area h-BN films is by using metal-catalysed chemical vapor deposition (CVD).^{6, 62, 132, 182} However, the h-BN films that are produced and their post-synthesis processes (i.e., the transfer process) often induce defects, strains, and contaminants. In particular, the increased surface roughness caused by thermally-induced wrinkles has remained a widespread problem which significantly hampers the effective utilization of CVD-grown h-BN films.

Wrinkles are out-of-plane lattice distortions which are ubiquitous in 2D films such as graphene and h-BN, which are grown on metallic substrates, due to the presence of thermal stress between the film and the underlying growth substrate. Briefly, upon thermal quenching at high growth temperatures of 1000 °C and above, the large difference in coefficient of thermal expansion (CTE) between graphene or h-BN and the metal substrate (i.e., Cu and Ni) causes the metal to corrugate by step bunching due to tensile strain and the graphene or h-BN overlayer to form wrinkles due to compressive strains.^{6, 110, 111, 183-185} Although wrinkles are usually detrimental as they result in uneven surfaces and alter the properties of the film,¹³⁷⁻¹³⁸ understanding its structure through in-depth characterization could lead to other creative and novel uses.^{186, 187} However, in comparison to graphene, the wrinkling structure of h-BN and methods to reduce the surface roughness have not been extensively explored.

In this chapter, the APCVD growth of h-BN films on Cu substrate was demonstrated. Particularly, detailed characterization to the h-BN wrinkles formed during CVD growth and after transferring onto SiO₂/Si substrates. Importantly, an effective solution to smoothen the wrinkles and thus enabling smoother films was provided. Efficient strain relaxation through corrugation of the Cu surface by step bunching is evident due to the large difference in CTE with the monolayer h-BN. When the h-BN film is transferred to a flat SiO₂ surface, the uneven corrugated structure can be released upon film detachment but wrinkles are still prevalent due to the excess h-BN along the Cu steps and terraces. These wrinkles, however, can be efficiently smoothened by simply annealing under air at 550 °C. During annealing, hydroxylation occur on both the h-BN film and SiO₂ surfaces which caused a reduction in adhesion energy between the h-BN/SiO₂ interface and resulted in the unwrinkling of the h-BN film. Due to the high temperature stability of h-BN, negligible amount of oxidative damages to the film at temperatures below 840 °C was recorded. Dehydroxylation occurs over time and the h-BN film is subsequently restored back to its original state.

6.2. Experimental sectionCVD growth of h-BN films

H-BN films were grown on Cu foils (Nilaco, 25 µm thick) via thermal CVD under atmosphere pressure. Firstly, the surface coating of Cu foil was removed using dilute nitric acid and the foil was further cleaned by rinsing in deionized (DI) water. Subsequently, the Cu foil was loaded into the center of a 1-inch quartz tube and 10 mg of ammonia borane (AB) (Sigma-Aldrich, product no. 682098, 97%) in a ceramic boat was placed outside the heating zone. A 200:20 sccm of Ar/H₂ as carrier gases was flowed into the system and kept constant throughout the whole process. The furnace was then ramped up to 1050 °C at a rate of 25 °C and remained constant for another 1 h for Cu annealing. After that, the AB was heated at ~85 °C to commence the film growth.

After keeping the furnace at 1050 °C for another 30 min to finish the film growth, the sample was rapidly cooled down without change the gases flow.

6.2.2. Thermal annealing

The transferred h-BN/SiO₂/Si samples were loaded into a 1 inch quartz tube with its ends exposed to ambient atmosphere. The furnace was ramped up to the specified temperature at a rate of 50 °C/min and kept constant for 10 min. After annealing, the furnace was allowed to cool down and the samples were extracted out from the quartz tube at room temperature.

6.3. Results and discussion

Figure 6-1a shows an optical image of a continuous h-BN film transferred onto a 285 nm SiO₂/Si substrate with a distinctive Raman peak at 1371 cm⁻¹, corresponding to the E_{2g} vibration mode of monolayer h-BN.¹⁸⁸ High-resolution TEM was utilized to determine the atomic structure of the film. Figure 6-1b shows a TEM image of a suspended h-BN membrane over a TEM grid hole. Presence of partial folds and tears within the film can be observed as a result of the rough handling procedures used during the transfer process. The edges of the suspended membranes within the TEM grid were surveyed and most regions comprise of a single layer as shown in Figure 6-1c. The crystalline structure within the interior of the membrane is consistent to that of h-BN which exhibits characteristic triangular-shaped defects due to the anisotropic etching by electron beam irradiation (Figure 6-1d).¹²⁷ Selected area electron diffraction (SAED) taken over the membrane shows a hexagonal pattern with measured d-spacings of 2.18 Å and 1.27 Å corresponding to the (10-10) and (21-10) planes of h-BN, respectively (inset of Figure 6-1d), in good agreement with previous reported values.¹¹⁰

Although the film may look smooth under an optical scope, atomic force microscopy (AFM) reveals the rough landscape of the h-BN film in the nano-scale (Figure 6-1e). Excess surface area relative to a flat surface ($\Delta A/A_0$) represents the percentage increase of the three-dimensional surface area over the two-dimensional surface area, and provides a good measure of the surface roughness.¹⁸⁹ Many seemingly parallel lines with step heights ranging from ~1-4 nm can be observed throughout the scanned region with a periodicity (λ) of ~153 nm and a measured $\Delta A/A_0$ of ~0.12%. To identify the origin of these wrinkles, the as-grown h-BN film prior to transfer was carefully examined. Figure 6-1f shows the AFM image of the highly-corrugated h-BN/Cu surface. Many uneven grooves with step heights ranging from ~3-18 nm and a similar λ of ~125 nm can be observed, demonstrating that the wrinkles observed in the transferred film are related to the morphology of the h-BN/Cu surface. However, the measured $\Delta A/A_0$ of the as-grown h-BN/Cu is ~2.55%, which is much larger than the transferred film. This huge disparity is attributed to the transfer process. In a typical transfer, the corrugated h-BN morphology is released during film detachment,¹⁴⁴ and upon transferring to a substrate, the film conforms to the flat SiO₂ surface with strong adhesive energy by van der Waals forces.^{190, 191} Hence, the effective excess h-BN surface area should reduce after transfer. It should be noted that different transfer processes will yield different degree of wrinkle density based on the duration of detachment process.^{6, 48, 192, 193}

