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# FORMATION AND OPTICAL PROPERTIES OF MIXED MULTI-LAYERED HETEROSTRUCTURES BASED ON ALL TWO- DIMENSIONAL MATERIALS

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AUGUST 2017

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Submitted in Conformity with the Requirements for the Degree of DPhil in Materials Science

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# Abstract

## **Formation and Optical Properties of Mixed Multi-layered Heterostructures Based on All 2D Materials**

*by Yuewen Sheng*

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*in pursuit of DPhil degree, Trinity Term, 2017*

The production of large area, high quality two-dimensional (2D) materials using chemical vapour deposition (CVD) has been an important and difficult topic in contemporary materials science research, after the discovery of the diverse and extraordinary properties exhibited by these materials. This thesis mainly focuses on the CVD synthesis of two 2D materials; bilayer graphene and monolayer tungsten disulphide ( $\text{WS}_2$ ). Various factors influencing the growth of each material were studied in order to understand how they affect the quality, uniformity, and size of the 2D films produced. Following this, these materials were combined to fabricate 2D vertical heterostructures, which were then spectroscopically examined and characterised.

By conducting ambient pressure CVD growth with a flat support, it was found that high uniform bilayer graphene could be grown on the centimetre scale. The flat support provides for the consistent delivery of precursor to the copper catalyst for graphene growth. These results provide important insights not only into the upscaling of CVD methods for growing large area, high quality graphene and but also in how to transfer the product onto flexible substrates for potential applications as a transparent conducting electrode.

Monolayer  $\text{WS}_2$  is of interest for use in optoelectronic devices due to its direct bandgap and high photoluminescence (PL) intensity. This thesis shows how the controlled addition of

hydrogen into the CVD growth of  $\text{WS}_2$  can lead to separately distributed domains or centimetre scale continuous monolayer films at ambient pressure without the need for seed molecules, specially prepared substrates or low pressure vacuum systems. This CVD reaction is simple and efficient, ideal for mass-production of large area monolayer  $\text{WS}_2$ .

Subsequent studies showed that hexagonal domains of monolayer  $\text{WS}_2$  can have discrete segmentation in their PL emission intensity, forming symmetric patterns with alternating bright and dark regions. Analysis of the PL spectra shows differences in the exciton to trion ratio, indicating variations in the exciton recombination dynamics. These results provide important insights into the spatially varying properties of these CVD-grown TMDs materials, which may be important for their effective implementation in fast photo sensors and optical switches.

Finally, by introducing a novel non-aqueous transfer method, it was possible to create vertical stacks of mixed 2D layers containing a strained monolayer of  $\text{WS}_2$ , boron nitride, and graphene. Stronger interactions between  $\text{WS}_2$  on graphene was found when swapping water for IPA, likely resulting from reduced contamination between the layers associated with aqueous impurities. This transfer method is suitable for layer by layer control of 2D material vertical stacks and is shown to be possible for all CVD grown samples, a result which opens up pathways for the rapid large scale fabrication of vertical heterostructure systems with large area coverage and controllable thickness on the atomic level.

# Acknowledgements

Executing the research outlined in this thesis would not have been possible without the guidance, contribution and support of my supervisors, colleagues, friends, and family. First of all, I would like to express gratitude and profound thanks to my supervisor, Prof. Jamie Warner, for providing me with the patient guidance and unconditional support throughout the project. The success of this Ph.D. project owes a considerable amount to his exceptional supervision. Prof. Andrew Watt, in his role as my co-supervisor, was a valuable mentor and supported me throughout with encouragement and wisdom. As such he also deserves special thanks.

Besides, this project involves several individuals who had been most helpful in providing their specialist expertise and knowledge when using certain characterisation facilities. Dr. Youmin Rong made an enormous contribution by setting up the two CVD systems for the growth of graphene and tungsten disulphide ( $\text{WS}_2$ ). This served as a cornerstone for my investigation and modification of the synthesis strategies of these materials. Dr. Zhengyu He was kind and helpful when doing the sheet resistance and optical transmission measurement on transferred graphene samples. The expertise and generous support of Mr. Xiaochen Wang on the use of the atomic force microscope in Prof. Harish Bhaskaran's group and the Carl Zeiss Merlin scanning electron microscope in Materials Department was greatly appreciated, as well as his supply of high-quality, continuous multilayer h-BN films, which is one of the building block for the layer by layer fabrication of 2D heterostructures. Mr. Haijie Tan provided a deep insight into the fabrication and electrical measurement of  $\text{WS}_2$  field effect transistors, which greatly aided in its use. Additionally, I would like to thank Ms. Wenshuo Xu and Ms. Yingqiu Zhou for providing fresh  $\text{WS}_2$  samples. The rest of my colleagues, Dr. Alex Robertson, Dr. Kuang He, Dr. Ye Fan, Dr. Shanshan Wang, Dr. Chuncheng Gong, Mr.

Thomas Samuels, Mr. Martin Tweedie, Mr. Hefu Huang, Ms Sha Li, Ms Qu Chen, Mr. Tongxin Chen, Mr. Ren-Jie Chang, Mr. Si Zhou and others, generously supplied their opinions during discussion, which broaden my horizon and improved my research. Among my collaborators, I would like to thank Mr. Siqi Ying from Prof. Alexander Korsunsky's group in the Department of Engineering, who was constantly genial and supportive to assist with characterisation using their energy dispersive X-ray spectroscopy. In addition, I would like to thank Dr. Kazunori Fujisawa, Dr. Ana Laura Elias, Mr. Zhong Lin and Prof. Mauricio Terrones from the Pennsylvania State University for conducting photoluminescence (PL) spectroscopy under low temperature and transmission electron microscopy on the study of PL segmentation within hexagonal WS<sub>2</sub> domains.

Lastly, I would like to give my deepest gratitude to my parents for their unconditional love and financial support throughout. Special thanks to my wife for her meticulous care and companionship.

# Publications

Here is presented a list of published first-/co-author research accomplished during the course of this project. The four first-author publications are enumerated individually corresponding to the result chapters in the thesis and the co-author publications are beyond the purview of this thesis.

## Chapter 4

1. **Sheng, Y.**; Rong, Y.; He, Z.; Fan, Y.; Warner, J. H. Uniformity of Large-Area Bilayer Graphene Grown by Chemical Vapour Deposition. *Nanotechnology* **2015**, 26, 395601.

## Chapter 5

2. **Sheng, Y.**; Tan, H.; Wang, X.; Warner, J. H. Hydrogen Addition for Centimetre-sized Monolayer Tungsten Disulphide Continuous Films by Ambient Pressure Chemical Vapour Deposition. *Chem. Mater.* **2017**, 29, 4904-4911.

## Chapter 6

3. **Sheng, Y.**; Wang, X.; Fujisawa, K.; Ying, S.; Elias, A. L.; Lin, Z.; Xu, W.; Zhou, Y.; Korsunsky, A. M.; Bhaskaran, H.; Terrones, M.; Warner, J. H. Photoluminescence Segmentation within Individual Hexagonal Monolayer Tungsten Disulphide Domains Grown by Chemical Vapour Deposition. *ACS Appl. Mater. Interfaces* **2017**, 9, 15005-15014.

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4. **Sheng, Y.**; Xu, W.; Wang, X.; He, Z.; Rong, Y.; Warner, J. H. Mixed Multilayered Vertical Heterostructures utilizing Strained Monolayer WS<sub>2</sub>. *Nanoscale* **2016**, 8, 2639-2647.

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# Abbreviations

|        |                                                       |
|--------|-------------------------------------------------------|
| CVD    | Chemical Vapour Deposition                            |
| APCVD  | Ambient Pressure Chemical Vapour Deposition           |
| LPCVD  | Low Pressure Chemical Vapour Deposition               |
| MOCVD  | Metal-Organic Chemical Vapour Deposition              |
| LPE    | Liquid-Phase Exfoliation                              |
| HOPG   | Highly Oriented Pyrolytic Graphite                    |
| TMDs   | Transition Metal Dichalcogenides                      |
| TCE    | Transparent Conductive Electrode                      |
| ITO    | Indium Tin Oxide                                      |
| PET    | Polyethylene Terephthalate                            |
| LEDs   | Light Emitting Diodes                                 |
| FETs   | Field Effect Transistors                              |
| FWHM   | Full Width Half Maximum                               |
| UHV    | Ultra-High Vacuum                                     |
| AC-TEM | Aberration Corrected Transmission Electron Microscopy |
| AFM    | Atomic Force Microscopy                               |
| EDX    | Energy Dispersive X-ray                               |
| SEM    | Scanning Electron Microscopy                          |
| LEED   | Low Energy Electron Diffraction                       |

# Chapter 1

## *Introduction*

### **1.1 Project Aims**

The objective of this doctoral project is to establish, develop and optimize the chemical vapour deposition (CVD) techniques for the growth of two two-dimensional (2D) materials; bilayer graphene and monolayer tungsten disulphide ( $\text{WS}_2$ ), and investigate the materials properties of the product throughout this development and optimisation *via* a range of characterisation techniques.

### **1.2 The Scope of this Thesis**

The thesis covers the research that has been carried out over the time span of four years of a UK DPhil degree at the Department of Materials, University of Oxford. It unfolds with a literature review chapter (Chapter 2) that summarizes the recent progress on the research of properties, CVD synthesis, characterisation techniques and applications of two 2D materials; graphene and  $\text{WS}_2$ . In Chapter 3, the basic CVD setups for the growth of graphene and  $\text{WS}_2$  and a section of characterisation techniques employed in this project are briefly described.

The first task, as the prerequisite of all results, was to establish a functional 4-inch CVD system for the synthesis of large area, high quality bilayer graphene films under ambient pressure. The purpose of this work is to gain a comprehensive understanding of the growth mechanism, which has a potential of being expanded to other 2D materials. In the process of optimising the CVD parameters for batch production, the first novel result was obtained, which will be further explained in Chapter 4. The as-developed bilayer graphene films were later used as nanoelectrodes by the collaborators and other members of this research group, facilitating several new research projects in areas of photo-detector/-transistor and single-molecule device.

Subsequent to the CVD synthesis of bilayer graphene films, the study then turned to the fabrication of monolayer WS<sub>2</sub> continuous films based on the previous parameters. The purpose of this research is to establish practical synthesis strategies, which can produce large area WS<sub>2</sub> monolayers for further device fabrications. Hydrogen gas was newly brought into the double-furnace system, which allowed the rapid formation of monolayer WS<sub>2</sub> continuous films or separately distributed large domains (Chapter 5). Following this, the vibrational and optical properties of the WS<sub>2</sub> monolayers were observed *via* Raman and photoluminescence (PL) spectroscopies, which unveiled an interesting and unusual fact that hexagonal domains of monolayer WS<sub>2</sub> have symmetric patterns in their PL emission intensity. Further characterisations, such as atomic force microscopy (AFM) and energy dispersive X-ray spectroscopy (EDX), were carried out to elucidate the connection between the structure and PL (Chapter 6).

The project focus then shifted towards the formation and optical properties of the 2D heterostructures based on the aforementioned materials. By introducing a novel alcohol-based transfer approach, it was possible to enable layer by layer transfer of 2D materials.

The research in Chapter 7 was accomplished by fabricating and characterising mixed vertical 2D heterostructures and comparing this non-aqueous sliding transfer with the traditional aqueous-based wet transfer method.

The final chapter summarizes and concludes the whole thesis. A potential future research as extension to this thesis is also envisioned.

## Chapter 2

### *Literature Review*

#### **2.1 Introduction**

The ever-increasing demands for faster, lighter, smaller and more energy efficient electronic and optoelectronic devices have almost reached the limits of the existing materials. The appearance of the 2D families including graphene and transition metal dichalcogenides (TMDs) are expected to narrow this gap. In this chapter, a review of the nascent development of two 2D materials: graphene and 2D WS<sub>2</sub>, will be presented to introduce their structures, properties and synthesis approaches. Based on the thesis subject, the focus of this review will be arranged on the discussion about different CVD growth strategies, transfer methods, and formation of 2D heterostructures, as well as this research's possible applications.

#### **2.2 Graphene**

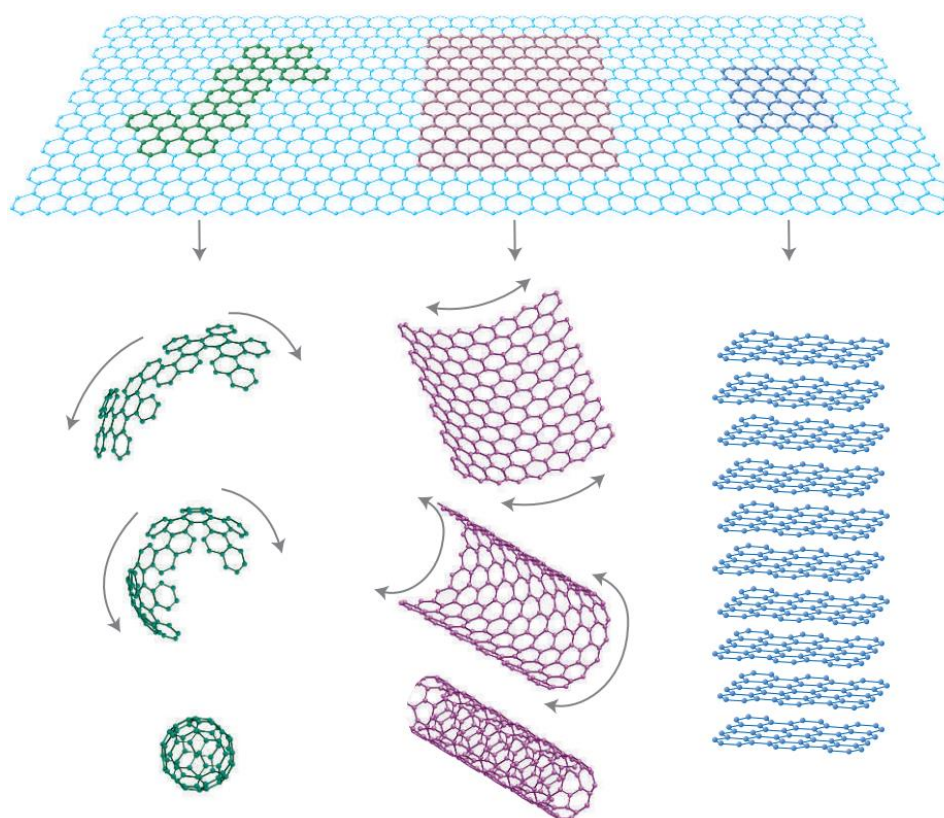
In this section, a review of graphene will be presented to introduce its structure, properties, synthesis approaches and transfer methods. This study focuses on graphene's optoelectronic properties, large area techniques for the CVD growth of graphene on Cu catalysts and its subsequent transfer processes.

### 2.2.1 What is Graphene?

Graphene is a novel two-dimensional (2D) carbon material whose extended honeycomb network is the basic building block of other important allotropes. For example, carbon sheets can be stacked to form three-dimensional (3D) graphite, rolled to form one-dimensional (1D) nanotubes, or wrapped to form zero-dimensional (0D) fullerenes, as illustrated in **Figure 2.1**.<sup>1</sup> More than 80 years ago, the previous work on atomically thin crystals by Landau and Peierls suggested that such 2D crystals would be thermodynamically unstable and could not exist.<sup>2,3</sup> Their theory claimed that the thermal fluctuations in low-dimensional crystal lattices should lead to such displacements of atoms that they become comparable to interatomic distances, thus destroying the crystals at any finite temperature.<sup>4</sup> It was not until the isolation of graphene from highly oriented pyrolytic graphite (HOPG) in 2004 using mechanical exfoliation method by Prof. Andre K. Geim and Prof. Konstantin S. Novoselov from the University of Manchester that 2D materials were proven to exist.<sup>5</sup> Since its discovery, graphene has attracted tremendous interests over the past decade from both the fields of theoretical research and commercial industry, primarily for its exceptional chemical and electronic properties. Prof. Geim and Prof. Novoselov were therefore awarded the Nobel Prize in Physics in 2010 for this breakthrough in 2D materials.

Graphene was once perceived to be the most ideal replacement for silicon, the development of which approaches the physical limits of speed and scaling.<sup>6</sup> Although graphene-based logic transistors are quite fast, research suggests that they lack traditional current saturation, have poor on/off current ratios, and are much slower (typically 100 times) in real circuit applications. These serious limitations are the result of graphene lacking a bandgap.<sup>7,8</sup> Currently many researchers are investigating methods to create one,<sup>9,10</sup> but it appears wiser to take advantage of its fundamental properties, rather than trying to overcome them.<sup>8</sup>

Examples include ambipolar electronics,<sup>11,12</sup> infrared detectors,<sup>13</sup> and heterogeneous graphene-silicon systems,<sup>14</sup> yet each of these still has a long way to go to compete with conventional silicon and compound semiconductor electronics.<sup>8</sup> Another important and promising application for graphene is its use as a transparent conductive electrode (TCE) in optoelectronic thin-film devices, such as displays, touch screens, photodetectors, light emitting diodes (LEDs) and solar cells.<sup>15</sup>



**Figure 2.1. Graphene as the building block for all other carbon materials in all dimensions.** Carbon sheets can be wrapped into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite. Reprinted with permission from ref. [1]. © 2007 Nature Publishing Group.

### 2.2.2 Properties of Graphene

For this section, some of the characteristic properties of graphene shall be discussed. The majority of graphene-related research interest has been on graphene's novel electronic

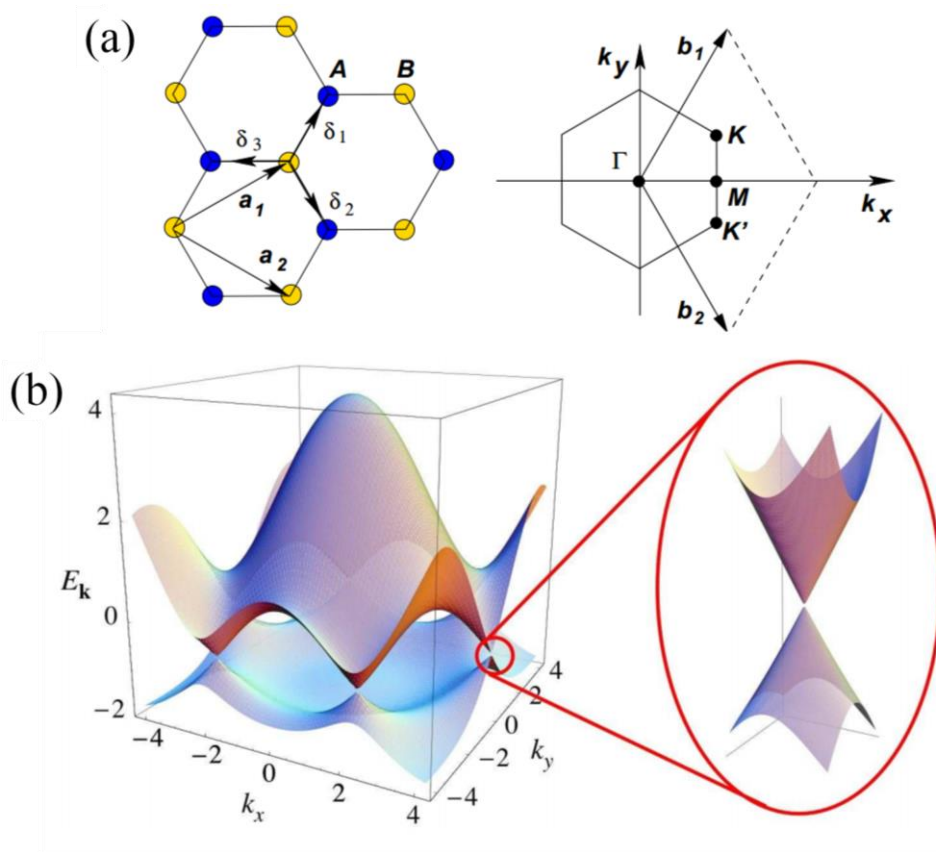
properties, such as its exceptional measured carrier mobilities or the physical existence of a massless Dirac fermion system. Yet, the other properties of graphene, *i.e.* optoelectronic, mechanical, thermal and vibrational properties, could also lead to interesting commercial applications, as will be reviewed here with a focus on its use as a TCE in optoelectronics.

### 2.2.2.1 Electronic Properties

Graphene, much like its parent graphite, is a lattice of  $sp^2$  hybrid bonded carbon. This composition yields a planar structure with a hexagonal symmetry, with the bonds spreading out to their maximum  $120^\circ$  separation. It is a zero-band gap semiconductor (or semimetal) meaning that its valence and conduction bands touch across  $k$ -space at two different points (noted as  $K$  and  $K'$ ) originating from the two unique lattice vectors that define the graphene lattice, **Figure 2.2(a)**. There are six of these intersection points across the Brillouin zone, **Figure 2.2(b)**, called Dirac points, at which the conduction band and valence band touch one another. In pristine graphene, theoretically, the valence band is completely filled and the conduction band is empty. Near the Dirac points, there is a linear relationship between energy and momentum,<sup>16</sup> causing the charge carriers in graphene to act as massless Dirac fermions,<sup>17</sup> relativistic particles described by Dirac's equations that travel with zero mass having an effective speed of light ( $\sim 10^6$  m/s).

In addition, the linear dispersion relation causes graphene to present an ambipolar field effect, whereby either electrons or holes can become the majority carriers by changing the Fermi level with an applied gate voltage.<sup>18</sup> This allows graphene to have an intrinsic carrier mobility of  $\sim 200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at room temperature,<sup>19</sup> which is higher than any other well-developed semiconductors, including semiconducting carbon nanotubes ( $\sim 100,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ),<sup>20</sup> indium antimonide (InSb) ( $77,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ),<sup>21</sup> gallium arsenide (GaAs) ( $4,600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )<sup>18</sup> and silicon ( $1,400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).<sup>22</sup> This result yields promise for the production of

graphene films of ultra-low sheet resistance and gives it potential for use in high speed electronics, such as field effect transistors (FETs), nanoelectronics and high frequency applications.<sup>1,23</sup> In practice, carrier scattering from grain boundaries, defects, impurities, and phonon interactions from the interface between graphene and the substrates are the main factors that lower the mobility of graphene.<sup>22,24,25</sup> Different substrates have been used to minimize these effects, giving a mobility of  $16,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  on silicon wafer coated with a layer of silicon oxide ( $\text{SiO}_2/\text{Si}$ )<sup>1</sup> and  $40,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  on boron nitride (BN).<sup>26</sup>



**Figure 2.2. The lattice and band structure of monolayer graphene.** (a) Lattice structure of graphene and its corresponding Brillouin zone. The Dirac cones are located at the  $K$  and  $K'$  points. (b) Energy spectrum and zoom-in of the energy bands close to one of the Dirac points. Reprinted with permission from ref. [16]. © 2007 Nature Publishing Group.

### 2.2.2.2 Optoelectronic Properties

All optoelectronic devices require TCEs that not only provide excellent charge transport and light transmission, but also good band matching with active layer materials. The two important parameters for a TCE are the sheet resistance and the optical transmittance. Typically, the commercially available product is a layer of 140 nm indium tin oxide (ITO) sputtered onto a glass substrate with sheet resistance of  $\sim 10 \Omega/\square$  and optical transmittance of 85% at 550 nm.<sup>27</sup> Additionally, the sheet resistance of ITO coated on polyethylene terephthalate (PET), a common flexible device substrate, is 60-300  $\Omega/\square$ .<sup>28</sup> The excellent electrical and optical performances have enabled ITO to dominate the TCEs market for over four decades,<sup>29</sup> but it has several disadvantages, including high cost,<sup>30</sup> toxicity and lack of flexibility.<sup>31</sup> The development of flexible optoelectronic devices has drawn great attention to new and lower cost materials for TCEs. Therefore, a substitute for ITO with a similar performance is urgently needed. Recent work on transparent conductive polymers (TCPs), carbon nanotube networks,<sup>32-34</sup> and metal nanowires meshes<sup>35-37</sup> has resulted in solution-processed, conductive, transparent electrodes with optoelectronic properties that approach or exceed that of ITO.

The 2D graphene<sup>38-44</sup> is also regarded as a promising transparent conductor because of its optical and electrical properties. Pang *et al.*<sup>45</sup> reported that the sheet resistance of pristine graphene is strongly affected not only by its surface morphology and crystal quality, which is mainly determined by its growth method, but also by the concentration of impurities, which usually emerges during the preparation and post-treatment processes. In a very thin film like graphene, the sheet resistance can be written as **Equation 2.1**, where  $t$  is the film thickness and  $\rho$  is the resistivity.

$$R_s = \frac{\rho}{t}, \quad \text{Equation 2.1}$$

For a film of length  $L$  and width  $W$ , the resistance  $R$  can be derived as **Equation 2.2**. The length and the width of the film often varies, so  $R_s$  is historically quoted in ohms per square,  $\Omega/\square$ .

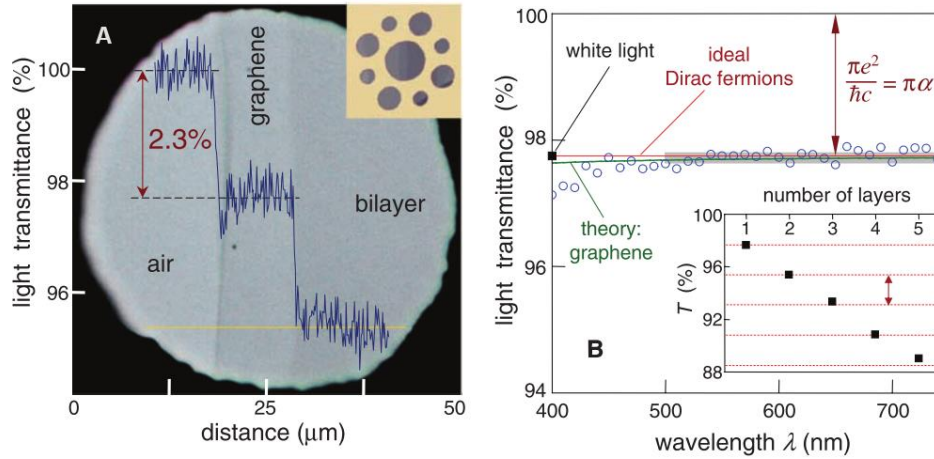
$$R = \frac{\rho}{t} \times \frac{L}{W} = R_s \times \frac{L}{W}, \quad \text{Equation 2.2}$$

As to the theoretical calculation of optical transmittance, Kuzmenko *et al.*<sup>46</sup> claimed that the optical transmittance of a single layer graphene is determined solely via the fine structure constant  $\alpha$ , which describes the coupling between light and relativistic electrons. Then the theoretical value of graphene can be acquired with the help of **Equation 2.3 and 2.4**.

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}, \quad \text{Equation 2.3}$$

$$T = (1 + \frac{\pi\alpha}{2})^{-2} \approx 1 - \pi\alpha \approx 97.7\%, \quad \text{Equation 2.4}$$

The result that Nair *et al.*<sup>47</sup> obtained from the experiment is surprisingly in agreement with this theoretical value. Despite only being one atom thick, graphene absorbs about 2.3% of normal incident light per layer, **Figure 2.3**, and its high optical transmittance is much better than ITO.<sup>47–49</sup>



**Figure 2.3. Light transmittance of single layer graphene and bilayer graphene.** Despite only being one atom thick, graphene absorbs about 2.3% of normal incident light per layer. Reprinted with permission from ref. [47]. © 2008 American Association for the Advancement of Science.