Figure 6-1g shows a magnified scanning electron microscopy (SEM) image of the corresponding h-BN monolayer film on Cu. The periodic lines can be easily identified which are consistent over an individual Cu grain but may change over different grains in the polycrystalline Cu as shown in the SEM image of h-BN/Cu (Figure 6-2). This indicates that they are reconstructed Cu surfaces formed by step bunching as a consequence of strain relaxation with an h-BN overlayer.^{183, 185} The formation of the

Figure 6-1 Characterization of wrinkles in monolayer h-BN films. (a) Optical image of transferred monolayer h-BN on SiO₂/Si substrate. Inset shows the corresponding Raman spectrum. (b) TEM image of a suspended h-BN membrane over a grid hole with several folded regions. High-resolution TEM images of (c) a folded edge and (d) interior of a monolayer h-BN. Inset in (d) show the corresponding SAED. (e) AFM image of the transferred h-BN in (a). (f) AFM and (g) SEM image of the as-grown h-BN film on Cu prior to transfer. (g) Schematic of the formation of wrinkles on monolayer h-BN film during thermal quenching. The red and green arrows indicate the contraction of bulk Cu and expansion of h-BN film, respectively

corrugated surface structure is further illustrated in the schematic in Figure 6-1g. Similar to graphene, h-BN has an anisotropic thermal expansion behavior. The CTE of h-BN along the c-crystallographic axis, α_c , remained relatively constant at $\sim 40 \times 10^{-6} \text{ K}^{-1}$ in the range of 273-800 K, while it is negative along the in-plane direction, α_a , with measured values of $-2.8 \times 10^{-6} \text{ K}^{-1}$ at 293 K and $-0.9 \times 10^{-6} \text{ K}^{-1}$ at 800 K.¹⁹⁴ This indicates that the in-plane structure of the h-BN expands as temperature decreases. On the other hand, Cu has a positive CTE of $16.85 \times 10^{-6} \text{ K}^{-1}$ at 293 K and increases to $\sim 25 \times 10^{-6} \text{ K}^{-1}$ at 1300 K with an overall uniaxial expansion of 2.088% over the temperature range.¹⁹⁵

Figure 6-2 (a) SEM image of as-synthesized h-BN film on Cu. (b, c) Magnified SEM images in (a) showing the different orientation of the step bunches on different Cu grains.

Hence, upon thermal quenching at the high growth temperature of 1050 °C, the in-plane structure of the h-BN expands while the bulk Cu contracts, causing strains along the h-BN/Cu interface. The Cu surface corrugates due to tensile stress by forming step bunches,^{183, 185} while the excess h-BN forms wrinkles by mechanical deformation along more susceptible regions such as Cu step edges and Cu grain boundaries.¹⁹⁶ It should be noted that the corrugated Cu surfaces are independent of h-BN grain boundaries as they remained continuous over merged h-BN domains (Figure 6-3). Since the corrugated h-BN structures are released upon transfer, the wrinkles that are observed on the transferred h-BN originated from the excess h-BN which mechanically deformed over the Cu steps and hence, retained the similar periodic parallel lines.

It has been reported that unwrinkling in graphene by thermal annealing is accompanied by the formation of nanoscale pits and cracks as the result of oxidative etching.¹⁴⁸ This simple yet efficient technique, however, has not been extended to h-BN

Figure 6-3 (a) SEM image of a noncontinuous monolayer h-BN film. (b–d) Magnified SEM images revealing the Cu corrugation across multiple h-BN grain boundaries.

films, whose high-temperature and chemical stability make them resistant to oxidation at elevated temperatures of up to 850 °C for monolayers in air.^{39, 197} For our CVD-grown h-BN films, Raman and AFM were utilized to determine the crystallinity and surface morphology of h-BN films before and after air annealing at different temperatures (550 °C, 800 °C, and 840 °C). As shown in the optical images (Figure 6-4 a-d), no noticeable difference in h-BN/SiO₂ before and after air annealing is observed due to the high transparency of the film. However, the corresponding Raman spectra and fitted peaks (Figure 6-4e,f) show the broadening of E_{2g} peak when the film is annealed in air at 800 °C and 840 °C, indicating the reduced crystal size and increased defect level induced by oxidation.¹⁹⁸ In contrast, negligible change to the Raman spectrum is observed at a lower annealing temperature of 550 °C, which indicates no oxidative damages to the film. Severe etch pits and lines due to oxidation are observed in the optical and AFM image of h-BN film annealed in air at 840 °C for 2h (Figure 6-5b), further indicating the oxidation of h-BN.

Figure 6-4 Optical images of (a) as-transferred h-BN film on SiO₂/Si substrate and after annealing in air at (b) 550 °C, (c) 800 °C and (d) 840 °C. (e,f) Raman spectra and their corresponding fitted peaks of the respective h-BN films in (a – d).

To determine the temperature needed to smoothen the wrinkles, the as-transferred h-BN films on SiO₂/Si were respectively annealed at 350 °C, 450 °C, and 550 °C in air for 10 min. Figure 6-6 shows the AFM images of the transferred monolayer h-BN film before and after thermal annealing at various temperatures. The root-mean-square roughness (R_q) in AFM image is a parameter obtained by calculating the standard deviation of the data within sampling area, which gives insights into height profile and surface uniformity.¹⁹⁹ It is observed that the wrinkles could not be effectively smoothed at temperatures below 550 °C. However, when the film is annealed at 550 °C (or higher),

Figure 6-5. (a) Optical and (b) AFM images of transferred h-BN film after annealing at 840 °C for 2 h. The onset of oxidation can be observed by the presences of nanoscale pits and the elongated etch lines along the wrinkled structures.

most of the wrinkles were effectively smoothened with reduced height and width, resulting in a dramatic improvement in surface smoothness from a measured R_q of ~ 0.9 nm down to ~ 0.3 nm and a reduced $\Delta A/A_0$ from 0.19% down to 0.045%. No observable etching lines or cracks indicate that h-BN is indeed more resistant to oxidation as compared to graphene.

To probe the early stages of the smoothening process, we performed the same annealing procedure on the h-BN film with multilayers where there is higher density of wrinkles. Figure 6-7a–d shows the AFM images of the as-transferred h-BN film and the same sample which subsequently underwent 10, 20 and 30 min of thermal annealing at 550 °C under air. We observed a systematic decline in the height and width of the wrinkles with no oxidation-related etching to the film. The boxed regions indicate the measured surface roughness within the interior of an h-BN grain. Remarkably, most of the wrinkles have been eliminated after 30 min of annealing and the surface became very smooth (R_q of ~ 0.3 nm). It should be noted that the particles observed along the multilayer regions are carbonaceous contaminants from the environment due to prolonged annealing in air (Figure 6-8). Importantly, the presence of oxygen or other oxygen-

containing molecules during the annealing is critical for the unwrinkling process as wrinkles are still prevalent even after 1 h of annealing under inert conditions (Figure 6-9).

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical bonding and elemental compositions of the transferred h-BN film on SiO₂/Si substrate. Figure 6-10a–f shows the high resolution B 1s, N 1s and C 1s spectra of the h-BN film before

Figure 6-6 Smoothing of wrinkles in a transferred monolayer h-BN film. AFM images of a transferred monolayer h-BN film on SiO₂/Si substrate (a) before and after annealing in air for 10 min at (b) 350 °C, (c) 450 °C, and (d) 550 °C, respectively. Their corresponding height profiles across the black lines are plotted below.

Figure 6-7 Smoothing of wrinkles in transferred h-BN film with multilayers. AFM images of a transferred h-BN film with multilayers on SiO₂/Si substrate (a) before and after annealing under air at 550 °C for (b) 10 min, (c) 20 min, (d) 30 min, respectively. Their corresponding height profiles across the black lines are plotted below.

and after thermal annealing at 550 °C, respectively. It is observed that both samples displayed a single peak in the B 1s and N 1s core levels with a binding energy of around 191 eV and 398.3 eV, respectively, assigning to B–N bond.²⁰⁰ The as-transferred h-BN film showed a relatively high amount of C composition of 59.8% with respect to B and N. Note that O was not included in the calculation due to presence of the underlying SiO₂ surface. Three deconvoluted peaks in the C 1s core level centering at 284.8, 286.3 and 288.2 eV, correspond to C–C/C=C, C–O and C=O bonds, respectively.²⁰¹ These are attributed to the residues and trapped absorbents by the PMMA,²⁰² which was used to coat the BN film during the transfer process. The C composition was significantly reduced to 39.7% for sample annealed at 350 °C and to ~32% for samples annealed at 450 °C and 550 °C, indicating that the majority of the PMMA impurities have been effectively removed.²⁰² This shows that a much cleaner h-BN surface can be obtained after performing this simple annealing process.¹⁰⁶

Figure 6-8 Representative Raman spectrum in some regions of the annealed h-BN film with multilayers indicating the presence of carbonaceous contamination by the presence of D and G bands.

Fourier transform infrared spectroscopy (FT-IR) characterization, which is sensitive to oxygen-containing group, was performed on target surfaces to further investigate the role of oxygen in the unwrinkling of h-BN films by air annealing. The comparative FTIR spectra for Si substrates and h-BN/Si samples before and after air annealing are shown in Figure 6-11. The transferred h-BN film can be detected as indicated by the characteristic peak at 1370 cm^{-1} which corresponds to the in-plane B-N stretching mode.^{66, 203-205} Incorporation of hydroxyl group is evident on both bare Si and h-BN/Si

Figure 6-9 AFM images of (a) as-transferred h-BN film and after annealing at $550\text{ }^{\circ}\text{C}$ under 200:20 sccm of Ar/H₂ for (b) 10 min and (c) 1 h. The h-BN wrinkles are still prevalent even after 1 h of annealing in Ar and H₂.

Figure 6-10 High-resolution XPS spectra of B 1s, N 1s and C 1s core levels for transferred h-BN film on SiO₂/Si substrate (a–c) before and (d–f) after annealing in air at $550\text{ }^{\circ}\text{C}$, respectively.

samples after air annealing, as revealed by the new additional peaks at 3570 cm^{-1} and 3740 cm^{-1} which correspond to O-H stretching vibrational mode,²⁰⁶⁻²⁰⁹ confirming the presence of hydroxyl group on h-BN/Si after air annealing.

To investigate the changes that occur in the h-BN film during and after the unwrinkling process, a fresh piece of monolayer h-BN film was transferred onto quartz substrate to examine its optical properties using ultraviolet-visible (UV-vis) spectroscopy. Figure 6-12a shows the absorbance spectra of the monolayer h-BN film before and after thermal annealing at $550\text{ }^{\circ}\text{C}$ for 10 min, and after an additional week under ambient conditions at room temperature, respectively. Their corresponding spectra are converted into Tauc's plots in Figure 6-12b for optical bandgap (OBG) extraction.¹³⁸ To convert the absorbance spectra into Tauc's plots for bandgap extraction, we use the derived formula for a direct band gap semiconductor,¹³⁸ where α is the

$$\alpha = C(E - E_g)^{1/2}/E \quad (1)$$

Figure 6-11 FTIR spectra of (a, b) bare Si and (c, d) h-BN/Si samples before and after annealing in air at $550\text{ }^{\circ}\text{C}$ for 10min, respectively.

absorption coefficient, C is a constant and E is the photon energy. α is calculated by the measured optical absorption divided by the film thickness. By plotting $(\alpha E)^2$ against E , a straight line can be extrapolated from the energy dispersion curves and their bandgaps, E_g , can be extracted at the intersection of the extrapolated lines and the x-axis. Initially, the as-transferred h-BN film has an OBG of 6.1 eV, which is consistent with theorized value.¹³⁹ After annealing, the OBG decreased slightly to 5.985 eV, and subsequently recovered back to 6.085 eV after another week of inactivity under ambient conditions at room temperature. The temporal change in optical properties (i.e., lower OBG or broadening of absorption peak) is associated to the absorption of oxygen-containing functional groups such as hydroxyl groups during annealing under air, which modifies

Figure 6-12 Surface functionalization of h-BN films. (a) UV-vis absorbance curves and the extracted (b) Tauc's plot of an as-transferred monolayer h-BN film (black trace), after annealing in air at 550 °C for 10 min (red trace) and after another week of inactivity under ambient conditions at room temperature (blue trace), on quartz substrate. CA of DI water droplets on (c) as-transferred monolayer h-BN film, (d) after annealing in air at 550 °C for 10 min and (e) after another week of inactivity under ambient conditions at room temperature, on SiO₂/Si substrate.

its surface chemistry.^{210, 211} After the annealing, as dehydroxylation take place over time,²⁰⁷ the h-BN film recovered back to its intrinsic optical properties.