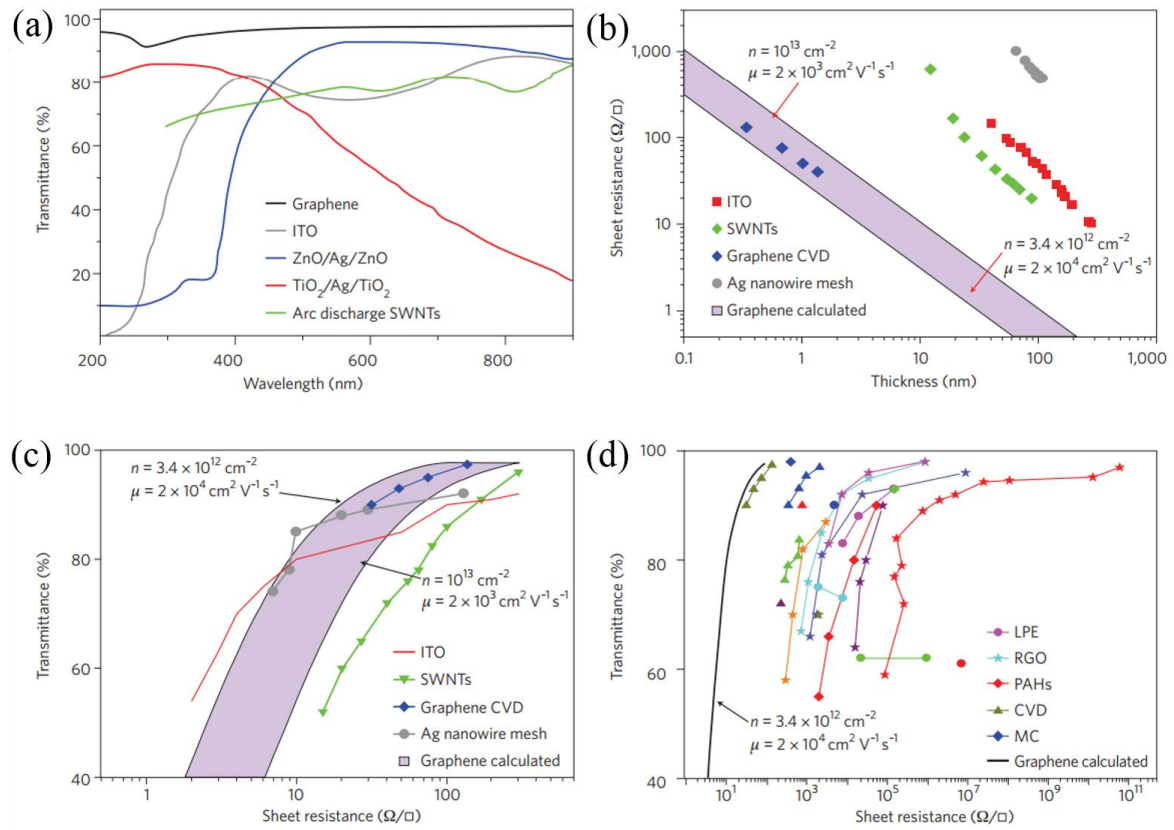
While it is important to understand the correlation between sheet resistance and optical transmittance, an effective transparent conductor should have high electrical conductivity combined with low absorption of visible light. Thus, an appropriate quantitative parameter of the performance of a transparent conductor is the ratio of the electrical conductivity  $\sigma$  to the visible absorption coefficient  $\alpha$ , which can be written as **Equation 2.5**, where  $R_s$  is the sheet resistance in  $\Omega/\square$ ,  $T$  is the total visible transmission and  $R$  is the total visible reflectance.<sup>50</sup>

$$\frac{\sigma}{\alpha} = -\frac{1}{R_s \ln(T + R)}, \quad \text{Equation 2.5}$$

The value of  $\sigma/\alpha$  is a figure of merit, which can be used to rate the efficacy of transparent conductors. The larger the value of  $\sigma/\alpha$ , the better performance of transparent conductors one can have.

**Figure 2.4** shows that graphene films have optical transmittance and thickness advantages over other competitors, but higher sheet resistance than ITO. To challenge the sheet

resistance values of ITO samples and produce a commercially viable product, some methods are urgently needed to reduce the sheet resistance of graphene. It was calculated that improved synthesis and transfer processes would improve sheet resistance values and quality consistency of as-prepared graphene samples.<sup>28</sup> It was also proven that the sheet resistance of graphene could be reduced by chemical doping.<sup>51–56</sup> Several dopants, such as gold chloride ( $\text{AuCl}_3$ ),<sup>52,57</sup> nitric acid ( $\text{HNO}_3$ )<sup>58,59</sup> and iron (III) chloride ( $\text{FeCl}_3$ )<sup>52,56,60</sup> have been used and demonstrated to be effective. The best sheet resistance of large area graphene films prepared by CVD so far is  $30 \, \Omega/\square$  after doping.<sup>59</sup>



**Figure 2.4. Property comparisons among next-generation TCEs candidates.** (a) Comparison of optical transmittance in visible range for different transparent conductors. (b) Thickness dependence of the sheet resistance. (c) Transmittance versus sheet resistance for different transparent conductors. (d) Transmittance versus sheet resistance for graphene TCEs grouped according to production strategies. Reprinted with permission from ref. [23]. © 2010 Macmillan Publishers Limited.

### 2.2.2.3 Mechanical Properties

A theoretical study of its mechanical properties predicted that graphene would be the strongest of the known materials usually used for this purpose.<sup>61</sup> The first thorough experimental measurements used a graphene sheet suspended over an array of micrometre scale perforations in the underlying substrate,<sup>62</sup> a technique originally outlined in a study of few layer graphene.<sup>63,64</sup> By applying force with a diamond atomic force microscope (AFM) tip on the free-standing area of graphene, it was possible to determine its elastic and inelastic breaking strength. A Young's modulus of  $1.0 \pm 0.1$  TPa and an intrinsic strength (*i.e.*, assuming no defects or flaws) of  $130 \pm 10$  GPa were found in this observation.<sup>62</sup> This extraordinarily high strength can be attributed not only to the covalent sigma bonds, but also to the fact that the measurement is of a defect free atomic-scale region. The measured breaking forces were justified as representative of an ideal defect free graphene due to the high level of their good agreement with *ab initio* calculations performed for monolayer graphene,<sup>65,66</sup> and the distribution of breaking forces recorded was narrow; a defective sheet would have a large variance in measured values due to the differing number, size and type of defects one would find under the tip.

Theoretical work has shown that a strain induced gap in the band structure should only manifest for strains in excess of 20%, and that graphene should be perfectly elastic for deformations in excess of 20%.<sup>67</sup> Graphene's flexibility, elasticity and mechanical stability have been tested in the fabrication of a flexible film on a PET substrate.<sup>68</sup> It was found that the original resistance could be restored when strains of up to 18.7% were applied. The further experiments showed that graphene has a high degree of flexibility, which places it in a unique position over ITO in the TCEs market, as it has great potential for use as a replacement for ITO in optoelectronic devices.<sup>68</sup>

#### 2.2.2.4 Thermal Properties

Theoretical predictions and experimental measurements have shown that freely suspended monolayer graphene exhibits an exceptionally large thermal conductivity of approximately  $5,000 \text{ W m}^{-1} \text{ K}^{-1}$  at room temperature.<sup>69–72</sup> This was measured using a non-contact optical technique reliant on graphene's characteristic Raman signal, specifically the temperature dependence of the G peak position (see section 2.2.2.5). Thermal conductivity is a critical issue for microelectronics, as the heat dissipation needs have risen with increased miniaturisation.

The practical use of graphene will require its interaction with a substrate. It cannot merely be suspended in ideal conditions. Such measurements yield a thermal conductivity of  $600 \text{ W m}^{-1} \text{ K}^{-1}$  for graphene on a  $\text{SiO}_2/\text{Si}$  substrate at room temperature.<sup>73</sup> This reduction is likely arises because of phonon coupling with the substrate.<sup>74</sup>

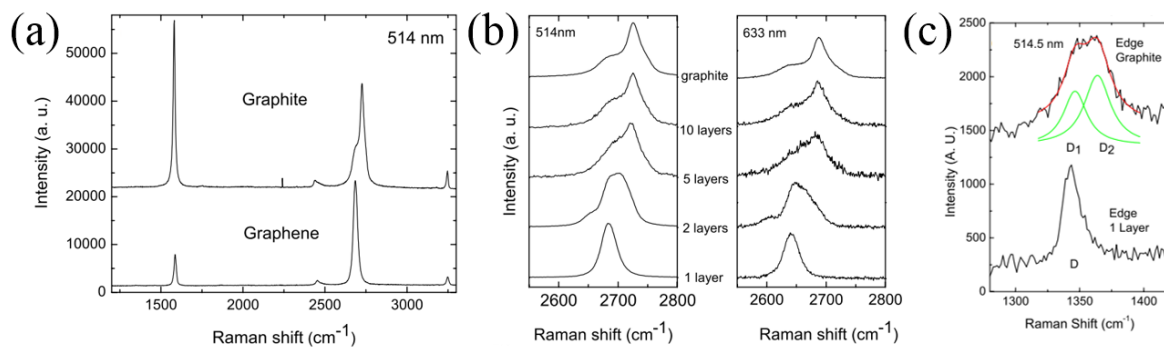
#### 2.2.2.5 Vibrational Properties

The vibrational properties of graphene are determined by Raman spectroscopy, which is a widely-used, non-invasive technique that relies on inelastic scattering.<sup>75–78</sup> The two most prominent peaks in a Raman spectrum taken of graphene, or of bulk graphite are the G peak at  $\sim 1580 \text{ cm}^{-1}$ , a signature of the carbon-carbon stretching mode and found in all  $sp^2$  carbons, and the 2D peak at  $\sim 2700 \text{ cm}^{-1}$ , originating from second order zone boundary phonons. **Figure 2.5(a)** shows that Raman spectra for monolayer graphene and graphite. The two spectra are readily distinguished by the shape of the 2D peak, as well as its relative position and intensity.<sup>76</sup> The G peak is red shifted slightly by  $3\text{--}5 \text{ cm}^{-1}$  at higher thicknesses, and the full width half maximum (FWHM) begins to increase. For monolayer graphene, the 2D peak can be well fitted with one single Lorentzian peak, but it blue shifts noticeably and broadens

into a shape composed of several Lorentzian peaks with incremental layer increases. As the layer count increases, the lower frequency Lorentzian peaks comprising the 2D profile decrease in intensity, eventually leading to the shape found for bulk graphite, **Figure 2.5(b)**. In particular, turbostratic graphene, which is graphene that lacks the AB Bernal arrangement in its layering, also shows a single Lorentzian 2D peak. However, it is blue shifted by  $\sim 20 \text{ cm}^{-1}$  and has a FWHM of  $50 \text{ cm}^{-1}$ , double that of single layer graphene.<sup>76</sup>

Other peaks for graphene can occur at  $\sim 1350 \text{ cm}^{-1}$  and  $\sim 1600 \text{ cm}^{-1}$ , attributed to the D and D' peak, respectively. The D' peak is normally seen as part of the much larger G peak, and is only apparent in strongly disordered graphene. The D peak, which is not present in theoretically ideal graphene due to polarisation symmetry, is visible in defective graphene or at graphene edges as the mode only remains inactive for perfect and infinite crystals, **Figure 2.5(c)**.<sup>76</sup> The relative intensity of the D and G peaks provides an effective way to identify the defect level and evaluate the quality of a graphene.<sup>75</sup>

When optically identified, it is often difficult to discriminate between layers that are different by a magnitude of one purely by contrast, and even when it is possible, a qualitative contrast measurement is not always ideal. The vibrational features of graphene exhibit different peak positions and profile shapes when the incident light interacts with particular graphene sheets, an understanding which can provide a quantitative means of thickness evaluation.



**Figure 2.5. The vibrational properties of graphene.** (a) Raman spectra for both graphite and graphene. (b) 2D peak variation as a function of layer number under two excitation wavelengths; 514 nm and 633 nm. (c) D peak of graphene and graphite edges. Reprinted with permission from ref. [76]. © 2006 American Physical Society.

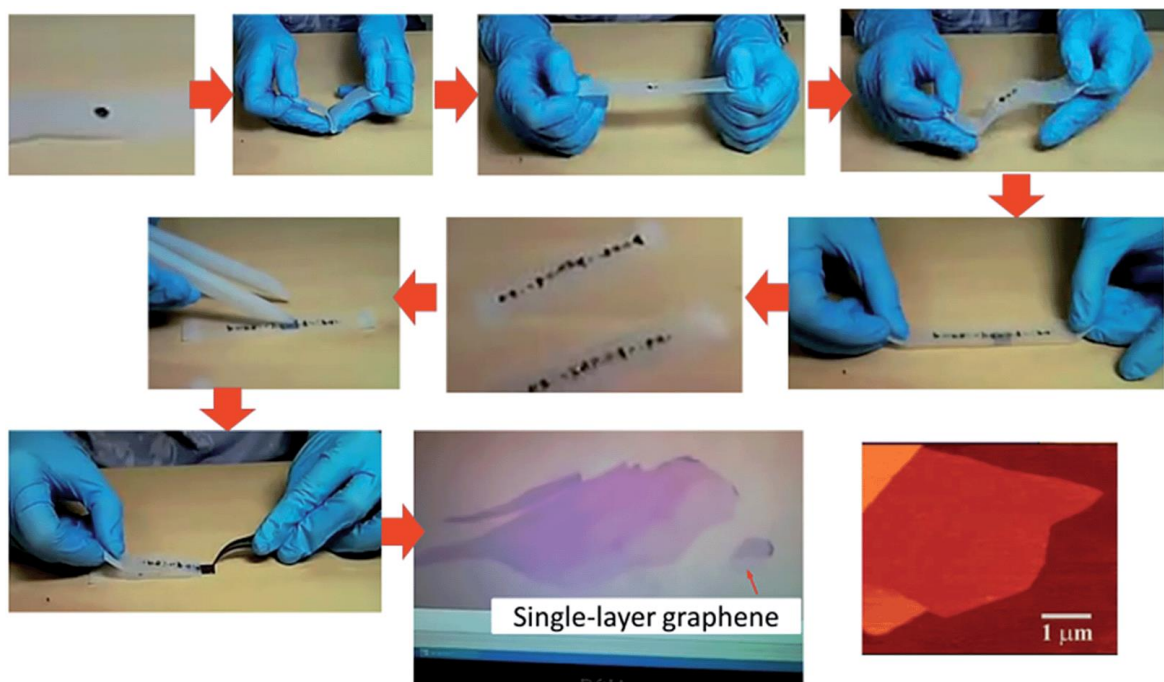
### 2.2.3 Synthesis of Graphene

The 2D character of graphene gives an advantage over the other novel carbon nanomaterial in the field, carbon nanotubes, as graphene can be processed by already established planar techniques, which are extensively used in the silicon based microelectronics sector. If a synthesis method that can generate large areas of high quality graphene can be found, then one of the main problems preventing the implementation of graphene into devices will have been solved. Two types of synthesis routes have been reported since the first discovery of graphene in 2004; top-down and bottom-up methods. The top-down method breaks the van der Waals force between two graphite layers and peels the graphite apart, whereas the bottom-up approach produces graphene from alternative carbon precursors. Although the number of synthesis routes for growing graphene increases, only 4 major relevant methods, namely mechanical exfoliation, chemical exfoliation, epitaxial growth on silicon carbide and CVD, shall be reviewed in this section.

### 2.2.3.1 Mechanical Exfoliation

The mechanical exfoliation, also known as the “scotch tape” or “peel-off” method, as illustrated in **Figure 2.6**, was first developed by Geim *et al.*<sup>5</sup> in 2004, and is the most readily available way to fabricate graphene.<sup>79</sup> After several peeling iterations, small graphene flakes of varying thickness are obtained from HOPG. The number of layers is identified by examining the contrast of graphene flakes using an optical microscope after applying the graphitic residue from the tape to a silicon substrate, with an oxide layer of 300 nm thickness.

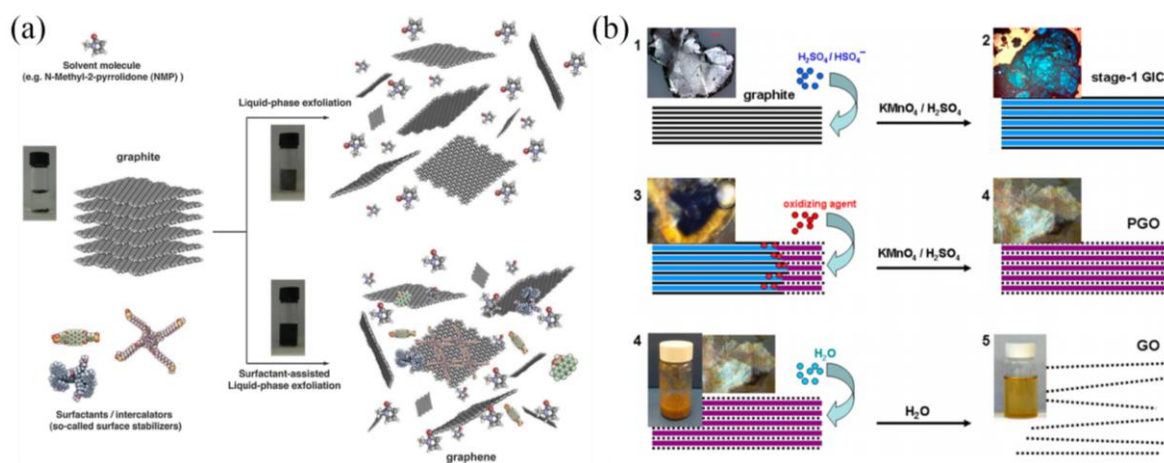
This technique has seen the best quality graphene fabricated to date, with a carrier mobility of  $15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , for non-suspended graphene measured under ambient conditions.<sup>1</sup> However, the locating of the isolated graphene flakes is particularly time consuming and the size is limited to micron scale. Therefore, this technique is widely used by researchers investigating graphene’s fundamental properties, but not suitable for mass production.



**Figure 2.6.** An illustrative procedure of the Scotch-tape based micromechanical cleavage of HOPG. Reprinted with permission from ref. [79]. © 2006 The Royal Society of Chemistry.

### 2.2.3.2 Chemical Exfoliation

The chemical exfoliation methods can be divided into two different subsections; liquid-phase exfoliation (LPE),<sup>80</sup> or the intercalation of graphite oxide (GO) and the subsequent reduction to graphene.<sup>81</sup> LPE typically involves a dispersion of graphite in a strong solvent, such as N-methyl-pyrrolidone (NMP), to extract individual layers, **Figure 2.7(a)**.<sup>82</sup> On the other hand, the Hummers method is the most frequently used protocol for preparing GO and its single layers.<sup>83</sup> The chemical reduction of GO sheets has been performed with reducing agents, such as hydriodic acid (HI),<sup>84</sup> hydrazine (N<sub>2</sub>H<sub>4</sub>),<sup>85</sup> sodium borohydride (NaBH<sub>4</sub>),<sup>86</sup> and dimethyl hydrazine.<sup>87</sup> Recent work demonstrated a highly efficient chemical reduction of GO achieved in a sodium-ammonia (Na-NH<sub>3</sub>) system.<sup>88</sup> **Figure 2.7(b)** summarizes and schematically represents the three steps constituting the process of conversion of bulk graphite into GO.<sup>89</sup> This method appears to provide a solution for the large-scale production of graphene because of its potential scalability, high yield and excellent dispersibility in various solvents, but it suffers from extremely poor quality and structural inhomogeneity, which is not suitable for electronic or optoelectronic applications.<sup>90</sup>

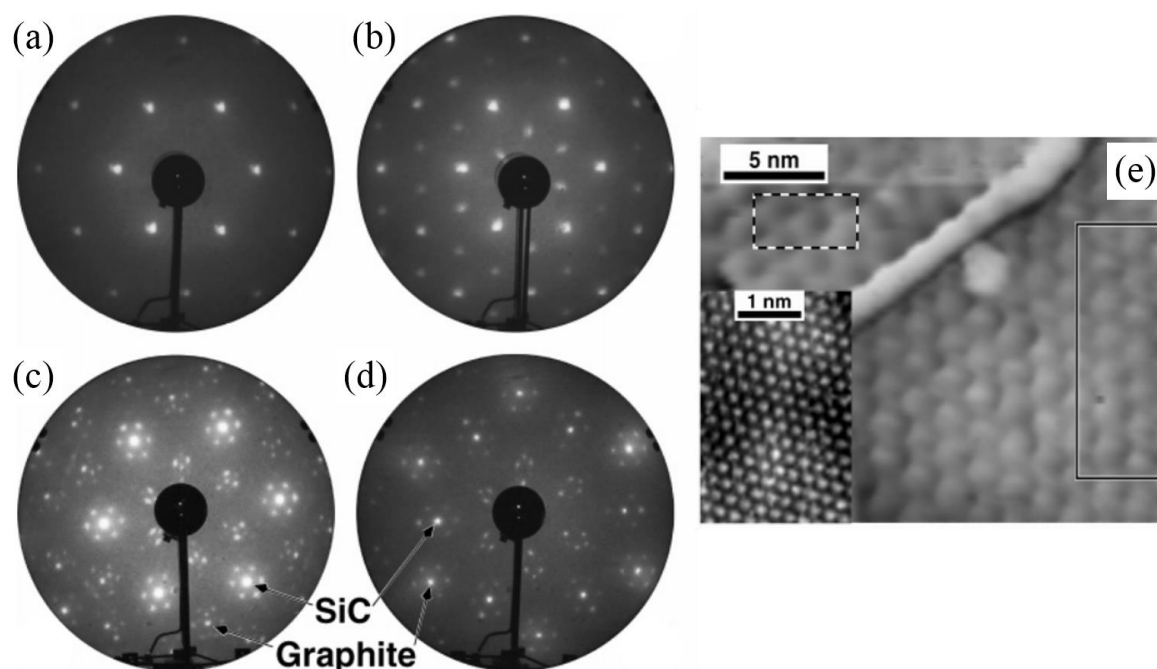


**Figure 2.7. Chemical exfoliation methods for producing graphene and GO.** (a) Schematics of the LPE process of graphite in the absence (top-right) and presence (bottom-right) of surfactant molecules. Reprinted with permission from ref. [82]. © 2014 The Royal Society of Chemistry. (b) Schematics of conversion of bulk graphite into GO with corresponding micrographic images or sample appearances at each phase. The three steps signify formation of the two intermediate products (stage-1 GIC and PGO) and the final GO product. The solid black lines represent graphene layers and the dotted black lines represent single layers of GO. Reprinted with permission from ref. [89]. © 2014 American Chemical Society.

### 2.2.3.3 Epitaxial Growth on Silicon Carbide

Berger *et al.*<sup>91</sup> reported the heat treatment of single-crystal silicon carbide (SiC) under an ultra-high vacuum (UHV) to form a graphene film at the SiC interface, which involves the evaporation of silicon atoms from the SiC surface, followed by the rearrangement and re-bonding of the remaining carbon atoms to form epitaxial graphene layers.<sup>91,92</sup> Typically, graphene samples with thicknesses of one to three layers can be formed depending on the temperature of decomposition. **Figure 2.8(a-d)** show low energy electron diffraction patterns (LEED) at different stages during the growth of a 2.5-monolayer graphite film grown *in situ*. **Figure 2.8(e)** displays an STM image from the sample obtained after growth. Although this method is suitable for the preparation of relatively high-quality graphene with mobilities exceeding  $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,<sup>92</sup> the size of a single domain with uniform layer thickness is still

limited to micron scale.<sup>18</sup> To conquer this matter, Emtsev *et al.*<sup>93</sup> heated the SiC under an argon atmosphere at 900 mbar as opposed to UHV. They were able to reduce the surface roughness and produce continuous graphene layers up to 50  $\mu\text{m}$  in length with much larger domain sizes. Electronic mobilities of up to  $2,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  were then found at a low temperature of  $\sim 27\text{K}$ . Epitaxial growth of graphene on silicon carbide is expected to potentially generating wafer-size graphene films. However, the graphene transfer from SiC to any other substrate is extremely difficult, which dramatically limits the versatility of the process in a wide range of electronic applications.



**Figure 2.8. Epitaxial Growth on Silicon Carbide.** (a-d) LEED patterns from graphite/SiC(0001). The sample was heated several times to successively higher temperatures. (a) 1050 °C. (b) 1100 °C. (c) 1250 °C. (d) 1400 °C. (e) STM image of a surface region of the sample described in (d). Inset is the atomically resolved region. Reprinted with permission from ref. [91]. © 2004 American Chemical Society.

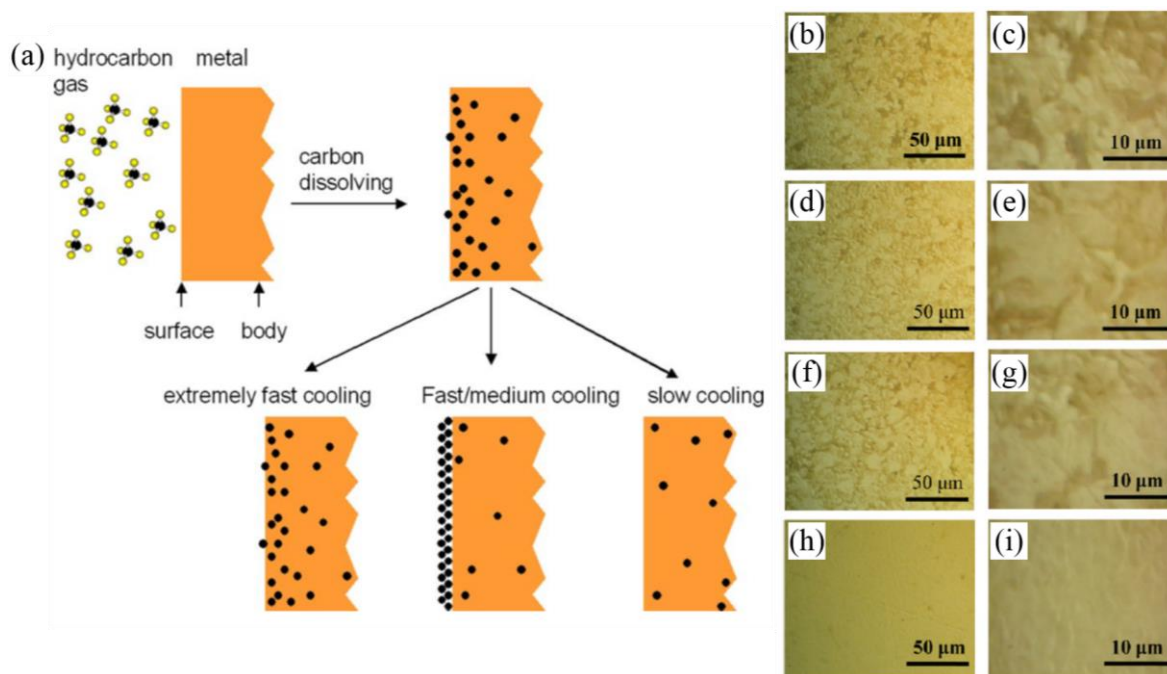
### 2.2.3.4 Chemical Vapour Deposition

CVD has been extensively used to synthesize graphene on metal substrates from gaseous carbon sources. It is also one of the most promising methods to produce graphene on an industrial-scale due to its ability to yield high-quality, continuous films over large areas that are only limited in extent to the size of the substrate on which they are grown. During CVD, carbon precursors decompose on a catalyst surface to form hydrocarbon intermediate species, which subsequently react to generate graphene layers. The first CVD growth of thin graphite films was demonstrated in 1969 using Pt as substrate.<sup>94</sup> Since then, graphene growth has been carried out on a wide range of metals, such as Ni,<sup>95,96</sup> Cu,<sup>38,68</sup> Fe,<sup>97</sup> Ru,<sup>98</sup> Co,<sup>99</sup> Rh,<sup>100</sup> Ir,<sup>101</sup> Pd,<sup>102</sup> Pt,<sup>103</sup> and Au.<sup>104</sup> Among these, Ni and Cu have attracted the most research attention because of their low cost and catalytic efficiency.

#### 2.2.3.4.1 CVD Growth on Ni

The graphene grown on Ni substrates is a surface segregation process. The solubility of carbon in Ni films is relatively high at elevated temperatures. Hence, graphene can be formed *via* the precipitation of carbon atoms from a metal surface during the cooling process. Yu *et al.*<sup>105</sup> claimed that the thickness and quality of the graphene sheets strongly depend on the rate of cooling, as illustrated in **Figure 2.9(a)**. In the early years of graphene study, graphene grown on Ni was believed to be an ideal platform for graphene synthesis, as Ni(111) has a lattice constant similar to graphene. Zhang *et al.*<sup>106</sup> demonstrated a comparative study of the growth of graphene on single-crystalline Ni(111) and polycrystalline Ni substrates. As shown in **Figure 2.9(b-i)**, the use of single crystal substrates allows a preferential formation of monolayer/bilayer graphene because of its atomically smooth surface and the absence of grain boundaries. However, it is still difficult to control the layer number and homogeneity

of the graphene films produced by this technique, mainly due to the high solubility of carbon in Ni at high temperatures.