To further confirm this mechanism, contact angle (CA) measurements were done on the transferred h-BN film on SiO₂/Si following the same procedure. Initially, the as-transferred h-BN film exhibits a hydrophobic behavior with a CA of ~100 ° (Figure 6-12c). After annealing, the film surface became more hydrophilic and the CA dropped to ~40 ° (Figure 6-12d). This trend of decreasing CA is consistent to a hydroxylated surface.^{210, 212} After one week of resting under ambient conditions at room temperature, the CA partially recovered to ~65 ° (Figure 6-12e). The increase in hydrophobicity is attributed to the dissociation of the oxygen or hydroxyl groups due to the high resistivity of the h-BN film towards molecular oxygen, making it an energetically favorable process.^{210, 213} On the other hand, the incomplete recovery of hydrophobicity of the film surface is because of the decrease in surface roughness of the unwrinkled film, where the measured CA is governed by:

$$\cos(\theta_w) = R_w \cos(\theta_0) \quad (1)$$

where θ_w is the measured CA, R_w is the surface roughness factor and θ_0 is the CA in

Figure 6-13 CA of DI water droplets on SiO₂/Si substrate (a) before and after annealing in air for 10 min at (b) 250 °C, (c) 350 °C, (d) 450 °C, (e) 550 °C, respectively.

Young's mode.²¹⁴ Hence, the decrease in surface roughness of the h-BN film and removal of polymer residues resulted in an overall decrease in hydrophobicity. Additionally, the thermal annealing effects on bare SiO₂ and quartz surfaces were investigated. It is apparent that both the surfaces became more hydrophilic with increasing annealing temperature (Figure 6-13 and Figure 6-14), indicating the increase in oxygen intercalation at the surface.

Figure 6-15 presents a schematic of the unwrinkling process. When transferred h-BN film on SiO₂/Si is exposed to air at 550 °C, oxygen and other oxygen-containing molecules from the air seep into the wrinkled h-BN/substrate interface through the edges of the transferred film or cracks induced by imperfect transfer. Upon thermal annealing, hydroxylation occurs on both the h-BN film and the surface of the substrate. As the interaction between the h-BN film and the SiO₂ surface is dominated by van der Waals forces, the adhesion energy is effectively reduced when the surfaces are hydroxylated and further decreases with absorbed water molecules, resulting in a reduction in the equilibrium separation distance between the film and substrate.²¹⁵ Hence, the lifted h-BN wrinkle descends towards the hydroxylated SiO₂ surface over time. After annealing, dehydroxylation occurs on both the unwrinkled h-BN film and SiO₂ surface.

Figure 6-14 CA of DI water droplets on quartz substrates (a) before and (b) after annealing in air at 550 °C for 10min.

Figure 6-15 Schematic illustration of the smoothening process of transferred h-BN film when subjected to thermal annealing in air and its subsequent dissociation at room temperature.

6.4. Summary

In summary, the microstructure of wrinkles in CVD-grown h-BN films and their smoothening process by thermal annealing were investigated. The high density of wrinkles that are commonly observed in h-BN films are attributed to the large difference in CTE between h-BN and Cu which are formed upon thermal quenching. The Cu corrugates by step bunching while the excess h-BN form wrinkles and conforms to the corrugated structure as the consequence of strain relaxation. Although the corrugated h-BN/Cu structure can be released upon film detachment, the h-BN wrinkles prevailed after transferring to a relatively flat substrate such as SiO_2/Si . By simply annealing the transferred h-BN film under air at 550°C , the wrinkles diminish over time with no observable oxidative detriment to the film. We concluded that the unwrinkling behavior is associated to the hydroxylation of the h-BN film as well as the substrate surface which resulted in a reduction in adhesion energy. When the unwrinkled film is brought to rest under ambient conditions at room temperature, dehydroxylation occurs over time and the film is restored back to its originally unmodified state. This work provides important insights into the microstructure of wrinkles in CVD-grown h-BN films and demonstrates an effective post-synthesis treatment to obtain smoother and cleaner films which is critical for the fabrication of scalable 2D heterostructure devices. Further improvement

of the growth process is still required to realize larger grain size, more uniform thickness, and lower growth temperature.

7. Vertically Aligned MoTe₂ on Mo Foils

7.1. Introduction

Two-dimensional molybdenum ditelluride (MoTe₂), an important member of transition metal chalcogenides (TMDs), has aroused increasing research interests due to its exceptional optical and electrochemical properties. These unique properties of MoTe₂ are reported to be highly related to the phase (2H and 1T'-phase) and orientation. 2H-phase MoTe₂ with hexagonal lattice in three fold symmetry is semiconducting and possesses a narrow bandgap (~1.1 eV) and a strong spin-orbit coupling, making it desirable for near-infrared photodetector and valleytronics.^{119, 216-218} 1T'-phase MoTe₂ with distorted octahedral structure is semi-metallic and exhibits a high electron mobility (4000 cm² V⁻¹ s⁻¹) and a giant magnetoresistance, showing great potentials in ohmic homojunction and spintronics.^{101, 119, 121, 122} Moreover, laterally orientated MoTe₂ with its basal planes exposed on the surface has been extensively utilized for transistors and ohmic homojunction devices.²¹⁹ On the other hand, vertically aligned MoTe₂ is expected to enhance the density of exposed active edge sites, which in turn should enable it more promising for optoelectronic and electrochemical applications.^{112, 113, 115-117, 220, 221}