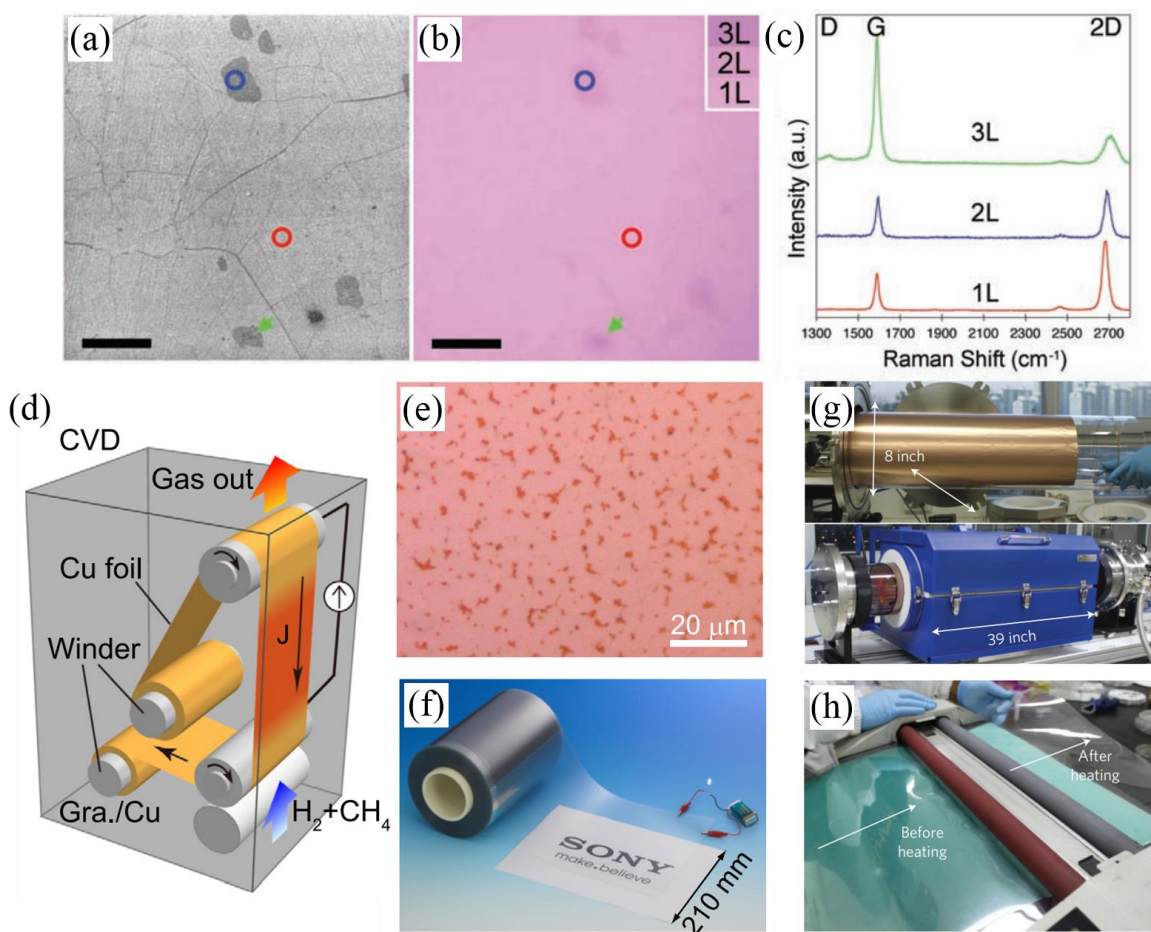


**Figure 2.9. CVD growth of graphene on Ni substrates.** (a) Illustration of carbon segregation at metal surface with different cooling rates. Reprinted with permission from ref. [105]. © 2008 American Institute of Physics. (b-i) Optical images taken after graphene CVD growth from polycrystalline Ni with (b,c) fast, (d,e) medium and (f,g) slow annealing rates; (h,i) optical images taken after graphene CVD growth from Ni (111). (b-i) are reprinted with permission from ref. [106]. © 2004 American Chemical Society.

#### 2.2.3.4.2 CVD Growth on Cu

In contrast, Cu has a low carbon solubility, which only allows limited carbon diffusion from substrate to surface. Instead, the Cu substrate catalyses the decomposition of the carbon containing species, which subsequently leads to the formation of graphene on its surface. Li *et al.*<sup>38</sup> used a similar CVD process to produce large scale monolayer graphene on copper foils in 2009. SEM imaging, optical microscopy and Raman spectroscopy, **Figure 2.10(a-c)**, confirmed the graphene to be primarily monolayer with a small percentage (less than 5%) of

few-layer graphene. The low solubility of carbon in Cu appears to allow the process self-limiting. The FETs they fabricated showed carrier mobilities as high as  $4,050 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at room temperature. A detailed comparative study of graphene grown on Ni and Cu has indicated that the graphene on polycrystalline Cu is much more uniform than that on Ni, which has several multilayer regions.<sup>107</sup> However, most work to date has specialised in optimizing graphene synthesis and devices on the 1 cm scale, with only a few reports of graphene in areas over  $10 \text{ cm}^2$ . Recent work by Sony demonstrated a 100-metre-long graphene film by low pressure CVD (LPCVD) using selective Joule heating, **Figure 2.10(d-f)**.<sup>108</sup> The sheet resistance was reported to be comparable to the conventional CVD-grown graphene. Another roll-to-roll process was reported to produce graphene films with a diagonal of up to 30 inches, **Figure 2.10(g) and (h)**. The graphene produced was reported to be predominantly monolayer with excellent sheet resistance and high optical transmittance. This roll-to-roll method will be perfect for the future commercial production of large-scale transparent electrodes.



**Figure 2.10. CVD growth of graphene on Cu substrates.** (a) SEM image of graphene transferred on SiO<sub>2</sub>/Si showing wrinkles, as well as bi- and three-layer regions. (b) Optical microscope image of the same regions as in (a). (c) Raman spectra from the marked spots with corresponding coloured circles or arrows, showing the presence of one, two, and three layers of graphene. (a-c) are reprinted with permission from ref. [38]. © 2008 American Association for the Advancement of Science. (d) Continuous roll-to-roll CVD system using selective Joule heating to heat a copper foil suspended between two current-feeding electrode rollers to grow graphene. (e) Optical microscopy image of the graphene film. (f) Photograph of the graphene/epoxy/PET roll before doping. (d-f) are reprinted with permission from ref. [108]. © 2013 American Institute of Physics. (g) Copper foil wrapping around a 7.5-inch quartz tube to be inserted into an 8-inch quartz reactor. The lower image shows the stage in which the copper foil reacts with CH<sub>4</sub> and H<sub>2</sub> gases at high temperatures. (h) Roll-to-roll transfer of graphene films from a thermal release tape to a PET film. (g) and (f) are reprinted with permission from ref. [59]. © 2010 Macmillan Publishers Limited.

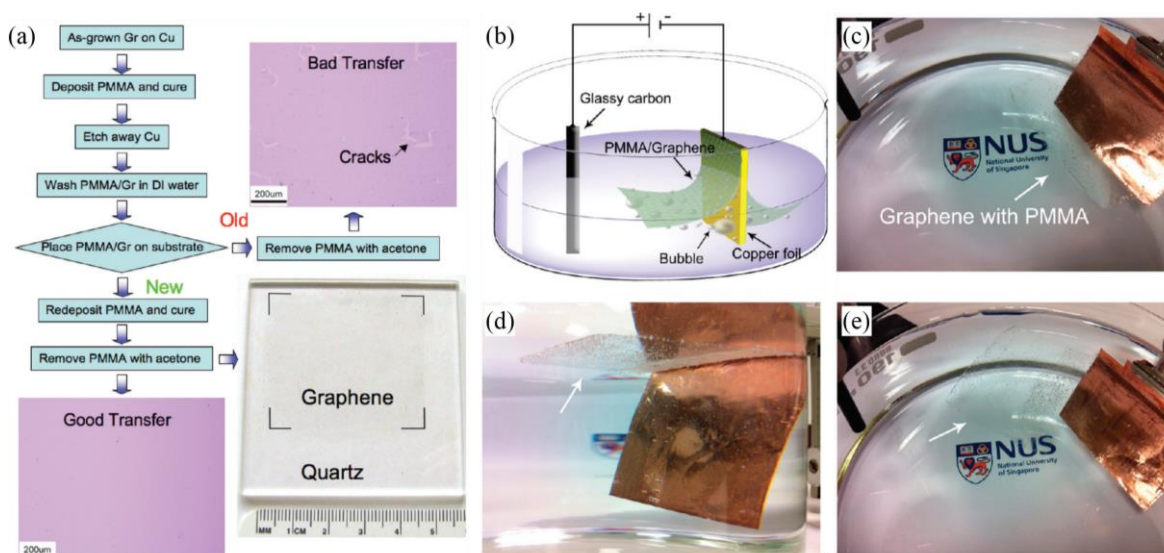
## 2.2.4 Transfer of Graphene

Graphene grown directly on metal surfaces, such as Cu, Ni, and Pt, has limited use; most applications require the graphene to be on non-metallic substrates, in most cases dielectric materials. A selection of transfer methods have been developed specifically according to various graphene synthesis methods, among which transfer techniques for CVD graphene is the major thought. The rapid development of large-area graphene growth through CVD reactions on Cu requires efficient routes for transferring them onto arbitrary substrates before characterisation.

### 2.2.4.1 Wet Transfer

The most commonly used transfer technique used today in research laboratories is still the wet transfer method utilising poly(methyl methacrylate) (PMMA) as a polymer scaffold, due to its advantage of maintaining the integrity of the graphene film.<sup>38</sup> The metal can then be removed by the action of an appropriate etchant, such as iron (III) chloride or ammonium persulfate (APS) solution, which does not damage the graphene layer. The PMMA/graphene film is subsequently rinsed with deionized (DI) water to remove chemical residues. It has been shown to be beneficial to apply an extra coat of PMMA in anisole solution to allow the film to relax to the substrate, as illustrated in **Figure 2.11(a)**.<sup>109</sup> Once transferred, the PMMA can be removed by the action of a solvent such as acetone. There are numerous drawbacks inherent in this technique, including difficult manufacturability, because of the fragile nature of the polymer carrier film; contaminations from the etchant salt and polymer residues; cost; and excessive chemical waste.<sup>110</sup> Delaminating graphene from the Cu substrate *via* an electrochemical process known as the “bubbling transfer” method, has also been successfully used, **Figure 2.11(b-e)**.<sup>111</sup> In this process, electrolysis of water with graphene/Cu as the cathode and glassy carbon as the anode generates hydrogen bubbles between the graphene

and the Cu substrate, which delaminates the graphene from the Cu without consuming any chemicals other than water and electricity. This method may significantly lower the cost of graphene production by the recycle of Cu substrate, which will not only cause a reduction in the amount of chemicals used, but also a possible reduction in environmental pollution.

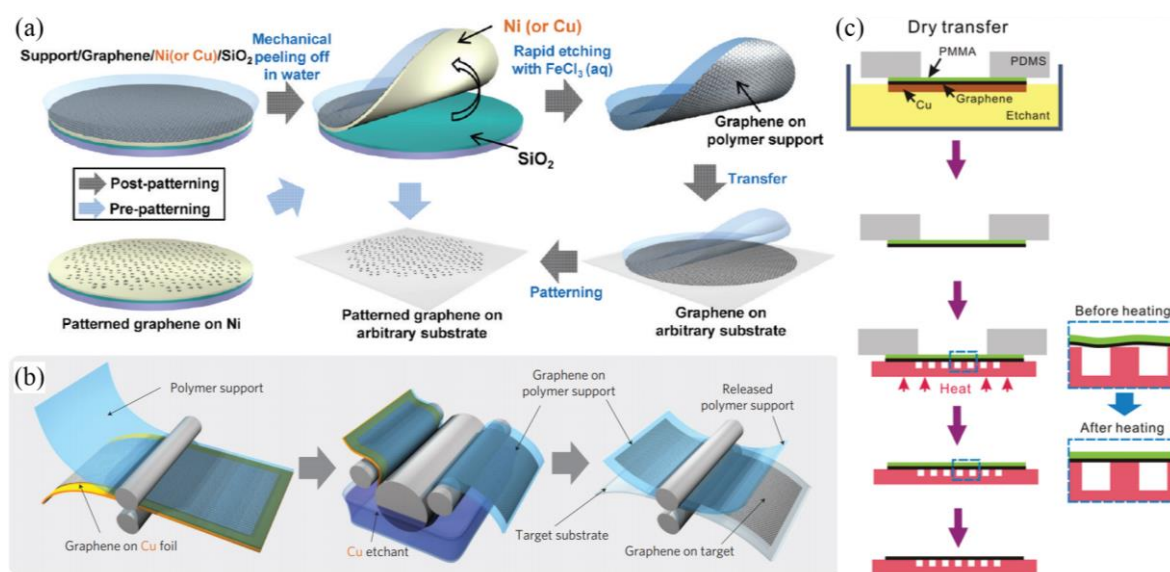


**Figure 2.11. Wet transfer of graphene on Cu.** (a) Processes for transfer of graphene films. The top-right and bottom-left insets are the optical micrographs of graphene transferred on SiO<sub>2</sub>/Si wafers with “Old” and “New” transfer, respectively. The bottom-right is a photograph of graphene on quartz substrate. Reprinted with permission from ref. [109]. © 2009 American Chemical Society. (b) Schematic diagram of electrochemical cell used for the electrochemical exfoliation. (c-e) Optical images showing the “whole film” peeling of PMMA-covered graphene from the copper foil. (b-e) are reprinted with permission from ref. [111]. © 2011 American Chemical Society.

#### 2.2.4.2 Dry Transfer

The dry transfer method is quite similar to the standard wet transfer, but utilises a polymer support such as a polydimethylsiloxane (PDMS) stamp or a thermal release tape (TRT). Here, once the metal etching and cleaning stages are performed, the graphene on the polymer support can be dry transferred to a desired substrate. As illustrated in **Figure 2.12(a)**, Lee *et al.*<sup>112</sup> introduced a polymer-supported process, which involves the dry transfer of wafer-scale

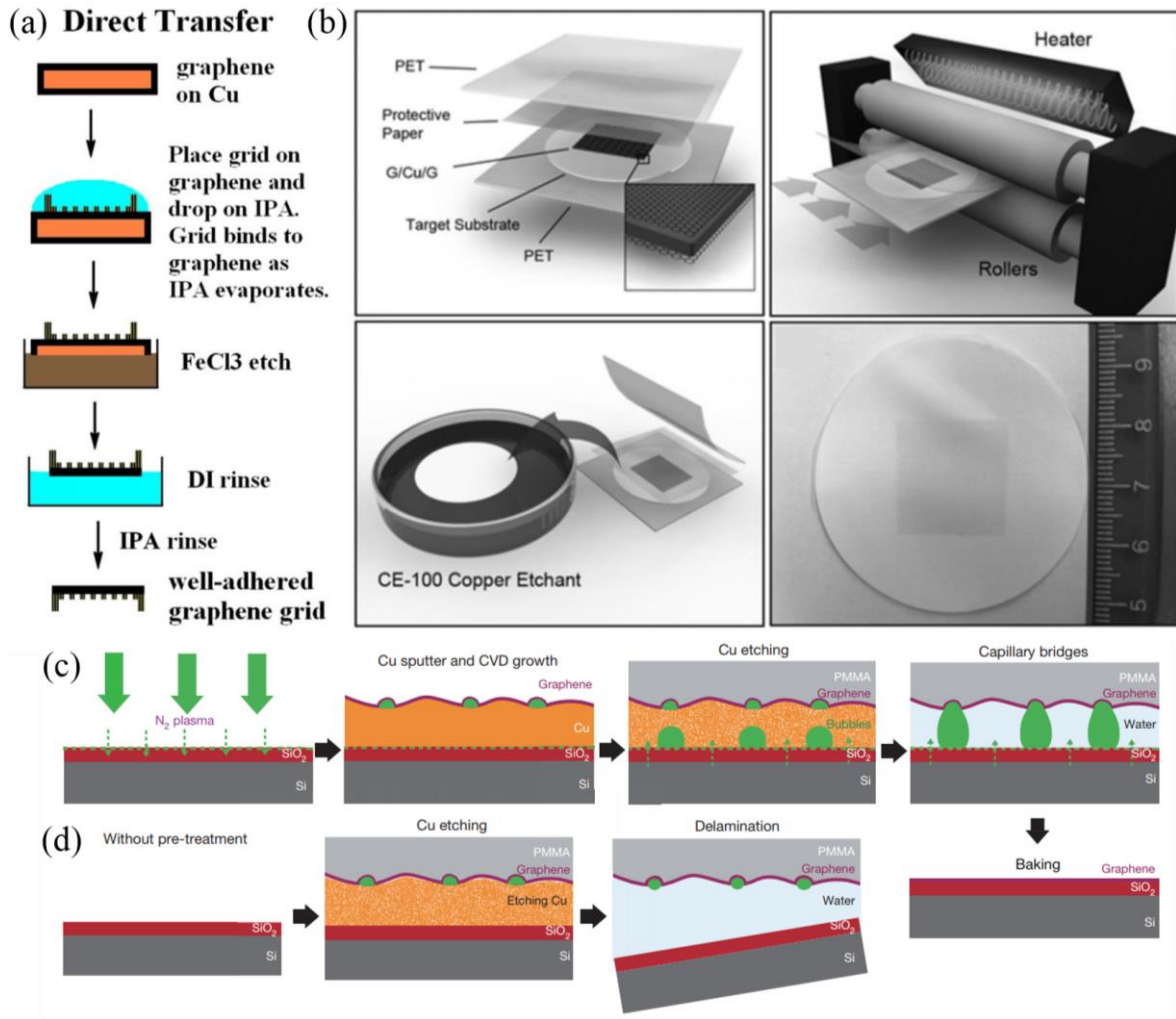
graphene onto arbitrary substrates and the batch fabrication of FET arrays. Following the trend, Bae *et al.*<sup>59</sup> presented a roll-based transfer process that includes adhesion of polymer supports, copper etching (rinsing) and dry transfer-printing onto a target substrate, **Figure 2.12(b)**. By repeating these steps (*i.e.*, transferring multiple graphene sheets) on the same substrate, multilayer graphene films can be stacked and exhibit enhanced electrical and optical properties. Another novel dry transfer method was demonstrated by Suk *et al.*<sup>113</sup> using both PMMA and PDMS, **Figure 2.12(c)**. This technique was used to make graphene-sealed micro-chambers without trapping liquid inside. The dry transfer method is suitable for the transfer of large scale graphene, but polymer residues will always accompany this process.



**Figure 2.12. Dry transfer of graphene on Cu.** (a) Schematic illustration for synthesis, etching, and transfer of large-area graphene films. After fast etching of metal, the graphene films can be transferred to arbitrary substrates and then patterned using conventional lithography. Reprinted with permission from ref. [112]. © 2010 American Chemical Society. (b) Schematic of the roll-based production of graphene films grown on a copper foil. Reprinted with permission from ref. [59]. © 2010 Macmillan Publishers Limited. (c) Schematics of the dry transfer process onto shallow depressions. Reprinted with permission from ref. [113]. © 2011 American Chemical Society.

### 2.2.4.3 Direct Transfer

A more elegant, but inherently limited solution, **Figure 2.13(a)**, is to use the surface tension effect of the evaporation of IPA to adhere a TEM grid to the graphene/catalyst surface and then etch the metal away, thus removing the need for any PMMA scaffold stages.<sup>114</sup> This method, however, is not transferrable across different substrates. Another novel direct transfer method *via* lamination is designed for flexible substrates, **Figure 2.13(b)**.<sup>115</sup> This approach does not require an intermediate transfer membrane, and is most effective on hydrophobic substrates with low glass transition temperature. In addition, Gao *et al.*<sup>116</sup> developed a face-to-face transfer method for wafer-scale graphene films that is so far the only known way to accomplish both the growth and transfer steps on one wafer. This spontaneous transfer method relies on nascent gas bubbles and capillary bridges between the graphene film and the underlying substrate during etching of the metal catalyst, as shown in **Figure 2.13(c)** and (d). The face-to-face transfer has advantages over the previous wet or dry transfer, and will facilitate batch processing for the future technological application of graphene.



**Figure 2.13. Direct transfer of graphene.** (a) Direct transfer of layer-area graphene to holey a-C TEM grids. Reprinted with permission from ref. [114]. © 2010 American Institute of Physics. (b) Schematic diagram of the direct transfer technique via lamination. Reprinted with permission from ref. [115]. © 2013 National Academy of Sciences. (c,d) Illustration of the face-to-face method for transferring graphene mediated by capillary bridges. (c) and (d) are reprinted with permission from ref. [116]. © 2014 Macmillan Publishers Limited.

## 2.2.5 Conclusion

Graphene has attracted great scientific and technological interest not only due to its electronic properties, but also because of its remarkable mechanical, thermal and optoelectronic properties. However, it is still difficult to evaluate the impact graphene will have on the world beyond the confines of academia. Regardless of the application, the

exploitation of graphene requires refining of many different synthesis strategies. CVD synthesis of graphene on Cu catalysts has made significant progress in the past decades, in both fundamental mechanism understanding and process development. However, challenges associated with this process remain. The precise mechanism of graphene growth are still under investigation, and it is still difficult to obtain high single-crystalline-graphene growth rate. The size of a single graphene domain is limited to the centimetre scale, mainly due to the low growth rate. Control of the layer number and stacking order is another big challenge for graphene synthesis. At this point, the optimized growth conditions still need high temperature and low pressure, while low temperature and ambient pressure lower the cost. A range of transfer methods for CVD graphene have been reported to match different needs, however, no one method has provided universal success. The development of techniques for the direct growth of graphene on target substrates, such as dielectrics, is a top priority to eliminate the film-transfer process, which not only degrades the graphene quality, but also increases the total production cost. Further work on the improvement of graphene synthesis and transfer is still needed to meet the most demanding applications, such as the potential use for electronic and optoelectronic devices.

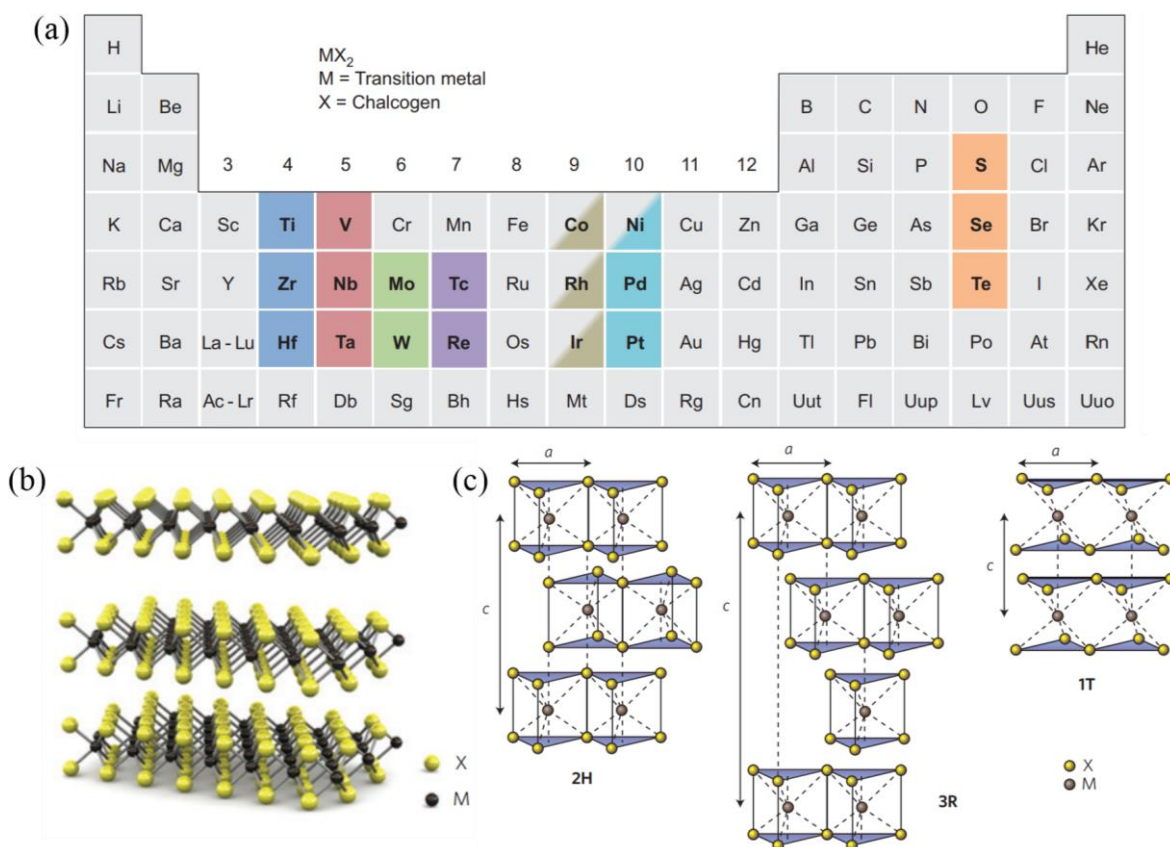
## **2.3 Tungsten Disulphide (WS<sub>2</sub>)**

Two-dimensional (2D) materials offer an exciting platform for fundamental research as well as prospects for technological breakthroughs in many different applications. Since the observation of unusual physical properties of graphene triggered an explosion of research in 2004, a wide variety of other 2D materials, like transition metal dichalcogenides (TMDs) have also received increasing attention, particularly in the last couple of years. The diversity of materials that exist in van der Waals layer structure offers an unlimited catalogue of 2D materials with a range of intriguing properties. These emerging 2D materials and their

heterostructures offer tremendous opportunities in the exploration of fundamental condensed matter phenomena as well as realization of novel technologies. This section will mainly cover the properties, synthesis and transfer of 2D WS<sub>2</sub>, although work on other 2D TMDs will also be introduced when needed.

### 2.3.1 What is WS<sub>2</sub>?

TMDs are a class of materials, **Figure 2.14(a)**, with the formula MX<sub>2</sub>, where M is a transition metal element from group IV (for instance Ti, Zr or Hf), group V (V, Nb, Ta and so on) or group VI (Mo, W), and X is a chalcogen (S, Se or Te).<sup>117</sup> These materials form layered structures of the form X–M–X, with the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms, as illustrated in **Figure 2.14(b)**, ranging from metals (e.g. NbS<sub>2</sub> and VSe<sub>2</sub>), semi-metals (e.g. WTe<sub>2</sub> and TiSe<sub>2</sub>), semiconductors (e.g. MoS<sub>2</sub> and WS<sub>2</sub>) to insulators (e.g. HfS<sub>2</sub>).<sup>118</sup> Layered TMDs often occur in different polytypes (stacking order) and polymorphs (metal coordination geometry). The three common polytypes are 1T, 2H and 3R, where the letters represent different crystal symmetry systems of trigonal, hexagonal and rhombohedral, respectively, and the digits stand for the number of layers in each unit cell, **Figure 2.14(c)**. In particular, group VI 2H-MX<sub>2</sub> (*i.e.*, MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub>) are thermodynamically stable under ambient conditions, compared with semiconducting TMDs from other group such as TiS<sub>2</sub>.<sup>119</sup> and other semiconducting 2D materials such as phosphorene,<sup>120,121</sup> which enables the application of 2D semiconducting TMDs in areas that were never viable with graphene, such as flexible and transparent optoelectronics.<sup>122</sup>



**Figure 2.14. Structure of TMDs.** (a) About 40 different layered TMD compounds exist. The transition metals and the three chalcogen elements that predominantly crystallize in those layered structure are highlighted in the periodic table. Partial highlights for Co, Rh, Ir and Ni indicate that only some of the dichalcogenides form layered structures. For example, NiS<sub>2</sub> is found to have apyrite structure but NiTe<sub>2</sub> is a layered compound. Reprinted with permission from ref. [117]. © 2013 Macmillan Publishers Limited. (b) Three-dimensional schematic representation of a typical MX<sub>2</sub> structure, with the chalcogen atoms (X) in yellow and the metal atoms (M) in grey. (c) Schematics of the structural polytypes: 2H (hexagonal symmetry, two layers per repeat unit, trigonal prismatic coordination), 3R (rhombohedral symmetry, three layers per repeat unit, trigonal prismatic coordination) and 1T (tetragonal symmetry, one layer per repeat unit, octahedral coordination). The chalcogen atoms (X) are yellow and the metal atoms (M) are grey. (b) and (c) are reprinted with permission from ref. [118]. © 2012 Macmillan Publishers Limited.

MoS<sub>2</sub> was the first semiconducting TMD obtained in a monolayer form, but monolayer WS<sub>2</sub> has gained its popularity as a result of the exotic properties. Theoretical models predict that monolayer WS<sub>2</sub> would have the highest mobility among all 2D semiconducting TMDs because of its reduced effective mass.<sup>123</sup> Monolayer WS<sub>2</sub> was reported to have several tens

of times higher PL yield than MoS<sub>2</sub>, which indicates that the optoelectronic devices based on WS<sub>2</sub> are more viable to obtain high quantum efficiency. Monolayer WS<sub>2</sub> is also expected to endure working conditions at higher temperatures, as the melting point of bulk WS<sub>2</sub> is higher than that of MoS<sub>2</sub>. In addition, the research interest in 2D WS<sub>2</sub> monolayer also stems from its semiconducting properties with a direct band gap in the visible spectrum,<sup>124</sup> large exciton binding energy, large absorption coefficient, and sensitivity to interlayer interactions. Despite the difficulty to produce, WS<sub>2</sub> monolayers have been utilized in the demonstration of nanoelectronic and optoelectronic devices such as excitonic laser,<sup>125</sup> valley-LED,<sup>126</sup> FETs,<sup>127</sup> and solar cells.<sup>128</sup>

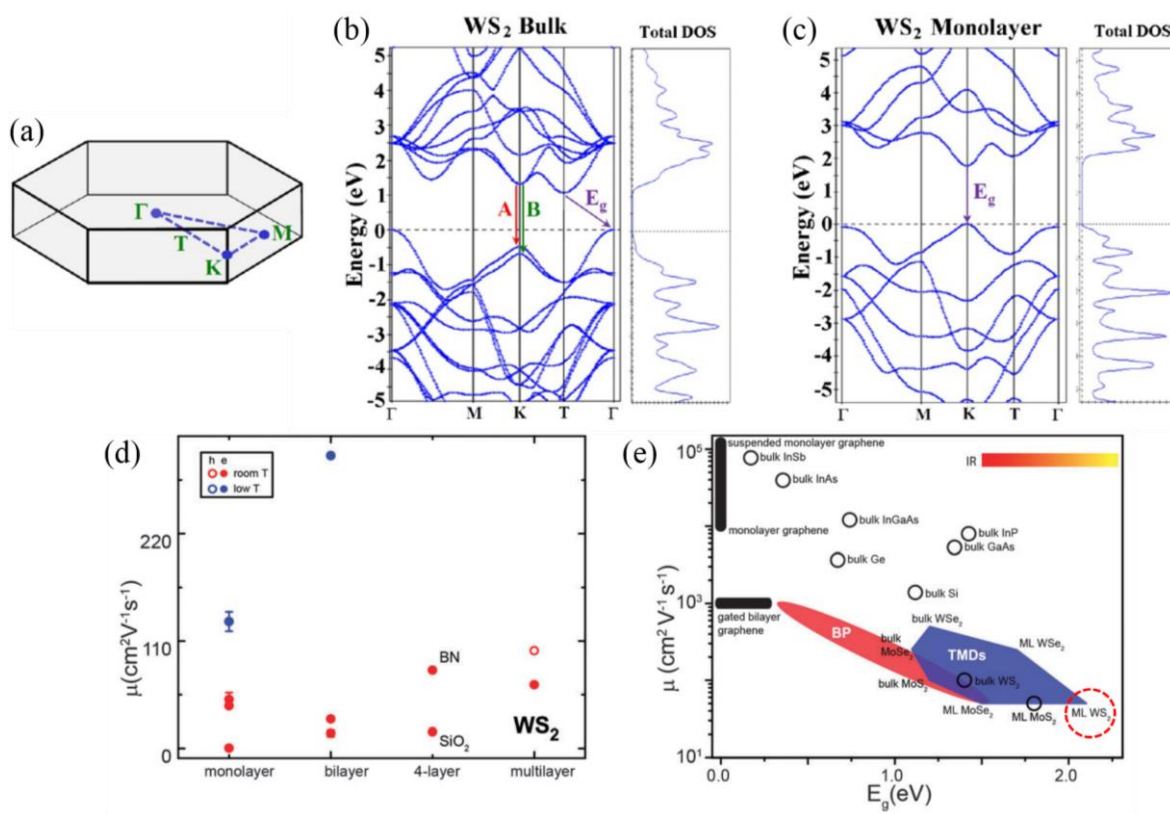
### 2.3.2 Properties of WS<sub>2</sub>

The basic properties of TMD crystals have been studied for over half a century.<sup>129</sup> No further discussion is meaningful unless I first address what properties have made 2D WS<sub>2</sub> monolayer so unique in the family of 2D materials. In this section, some of the properties of WS<sub>2</sub> shall be reviewed, with an emphasis on optical properties.

#### 2.3.2.1 Electronic Properties

The fundamental band structure physics is basically the same for all the group VI TMDs.<sup>130</sup> Theoretical band structures are normally calculated from first principles density functional theory (DFT) to gain an insight into the influence of low-dimension quantum confinement. A fundamental indirect bandgap derives from the energy required for transition of electrons from the top of valence band at the  $\Gamma$  point of the Brillouin zone to the bottom of conduction band halfway between  $\Gamma$  and K at the T symmetry point, **Figure 2.15(a)**.<sup>131</sup> The conduction band states at the T point result from the hybridization between the *d* orbitals of W and the antibonding *p<sub>z</sub>* orbitals of S and hence are susceptible to interlayer interactions. In contrast,

the conduction band states at the K point are solely due to localized  $d$  orbitals on the W atoms, located within the S-W-S sandwich structure, which are relatively insensitive to layer number.<sup>131–133</sup> Therefore, as the WS<sub>2</sub> becomes thinner, lowest conduction band at the T point shifts upward remarkably, while the conduction band at the K point barely moves. When the WS<sub>2</sub> thickness is reduced to monolayer, the indirect transition gap surpasses the direct bandgap, allowing it transit from indirect to direct semiconductor. The optical direct bandgap of monolayer WS<sub>2</sub> proposed by theoretical models varies slightly, ranging from 2.05 to 2.1 eV, while bulk WS<sub>2</sub> has an indirect bandgap of 1.3 eV.<sup>131,134</sup> An evolution of band structure from indirect to direct was presented in **Figure 2.15(b)** and (c), corresponding to bulk and monolayer WS<sub>2</sub>, respectively. It also exhibits the splitting of the valence band in bulk WS<sub>2</sub> that leads to two distinct direct electronic transitions at the K point, which have been experimentally observed and known as excitons A at 1.95 eV and B at 2.36 eV.<sup>135–137</sup> This feature is the consequence of interlayer coupling that is absent in monolayers.<sup>138</sup> **Figure 2.15(d)** shows the electron mobilities of exfoliated monolayer WS<sub>2</sub> ranging from <1 to 140 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, where the application of hexagonal boron nitride (h-BN) substrate has successfully enhanced the electron mobility at room-temperature.<sup>127,139,140</sup> **Figure 2.15(e)** unveils the correlation between carrier mobilities and the bandgaps of semiconducting TMDs along with representative semiconductors and other 2D materials including graphene and black phosphorous. At similar bandgap sizes, semiconducting TMDs are of lower carrier mobilities compared with conventional bulk semiconductors, such as bulk InP and bulk GaAs. Among monolayer TMDs, WS<sub>2</sub> exhibits carrier mobility similar to MoS<sub>2</sub> and MoSe<sub>2</sub>, whereas all three rank in the bottom of the contest.



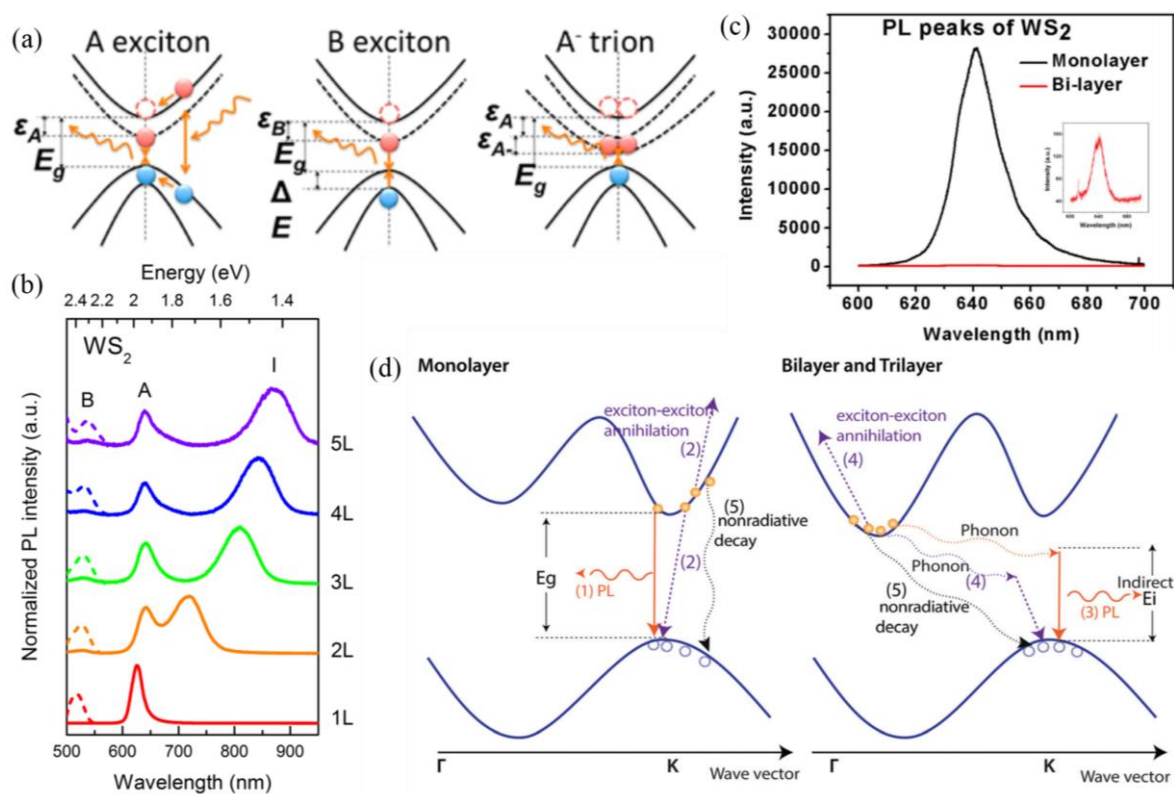
**Figure 2.15. Electronic properties of WS<sub>2</sub>.** (a) Brillouin zone for WS<sub>2</sub> monolayer. (b,c) Electronic band structure (left) and total density of states (right) for the WS<sub>2</sub> bulk and monolayer, respectively. (a-c) are reprinted with permission from ref. [131]. © 2013 American Chemical Society. (d) Carrier mobility values reported for WS<sub>2</sub> at room-/low-temperatures. (e) Demonstration of mobility vs. band gap in various 2D semiconductors (BP = black phosphorus; ML = monolayer). The colour scale (top right) represents the infrared-visible light range corresponding to the bandgap energy. (d) and (e) are reprinted with permission from ref. [122]. © 2015 The Royal Society of Chemistry.

### 2.3.2.2 Photoluminescence Emission Characteristics

The PL peak energy of direct bandgap semiconductors, usually called the optical band gap, is equal to the electronic band gap calculated from the electronic dispersion relation minus the binding energy of the quasiparticles (excitons or trions) originating from the Coulomb interactions between the electrons and holes.<sup>141</sup> **Figure 2.16(a)** elucidates, in the case of negatively doped monolayer TMDs, three possible quasiparticles: A exciton, B exciton, and A<sup>-</sup> trion (*i.e.*, a quasiparticle composed of a neutral exciton and a free electron). In the PL

spectrum of monolayer WS<sub>2</sub>, only one dominant peak located at ~1.98 eV is found at room temperature,<sup>131,142–147</sup> which corresponds to the direct A-excitonic transition at the K point in the Brillouin zone. The exciton binding energy in WS<sub>2</sub> was discovered to be  $0.71 \pm 0.01$  eV by two-photon PL excitation spectroscopy, which is around one third of its optical direct gap.<sup>148</sup> The B exciton component, which is found notably next to A exciton in monolayer MoS<sub>2</sub>, however, has negligible contribution to the PL of monolayer WS<sub>2</sub>, **Figure 2.16(b)**, possibly due to its greater spin splitting in valence band.<sup>149–151</sup> A<sup>-</sup> trion is formed at lower density states of the direct bandgap compared to A/B exciton, as an extra peak on the low energy (*i.e.*, large wavelength) side of the A exciton peak. The trion binding energy in WS<sub>2</sub> was found to be in the range of 20–45 meV, which is sensitive to laser excitation power, dielectric environment and doping level.<sup>148,152–154</sup>

As illustrated in **Figure 2.16(c)**, the direct bandgap nature of monolayer WS<sub>2</sub> triggers the emergence of strong PL emission, while the PL intensity for bilayer WS<sub>2</sub> was greatly compromised due to the band gap transitioning from direct to indirect, about ~150 times lower than that for monolayer, **Figure 2.16(d)**.<sup>155</sup> Methods of applying mechanical strain,<sup>156</sup> chemical dopants,<sup>151,157</sup> electric field<sup>158</sup> and low-temperature treatment<sup>159</sup> have been reported to engineer the bandgap of 2D WS<sub>2</sub>, and thus tune the electrical and optical properties. Furthermore, the PL quantum yield for monolayer WS<sub>2</sub> was measured to be ~6%, higher than the other 2D semiconducting TMDs because of its relatively low defect density.



**Figure 2.16. PL emission characteristics of WS<sub>2</sub>.** (a) Schematics of the exciton-related radiative transition at the K point in the Brillouin zone.  $E_g$ ,  $\Delta$ ,  $\epsilon_A$ ,  $\epsilon_B$ ,  $\epsilon_{A^-}$  denote the band gap, valence band splitting, binding energy of the A, B exciton and A<sup>-</sup> trion, respectively. Reprinted with permission from ref. [141]. © 2014 American Chemical Society. (b) Normalized PL spectra of mechanically exfoliated WS<sub>2</sub> flakes consisting of 1–5 layers. Reprinted with permission from ref. [146]. © 2012 American Chemical Society. (c) PL spectra of mono and bi-layer WS<sub>2</sub>. Inset: the magnified PL peak of bilayer WS<sub>2</sub>. Reprinted with permission from ref. [148]. © 2015 Macmillan Publishers Limited. (d) Schematic summary of possible relaxation pathways for monolayer and few-layer WS<sub>2</sub>: (1) direct exciton recombination; (2) direct exciton–exciton annihilation; (3) indirect exciton recombination; (4) indirect exciton–exciton annihilation; and (5) other nonradiative pathways. Reprinted with permission from ref. [155]. © 2015 The Royal Society of Chemistry.

### 2.3.2.3 Vibrational Properties

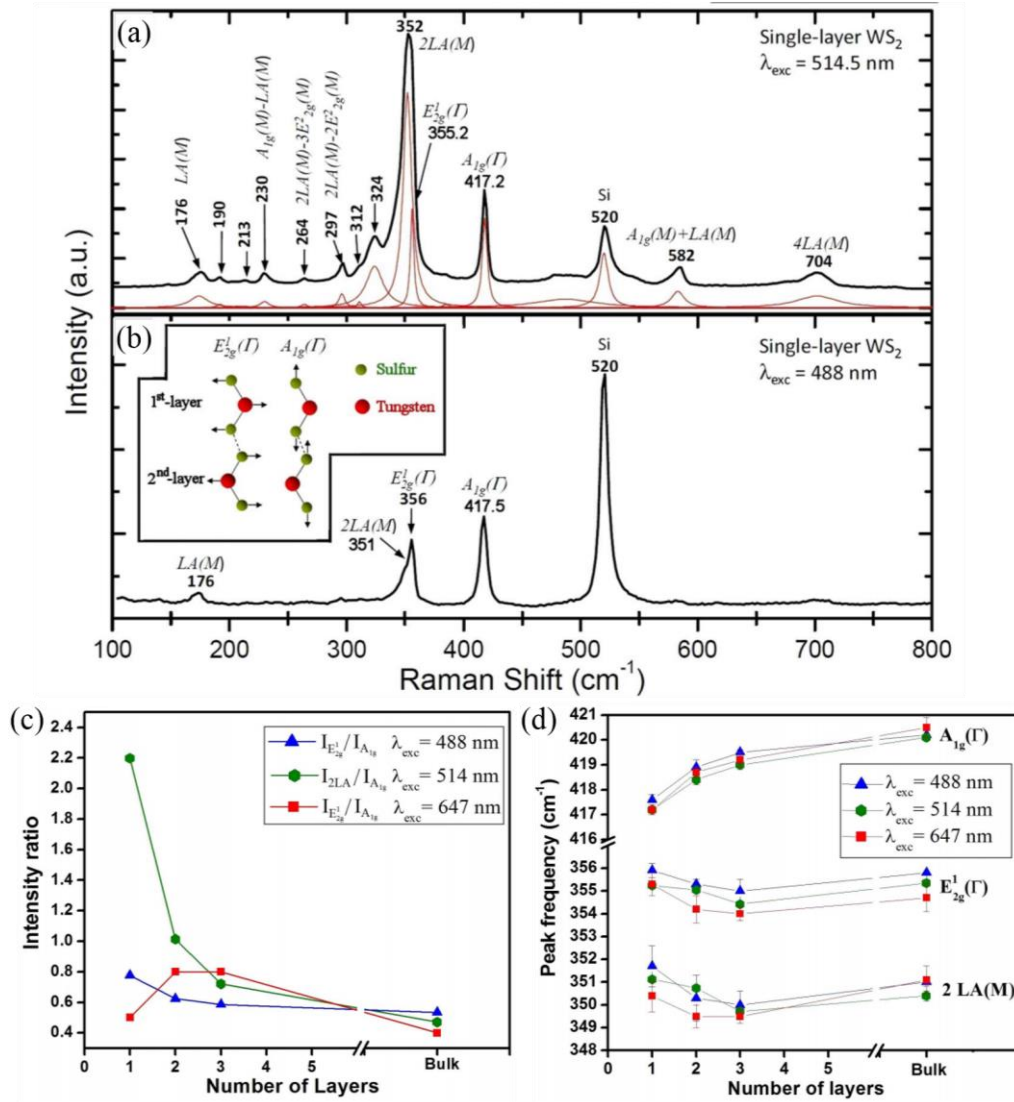
The vibrational properties of WS<sub>2</sub> are characterised *via* Raman spectroscopy, a powerful technique to reveal structural and electronic information including but not limited to layer number, layer stacking order, lattice strain and doping level. When a monochromatic light

source illuminates on a sample, a majority of the light is scattered elastically, in a process known as Rayleigh scattering, while a tiny amount remains. Raman spectroscopy can detect the energy variations from the excitation source caused by inelastic scattering from the vibrational phonons in the lattice. The intensity of this inelastically scattered light and its corresponding frequency shift, corresponding to Raman peak intensity and position, is subject to change with the lattice structure and the incident light source.

Semiconducting WS<sub>2</sub> has two prominent first-order vibration modes; E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub>. The E<sub>2g</sub><sup>1</sup> mode represents in-plane vibration where two S atoms and the W atom move in opposite directions within the atomic plane, while the A<sub>1g</sub> mode is related to the out-of-plane vibration where the W atom remains still and two S atoms move in opposite directions perpendicularly against the atomic plane.<sup>160</sup> **Figure 2.17(a)** and **(b)** present two typical Raman spectra of monolayer WS<sub>2</sub> acquired at different laser wavelengths; 514.5 and 488 nm. In addition to two dominant peaks: E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub>, two extra peaks, LA(M) and 2LA(M), are found in the Raman spectrum of monolayer WS<sub>2</sub> at an excitation wavelength of 488 nm. They are known as the first-order and the second-order longitudinal acoustic modes at the M point of the Brillouin Zone.<sup>161</sup> Many other second-order peaks have been revealed when shining the 2D WS<sub>2</sub> under resonant excitation with an incident laser of 514.5 nm wavelength. The strong 2LA(M) signal is most likely due to a double-resonant Raman process that occurs only in the specific electronic band structure of the monolayer.<sup>161</sup> Therefore, the relative intensity of 2LA(M) and A<sub>1g</sub> at 514 nm excitation wavelength provides a unique way to distinguish monolayer from multilayer WS<sub>2</sub>, **Figure 2.17(c)**.

In addition, the A<sub>1g</sub> mode is sensitive to interlayer interactions (e.g. layer number and substrate) as well as doping either from surface adsorbates or gate-induced electron injection. **Figure 2.17(d)** shows the evolution of Raman signatures in WS<sub>2</sub> as the layer number

changes. It is obvious to notice that the  $E_{2g}^1$  and  $2LA(M)$  peaks show negligible shifts, while  $A_{1g}$  peak blue-shifts when increasing the layer number. One can also unveil the lattice strain by examining the frequency change of the  $E_{2g}^1$  vibration mode, with a red/blue shift enacted under a tensile/compressive strain.



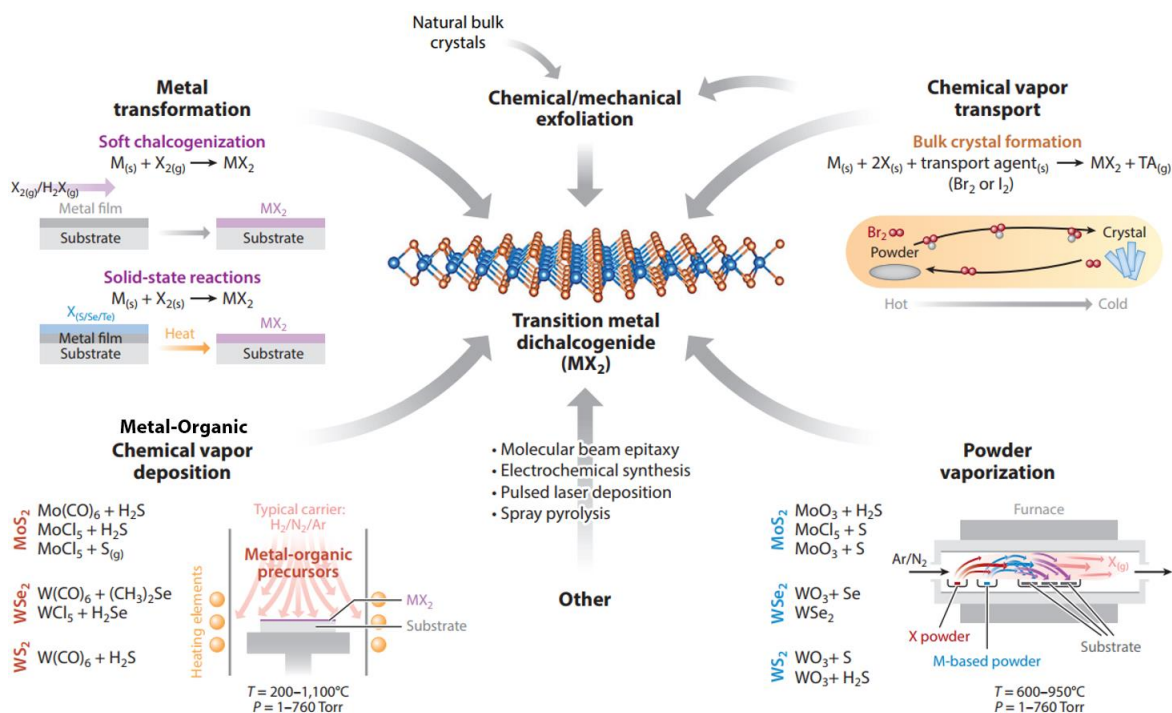
**Figure 2.17. Vibrational properties of WS<sub>2</sub>.** Raman spectra of monolayer WS<sub>2</sub> using (a) 514.5 and (b) 488 nm laser excitation, respectively, including Lorentzian peak fits for 514.5 nm data. The inset in (b) shows the atomic displacements for the in-plane phonon mode  $E_{2g}^1$  and the out-of-plane phonon mode  $A_{1g}$  for two adjacent layers, the dashed line represents the weak inter-layer van der Waals interaction. Thickness-dependent (c) Raman peak intensity ratios and (d) frequencies of WS<sub>2</sub> at 488 nm, 514 nm and 647 nm laser excitation wavelength. Reprinted with permission from ref. [161]. © 2013 Macmillan Publishers Limited.

### 2.3.2.4 Mechanical Properties

In addition to their extensively studied electrical and optical properties, elastic and mechanical properties of 2D TMDs and their heterostructures have also been observed. An elastic modulus is a number used to determine the mechanical property of an object or substance, and has recently played a vital role in the applications of flexible and stretchable electronics and photonics. 2D WS<sub>2</sub> possesses outstanding mechanical properties observed in recent experiments using an AFM probe. The CVD-grown monolayer WS<sub>2</sub> is found to have a high 2D elastic modulus of  $177 \pm 12 \text{ N m}^{-1}$ ,<sup>162</sup> very close to the value of exfoliated MoS<sub>2</sub> ( $180 \pm 60 \text{ N m}^{-1}$ ),<sup>163</sup> and almost half of that of graphene ( $\sim 340 \text{ N m}^{-1}$ ), which is the strongest 2D material.<sup>62,164</sup> In addition, the modulus of MoS<sub>2</sub>/WS<sub>2</sub> bilayer heterostructure is measured to be  $314 \pm 31 \text{ N m}^{-1}$ , slightly lower than the summed modulus of each layer ( $348 \text{ N m}^{-1}$ ), but comparable to the corresponding bilayer homostructures.<sup>162</sup> These advantages render 2D WS<sub>2</sub> a promising candidate for use in flexible devices.

### 2.3.3 Synthesis of WS<sub>2</sub>

To meet the demand for the fundamental study and the future application, many synthesis techniques have been developed, **Figure 2.18**. In many respects closely related to graphene synthesis, the methods for the growth of 2D TMDs can be divided into two groups: top-down and bottom-up methods.<sup>165</sup> The top-down methods are comprised of mechanical exfoliation and chemical exfoliation, and the bottom-up approaches include but not are limited to physical vapour deposition, thermal decomposition and CVD, which have shown promising advantages over large-area production. A review of synthesis methods for growing 2D WS<sub>2</sub> will be provided in this section, with a special focus on the CVD methods.



**Figure 2.18. Summary of primary growth techniques for the formation of monolayer TMDs.** These methods include but not limited to mechanical exfoliation, chemical exfoliation, metal transformation, powder vaporization and Metal-Organic CVD. Reprinted with permission from ref. [165]. © 2015 Annual Reviews.

### 2.3.3.1 Mechanical Exfoliation

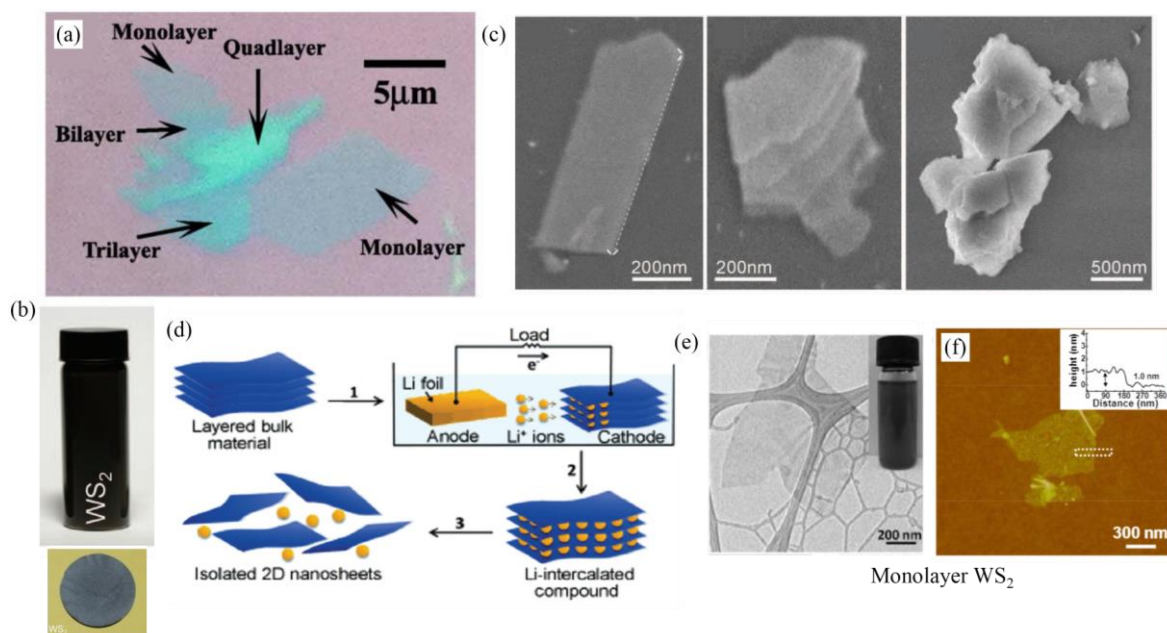
Utilising the same technique that was developed for graphene, atomically thin WS<sub>2</sub> flakes can be peeled off from its parent bulk crystals by mechanical exfoliation through the use of an adhesive tape, applied to substrates and identified by optical contrast, **Figure 2.19(a)**.<sup>166</sup> The bulk crystals are synthesised via chemical vapour transport, **Figure 2.18**, a process that usually takes days or weeks to complete under new equilibrium conditions. This method produces single-crystalline monolayer flakes with both a high purity level and high levels of cleanliness. Therefore, it enables the intrinsic property study of monolayer WS<sub>2</sub> without the interference of structural defects and chemical dopants, which are easily generated during

material synthesis and processing. However, mechanical exfoliation suffers from low-yield production of the desired materials, and thus is not scalable.<sup>118,167</sup>

### 2.3.3.2 Chemical Exfoliation

Following the successful dispersion of graphite,<sup>80</sup> ultrasonication in appropriate liquids, including organic solvents<sup>168</sup> and aqueous surfactant solutions,<sup>169</sup> was quickly adopted and has proven effective in producing TMDs nanosheets. Photo of 2D layered WS<sub>2</sub> exfoliated in NMP is shown in **Figure 2.19(b)**, along with a free-standing film from filtration of solution-based materials. For obtaining exfoliated nanosheets in large quantities, the liquid-phase preparations look very promising, but the most flakes it generates are only a few hundred nanometres in size with random thickness, **Figure 2.19(c)**, which hinders the viability for device fabrication.

Alternatively, the intercalation by ionic species<sup>149,170–173</sup> allows the bulk TMDs crystals to be exfoliated in solution. The basic principle for the intercalation-based exfoliation is to increase the layer spacing by inserting foreign species, and thus weaken the interlayer adhesion and reduce the energy barrier to exfoliation.<sup>174</sup> In particular, the intercalation of WS<sub>2</sub> by lithium was shown to produce quantities of submicrometre-sized monolayers,<sup>175</sup> but the resulting product differs structurally and electronically from its bulk crystal (e.g. phase change from the semiconducting 2H to the metallic 1T phase).<sup>149,176,177</sup> To improve on these methods, Zeng *et al.*<sup>173</sup> developed a faster and more controllable approach that used an electrochemical cell with a lithium foil anode and a bulk WS<sub>2</sub> crystal as cathode, as depicted in **Figure 2.19(d)**. The subsequent ultrasonication and exfoliation of the lithium-intercalated compounds in water or ethanol resulted in high-yield WS<sub>2</sub> monolayers in large amounts, **Figure 2.19(e)**.