To date, MoTe₂ nanosheets have been mainly fabricated by top-down (mechanical/chemical exfoliation) and bottom-up (chemical vapor deposition (CVD) and molecular beam epitaxy) methods.²²² Although mechanical exfoliation produces high-quality nanosheets by physically peeling off layers from bulk crystals, the resulting MoTe₂ flakes are usually with limited dimension and random yield.^{223, 224} The chemical exfoliation method is promising for mass production of MoTe₂ nanosheets, but the obtained products inevitably suffer from severe defects and low quality, which hinder their further practical applications.^{225, 226} Alternatively, CVD and molecular beam epitaxy offer more pragmatic approaches to scalable fabricate high-quality MoTe₂ with

controllable thickness.²²⁷⁻²³⁰ Although considerable efforts have been devoted to synthesizing laterally oriented MoTe₂, the fabrication of vertically aligned MoTe₂ has not been reported yet. Therefore, development of new fabrication strategy for large-scale growth of high-quality vertically aligned MoTe₂ with controllable properties is highly desirable towards high-performance optoelectronic and electrochemical devices.

Herein, this chapter presents a versatile and scalable CVD growth of vertically aligned MoTe₂ on reusable Mo foil, and further demonstrated the feasibility for mass production of high-quality MoTe₂ nanosheets. The typical length of the as-grown vertically aligned MoTe₂ ranges from 0.66 μm to 7.5 μm . Importantly, the dominant phase of the MoTe₂ can be effectively tuned from 2H to 1T' by increasing the growth temperature from 630 to 780 °C. The vertical growth of MoTe₂ is proposed to be caused by the internal strain generated during tellurization of Mo foil. Moreover, the as-grown MoTe₂ was easily detached from the Mo surface and the Mo foil was able to be repeatedly used for subsequent growths. The as-obtained MoTe₂ can also be dispersed in IPA to produce high-quality MoTe₂ nanosheets. The growth of vertically aligned TaTe₂ and MoSe₂ were further demonstrated by using the same fabrication method.

7.2. Experimental section

Vertically aligned MoTe₂ are grown via thermal CVD under atmospheric pressure (AP). Prior to growth, a 3×1 cm piece of Mo foil (Alfa Aesar, 25 μm , 99%) is dipped into aqueous ammonia hydroxide for a few seconds and then rinsed with deionized (DI) water to clean the surface. The Mo foil was then put inside a quartz crucible and loaded into a 1-inch quartz tube. Tellurium powder is placed upstream of the quartz tube to supply Te vapor continuously during growth. The system is purged with Ar/H₂ flow of 500/20 sccm for 10 min to remove the oxygen, after that the Ar/H₂ flow is changed to

70/20 sccm and remained constant during the following process. The furnace is ramped up to desired temperature at a rate of 50 °C/min and then maintained for a specific time to finish the growth. After the growth process, the sample is cooled down rapidly under 300/20 sccm Ar/H₂ flow.

7.3. Results and discussion

Figure 7-1a shows the schematic setup of APCVD used to grow vertically aligned MoTe₂. For this growth, commercially available Mo foil was chosen both as a support substrate and Mo source. At high temperature (of 630 °C or more), Te vapor is carried into the reaction zone by Ar/H₂ flow to react with the Mo foil and produce vertically aligned MoTe₂. Due to weak

Figure 7-1. (a) Schematic diagram of CVD growth of vertically aligned MoTe₂. Cross-section SEM images of vertically aligned MoTe₂ grown at 630 °C for different times of (b) 5 min, (c) 15 min, (d) 30 min, and (e) 40 min. (f) Length of MoTe₂ as a function of growth time. (g) Representative Raman spectrum of MoTe₂ grown at 630 °C. Deconvoluted high-resolution (h) Mo 3d and (i) Te 3d XPS spectra of vertically aligned MoTe₂.

interaction between the as-synthesized MoTe₂ and the surface of the Mo foil, MoTe₂ can be easily detached from the Mo foil after growth by providing it with slight agitations such as bending or shaking gently. The yield from one growth is only limited by the size of the furnace and the Mo foil area, demonstrating the scalability of this process. Among the many parameters in our experiments, we found that the growth time and temperature are two key factors that control the growth of MoTe₂. Therefore, systematic studies were conducted to investigate the growth behavior of the vertically aligned MoTe₂.

To investigate the growth-time-dependent morphology evolution of the MoTe₂, SEM images (Figure 7-1b–e) were taken at the cross-section of the detached MoTe₂ samples that were grown at 630 °C for distinct times of 5, 15, 30 and 40 min, respectively. As summarized in Figure 7-1f, the average length of the as-grown MoTe₂ increase gradually from ~0.66 μm after 5 min of growth to ~2.7 μm after 40 min. Further extension of the growth time to 60 min resulted in negligible change in length (Figure

Figure 7-2. Cross-section SEM image of vertically aligned MoTe₂ grown at 630 °C for 60 min, which shows negligible change in terms of morphology as compared to sample grown at 630 °C for 40 min.

7-2), which might be due to the limited diffusivity of Te vapor after MoTe₂ grows longer over time.²³¹ Raman spectroscopy was performed to determine the crystal structure of the MoTe₂. As shown in Figure 7-1g, several well-resolved Raman peaks at $\sim 118\text{ cm}^{-1}$, $\sim 172\text{ cm}^{-1}$, $\sim 232\text{ cm}^{-1}$, and $\sim 287\text{ cm}^{-1}$ were observed and assigned to the in-plane E_{1g} , the out-of-plane A_{1g} , the prominent in-plane E_{12g} , and the out-of-plane B_{12g} vibrational modes of 2H MoTe₂, respectively.²²² Note that B_{12g} mode is Raman-inactive in monolayer and bulk 2H MoTe₂. Hence, the presence of B_{12g} peak indicate that they are relatively thick MoTe₂ flakes.^{222, 232} X-ray photoelectron spectroscopy (XPS) was further utilized to determine the chemical bonding and elemental composition of the MoTe₂. The survey spectrum reveals the presence of Mo, Te, C, and O elements in the samples (Figure 7-3). Figure 1h,i shows the high-resolution Mo 3d and Te 3d spectra, respectively. The Mo 3d spectrum can be deconvoluted into four peaks: the prominent peaks centered at 228.3 eV and 231.5 eV are assigned to Mo–Te bonds, whereas the peaks located at 232.7 eV and 235.9 eV correspond to Mo–O bonds. For the Te 3d spectrum, four components can be distinguished. The peaks centered at 573.0 eV and 583.3 eV correspond to Te–Mo bonds, while the peaks at 576.4 eV and 586.8 eV are attributed to Te–O bonds.²³³⁻²³⁵ The presence of oxide components in the XPS spectra