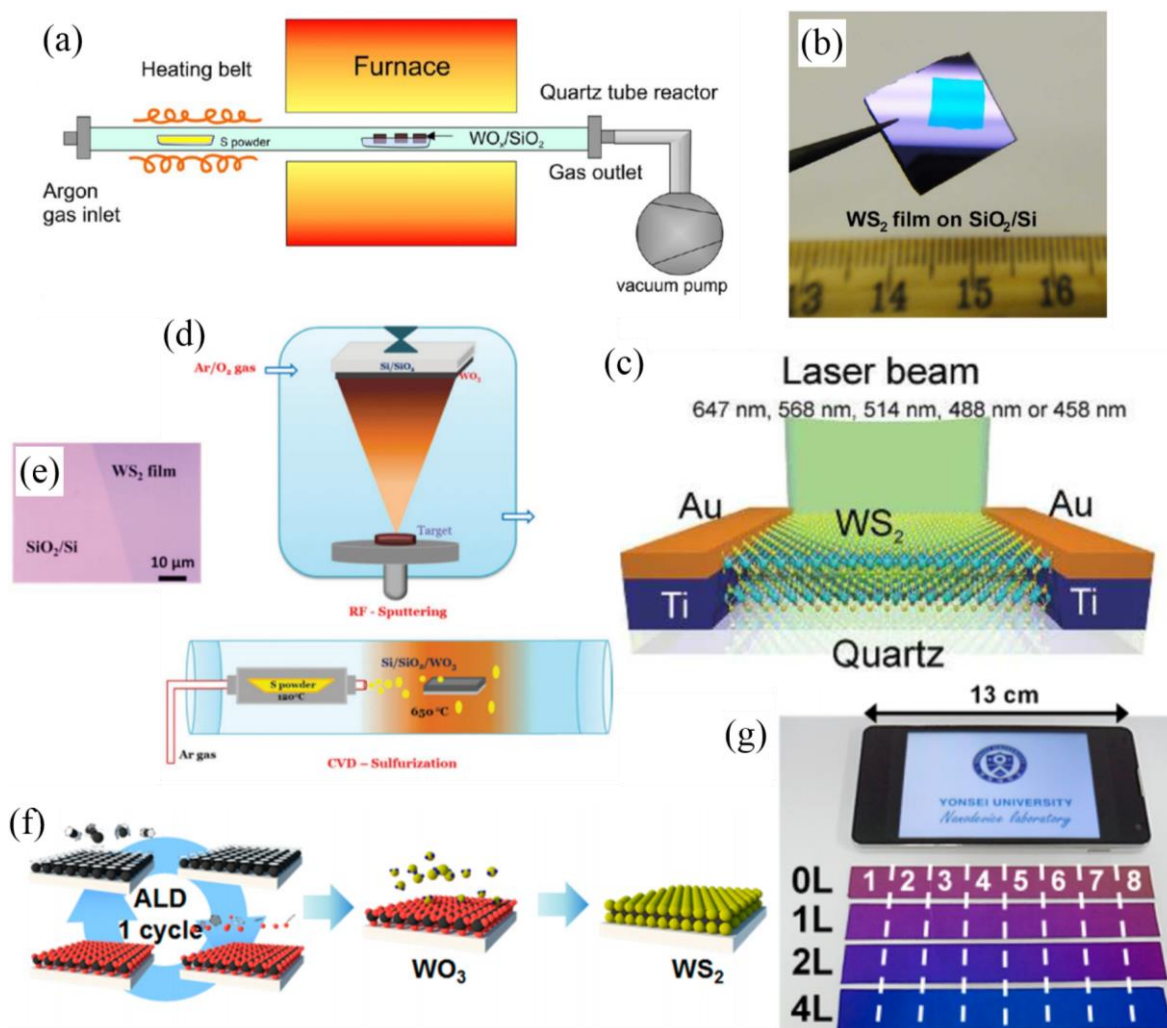
**Figure 2.19. Mechanical and chemical exfoliation of WS<sub>2</sub>.** (a) Optical image of mechanically exfoliated WS<sub>2</sub> flake on Si substrate with 300 nm SiO<sub>2</sub> (SiO<sub>2</sub>/Si). The layer number is identified by optical contrast. Reprinted with permission from ref. [166]. © 2013 Macmillan Publishers Limited. (b) Photographs of exfoliated WS<sub>2</sub> in NMP and the free-standing film developed from the suspensions above. (c) SEM images of a very thin flake, a multilayer and a cluster of aggregated multilayers, obtained from the solution in (b). (b) and (c) are reprinted with permission from ref. [168]. © 2011 American Association for the Advancement of Science. (d) Schematic illustration for the electrochemical Li<sup>+</sup> intercalation of 2D WS<sub>2</sub>. (e) TEM image and (f) AFM measurement of a typical WS<sub>2</sub> nanosheet, Inset in (e): Photograph of the WS<sub>2</sub> solution. Inset in (f): Height profile showing a thickness of ~1.0 nm. (d-f) are reprinted with permission from ref. [173]. © 2011 Wiley.

### 2.3.3.3 Chemical Vapour Deposition

Unlike the top-down methods, the CVD approach, one of the bottom-up methods, has been developed to meet the industrial demand of large area, high quality WS<sub>2</sub> with controllable thickness. It can be categorized into three routes: metal transformation (soft sulphurization), powder vaporisation and Metal-Organic CVD. This section will focus on introducing the CVD techniques for the large-area (~cm<sup>2</sup>) growth of monolayer WS<sub>2</sub>.

### 2.3.3.3.1 Sulphurization of Metal or Metal Oxide

This method usually involves a pre-coating of the W-based precursors on the substrate, followed by a transformation into WS<sub>2</sub> via exposure to a sulphur vapour. Prior work has reported, for the first time, the synthesis of large-area WS<sub>2</sub> films using a two-step process, **Figure 2.20(a)**.<sup>178</sup> WO<sub>3</sub> thin films with different thicknesses were deposited onto SiO<sub>2</sub>/Si substrates by thermal evaporation, and then sulphurized under vacuum at high temperatures to form WS<sub>2</sub> sheets with thicknesses ranging from one to several layers, **Figure 2.20(b)**. Following this, a wavelength sensitive photo detector, **Figure 2.20(c)**, was fabricated based on the few-layer WS<sub>2</sub> films grown by the same method using a quartz substrate.<sup>179</sup> The photocurrent measurements revealed strong dependence of the electrical response and the excitation laser (*i.e.*, wavelength and illumination power), which makes it a strong candidate for ultrathin optoelectronic devices. Hussain *et al.*<sup>180</sup> presented a similar preparation technique *via* sulfurization of a RF-sputtered WO<sub>3</sub> film to produce continuous and wafer-scale uniform WS<sub>2</sub> layers, as depicted in **Figure 2.20(d)**. The thickness of the prepared WS<sub>2</sub> film was controlled by adjusting the sputtering time, **Figure 2.20(e)**. The WS<sub>2</sub> FET exhibited better performance (*i.e.*, higher field-effect mobility and higher current on/off ratio) when increasing the sputter time. The photosensitivity was also investigated in the report based on the few-layer samples, showing linear dependence on bias voltage. Alternatively, a novel synthesis method was reported to grow WS<sub>2</sub> nanosheets by the sulphurization of a WO<sub>3</sub> film deposited using atomic layer deposition (ALD), **Figure 2.20(f)**.<sup>181</sup> The advantages of the ALD process are high thickness controllability, reproducibility and wafer-level uniformity, **Figure 2.20(g)**. The WS<sub>2</sub>-based top-gate FET has an electron mobility of  $\sim 3.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a low subthreshold swing of 0.6 V/dec. These methods seem to be appropriate for growing wafer size continuous WS<sub>2</sub> films. However, the grain size of the film is mostly limited to nanoscale, which will result in poor device performance.



**Figure 2.20. Synthesis of  $\text{WS}_2$  via sulphurization of metal or metal oxide.** (a) Schematic representation of the experimental setup used for the synthesis of  $\text{WS}_2$  films. (b) Photograph of a  $\text{WS}_2$  film on a  $\text{SiO}_2/\text{Si}$  substrate after transfer, exhibiting the high contrast and colour change. (a) and (b) are reprinted with permission from ref. [178]. © 2013 American Chemical Society. (c) Schematic representation of the photo detector device consisting of a few-layered  $\text{WS}_2$  film on quartz, the Au/Ti contacts and the different laser wavelengths were applied perpendicularly to the film. Reprinted with permission from ref. [179]. © 2013 Wiley. (d) Schematic illustration of CVD synthesis setup *via* RF sputtering. (e) Optical image of the  $\text{WS}_2$  film prepared with 80 s sputtering time. (d) and (e) are reprinted with permission from ref. [180]. © 2011 The Royal Society of Chemistry. (f) Synthesis procedure for the ALD-based  $\text{WS}_2$  nanosheets. (g) Large-area mono-, bi- and tetralayer  $\text{WS}_2$  films fabricated by ALD-based method. (f) and (g) are reprinted with permission from ref. [181]. © 2013 American Chemical Society.

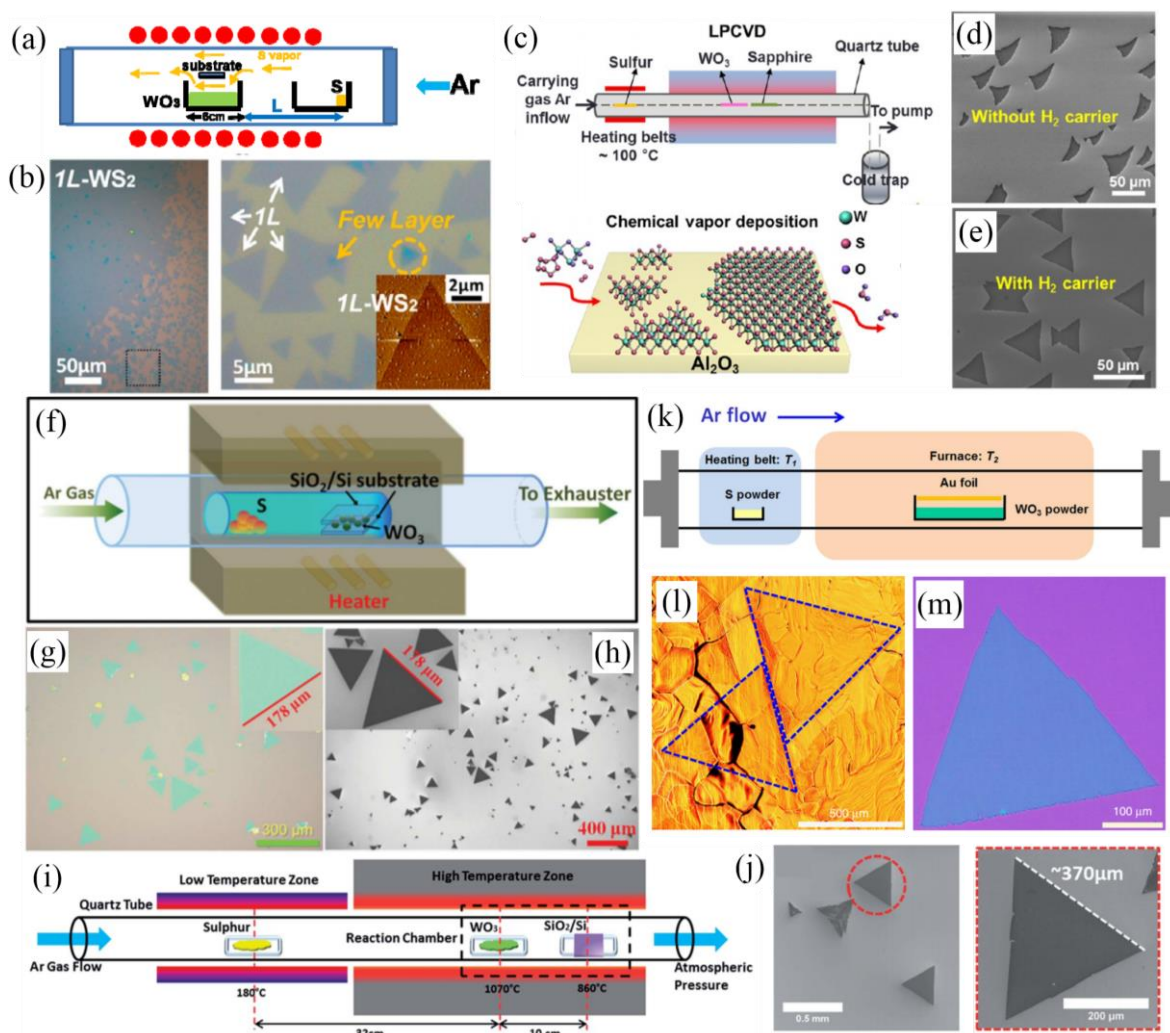
### 2.3.3.3.2 Powder Vaporisation

The powder vaporisation occurs through the chemical vapour reaction, where solid powder precursors (*i.e.*,  $\text{WO}_3$  and S) are first vaporised and then transported into the reaction zone (substrate) to form  $\text{WS}_2$ . These processes typically utilize a horizontal tube furnace, where the S powder is placed upstream of the reaction zone and the  $\text{WO}_3$  powder is placed in the hot zone of the furnace. The sample substrates are normally placed downstream of the  $\text{WO}_3$  precursor or face down directly on top of it.

The first work for the growth of monolayer  $\text{WS}_2$  *via* powder vaporisation was a scalable APCVD process with the seeding of perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS), as shown in **Figure 2.21(a)**.<sup>182</sup> The domain size of the as-grown  $\text{WS}_2$  is  $\sim 10\ \mu\text{m}$ , **Figure 2.21(b)**, and the  $\text{WS}_2$  FET measured at room temperature showed an on/off current ratio of  $\sim 10^5$  and a low carrier mobility of  $0.01\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ . Alternatively, Zhang *et al.*<sup>147</sup> presented a synthesis method for the growth of  $\text{WS}_2$  monolayer flakes on sapphire ( $\text{Al}_2\text{O}_3$ ) *via* LPCVD, **Figure 2.21(c)**. The shape of the product was modified by adding  $\text{H}_2$  to the system, as shown in **Figure 2.21(d)** and (e). The domain size of the single crystal domains was measured to be as large as  $\sim 50\ \mu\text{m}$ . The FET devices based on these monolayers exhibited an improved electron mobility of  $0.46\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$  and a relatively low on/off ratio of  $\sim 10^2$ .

To obtain single crystals with larger domain size, Cong *et al.*<sup>183</sup> introduced a one-step APCVD process with two  $\text{SiO}_2/\text{Si}$  substrates in the reaction zone, **Figure 2.21(f)**. Before heated, one substrate was spread with  $\text{WO}_3$  powders, and the other blank piece was placed face down above it. This approach resulted in monolayer  $\text{WS}_2$  single crystals with sizes up to  $178\ \mu\text{m}$ . Based on the abovementioned methods, Rong *et al.*<sup>142</sup> presented another APCVD method to produce single-crystal monolayer  $\text{WS}_2$ , **Figure 2.21(i)**, where a double-furnace

system was used to separately control the S and WO<sub>3</sub> vapour introduction. Large triangular monolayer domains (~370 μm) were obtained, as shown in **Figure 2.21(j)**. In addition, considering the key role of metallic substrates in graphene CVD synthesis, Gao *et al.*<sup>144</sup> demonstrated the first WS<sub>2</sub> CVD synthesis on Au, perhaps the only metal that do not react with S, as illustrated in **Figure 2.21(k)**. The low solubility of W in Au allows self-limiting growth, making it possible to grow uniform high-quality monolayer WS<sub>2</sub> single crystals of millimetre size without any multilayer islands, **Figure 2.21(l)** and (m). This method also holds promise for the large-scale roll-to-roll production of transparent and flexible devices.

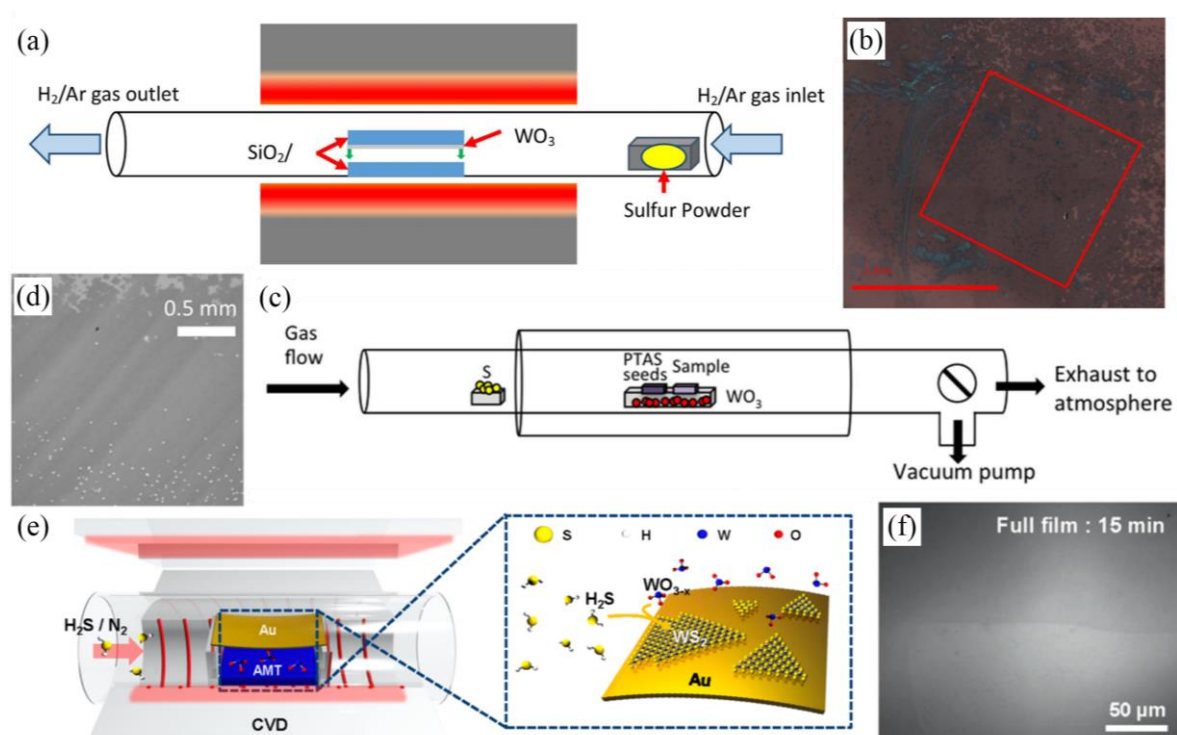


**Figure 2.21. Synthesis of single-crystal  $\text{WS}_2$  domains via powder vaporisation.** (a) Schematic diagram of experimental setup for the  $\text{WS}_2$  synthesis. (b) Optical images of the  $\text{WS}_2$  monolayer. (a) and (b) are reprinted with permission from ref. [182]. © 2013 American Chemical Society. (c) Experimental setup of the LPCVD system and schematic view of the related chemical reaction. (d,e) SEM images of the  $\text{WS}_2$  flakes (d) without and (e) with  $\text{H}_2$ . (c-e) are reprinted with permission from ref. [147]. © 2013 American Chemical Society. (f) Schematics of the CVD system with two stacked substrates. (g) Optical image and (h) SEM image of  $\text{WS}_2$  on  $\text{SiO}_2/\text{Si}$  substrate. Insets show the same triangular monolayer with a domain size of  $178\ \mu\text{m}$ . (f-h) are reprinted with permission from ref. [183]. © 2014 Wiley. (i) Schematic presentation of the corresponding CVD setup. (j) SEM images of the as-deposited area, showing large  $\text{WS}_2$  single crystal domains  $\sim 370\ \mu\text{m}$ . (i) and (j) are reprinted with permission from ref. [142]. © 2014 The Royal Society of Chemistry. (k) Schematic for the growth of high-quality uniform monolayer  $\text{WS}_2$  on Au. (l) Optical image of the  $\text{WS}_2$  domains on Au foil. (m) Optical image of a  $400\ \mu\text{m}$  transferred  $\text{WS}_2$  domain on  $\text{SiO}_2/\text{Si}$  substrate. (k-m) are reprinted with permission from ref. [144]. © 2015 Macmillan Publishers Limited.

From an industrial perspective, batch fabrication of device arrays on continuous films instead of separately distributed WS<sub>2</sub> domains could lead to a greater yield. Only until recently, Kang *et al.*<sup>184</sup> reported a LPCVD process using two stacked substrates facing each other, one for the tungsten source and the other for growth, **Figure 2.22(a)** and (b), similar to the previous work published by Cong *et al.*,<sup>183</sup> but they successfully achieved polycrystalline WS<sub>2</sub> monolayers up to mm<sup>2</sup>, and also studied the effect of H<sub>2</sub> concentration on the growth results, including nucleation density, crystal size and growth formation. However, this method was carried out under low pressure with a growth duration of ~30 min, which hindered the viability for mass-production.

To alleviate the difficulty of CVD setup and shorten the growth time, alternative strategies have been attempted. In particular, as derived from the PTAS-based approach for growing WS<sub>2</sub> domains,<sup>182</sup> McCreary *et al.*<sup>185</sup> further demonstrated that large area production of monolayer WS<sub>2</sub> films was likewise feasible, as shown in **Figure 2.22(c)** and (d). The APCVD reaction was quite efficient, which allows the formation of a fully-merged film (~mm<sup>2</sup>) in just 10 min. However, the seeding promotor may produce impurities on the surface, and it is rather difficult to achieve full coverage without multilayer regions. As illustrated by **Figure 2.22(e)** and (f), Yun *et al.*<sup>186</sup> reported another APCVD method, by inheriting the previous reported technique, to use an Au substrate instead of an insulation substrate. Centimetre-sized WS<sub>2</sub> films were fabricated with hydrogen sulphide (H<sub>2</sub>S) gas as a S source and ammonium metatungstate (AMT, (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·x(H<sub>2</sub>O)) as W precursor. The FET fabrication revealed an electron mobility of 20 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with a high on/off ratio of ~10<sup>8</sup> at room temperature, outperforming the previously reported values based on CVD-grown WS<sub>2</sub> films. However, special treatment is required for preparing Au substrates and the compulsory transfer of the product may slow and hinder device fabrication.

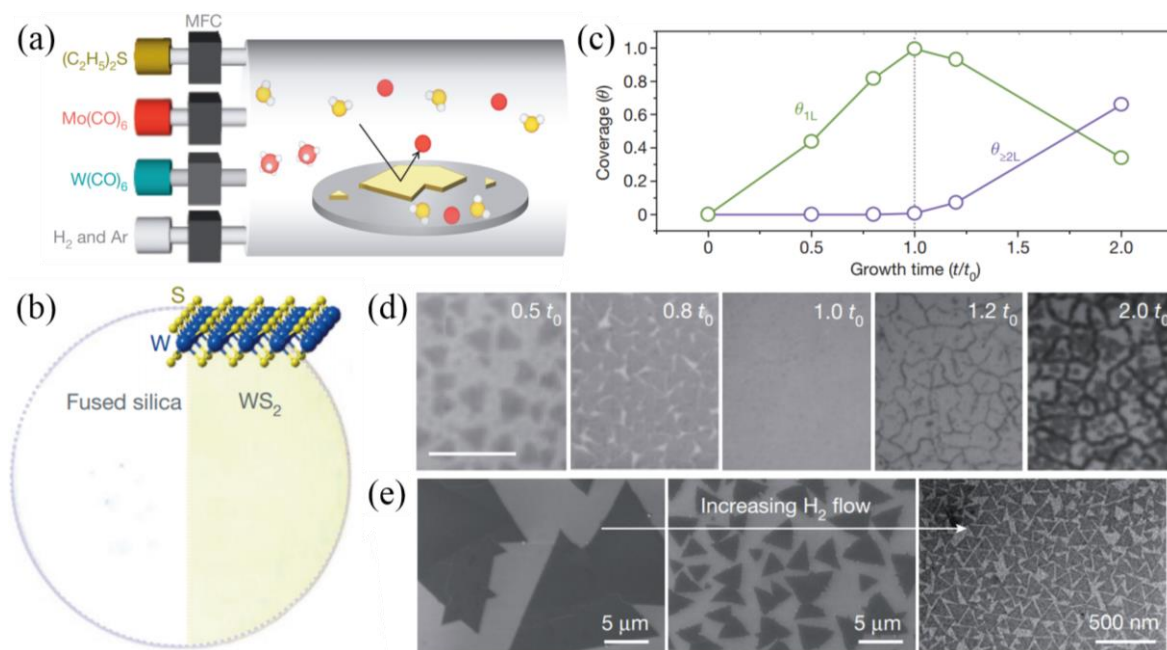
In general, CVD techniques *via* powder vaporisation are very successful in fabricating monolayer  $\text{WS}_2$  continuous films over large areas. However, little control over vaporisation rates of the powder precursors often leads to a gradient of product quality. For example, regions near the W-based powder are typically rough, continuous film with excess multilayer islands, whereas, a gradual change occurs further downstream to uniform continuous films which ultimately ends in semi-continuous films.



**Figure 2.22. Synthesis of  $\text{WS}_2$  continuous films *via* powder vaporisation.** (a) Schematic diagram of experimental setup for  $\text{WS}_2$  continuous film. (b) Optical image of the mm scale  $\text{WS}_2$  monolayer. (a) and (b) are reprinted with permission from ref. [184]. © 2015 Macmillan Publishers Limited. (c) Schematic of the PTAS-based approach used for  $\text{WS}_2$  monolayer synthesis. (d) The optical image displays large areas ( $\sim 1 \text{ mm} \times 1 \text{ mm}$ ) of continuous monolayer  $\text{WS}_2$  (dark grey). (c) and (d) are reprinted with permission from ref. [185]. © 2016 Macmillan Publishers Limited. (e) Schematic diagram of the chemical vapour deposition setup and illustration of the growth behaviour of  $\text{WS}_2$  on Au foil. (f) SEM image of a fully-merged film with a growth time of 15 min. (e) and (f) are reprinted with permission from ref. [186]. © 2015 American Chemical Society.

### 2.3.3.3 Metal-Organic Chemical Vapour Deposition

The utilization of Metal-Organic CVD (MOCVD) with controlled introduction of chemical or molecular precursors into the hot zone of a furnace) shows significant promise for a truly scalable synthesis technique for TMDs. As illustrated in **Figure 2.23(a)**, the most recent progress was accomplished by Kang *et al.*,<sup>187</sup> who demonstrated a versatile MOCVD growth of 4-inch wafer scale, high-quality monolayer WS<sub>2</sub> films on silicon oxide with gaseous precursors; W(CO)<sub>6</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S. The WS<sub>2</sub> continuous monolayers, **Figure 2.23(b)**, are spatially uniform over the entire 4 inch growth substrates with intrinsic optical properties. This method enables the layer by layer growth mode, which is crucial for uniform layer control over the large scale, as shown in **Figure 2.23(c)**. **Figure 2.23(d)** shows the optical images at corresponding growth time, revealing the morphology change: the initial nucleation of isolated domains; subsequent formation of fully-merged monolayer film; and the emergence of bilayer growth starting at grain boundaries. The presence of H<sub>2</sub> facilitates the removal of carbonaceous species generated during the MOCVD growth, leading to a higher nucleation density at a higher concentration, **Figure 2.23(e)**. The batch fabrication of the WS<sub>2</sub> FETs was then carried out and the devices showed uniquely powerful electrical properties, with their electron mobilities as high as 18 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and a high on/off ratio of 10<sup>6</sup> at room temperature.



**Figure 2.23. Synthesis of  $WS_2$  continuous films via MOCVD.** (a) Diagram of the MOCVD growth setup. (b) Photograph of monolayer  $WS_2$  films grown on 4-inch fused silica substrates. (c) Coverage ratio for monolayer (green) and multi-layer (purple) regions as a function of growth time. (d) Optical images of MOCVD-grown product at the indicated growth times, where  $t_0$  was the optimal growth time for full monolayer coverage. Scale bar: 10  $\mu m$ . (e) Grain size variation of monolayer product depending on the hydrogen flow rate. Reprinted with permission from ref. [187]. © 2015 Macmillan Publishers Limited.

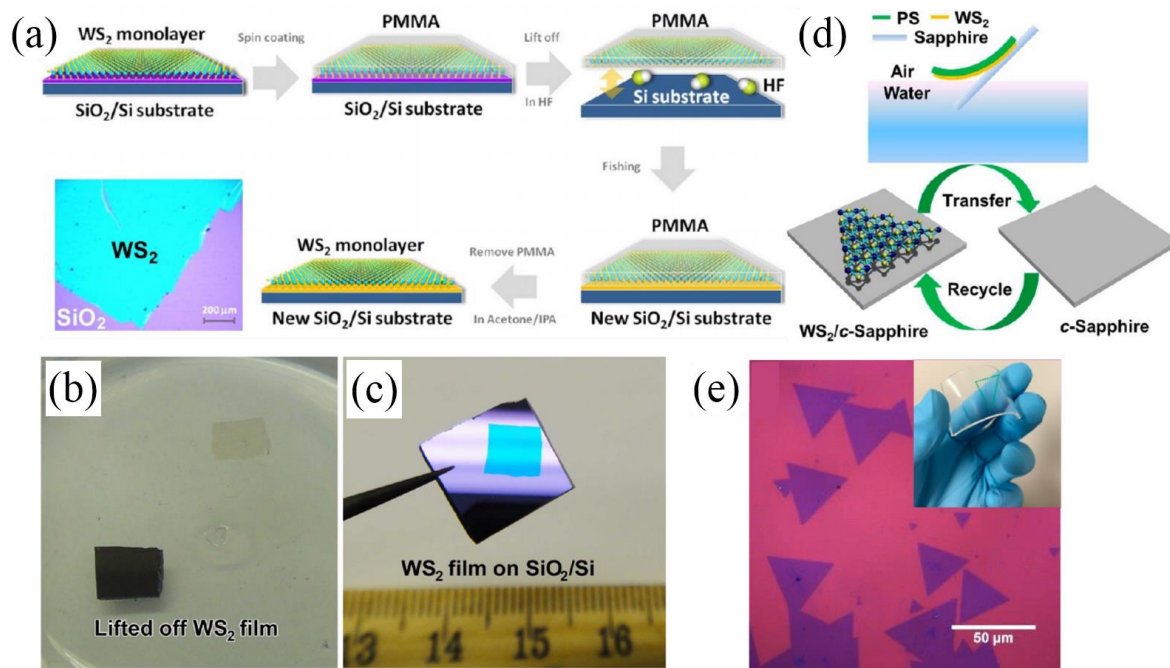
### 2.3.4 Transfer of $WS_2$

As with graphene, the TMD samples fabricated either on insulating or metallic substrates are expected to be transferred for further characterisation and device fabrication. The transfer approaches developed to date only differ depending on the underneath substrate, which means that a transfer method designed for one single TMD is applicable to all TMDs grown on the same substrate.

### 2.3.4.1 Insulating Substrates

Insulating substrates have been used more often for the growth of WS<sub>2</sub>. As illustrated in **Figure 2.24(a)**, PMMA was chosen to act as a temporary scaffold. The PMMA/WS<sub>2</sub> was then lifted off by floating on hydrofluoric acid (HF), **Figure 2.24(b)**. After cleaned in DI water, the PMMA/WS<sub>2</sub> stack was scooped out and transferred onto a new substrate, followed by PMMA removal in acetone. **Figure 2.24(c)** shows the appearance of a transferred sample, showing high uniformity. The HF solution was later proved effective for etching other insulating substrates, such as mica.<sup>188</sup> Alternative etchants for insulating growth substrates have also been introduced, for example, NaOH or NaOH/NaF for sapphire<sup>134,147</sup> and KOH for SiO<sub>2</sub>/Si.<sup>131</sup>

The involvement of the etching process during transfer introduces damage and contaminants to the WS<sub>2</sub> sample, which will inevitably degrade its optoelectronic properties. Based on the transfer approach demonstrated by Schneider *et al.*<sup>189</sup> in 2010, which occurs through the intercalation of a layer of water between a hydrophilic substrate and a hydrophobic nanostructure (e.g. graphene and carbon nanotubes) locked within a hydrophobic polymer thin films, a surface energy assisted transfer method was reported.<sup>190</sup> They successfully delaminated the layered materials (hydrophobic) from a sapphire substrate (hydrophilic) by water penetration. The non-destructive transfer process enables multiple reuses of the sapphire substrates and benefits from using polystyrene (PS), instead of PMMA, as the carrier polymer. A similar transfer technique was then demonstrated by Xu *et al.*,<sup>191</sup> where they detached the PS/WS<sub>2</sub> films from sapphire substrates via capillary force in water. Recent studies also reported using PDMS and cold water to lift off the monolayer films from SiO<sub>2</sub>/Si substrates.<sup>182</sup> However, this method requires the presence of a water-soluble layer beneath the as-fabricated sample, which is not typical in the growth techniques for TMDs.

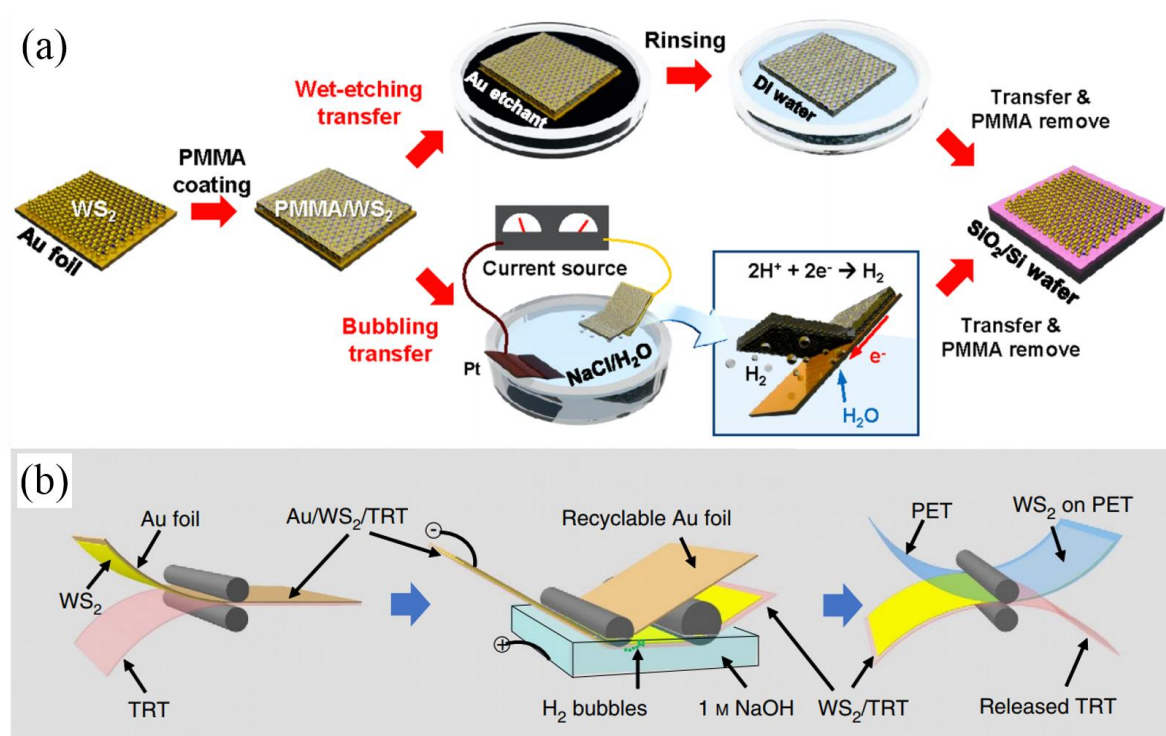


**Figure 2.24. Transfer of monolayer WS<sub>2</sub> grown on insulating substrates.** (a) Schematic representation of the PMMA-assisted transfer method onto different substrates. (b) Photograph of the WS<sub>2</sub> film floating on HF. (c) Photograph of a WS<sub>2</sub> film on a SiO<sub>2</sub>/Si substrate, exhibiting the high contrast and colour change (films appear in a cyan colour upon contrast with the SiO<sub>2</sub> substrate). (a-c) are reprinted with permission from ref. [178]. © 2013 American Chemical Society. (d) Schematic image of the capillary force assisted delamination process. (e) Optical image of WS<sub>2</sub> flakes transferred on SiO<sub>2</sub>/Si. Inset: A photograph of WS<sub>2</sub> monolayers transferred onto PDMS. The sample is marked with a green triangle. (d) and (e) are reprinted with permission from ref. [191]. © 2015 American Chemical Society.

### 2.3.4.1 Metallic Substrates

For further measurement of the WS<sub>2</sub> monolayers grown on Au substrates, researchers had to transfer the samples to other substrates. The wet-etching transfer, as illustrated in **Figure 2.25(a)**, involving the etching process in Au etchant, was tried and demonstrated as suitable for this purpose.<sup>186</sup> However, this method does not allow for the recycling of Au foil, leading to an extremely high cost for large scale synthesis. In response to that, an electrochemical H<sub>2</sub> bubbling transfer method was developed based on the previous techniques for graphene

transfer. The weak interaction between the WS<sub>2</sub> and Au enables the quick and intact delamination of the monolayers without sacrificing any Au. Compared with the wet-etching method, this method has advantages, such as its sustainable use of Au substrate and better device performance.<sup>186</sup> In particular, Gao *et al.*<sup>144</sup> demonstrated an integrated system, **Figure 2.25(b)**, combining APCVD growth, electrochemical bubbling transfer and roll-to-roll concept, to produce large-area monolayer WS<sub>2</sub> films on flexible substrates, which makes the future large scale production even more likely.



**Figure 2.25. Transfer of monolayer WS<sub>2</sub> grown on Au substrates.** (a) Schematic diagrams of wet-etching and bubble transfer. Reprinted with permission from ref. [186]. © 2015 American Chemical Society. (b) Schematic of the roll-to-roll/bubbling process. Reprinted with permission from ref. [144]. © 2015 Macmillan Publishers Limited.

### 2.3.5 Conclusion

Graphene's peculiar electronic properties are not suitable for modern electronics due to the lack of bandgap. Herein, it is reasonable to say that ultrathin 2D nanosheets of layered TMDs are fundamentally and technologically intriguing because each naturally provides a tuneable direct bandgap. However, the salient differences between conventional semiconductors and monolayer TMDs are just starting to be understood. The future application of 2D WS<sub>2</sub> would not be possible without a cost-effective and reliable synthesis method to produce large-area, high quality monolayer continuous films. In addition, the synthesis of WS<sub>2</sub> monolayers is slightly more difficult than MoS<sub>2</sub> due to the higher melting points of the W-based precursors, such as WO<sub>3</sub>, compared with Mo-based precursor counterparts and the corresponding higher growth temperatures needed for effective synthesis. A selection of synthesis approaches have been demonstrated to fulfil different demands. However, each has its drawbacks, such as small domain size (~400 μm) and limited control over uniform thickness. To date, the optimized growth conditions still require high temperature and a subsequent transfer process, which are not suitable for large scale production. The current approaches for the transfer of CVD WS<sub>2</sub> are found to damage and contaminate the sample, which leads to poor device performance. More work on the improvement of WS<sub>2</sub> synthesis and transfer is required to bring about real applications.

## 2.4 Two-Dimensional (2D) Heterostructures

The isolation of various ultrathin 2D materials, and the possibility to vertically or laterally stack them, has created a new page in materials science: 2D heterostructures. The van der Waals heterostructures based on TMDs and other 2D materials, such as graphene and hexagonal boron nitride (h-BN), where graphene is an ideal candidate for electrodes and h-

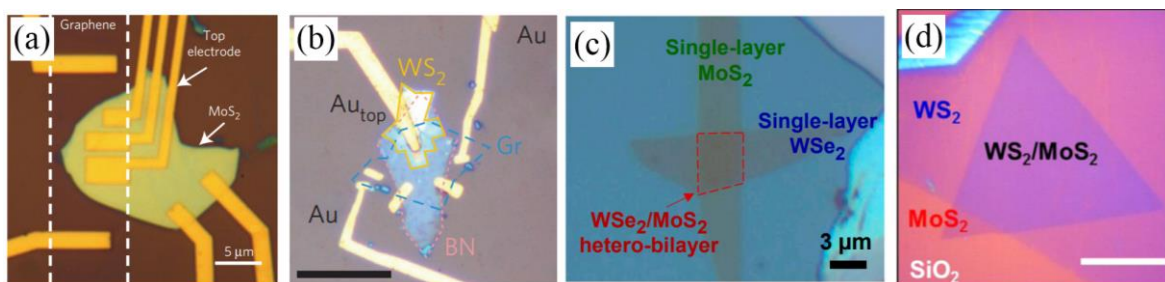
BN is a promising dielectric material, have already been proven as the fundamental platform for a wide range of future electronic and optoelectronic applications in the area of ultrathin, flexible, and transparent devices, such as transistors, phototransistors, solar cells, LEDs and photodetectors. This section will present a review of the recent developments of 2D van der Waals heterostructures with a highlight on fabrication and application based on 2D WS<sub>2</sub>.

### 2.4.1 Fabrication of 2D heterostructures

The synthesis of TMD heterostructures was achieved as early as 1985,<sup>192</sup> but the field is in many ways still in its infancy.<sup>193</sup> 2D heterostructures can be formed by either top-down transfer or bottom-up direct growth. The top-down method is realised *via* layer by layer stacking or transferring 2D layered materials, fabricated by mechanical exfoliation or CVD growth, on top of each other, whereas the bottom-up approach is completed *via* direct CVD growth.

#### 2.4.1.1 Layer by layer Transfer

The development of transfer methods for graphene (see section 2.2.4) and TMDs/WS<sub>2</sub> (see section 2.3.4) is essential for the layer by layer van der Waals reassembly. Different types of 2D stacks based on graphene or WS<sub>2</sub> have been fabricated, including graphene/MoS<sub>2</sub>,<sup>194–196</sup> graphene/WS<sub>2</sub>,<sup>197,198</sup> WSe<sub>2</sub>/MoS<sub>2</sub>,<sup>199,200</sup> and WS<sub>2</sub>/MoS<sub>2</sub>,<sup>162,201–203</sup> **Figure 2.26(a-d)**. The dry transfer method, such as the PDMS stamping technique, is mostly used by research groups,<sup>162,195–202</sup> allowing one 2D material to be transferred onto another 2D material, which was either mechanically exfoliated or transferred on an insulating substrate, such as SiO<sub>2</sub>/Si, for device fabrication. Manually stacking can yield impressively complex heterostructures. However, this method suffers from poor scalability, little control over the stacking orientation, and contaminations at the interface between layers.<sup>204,205</sup>



**Figure 2.26. Layer by layer transfer of 2D heterostructures.** (a) Optical image of graphene/MoS<sub>2</sub>. Reprinted with permission from ref. [196]. © 2013 Macmillan Publishers Limited. (b) Optical image of graphene/WS<sub>2</sub>. Reprinted with permission from ref. [198]. © 2012 Nature Publishing Group. (c) Optical image of WSe<sub>2</sub>/MoS<sub>2</sub>. Reprinted with permission from ref. [199]. © 2013 National Academy of Sciences. (d) Optical image of WS<sub>2</sub>/MoS<sub>2</sub> prepared by manually stacking. Reprinted with permission from ref. [201]. © 2014 American Chemical Society.

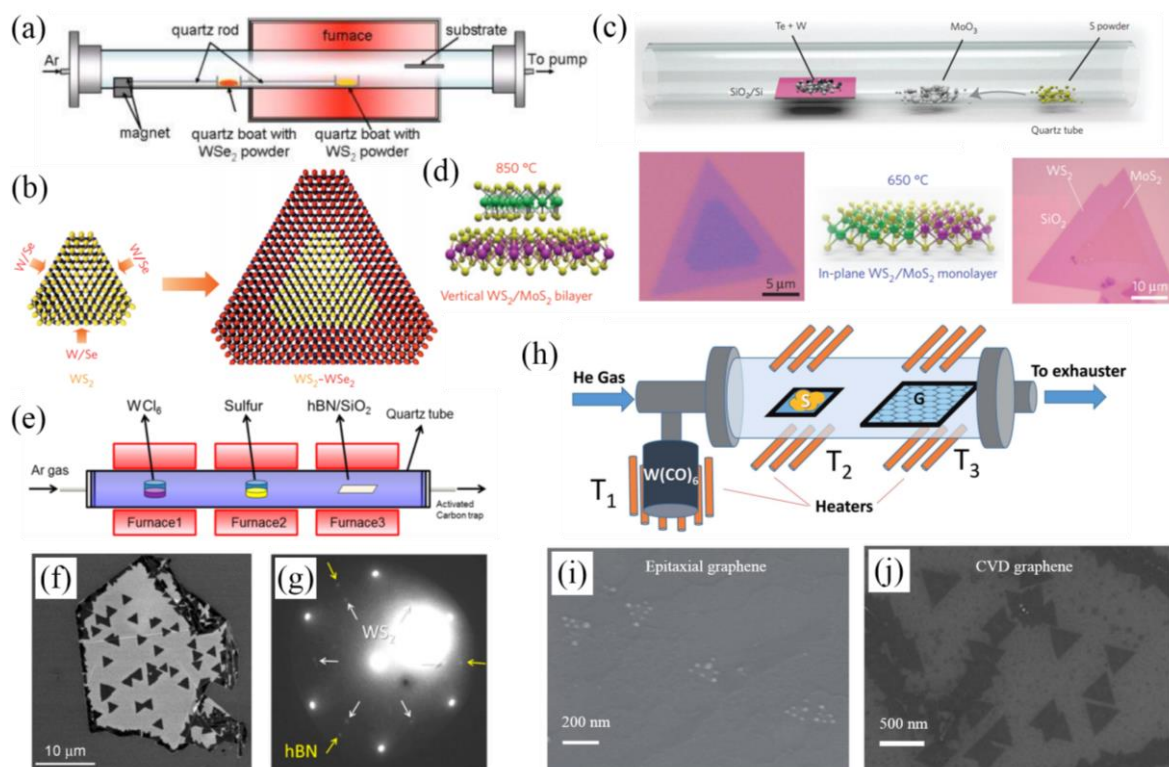
#### 2.4.1.2 Direct CVD Growth

In contrast to the top-down layer by layer transfer method, the bottom-up direct growth approach is more scalable and has better crystal orientation alignment. Different kinds of 2D heterostructures have been reported, such as MoS<sub>2</sub>/graphene,<sup>206</sup> WS<sub>2</sub>/graphene,<sup>207,208</sup> WS<sub>2</sub>/h-BN,<sup>207,209</sup> MoS<sub>2</sub>/h-BN,<sup>150</sup> WS<sub>2</sub>/WSe<sub>2</sub>,<sup>210</sup> WSe<sub>2</sub>/MoSe<sub>2</sub>,<sup>211</sup> MoS<sub>2</sub>/MoSe<sub>2</sub>,<sup>210</sup> MoS<sub>2</sub>/WSe<sub>2</sub>,<sup>212</sup> and WS<sub>2</sub>/MoS<sub>2</sub>.<sup>213</sup> In this section, typical CVD growth recipes regarding WS<sub>2</sub>-based 2D heterostructures will be introduced.

Duan *et al.*<sup>210</sup> demonstrated the synthesis of WSe<sub>2</sub>/WS<sub>2</sub> lateral heterostructures by *in situ* modulation of the vapour-phase reactants of these 2D crystals, **Figure 2.27(a)**. This approach involves two steps: a first growth of WS<sub>2</sub>; followed by a lateral epitaxial growth of WSe<sub>2</sub>, as illustrated in **Figure 2.27(b)**. The electrical measurements demonstrated that the WSe<sub>2</sub>/WS<sub>2</sub> heterojunctions form p–n diodes and photodiodes, which can subsequently be used to create complementary inverters with high voltage gain. At almost the same time, Cong *et al.*<sup>213</sup> reported a scalable single-step growth strategy for the creation of vertical stacked and in-

plane interconnected heterostructures based on WS<sub>2</sub> and MoS<sub>2</sub>, **Figure 2.27(c)**, respectively, by adjusting the reaction temperature. Accordingly, high-temperature growth creates mostly vertically stacked bilayers, as shown in **Figure 2.27(d)**, while low-temperature conditions usually produces lateral heterojunctions. The average carrier mobility and on/off ratio of the FETs based on the vertical WS<sub>2</sub>/MoS<sub>2</sub> bilayers are 25 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 10<sup>6</sup>, respectively, under vacuum.

The realisation of flexible and transparent devices requires not only 2D semiconducting TMDs, but also other 2D materials, such as insulating h-BN and metallic graphene. Okada *et al.*<sup>209</sup> demonstrated for the first time a direct CVD growth of 2D WS<sub>2</sub> on high-quality exfoliated h-BN flakes, as illustrated in **Figure 2.27(e)**, utilising a three-furnace system and a new liquid precursor WCl<sub>6</sub>. The domain size of the WS<sub>2</sub> on h-BN is about 2 μm, **Figure 2.27(f)**. The LEED pattern, **Figure 2.27(g)**, indicated that the triangular WS<sub>2</sub> sample was monolayer of extremely high quality. As to the graphene substrate, the first study was reported by Bianco *et al.*<sup>208</sup> to directly grow monolayer WS<sub>2</sub> on both epitaxial and CVD graphene with W(CO)<sub>6</sub> and S powder as precursors, **Figure 2.27(h)**. The WS<sub>2</sub> grown on epitaxial graphene was found to consist of a better quality owing to negligible strain at the interface and defect-free graphene substrate, as shown in **Figure 2.27(i)** and **(j)**. However, the domain size of the monolayer WS<sub>2</sub> was limited to nanoscale.



**Figure 2.27. Direct CVD growth of 2D heterostructures.** (a) Schematic illustration of the CVD system for WSe<sub>2</sub>/WS<sub>2</sub>. (b) Illustration of lateral epitaxial growth of WS<sub>2</sub>/WSe<sub>2</sub>. (a) and (b) are reprinted with permission from ref. [210]. © 2014 Macmillan Publishers Limited. (c) Schematic diagram of the synthesis process for MoS<sub>2</sub>/WS<sub>2</sub>. (d) Schematics and optical images of the vertical and in-plane MoS<sub>2</sub>/WS<sub>2</sub> heterostructures. (c) and (d) are reprinted with permission from ref. [213]. © 2014 Macmillan Publishers Limited. (e) Schematic of the CVD system for the epitaxial growth of monolayer WS<sub>2</sub> domains on mechanically exfoliated h-BN multi-layers. (f) SEM image of the triangular WS<sub>2</sub> domains epitaxially deposited on the h-BN flake. (g) LEED pattern of the WS<sub>2</sub>/h-BN heterostructure. (e-g) are reprinted with permission from ref. [209]. © 2014 American Chemical Society. (h) Schematic illustration of the CVD system used for the growth of WS<sub>2</sub> on graphene. (i, j) SEM images of the WS<sub>2</sub> grown on (i) epitaxial graphene and (j) CVD graphene with 5 min deposition time. (h-j) are reprinted with permission from ref. [208]. © 2015 The Royal Society of Chemistry.

## 2.4.2 Application of 2D Heterostructures

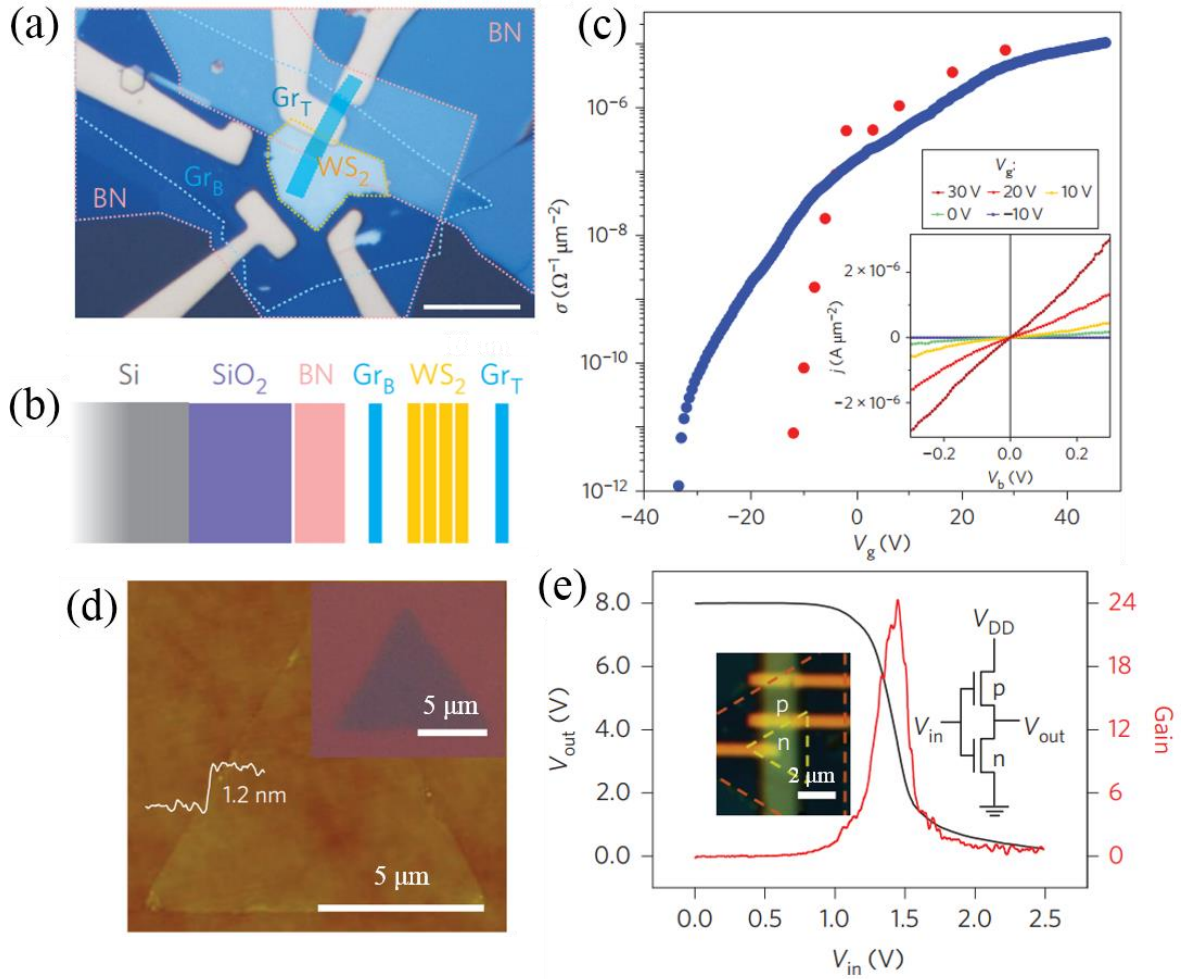
2D layered materials exhibiting unique and tuneable material properties are applicable to solving various scientific and technological problems. A great deal of work has been done in a relatively short period of time to both understand the intrinsic properties and to develop

the experimental techniques to validate the enormous potential that these novel materials can provide. The solid progress in the study of electronic devices based on a single 2D material underpins the development for creating 2D material assemblies with unique electronic and optoelectronic properties. In this section, some applications of the structures containing WS<sub>2</sub> and at least one more other 2D layered material will be reviewed.

#### **2.4.2.1 Electronics**

The evolutionary path of the modern digital electronics (Si-based) industry has come to an end, as the channel length of MOSFETs (metal oxide semiconductor field effect transistors) is approaching the limits set by the statistical and quantum effect.<sup>118</sup> There is an urgent and immediate need for alternative materials in order to overcome the challenges brought by the decreasing channel length for transistor miniaturisation.<sup>123,214</sup> FET is the basic building block for digital electronics that has two outputs; ON and OFF states. A fine FET in terms of performance generally exhibits a low leakage current (OFF state current), a high carrier mobility and a high on/off current ratio. Recent study on monolayer WS<sub>2</sub> FETs demonstrated a field-effect mobility of  $50 \pm 7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , a current on/off ratio of  $\sim 10^6$ , and a dark state current of  $10^{-9}$  at room temperature.<sup>127</sup> However, such a device structure with only one 2D material suffers from interface problems. First, contacting semiconducting TMDs with conventional metal electrodes forms Schottky junctions at the interfaces. The Schottky barrier induces contact resistance that is notably higher than channel resistance, which will lower the overall conductance of FETs. Second, the exposure of channel material to air and the contact with SiO<sub>2</sub> evokes charge carrier scattering, which will also impair the functioning of FETs. Therefore, it is essential to build heterostructures based on pure 2D materials, where semiconducting TMDs as active layers, metallic graphene as electrodes and insulating h-BN as substrates and encapsulants.

**Figure 2.28(a)** presents an ultrathin tunnelling field-effect transistor (TFET) created by a vertical heterostructure that comprises, a few-layer WS<sub>2</sub>, two graphene layers and a thin layer of h-BN. The stacking sequence of the transistor is demonstrated in **Figure 2.28(b)**. In this device structure, the tunnelling currents upon on/off states depend on WS<sub>2</sub> thickness, gate bias (inset in **Figure 2.28(c)**) and temperature. The combination of tunnelling (under the barrier) and thermionic (over the barrier) transport resulted in unprecedented current modulation exceeding  $1 \times 10^6$  at room temperature and very high ON current. Such vertical heterostructures exhibited similar tunnelling characteristics when prepared on a flexible PET film. It is worth mentioning that the recent study on lateral epitaxial synthesis strategy for the preparation of WS<sub>2</sub>/WSe<sub>2</sub> lateral heterostructures with both p- and n-type characteristics allows a CMOS inverter (a logic NOT gate) to be built, **Figure 2.28(d)**. Despite the use of conventional metal contacts, the inverter can still exhibit a voltage gain as large as 24, red curve in **Figure 2.28(e)**.