Figure 7-3. XPS survey spectrum of vertically aligned MoTe₂ grown at 630 °C.

indicates that the surface of the MoTe₂ is slightly oxidized due to its air-sensitive properties upon exposure to air.²³⁶⁻²³⁹ The extracted atomic ratio of Mo to Te was 1:2.2, in good agreement to the ideal stoichiometry of MoTe₂.

Varying growth temperature is known to change the crystallinity and quality of synthetic crystals. In our study, we conducted controlled experiments at different growth temperatures to investigate its influence on the crystal structure of MoTe₂. Figure 7-4a-d shows the cross-section SEM images of the vertically aligned MoTe₂ grown at different temperatures. By increasing the growth temperature to 680 °C, the length of the MoTe₂ increased dramatically from ~3.2 μm to ~7.2 μm, suggesting an increased growth rate in the vertical direction. Much less Te vapor could diffuse onto the Mo surface as the vertically MoTe₂ has grown longer, thus further increment of the growth

Figure 7-4. Cross-section SEM images of vertically aligned MoTe₂ grown at different temperatures of (a) 630 °C, (b) 680 °C, (c) 730 °C, and (d) 780 °C for 40 min. The insets show the corresponding magnified SEM images, scale bars: 300 nm.

and 51.9° were detected for the samples that were grown at 630 °C and 680 °C, corresponding to the (002), (004), (006), and (008) reflection of 2H MoTe₂, respectively.²⁴²⁻²⁴⁴ For MoTe₂ grown at higher temperatures of 730 °C and 780 °C, besides having similar peaks corresponding to (002) and (004) reflections of 2H MoTe₂, a slight “shoulder” at 26°, as well as many closely spaced peaks at 29°, 30°, 37.5°, 40°, and 42° can be observed, attributed to (004) reflection and low-symmetry monoclinic crystal structure of 1T' MoTe₂, respectively.^{235, 245, 246} This strongly indicates the coexistence of 2H and 1T' phases. Raman spectroscopy was used to further confirm the crystalline phase of the various MoTe₂ samples. As shown in Figure 7-5b, the Raman four distinctive peaks at 118 cm⁻¹, 172 cm⁻¹, 232 cm⁻¹, and 287 cm⁻¹, assigning to 2H polymorph of MoTe₂. For samples synthesized at 730 °C, both 1T' MoTe₂ Raman peaks at 163 cm⁻¹ (B_g) and 257 cm⁻¹ (A_g),^{101, 227, 247} as well as 2H MoTe₂ Raman peaks at 172 cm⁻¹ (A_{1g}) and 232 cm⁻¹ (E_{2g}) were detected, confirming the coexistence of 2H and 1T' phases, in consistent with the XRD analysis. The phase transition was further revealed in the Raman spectrum of MoTe₂ grown at 780 °C, where the intensity of B_{1g} mode of 1T' phase increased, while E_{12g} mode of 2H phase was suppressed.

Since the as-synthesized MoTe₂ can be easily detached from the surface of the Mo foil, we repeated the growth using the same Mo foil to explore its reusability. As shown in Figure 7-6a, b, MoTe₂ can be repeatedly grown on the same Mo foil without any observable change to its morphology even after 10 growths (@630 °C, 40 min). Furthermore, Raman spectra taken from the MoTe₂ samples after the 1st and the 10th growth showed identical peaks that belong to 2H MoTe₂ (Figure 7-6c), confirming that they are of equally high-quality. As depicted in Figure 7-6f, while the Mo foil retained its lateral shape and size, its thickness was decreased from 25 μm to 14 μm after 10 growths. This indicates that an average of ~1.1 μm of Mo foil was consumed in the

Figure 7-6. (a–d) SEM images of vertically aligned MoTe₂ obtained from (a, b) the 1st and (c, d) the 10th growth process using the same piece of Mo foil. (e) Raman spectra of MoTe₂ from the (black) 1st and (red) 10th growth. (f) Optical images of a piece of fresh Mo foil and the same Mo foil after 10th growth. Diagrams at the right indicate the corresponding thickness of the Mo foil. (g) Schematic illustration of the vertical growth process of MoTe₂.

vertical direction during each growth to produce vertically aligned MoTe₂ with a typical length of ~2.3 μm. Therefore, as expected, a significant volume expansion occurred during the conversion from Mo to MoTe₂.

It was observed from previous studies that tellurization of Mo into MoTe₂ produced horizontally grown films.^{228, 240, 241, 248} This is because most of the Mo films used were very thin (typically ≤ 3 nm) and were non-crystalline (deposited using either E-beam evaporator or sputtering). Similar to the sulfidation process on Mo where horizontal growth occurs with a thin Mo film (≤ 1 nm) while a thicker Mo film (≥ 4 nm) would be microns thick. The proposed growth process of the vertically aligned MoTe₂ is

schematically illustrated in Figure 7-6g. At high growth temperature, Te vapor was introduced into the reaction region which diffused and absorbed on the surface of the Mo foil. This was followed by nucleation of MoTe₂ where the absorbed Te reacts with the Mo atoms. However, note that the volume of each Mo unit in Mo and MoTe₂ are 15.6 Å³ and 74.9 Å³, respectively, which translate to an overall volume increment of 380%.²⁴⁰ Therefore, the huge volume expansion together with the physical confinement of the metal bulk caused internal strains which prevented the MoTe₂ from nucleating

Figure 7-7. (a) SEM image of MoTe₂ nanosheets obtained by tip-sonication in IPA for 8h followed by centrifugation at 500 rpm for 10 min. Inset shows the Tyndall effect of the MoTe₂ dispersion, indicating its colloidal nature. (b) AFM characterization of the MoTe₂ nanosheets. (c) Representative low-magnified TEM image of a single MoTe₂ nanosheet in size of $\sim 0.5 \times 2 \mu\text{m}$, consistent with SEM image above. (d) High-resolution TEM image of the MoTe₂ nanosheet. Inset at top right corner: high-magnified TEM image shows the (10 $\bar{1}$ 0) plane and its d-spacing of the MoTe₂ nanosheet. Inset at upper right corner: the corresponding SAED pattern.

horizontally. To effectively relieve the strain, MoTe₂ was forced to nucleate and grow in vertical direction that allows for unconstrained volume expansion. Upon extended growth, more Te were allowed to diffuse along the van der Waals gaps of MoTe₂ to reacted with fresh Mo at the Mo/MoTe₂ interface.¹¹² The growth then proceeded along the interface by “consuming” the Mo in the vertical direction. Hence, this resulted in the thinning of the Mo foil as the vertically aligned MoTe₂ continued to grow in length.

The promising performance of MoTe₂ in various energy-related applications promotes us to further explore the potential of our vertically aligned MoTe₂.^{245, 249-251} The as-grown and easily detachable vertically aligned MoTe₂ was further dispersed in solvent to produce high-quality MoTe₂ nanosheets. Briefly, MoTe₂ (@680 °C, 40 min) was immersed in IPA and sonicated to form nanosheets. The dispersion was then centrifuged and the supernatants was collected for further characterization. An obvious Tyndall effect can be observed in the MoTe₂ nanosheets dispersion (inset of Figure 7-7a) which indicates its colloidal nature. Figure 7-7a shows a representative SEM image of the obtained MoTe₂ nanosheets with a typical size of $\sim 3 \times 0.5 \mu\text{m}^2$. AFM was utilized to determine the thickness of the MoTe₂ nanosheets. Figure 5b shows an AFM image of a MoTe₂ flake with a thickness of ~ 55 nm. Typically, the thickness of the nanosheets can range between 20 ~ 90 nm (Figure 7-8). The morphology and crystallinity of the MoTe₂ nanosheets were further examined using TEM. Figure 7-7c shows a typical TEM

Figure 7-8. AFM images of MoTe₂ nanosheets indicate their thickness is within 20-90 nm range.

image of a single MoTe₂ nanosheet at low magnification. The corresponding selected-area electron diffraction (SAED) (inset of Figure 7-7d) shows a distinctive single set of hexagonal pattern, which indicates the single-crystalline nature of 2H-MoTe₂. Figure 7-7d shows the atomically resolved TEM image of the nanosheet with a d-spacing of 3.05 Å corresponding to the (10 $\bar{1}$ 0) plane, in good agreement with the crystal structure of 2H-MoTe₂.^{101, 119, 224, 227} Energy-dispersive X-ray spectroscopy (EDX) was performed on the SEM samples, and the elemental stoichiometry of the Mo:Te is extracted to be 1:2.1 (Figure 7-9), in consistent with our XPS analysis.

Finally, to demonstrate the versatility of our growth process, we further extended it to other TMDs as well. By replacing Te source with Se source or Mo foil with Ta foil, we successfully synthesized vertically aligned MoSe₂ and TaTe₂, respectively, as shown in Figure 7-10a,b. The corresponding magnified SEM image is shown in the inset. Figure 7-10c,d shows the Raman spectra of the as-grown MoSe₂ and TaTe₂,

Figure 7-9. EDX spectrum of MoTe₂ nanosheet. The inset shows the atomic ratio of Mo and Te, indicating a good stoichiometry.

respectively. For the vertically aligned MoSe₂, Raman peaks centered at 165 cm⁻¹, 239 cm⁻¹, and 282 cm⁻¹ were observed which are assigned to the E_{1g}, A_{1g}, and E_{2g}¹ vibration mode of 2H–MoSe₂.^{252, 253} For vertically aligned TaTe₂, several peaks located at 109 cm⁻¹, 141 cm⁻¹, 157 cm⁻¹ and 214 cm⁻¹ were distinguished corresponding to distorted 1T–TaTe₂.^{254, 255}

Figure 7-10. Cross-section SEM images of (a) vertically aligned MoSe₂ layers grown on Mo foil and (b) vertically aligned TaTe₂ layers grown on Ta foil. The insets show the corresponding magnified SEM images. Raman spectra shows distinctive Raman peaks of (c) 2H MoSe₂ and (d) distorted 1T TaTe₂, respectively.

7.4. Summary

In summary, a versatile and scalable CVD growth of high-quality vertically aligned MoTe₂ on Mo foil is demonstrated. By controlling the growth time and temperature, the length (up to ~7.5 μm) and dominant phase (2H and 1T') of the vertically aligned MoTe₂

can be effectively tuned. Due to weak interaction between MoTe₂ and Mo, the as-synthesized MoTe₂ were easily detached from the Mo foil. Having a fresh Mo surface each time after growth, the same Mo foil can be repeatedly used for multiple growths. The vertical growth of MoTe₂ is proposed to be caused by internal strains involving the huge volume expansion during tellurization and physical confinement of the metal bulk. High-quality MoTe₂ nanosheets were further attained by dispersing the vertically aligned MoTe₂ in solvent. Additionally, the same synthesis approach was applied to growth other vertically aligned TMDs such as TaTe₂ and MoSe₂. This work provides a versatile strategy for scalable production of vertically aligned TMDs which paves the way for studies of their unique properties and novel applications. Further research effort is still needed to explore the performance of vertically aligned MoTe₂ in electronic devices.

8. Conclusions and Recommendations for Future Work

8.1. Conclusions

In this thesis, novel CVD strategies have been developed for growth and engineering of 2D materials including graphene, h-BN, and MoTe₂. Particularly, systematic studies have been conducted to gain in-depth understanding these CVD processes.