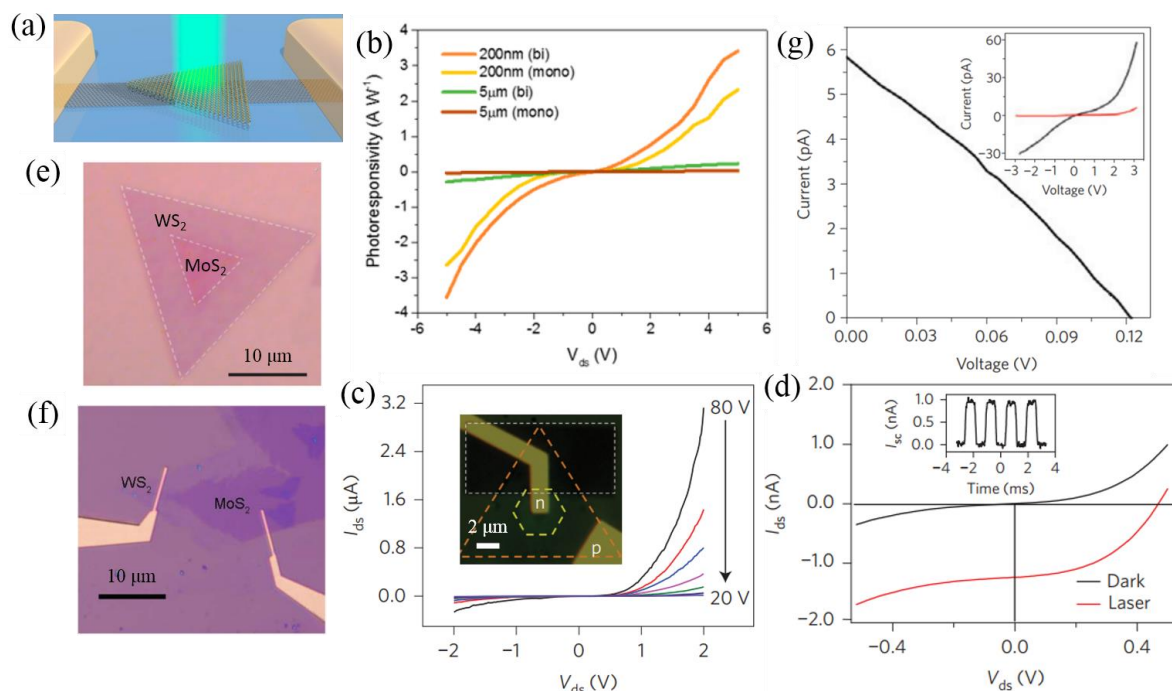
**Figure 2.28. WS<sub>2</sub>-based heterostructures for electronics.** (a) Optical image of a TFET based on WS<sub>2</sub>, graphene and h-BN. (b) Schematic of the materials stacking order. (c) Red circles: zero-bias conductivity as a function of gate voltage. Blue circles: conductivity measured at a bias voltage of 0.02 V as a function of gate voltage. Inset: I–V at different gate voltage (linear scale). T = 300 K. (a–c) are reprinted with permission from ref. [198]. © 2012 Nature Publishing Group. (d) AFM image of a triangular domain with a thickness of 1.2 nm. Inset: optical image of a triangular domain. (e) A CMOS inverter obtained by integrating a p-type WSe<sub>2</sub> and n-type WS<sub>2</sub> FET, showing the expected inverter function with a voltage gain as large as 24. The black curve is the output–input curve and the red curve indicates the voltage gain. Inset: Image and circuit diagram of the WSe<sub>2</sub>/WS<sub>2</sub> CMOS inverter. (d) and (e) are reprinted with permission from ref. [210]. © 2014 Macmillan Publishers Limited.

### 2.4.2.2 Optoelectronics

The field of optoelectronics represents the study of the interaction of light with matter. The optical response of a semiconductor is strongly dependent on its electronic band structure. In a direct bandgap semiconductor, photons with energy greater than its bandgap can be directly absorbed or emitted, while it requires the involvement of an additional phonon for opto-behaviour in an indirect bandgap semiconductor. Therefore, monolayer TMDs with direct bandgaps of visible-range wavelengths would be ideal candidates for optoelectronic applications in photodetectors, photovoltaic devices, LEDs, lasers and even novel optical switches for the future generations of nanotechnologies.

There are two classes of optoelectronics: light harvesting and light generating devices, which correspond to photon absorption and photon emission processes, respectively. An interesting light harvesting device of 2D materials is the photodetector, which forms excitons (electron-hole pairs) by absorbing photons and then generates electrical feedback by separating these excitons *via* a selection of methods. Photoresponsivity and response time are two essential measures that justify the performance of a photodetector, where photoresponsivity is the ratio of photocurrent over total incident light power and response time is the amount of time it take for the photodetector to reach the saturation current from dark current under fixed illumination. Due to the large contact resistance that limited the photocurrent collection, the preliminary photodetector based on multilayer WS<sub>2</sub> films had a photoresponsivity of ~92  $\mu\text{A W}^{-1}$  and a response time of 5.3 ms.<sup>179</sup> Recent study reported by Tan *et al.*<sup>215</sup> introduced the fabrication of ultrathin 2D photodetectors using WS<sub>2</sub> monolayers with graphene electrodes, as shown in **Figure 2.29(a)**. These lateral metal/semiconductor/metal (MSM) photodetectors exhibited high photoresponsivities (**Figure 2.29(b)**, ~3.5  $\text{A W}^{-1}$  for a bilayer WS<sub>2</sub> device and

$\sim 2.5 \text{ A W}^{-1}$  for monolayer) and photogain under ambient conditions, comparable to and in many cases outperforming the TMDs-based photodetectors with metal electrodes.<sup>179,216–222</sup>

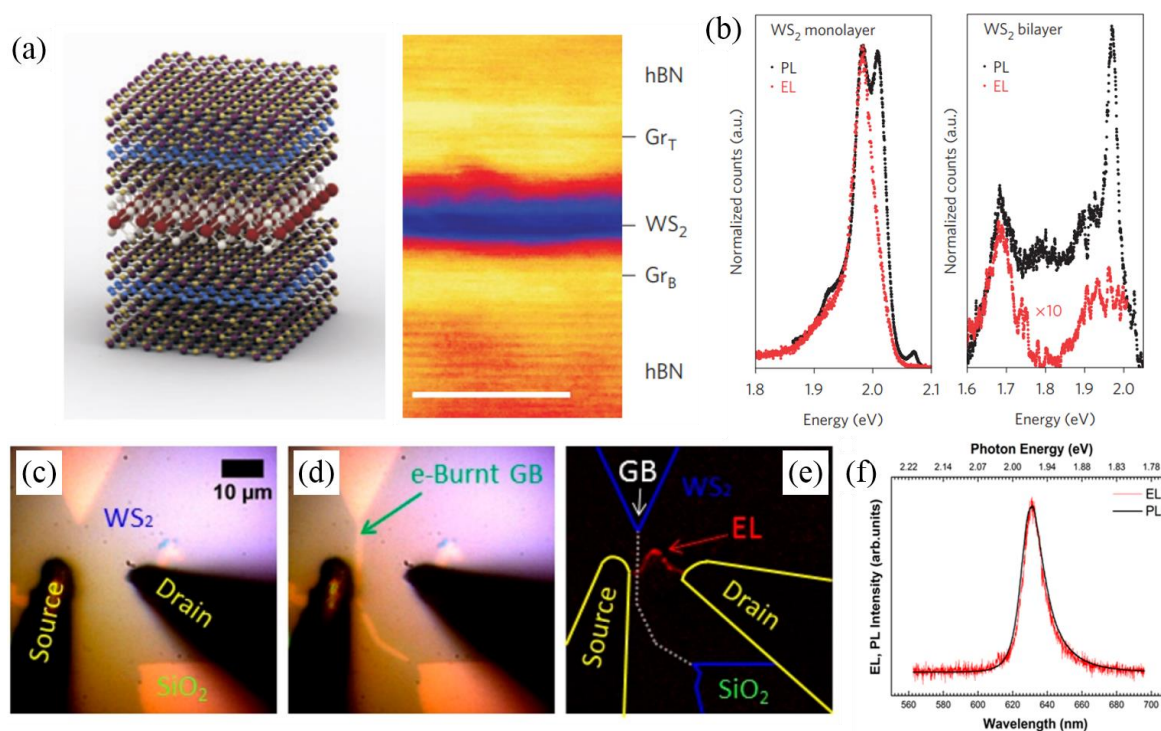


**Figure 2.29. WS<sub>2</sub>-based heterostructures for light harvesting devices.** (a) Schematic 3D view of graphene/WS<sub>2</sub>/graphene photodetector. (b) Photoresponsivity of the four types of detectors under an incident light density of  $3.8 \times 10^6 \text{ m W cm}^{-2}$ . (a) and (b) are reprinted with permission from ref. [215]. © 2016 American Chemical Society. (c) Gate-tunable output characteristics of a lateral WSe<sub>2</sub>/WS<sub>2</sub> heterojunction p–n diode. (d) Experimental output characteristics of the lateral p–n diode in the dark (black line) and under illumination (red line). Inset: temporal photocurrent response under periodic on/off laser illumination through a mechanical chopper. (c) and (d) are reprinted with permission from ref. [210]. © 2014 Macmillan Publishers Limited. (e) Optical image of a triangular in-plane WS<sub>2</sub>/MoS<sub>2</sub> Heterojunction. (f) A typical optical image of the device based on WS<sub>2</sub>/MoS<sub>2</sub> in-plane heterojunction, where one electrode is on the outer layer WS<sub>2</sub> and the other one is placed on the inner layer MoS<sub>2</sub>. (g) Photovoltaic effect of the in-plane heterojunction. Inset is the typical I–V curve of the junction with (black) and without (red) illumination, showing the p–n junction behaviour. (e–g) are reprinted with permission from ref. [213]. © 2014 Macmillan Publishers Limited.

Another interesting light harvesting device is the photovoltaic cell, a p–n junction that is characterised by a parameter termed external quantum efficiency (EQE), defined as the ratio

of the number of as-generated charge carriers over the number of incident photons. Prior work on the direct growth of WS<sub>2</sub>/WSe<sub>2</sub> lateral heterostructures facilitated the fabrication of a p-n diode with well-defined p-type characteristics in WSe<sub>2</sub> and n-type in WS<sub>2</sub>, **Figure 2.29(c)**. Such a natural p-n diode, **Figure 2.29(d)**, showed a clear photovoltaic effect with an open-loop voltage of ~0.47 V and close-loop current of ~1.2 nA. However, the EQE of this device was only ~9.9%, much lower than the value of the contemporary Si-based solar cells, ~80%. A similar in-plane heterostructure based on WS<sub>2</sub> and MoS<sub>2</sub>, **Figure 2.29(e)** and **(g)**, was also demonstrated to serve as an intrinsic monolayer p-n junction, where an open circuit voltage of 0.12 V and short circuit current of 5.7 pA was obtained.

Finally, the light-emitting diode, one of the light generating devices, requires current to be injected into the p-n junction, which results in light emission. Electroluminescence (EL) can be generated in TMDs-based nanoelectronic devices by applying source-drain bias and detecting the emission. Withers *et al.*<sup>223</sup> reported the LEDs made by combining metallic graphene, insulating h-BN and semiconducting TMDs monolayers into complex but carefully designed stacks, **Figure 2.30(a)**. It was found that, in contrast to PL, EL started only at the bias voltage above a certain threshold, and the frequency of EL is close to that of PL, **Figure 2.30(b)**, which attributed to radiative recombination of A<sup>-</sup>, negatively charged excitons. In addition to the above-mentioned vertical stacked heterostructures, EL across the grain boundary (GB) regions of monolayer WS<sub>2</sub> was also observed, as shown in **Figure 2.30(c-e)**. The similarity of the EL and PL spectra indicates that the EL originates from electron-hole pairs (excitons) recombination across the direct band gap, as shown in **Figure 2.30(f)**.



**Figure 2.30. WS<sub>2</sub>-based heterostructures for light generating devices.** (a) Schematic diagram of the hBN/Gr<sub>B</sub>/2hBN/WS<sub>2</sub>/2hBN/Gr<sub>T</sub>/hBN structure and cross-sectional bright-field STEM image of the same structure. (b) Comparison of the PL and EL spectra for the bilayer and monolayer WS<sub>2</sub>-based device. (a) and (b) are reprinted with permission from ref. [223]. © 2015 Macmillan Publishers Limited. (c) An optical image of W probes set in contact at two sides of a 2D WS<sub>2</sub> GB on a SiO<sub>2</sub>/Si substrate. (d) After source-drain bias is applied, the GB erodes to be visible under an optical microscope. (e) A red-channel optical image taken to capture a visible-range (red) EL emission arc generated in the GB region shown in (c) (*i.e.*, the image was background subtracted and “Red” colour coded to show only EL). (f) An EL spectrum is compared with a PL spectrum normalized to the EL intensity (*i.e.*, the PL is obtained at the EL domain region before source-drain bias is applied). (c-f) are reprinted with permission from ref. [224]. © 2015 American Chemical Society.

### 2.4.3 Conclusion

The growing interest in ultrathin 2D heterostructures is not limited to simply understanding the new science. Instead, the interest develops from a massive potential for real world, commercial applications, including but not limited to transistors, photodetectors, solar cells, LEDs, sensors, lasers and optical switch. To date, 2D vertical heterostructures have been

produced primarily through mechanical exfoliation and stacking. Manually stacking mechanically exfoliated 2D flakes can yield impressively complex heterostructures, but it is not suitable for large scale production and can also lead to uncontrollable interface. Direct CVD synthesis of 2D material epitaxially grown on top of each other seems to be a scalable and time-effective approach to form van der Waals assemblies with different building blocks and stacking sequences. The benefits of this approach over manual assembly through transfer techniques are that the interfaces are atomically sharp and that there are no residues from the transfer process. However, it is still a challenging task to find the right conditions for the formation of fully merged continuous film rather than island growth. As of now, the most viable approach to large scale production of 2D heterostructures seems to involve growing individual 2D layers on catalytic substrates, then isolating and layer by layer transferring these nanosheets. However, the production of particular heterostructures cannot be scaled up without trying a large number of available approach.

## **2.5 Conclusion**

Graphene is a material that could have great potential for a wide range of scientific areas. However, the world of 2D materials goes well beyond graphene, with a large number of 2D materials that have not been comprehensively studied or even synthesised yet, which hold promise for many more exciting discoveries. Material science through synthesis and formation of lateral and vertical homo- and heterostructures of these novel atomically thin layered materials writes a new chapter in the history of science that could lead to unprecedented future applications. Furthermore, this versatile 2D warehouse offers materials such as insulators, semiconductors, semi-metals, metals and even superconductors, which makes them ideal for future wearable applications.

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## Chapter 3

### *Methodology*

#### **3.1 Introduction**

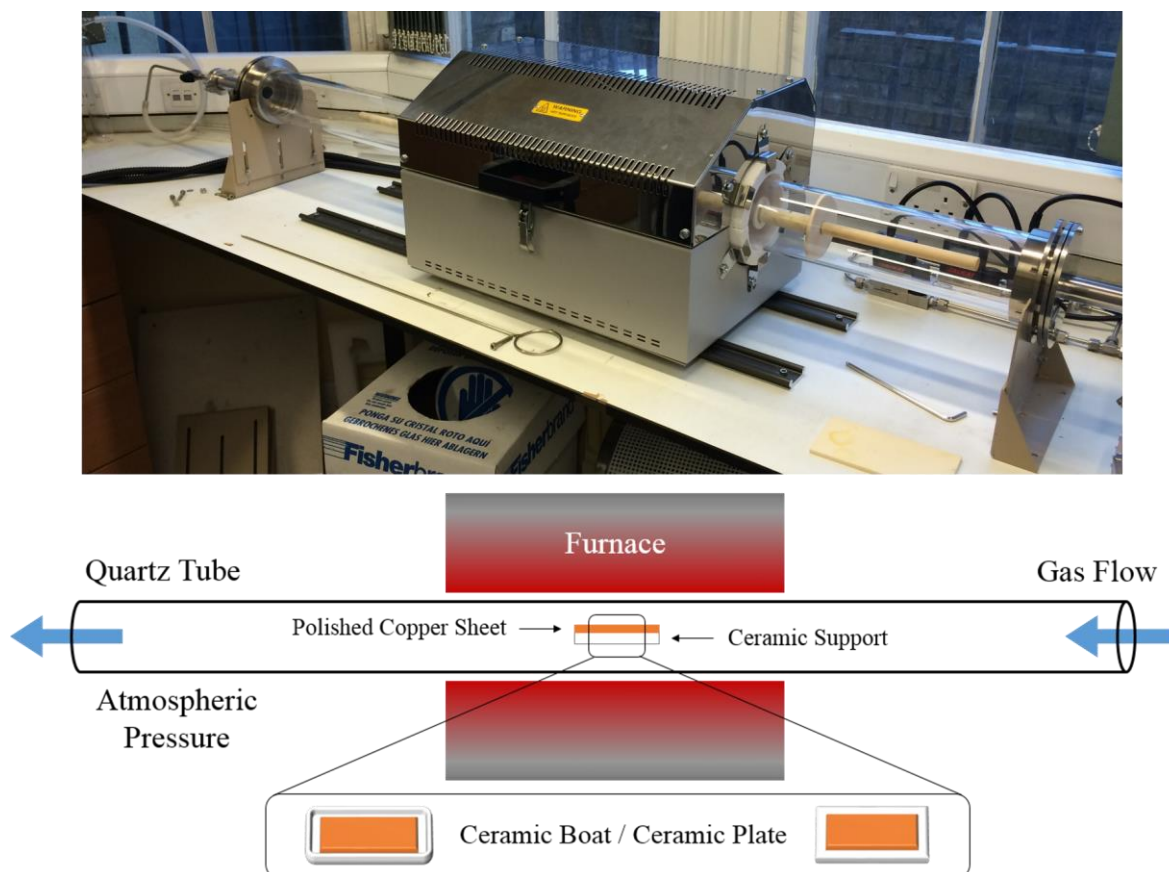
This chapter aims to give a brief introduction of the major characterization techniques from materials fabrication to property characterization, which are exclusively employed to aid the progression of this project. In lieu of looking into details of the general working principles of these techniques, this chapter will focus more on delivering operational details, such as CVD recipes, transfer procedures, equipment models and parameters. With the provided experimental details, I can expect that all the experiments and analysis performed in this thesis can be replicated.

#### **3.2 Graphene Synthesis and Transfer**

##### **3.2.1 Preparation and growth of graphene**

As the first objective of this project, a 4 inch CVD system illustrated in **Figure 3.1** was constructed for graphene synthesis by referring to the previous reports.<sup>1,2</sup> A piece of 25  $\mu\text{m}$  thick 14 cm  $\times$  6 cm copper (Alfa Aesar, Puratronic 99.8%) was first polished by metal polish liquid (Brasso) for at least 15 min. After that, oxides residue on the copper surface was

removed through sonication in diluted hydrochloric acid solution (HCl, Alfa Aesar, 37% HCl:H<sub>2</sub>O = 1:3) for two min, and then sonicated in acetone and isopropanol (IPA) for 5 min each. Finally, the whole piece of copper was put into a ceramic boat or a ceramic plate, and was then placed into an air tight 4 inch quartz tube. A horizontal tube furnace with accompanying control unit (Carbolite model HST 12/400) was moved to the sample's position by sliding it across mounted runners. In order to ensure a uniform temperature during growth, the copper sheet was positioned in the centre of the furnace. Three gases (BOC) were used within the system: 1% methane in argon, 25% hydrogen in argon and 100% argon (hereinafter referred to as CH<sub>4</sub>, H<sub>2</sub> and Ar). The flow rate of these gases could be individually controlled using Alicat mass flow controllers in conjunction with Flowvision computer software, and was measured in standard cubic centimetres per minute (sccm). The CVD growth was performed at atmospheric pressure and was first purged with 2000 sccm Ar, 500 sccm H<sub>2</sub> and 50 sccm CH<sub>4</sub> for 30 min. The temperature of the furnace was then set to 1060 °C at a ramping rate of 50 °C/min under a flow of 500 sccm of Ar and 100 sccm of H<sub>2</sub>. The copper was annealed at 1060 °C with the same flow rate for 1 hour. Graphene growth was carried out at 1060 °C under a flow of 500 sccm of Ar, 100 sccm of H<sub>2</sub> and 10 sccm of CH<sub>4</sub> for 1 hour. After growth, the furnace was slid away from the sample to the other end of the runners, which allow the sample to be fast cooled to room temperature.



**Figure 3.1.** The CVD setup for graphene synthesis in this thesis. Top: photograph. Bottom: schematic diagram.

### 3.2.2 Transfer of graphene

In this project, the as-grown graphene samples from CVD were transferred onto different substrates for further characterization. After cooling process, the graphene sample was first spin coated with a layer of Poly-methyl-methacrylate (PMMA, 8% wt. in anisole, 495k molecular weight) at 4500 rpm for 60 seconds using a spin coater (Laurell-WS-650MZ-23NPP), and then cured on a hot plate (Stuart-SD160) at 180 °C for 90 seconds to remove any anisole from the PMMA. Cotton buds were used to wipe away backside graphene and the copper was etched away by floating the sample on an aqueous solution of  $\text{FeCl}_3$  (Sigma-Aldrich, 1 M) or ammonium persulfate (APS, Sigma-Aldrich, 0.2 M). The PMMA/graphene

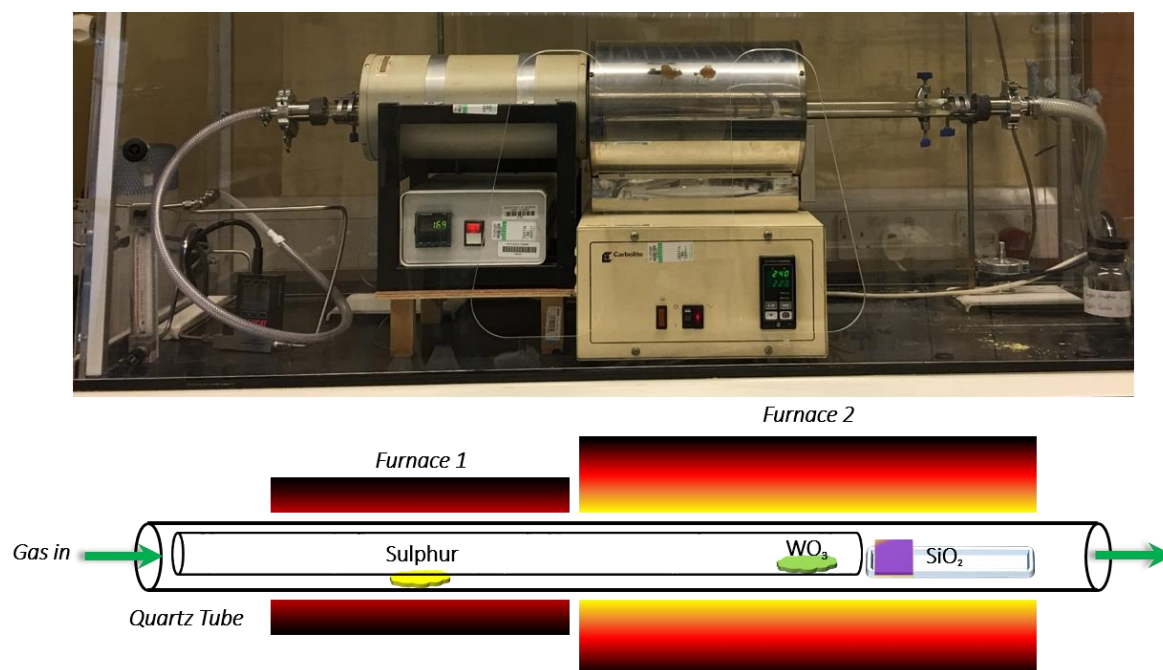
stack was then rinsed in deionised water three times for 30 min each to wash away any remaining chemicals. After the cleaning process was completed, the sample was transferred onto a cleaned substrate, such as Si chip with a 300 nm oxide layer ( $\text{SiO}_2/\text{Si}$ ), quartz and polyethylene terephthalate (PET) film, and then left in fume hood overnight to slowly evaporate the water trapped between the film and the substrate. The sample was then baked on the hot plate at 150 °C for 15 min and placed in warm acetone (~45 °C) for 2–3 hours to remove PMMA.

### 3.3 $\text{WS}_2$ Synthesis and Transfer

#### 3.3.1 Preparation and growth of $\text{WS}_2$

In addition to graphene growth, the CVD synthesis of monolayer  $\text{WS}_2$  is another major objective in this project. The CVD monolayer  $\text{WS}_2$  domains or films were fabricated on  $\text{SiO}_2/\text{Si}$  substrates (University Wafer) based on the previously reported CVD approach<sup>3,4</sup> using S and  $\text{WO}_3$  as precursors, with the addition of  $\text{H}_2$ , **Figure 3.2**. Before growth, the substrate was cleaned using sonication in acetone and isopropanol (IPA) for 15 min each, followed by a 10 min oxygen plasma treatment. 200 mg sulphur powder (>99.5%, Sigma-Aldrich) was loaded at the centre of furnace 1 in the outer 1 inch quartz tube, while 100 mg of  $\text{WO}_3$  powder (>99.5%, Sigma-Aldrich) was placed at the centre of furnace 2, in an inner quartz tube with a smaller diameter of 1cm. The 2 cm × 2 cm substrate was then placed downstream in furnace 2, about 8.5 cm away from  $\text{WO}_3$  powder. The whole system was first flushed with 500 sccm Ar gas for 30 min, followed by a pre-introduction of S by heating the S powder up to 180 °C. Then furnace 2 was heated up to 1150 °C with a ramping rate of 40 °C/min. The reaction was conducted under the temperature of 1150 °C for 3 min with a mixed gas flow of 250 sccm and a  $\text{H}_2/\text{Ar}$  ratio of 1:19. After that, furnace 2 was set down to

room temperature with an Ar flow of 10 sccm, whilst furnace 1 was heated up to 400 °C. The flow rate was set back to 500 sccm when furnace 2 reached 950 °C in order to purge the abundant S away from the system. A fast cooling process was then applied when furnace 2 reached 850 °C.



**Figure 3.2.** The CVD setup for WS<sub>2</sub> synthesis in this thesis. Top: photograph. Bottom: schematic diagram.

### 3.3.2 Transfer of WS<sub>2</sub>

Similar to the graphene transfer process, the as-grown CVD WS<sub>2</sub> samples were first spin-coated with a PMMA scaffold at 4500 rpm for 60 seconds and cured at 180 °C for 90 seconds. The PMMA/WS<sub>2</sub> film was separated from the growth substrate by potassium hydroxide (KOH, Sigma-Aldrich reagent grade 90%, 1 M) etching at 50 °C. The floating PMMA/WS<sub>2</sub> film was then carefully transferred into deionized water and rinsed for several times to dilute residual contaminations. The films were subsequently transferred onto other substrates and left in fume hood for overnight. After baked at 150 °C for 15 min, the

transferred sample was prepared by removing the PMMA *via* an acetone solution bath at 45 °C for 2–3 hours.

### 3.4 Optical Microscopy

Optical Microscopy (OM) is a useful tool in the context of this project and can be used to give a quick evaluation of certain samples. The substrate upon which the sample is placed limits the use of this technique. If the graphene or WS<sub>2</sub> is placed on top of glass then OM cannot be used. Monolayer graphene and WS<sub>2</sub> on SiO<sub>2</sub>/Si substrate, however, are visible under OM. OM also allows for a fast and non-harmful detection of multilayer areas as they appear darker. Furthermore, it can be used to check the coverage of the sample after transfer and to identify large dirt particles/contaminants. A custom-built optical microscope illuminated by a yellow LED was mainly used in this project. Mitutoyo objective lens with magnification of 10x and 50x were employed for different purposes. Thorlabs high-resolution 1280 × 1024 CMOS colour sensor was used as the camera to acquire the images and display on a computer. Optical images were normally brightness/contrast adjusted to show information of interest using ImageJ, an image processing software.

### 3.5 Scanning Electron Microscopy

Graphene and WS<sub>2</sub> samples were regularly characterised by scanning electron microscopy (SEM) in order to investigate nanoscale geometry and variation in layer number, and to identify the degree of damage incurred by the transfer process, which cannot be detected *via* OM. Two models were used in this project, namely the Hitachi S-4300 field-emission gun and the Zeiss Merlin Analytical. The accelerating voltages was set to 3 kV with a beam current of 10 µA. The choice of using such a low accelerating voltage is to obtain clearer surface structures with less charge-up and irradiation damage to samples. Both instruments

were capable of characterising graphene and WS<sub>2</sub> to a good resolution, but the Zeiss Merlin is a more modern instrument that provides much improved contrast and resolution at higher magnitude when comparing to the Hitachi.