Firstly, large hexagonal-shaped monolayer NG single crystals were grown on Cu substrates by CVD using HMTA as a single-source solid precursor. For the first time, it was demonstrated experimentally that dopant segregation exists in monolayer NG single crystals. The doping inhomogeneity is attributed to sublattice selectivity of the N dopants by attachment via zigzag or Klein edges, where the former resulted in higher doping concentration and the latter are N depleted regions. This work provides important insights into the growth mechanism of CVD-grown NG single crystals and enables new opportunities for tailoring the electronic and optical properties in graphene.

Secondly, this thesis investigated the microstructure of wrinkles in CVD-grown h-BN films and developed an effective smoothening process. Wrinkles are commonly observed in CVD-grown h-BN films which prevailed even after transferring to a relatively flat substrate such as SiO₂/Si. By simply annealing the transferred h-BN film under air at 550 °C, the wrinkles diminish over time with no observable oxidative detriment to the film. The unwrinkling behavior is associated to the hydroxylation of the h-BN film and the substrate surface after air annealing, which resulted in a reduction in adhesion energy. This work provides an effective post-synthesis treatment to obtain smoother and cleaner films which is highly desired for the scalable fabrication of 2D heterostructure devices.

Last but not least, this thesis presented a versatile and scalable CVD growth of high-quality vertically aligned MoTe₂ on commercially available Mo foil. Due to weak

interaction between MoTe₂ and Mo, the as-synthesized MoTe₂ were easily detached from the Mo foil, enabling the Mo foil to be reused for multiple growths. The vertical growth of MoTe₂ is proposed to be induced by internal strains involving the physical confinement of metal bulk and the huge volume expansion during tellurization. Additionally, the same synthesis approach was applied to growth other vertically aligned TMDs such as TaTe₂ and MoSe₂. This work provides a versatile strategy for scalable production of vertically aligned TMDs which paves the way for studies of their unique properties and novel applications.

8.2. Recommendations for future works

8.2.1. Performance of smoothened h-BN films as substrates

Insulating h-BN has been proven to be an appealing substrate to improve the carriers transport of other 2D materials devices because of its atomically smooth surface, low-density dangling bonds and charge traps as compared to SiO₂. Dean, C. R. et al. have reported that the carrier mobility of graphene field effect transistors on h-BN substrates can be one order of magnitude higher than the devices on SiO₂ substrates as shown in Figure 8-1a,b.⁴² The h-BN has also been used as encapsulation layers of MoS₂ to reduce the scattering from substrate phonons and charged impurities, leading to an ultrahigh hall mobility of 34000 cm² V⁻¹ s⁻¹ (Figure 8-1 c,d).²⁵⁶ But still mechanically exfoliated h-BN flakes were mainly used to date to construct various 2D stacks. Now that large-area unwrinkled CVD-grown h-BN films with clean surface and greatly improved surface smoothness have been achieved in this thesis, the next step for the work on smoothened h-BN will be to utilize it as a substrate or gate dielectric for 2D heterostructure devices.

Figure 8-1 (a) Optical images of graphene and h-BN flakes and devices.¹²⁹ (b) Schematic illustration of the transfer process for the fabrication of graphene/h-BN device.¹²⁹ (c) Optical image of h-BN/graphene/MoS₂/h-BN device.²²⁰ (d) Cross-sectional STEM image of the fabricated device. The zoom-in false color image shows the sharp interfaces between different layers.²²⁰

8.2.2. Growth of other vertically aligned TMDs on metal foils

Chapter 7 has demonstrated a novel CVD process for the growth of vertically aligned (VA) MoTe₂ on commercially available Mo foil. Given that the growth of VA MoSe₂ and TaTe₂ has also been realized using this process, more VA TMDs are expected to be synthesized by annealing the corresponding metal foils under specific chalcogen vapor. For example, it has been reported that VA PtSe₂ can be grown by selenizing pre-deposited Pt thin films (~ 10 nm) on SiO₂ substrates.¹¹⁷ Hence, by using commercially available Pt foil (micron scale in thickness) as source and substrates, large quantities of VA PtSe₂ arrays are expected to be produced. Therefore, these VA TMDs would enable a wide range of electrochemical applications such as catalysts, batteries, and supercapacitors.

Figure 8-2 (a) SEM images of 1T' MoTe₂ films with different density of holes (diameter: 5 μm) created by ion beam bombardment. (b) Polarization curves of the MoTe₂ shown in (a) in an electrochemical measurement. (c) Tafel plots derived from the polarization curves in (b).¹⁸⁵

8.2.3. Electrochemical performance of vertically aligned MoTe₂

MoTe₂ is an appealing material candidate for electrochemical applications due to its excellent catalytic performance. Recently, it was reported experimentally that the hydrogen evolution reaction (HER) performance of MoTe₂ can be significantly enhanced by creating more exposed edge sites using ion beam bombardment (Figure 8-2).²²¹

Besides, VA TMDs layers are to show excellent electrochemical performance in HER because of the much higher density of exposed edge sites than their laterally orientated counterparts. For example, it has been reported that VA MoS₂ exhibited a high exchange current densities than MoS₂ nanoparticle-based electrodes in electrochemical measurements (Figure 8-3).¹¹² In our VA MoTe₂ work, the as-grown MoTe₂ layers were

attached onto the electrically conductive Mo foil, therefore, the produced MoTe₂/Mo can be directly utilized as electrodes to test their HER performance. Given the high density of exposed edge sites on the VA MoTe₂ surface, VA-MoTe₂/Mo electrode is expected to show excellent electrochemical performance.

Figure 8-3 (a) TEM images of MoS₂ and MoSe₂ films showing exposed edges. (b) Schematic illustration of structure of edge-terminated molybdenum chalcogenide films. (c) Polarization curves of vertically aligned MoS₂, MoSe₂, and a blank glassy carbon substrate in electrochemical measurements.¹¹²

Publication List

Journals

1. **Lin, J. J.**; Tay, R. Y.; Li, H. L.; Jing, L.; Tsang, S. H.; Wang, H.; Zhu, M.; McCulloch, D. G.; Teo, E. H. T., Smoothing of Wrinkles in CVD-Grown Hexagonal Boron Nitride Films. *Nanoscale* **2018**, *10* (34), 16243-16251.
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