The SEM characterisations were carried out on WS<sub>2</sub> samples deposited on SiO<sub>2</sub>/Si substrates and graphene samples on either SiO<sub>2</sub>/Si or copper substrates. In preparing an SEM sample, silver paste or carbon sticky pads were used to paste the sample to a sample stub. The carbon sticky pads were more often used because of the easy recovery of samples from the stub, while the silver paste provides better conductivity, which can militate against unwanted charging. During imaging, the brightness and the contrast need to be adjusted properly with a correct focus value to obtain the best visual effect of the image. Astigmatism should also be corrected to avoid any distortion and thus increase the image sharpness. In Chapter 6, the energy dispersive X-ray (EDX) analysis was conducted by Mr. Siqi Ying using a Tescan Lyra Multibeam system equipped with an EDX detector (Oxford Instruments). EDX data were acquired at 5 keV for 6–8 hours to get a clear contrast difference within the hexagonal WS<sub>2</sub> domains.

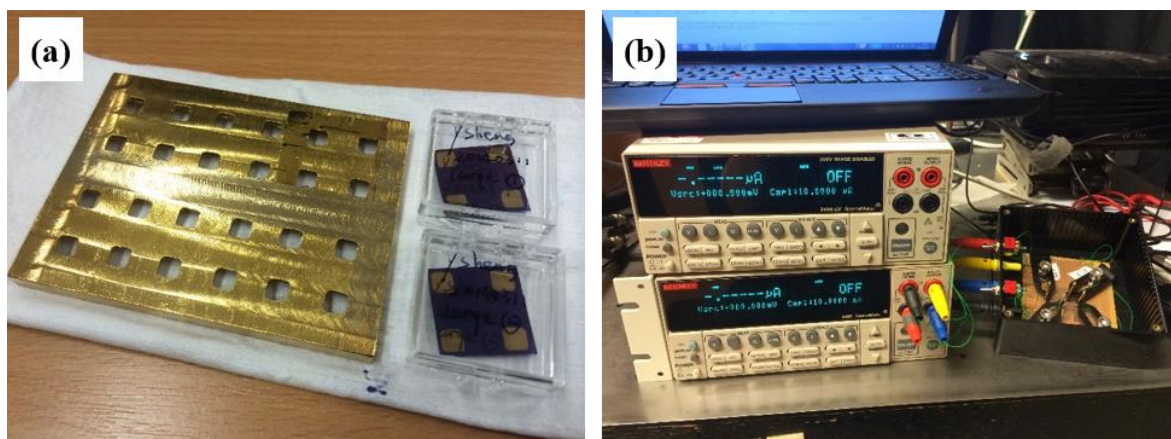
### **3.6 Transmission Electron Microscopy**

Transmission Electron Microscopy (TEM) provides an accurate way to measure the layer number and electron diffraction of the 2D materials, and, as it relates to this project, helps reveal the stacking order and lattice structure of the graphene film. Aberration-corrected transmission electron microscopy (AC-TEM) measurements in Chapter 4 was performed by Prof. Jamie Warner using the Oxford-JEOL JEM-2200MCO field emission gun TEM with a CEOS imaging aberration corrector and a double Wien Filter monochromator under an accelerating voltage of 80 kV. Before imaging, bilayer graphene was transferred onto a SiN TEM grid with 2 µm holes as outlined in section 3.2.2, however an additional overnight

baking at 380 °C was performed to thoroughly remove any residue from transfer. The AC-TEM images were processed using the software, ImageJ, and the atomic models were established *via* Accelrys Discovery Studio Visualizer.

### 3.7 Sheet Resistance Measurement

With graphene's role as the transparent conducting electrode in the devices, the sheet resistance of the graphene was an important parameter to measure, with the lowest value possible the most desirable. After transfer and PMMA removal, all the graphene samples were first thermally evaporated with a layer of metal (10 nm Cr and 90 nm Au) as electrodes with help of the shadow mask shown in **Figure 3.3(a)**. The sheet resistance measurements in Chapter 4 were carried out using a home-built instrument with wires connected to a Source Meter (Keithley 2400), **Figure 3.3(b)**.



**Figure 3.3. Photographs of experimental setup for sheet resistance measurement.** (a) Shadow mask for metal contact fabrication and graphene samples on SiO<sub>2</sub>/Si substrates after evaporation. (b) Home-built sheet resistance measurement instrument.

By applying a current through one side of the sample, a voltage can be measured across the other, which allows calculation of resistance using  $R=V/I$ . Measurement of the average

resistance across perpendicular directions of a film ( $R_1$  and  $R_2$ ) allows  $R_s$  to be determined by solving the Van Der Pauw equation, **Equation 3.1**.<sup>5</sup>

$$\exp\left(-\frac{\pi R_1}{R_s}\right) + \exp\left(-\frac{\pi R_2}{R_s}\right) = 1, \quad \text{Equation 3.1}$$

### 3.8 Optical Transmission Measurement

The optical transmission measurement is another way to determine the layer number and the quality of the graphene sample. Characterisation of the light transmission in Chapter 4 was performed using the JASCO V-570 spectrometer. This produces light from the ultraviolet to the near infrared regime and measures how much light is collected after passing through the sample. Before measurements, all graphene samples were transferred onto transparent and flexible substrates, PET in this project. The transmittance of a bare substrate was first taken to serve as a base line. The transmission of graphene samples was then measured in the range between 400 nm to 700 nm with a spectral resolution of 0.1 nm and a slow sweep speed for accuracy. As potential electrodes for solar cells, it is important that light transmission is high across the whole solar spectrum, however, if single values of transmission are quoted, it will be at 550nm. At this wavelength, it has been shown that a single layer of graphene absorbs approximately 2.3% of light with every additional layer absorbing about the same amount of light again.<sup>6,7</sup>

### 3.9 Raman and Photoluminescence Microscopy

Raman and photoluminescence (PL) spectroscopies were carried out in this project to investigate the layer number, lattice strain, doping level and interlayer interaction. The spectra were taken by a JY Horiba LabRAM Aramis imaging confocal Raman spectrometer. Switching between Raman and PL measurement mode was accessible from the software

package installed. The excitation light was a 532 nm frequency doubled Nd:YAG laser, linearly polarized, with an estimated laser spot size of 1  $\mu\text{m}$ . The full power of the laser power was 12.5 mW, but different filters can be applied to avoid signal saturation or damage to the sample. Two types of grating, 1800  $\text{mm}^{-1}$  (1800 slits per mm grating) and 600  $\text{mm}^{-1}$ , can be selected for different purposes. Before the measurement, the system was calibrated by a standard silicon chip (520.7  $\text{cm}^{-1}$ ) to exclude any instrumental error introduced after previous use.

Upon using Raman mode, 1800 g/mm was selected because of the better spectral resolution it provides. The measurement for graphene sample was normally taken at full laser power ranging from 1000 to 3000  $\text{cm}^{-1}$ , with an acquisition time of 5 seconds and an accumulation number of 2, while the Raman spectrum of  $\text{WS}_2$  sample was usually obtained at 10% laser power for 1 second and averaged 3 times over the range from 100 to 500  $\text{cm}^{-1}$ . It was found that both set-ups provided a good signal to noise ratio and avoid any sample damage by the thermal effect from the laser. As a result of the high PL efficiency from monolayer  $\text{WS}_2$ , the laser filter and acquisition time had to be further reduced to 1% and less than 1 second, respectively. The PL intensity as a function of wavelength (*i.e.*, 550-750 nm) was captured by using the coarse resolution 600 slits per mm grating. To investigate the uniformity of the as-grown and the treated  $\text{WS}_2$  monolayers, Raman and PL multi-point spectra across lateral dimensions (XY coordinates) in a fixed step size (1  $\mu\text{m}$ ), namely Raman and PL mappings, were collected. To expedite the acquisition process, SWIFT<sup>TM</sup> mapping mode was selected. The acquisition time at each spot was set to 0.5 second for Raman mapping and 0.1 second for PL mapping.

### 3.10 Atomic Force Measurement

Atomic force microscopy (AFM) is the most unambiguous characterisation tool to determine the layer number and surface morphology of 2D WS<sub>2</sub>. Characterisations of the as-grown and the treated WS<sub>2</sub> in Chapter 5, 6 and 7 were performed by Mr. Xiaochen Wang using an atomic force microscope (Asylum Research MFP-3D) in the AC mode with a silicon AC-160TS cantilever (Olympus, spring constant ~42 N/m and resonant frequency ~300 kHz). WS<sub>2</sub> samples grown directly on rigid SiO<sub>2</sub>/Si substrates can be directly investigated by AFM, excluding the necessity of sample transfer. Various imaging modes can be recorded simultaneously, including height, phase, amplitude and Kelvin probe microscopy (KPM). The topography mode normally displays the height change on material surface, which was employed to determine the thickness of the WS<sub>2</sub> samples on SiO<sub>2</sub>/Si substrates. The phase mode, which is sensitive to the elasticity changes of different materials, was used to show the variations in surface stiffness/softness and adhesion between the tip and surface. Furthermore, KPM was carried out to measure the difference in work function between two materials. The AFM mappings and corresponding profiles were generated by using the software, Gwyddion.

### 3.11 Electrical Measurement

Electrical measurement in Chapter 5 was conducted by Mr. Haijie Tan on the home-built probe station in an ambient environment. The probe station was equipped with a pair of ultrafine W probe tips (Signatone, 5 µm in diameter) controlled by micro-manipulators. The electrical measurements of the WS<sub>2</sub> FETs were programmed to run at designated values through a source meter (Keithley 2400 V).

Upon fabricating the WS<sub>2</sub> field effect transistors (FETs), JEOL 5500 FS electron-beam lithography (EBL) system was used to pattern bond pads in a bilayer PMMA resist. A thermal evaporator was used to deposit Au/Cr (80 nm/10 nm) bond pads onto a 300 nm SiO<sub>2</sub>/Si substrate, followed by a liftoff in acetone at 45 °C. The PMMA/graphene film was transferred onto the Si chip with prepatterned bond pads and baked overnight at 180 °C for better contact. The graphene film was then patterned using EBL with negative resist and oxygen plasma etching to define graphene channels with a length and width of 1 and 15 µm, respectively. Lastly, the PMMA/WS<sub>2</sub> film was transferred onto the sample. After being baked at 150 °C for 30 min, the sample was rinsed in hot acetone for PMMA removal.

### 3.12 References

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## Chapter 4

### *Uniformity of Large-Area Bilayer Graphene Grown by Chemical Vapour Deposition*

This chapter introduces the strategy for the CVD growth of bilayer graphene on Cu foils, which was developed in the first year of my DPhil program. I examine the spatial uniformity of large area films on the centimetre scale when transferred onto both silicon substrates coated with a thin oxide layer ( $\text{SiO}_2/\text{Si}$ ) and flexible transparent polyethylene terephthalate (PET) substrates. The sheet resistance and optical transmission of graphene are measured to investigate the effect of local gas flow dynamics on film quality through the alteration of the ceramic support used to hold the copper catalyst.

#### 4.1 Introduction

Graphene is a two-dimensional carbon material that is only one atom thick, first isolated in 2004 by mechanical exfoliation.<sup>1</sup> Its extended honeycomb network is the basic building block of other important carbon materials: 3D graphite, 1D nanotubes and 0D fullerenes.<sup>2,3</sup> Graphene has attracted interest due to its special properties, including both high charge carrier mobility and density, high optical transmittance and excellent thermal conductivity.<sup>4-</sup>

<sup>6</sup> It is believed to have potential for various applications, which include high-speed and radio

frequency logic devices, sensors, and transparent conducting electrodes (TCEs) for displays, touch screens, light emitting diodes and solar cells.<sup>7-13</sup>

The micromechanical cleavage of graphite necessary to isolate graphene is not compatible with large area TCE applications. Alternative methods<sup>14-19</sup> have been developed to achieve reliable and repeatable synthesis of large-area graphene sheets up to 30 inch size scales. Among these, chemical vapour deposition (CVD) is regarded as one of the most promising techniques that is compatible for TCE in flexible optoelectronics.<sup>10</sup> However, most reactions reported to date occurs under low pressure, which increases the complexity of the process and the requirements for the experimental equipment. Moreover, at normal low pressure CVD (LPCVD) condition, high sublimation of Cu results in significant surface evolution and hence a rougher surface of Cu is observed.<sup>20</sup> Therefore, atmospheric pressure CVD (APCVD) is more suitable for producing relatively high quality large-area graphene sheets in a simple, easy and low cost manner. For graphene to be useful in optoelectronic devices as a TCE it needs low sheet resistance and large light transmission. Most work to date has focused on optimizing graphene synthesis and devices on the 1 cm scale, with only a few reports of growing graphene in sizes above 10 cm and its detailed characterization. Upscaling growth from the 1–2 inch tube furnace systems routinely used in most CVD experiments for graphene growth to larger 4 inch systems and above is not trivial and more work is necessary to explore the factors that influence this upscaling process.

Recent results demonstrated a 100-meter-long graphene film by low pressure CVD using selective Joule heating.<sup>21</sup> The sheet resistance was reported to be comparable to that of the conventional CVD-grown graphene. A large scale low-pressure CVD process was reported to produce monolayer graphene films with a diagonal size of up to 30 inches, along with a roll-to-roll transfer process to flexible plastics.<sup>22</sup> Vlassiouk *et al.* also reported a similar large

scale (40 inches diagonal) graphene synthesis and studied the influence of copper foil morphology and its pretreatment.<sup>23</sup> However, a detailed analysis of the spatial uniformity of the samples was not thoroughly undertaken, which is important to see how the quality of the film varies on different size scales across the sample.

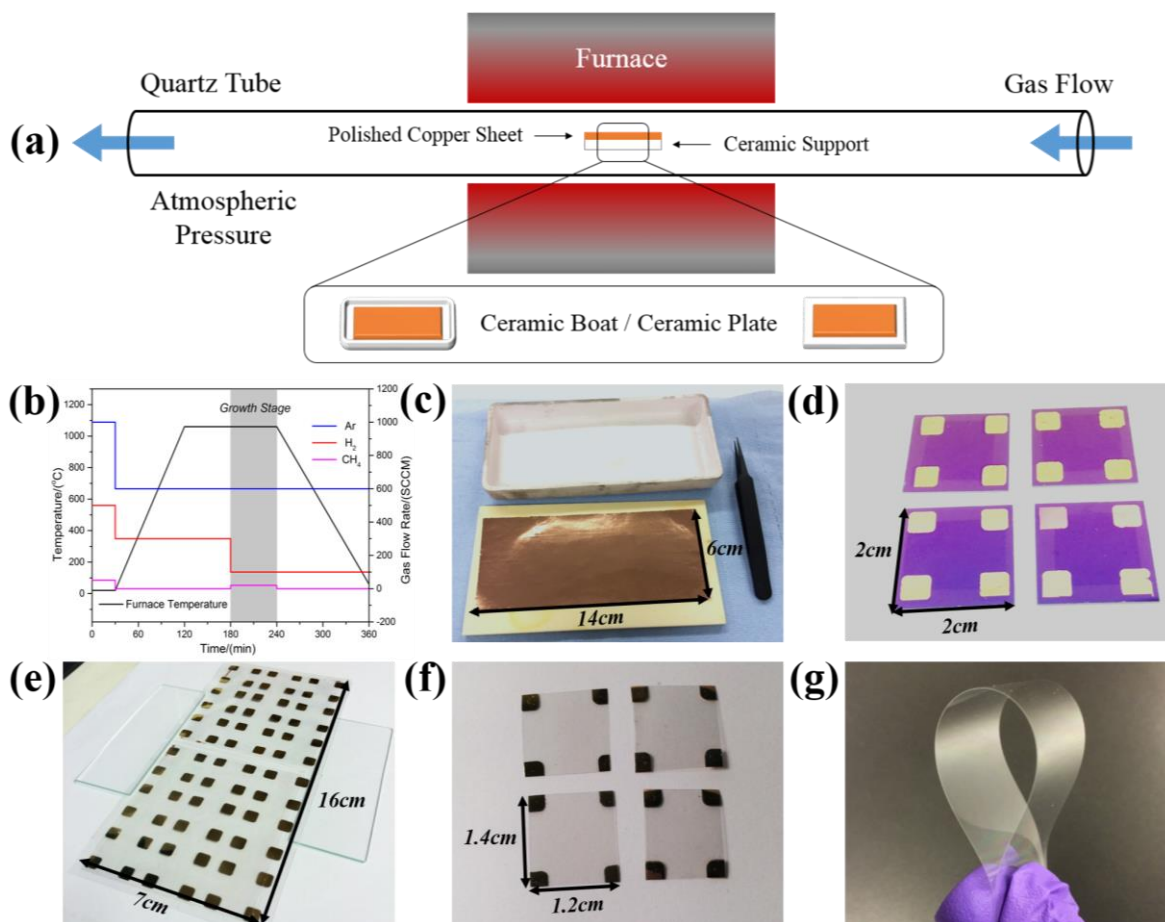
One approach for lowering the sheet resistance of graphene is to stack multiple layers one-by-one on top of each other to create a multi-layered film.<sup>22,24-28</sup> This can be a time-consuming method to obtain bilayer graphene, whereas directly growing bilayer graphene by CVD on Cu could lead to a reduced number of transfers and minimized cracks, residues and contamination during the layer by layer transfer, allowing for a more uniform graphene surface and better performance in TCE applications. In addition, bilayer graphene with Bernal (AB) stacking order has an advantage over monolayer graphene in its tunable band structure, which allows the development of semiconducting graphene for device applications based on electronic bands.<sup>29,30</sup> Recent work on the CVD synthesis of bilayer graphene film has been reported by studying the catalyst substrate, concentration of carbon source, growth temperature and total pressure.<sup>31-36</sup> In particular, Lee *et al.*<sup>34</sup> reported a bilayer graphene film across 2 inch  $\times$  2 inch area grown on a copper sheet by CVD. A method of producing Bernal stacked bilayer graphene (3 inch  $\times$  3 inch) was introduced by Liu *et al.*<sup>32</sup> using CVD on engineered alloy catalyst films. The homogeneity of their films was evaluated by Raman mapping<sup>32-36</sup> and further supported by electrical transport measurements.<sup>34,36</sup>

In this work, I examine the upscale growth of large area (14 cm  $\times$  6 cm) graphene films on copper sheets by ambient pressure CVD within a 4 inch tube furnace system. The quality of the graphene is measured by transferring it onto SiO<sub>2</sub>/Si and PET films that are compatible with flexible TCE applications. The effect of different local gas flow conditions on film uniformity is investigated through the alteration of the ceramic support used to hold the

copper catalyst. Bilayer graphene films with high coverage were successfully grown and characterised using optical microscopy, scanning electron microscopy (SEM), Raman spectroscopy, aberration-corrected transmission electron microscopy (AC-TEM), van der Pauw measurements of sheet resistance and optical transmittance spectroscopy.

## 4.2 Results and Discussion

The synthesis of large area graphene was carried out using a custom-built 4 inch CVD system with quartz tube and gas flow rates controlled by digital mass flow controllers. This builds on the prior experimental results of graphene growth on copper by CVD at the 1 inch scale.<sup>37</sup> Methane was introduced here as the gaseous carbon source and copper foil served as the catalyst metal substrate. **Figure 4.1(a)** shows the schematic diagram of the 4 inch quartz tube atmospheric pressure CVD system with copper sitting on a ceramic support. The whole system was first flushed with argon, hydrogen and methane and then ramped up to a high temperature. The copper was annealed for at least one hour after the furnace reached the desired temperature. Graphene was then grown on the copper by introducing the carbon source. In order to get a uniform bilayer graphene film with less grain boundaries and defects, the growth recipe in terms of argon/hydrogen/methane gas flow rate, growth temperature and growth time was evaluated and optimized. **Figure 4.1(b)** presents a temperature curve for the furnace as a function of time and the gas flow rate used for growing bilayer graphene during each timeline. This allowed me to produce a large bilayer graphene sheet with size up to 14 cm × 6 cm, **Figure 4.1(c)**. Before the samples were transferred onto SiO<sub>2</sub>/Si or PET substrates using a standard wet transfer method, a layer of metal (10 nm chromium and 90 nm gold) was thermally evaporated onto all the substrates as electrodes. The samples transferred onto SiO<sub>2</sub>/Si were cut into 40 pieces before wet etching.

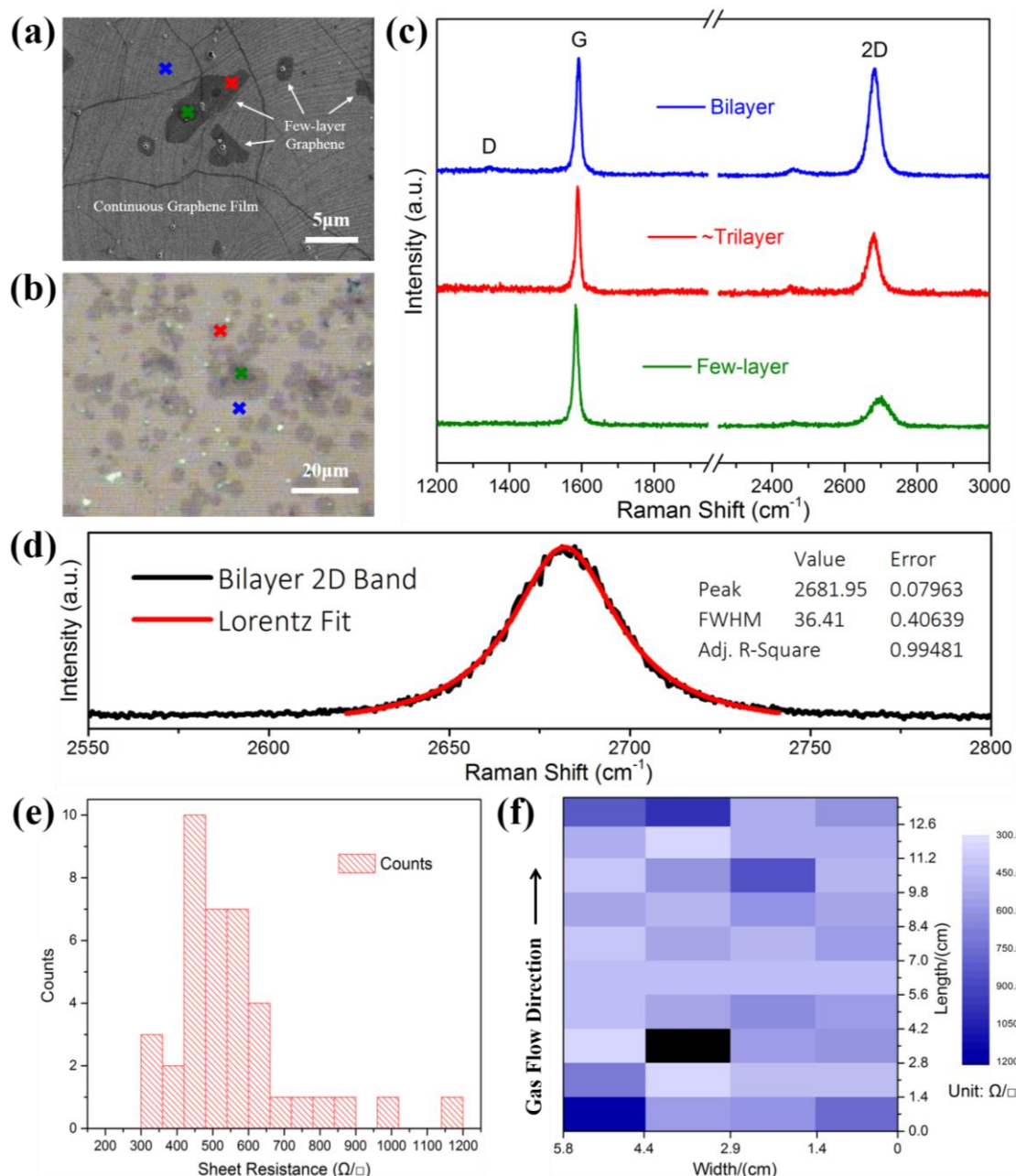


**Figure 4.1. Atmospheric pressure CVD synthesis of large-area (14 cm × 6 cm) bilayer graphene on copper.** (a) Schematic illustration of the CVD experimental set-up with polished copper sheet in a ceramic boat or a flat ceramic plate. (b) Temperature profiles of the furnace as a function of time and the gas flow rate of argon, hydrogen and methane during the growth, respectively. Black line: furnace temperature. Blue line: argon. Red line: hydrogen. Magenta line: methane. (c) Photo of large-area graphene sheet on copper. The photo also displays the ceramic boat and the ceramic plate used during the graphene synthesis. (d) Photo of four transferred graphene samples on SiO<sub>2</sub>/Si with pre-patterned metal contacts. The SiO<sub>2</sub>/Si used here is 2 cm × 2 cm. (e) Photo of two large pieces of graphene sheet on pre-patterned PET substrates before PMMA removal. The area for each PET substrate is about 8 cm × 7 cm. (f) Photo of four transferred graphene samples on PET substrates with pre-patterned electrodes. The area of the PET varies from 1 to 2 cm<sup>2</sup>. (g) Photo of the flexible PET substrate used for transfer. The thickness is 5 μm.

**Figure 4.1(d)** shows four of the graphene samples transferred on SiO<sub>2</sub>/Si. For the samples transferred onto PET, the whole piece of graphene was first transferred onto two big PET substrates, as shown in **Figure 4.1(e)**. After removing the PMMA using acetone, the samples

were then cut into 50 pieces for further characterization. **Figure 4.1(f)** shows four typical graphene samples that were transferred on PET and **Figure 4.1(g)** demonstrates the flexible nature of the thin PET film used for flexible TCE of graphene.

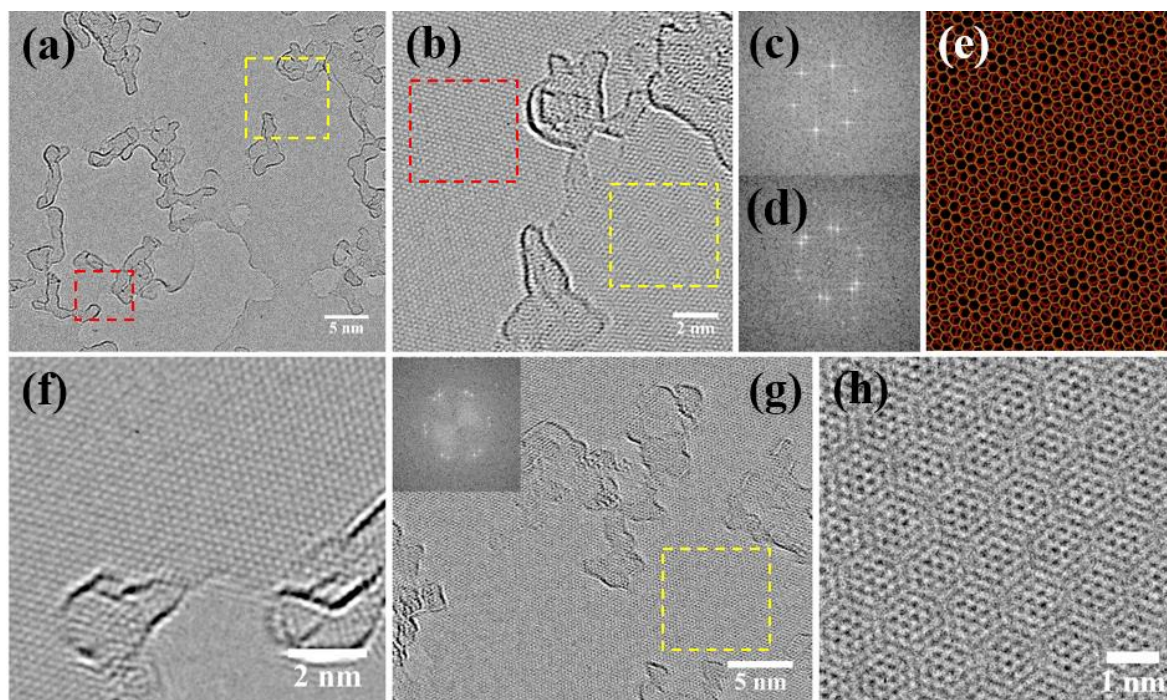
**Figure 4.2(a)** and **(b)** present some typical areas of the transferred graphene on SiO<sub>2</sub>/Si examined by SEM and optical microscopy, respectively. The non-uniform contrast indicates the variation of the film thickness. The graphene film is continuous with about 30% of the area containing smaller thicker graphene islands. Raman spectroscopy was used to evaluate the quality of the graphene films and interpret the thickness. **Figure 4.2(c)** shows the Raman spectra of three marked spots with different colour in the panels (blue cross, red cross, green cross in **Figures 4.2(a)** and **(b)**). All three spectra present the two important features related to graphene: a G peak at  $\sim 1590\text{ cm}^{-1}$  and a 2D peak at  $\sim 2690\text{ cm}^{-1}$ .<sup>16,17,38</sup> The 2D/G intensity ratio of the spectra in blue is  $\sim 1$ , which indicates bilayer graphene.<sup>16,17,33,36</sup> The red one with a ratio of  $\sim 0.7$  indicates that the graphene is about 2-4 layers thick,<sup>38</sup> and the green one showing 2D/G ratio less than 0.3 represents few-layer ( $>4$ ) graphene.<sup>16</sup> The D peak ( $\sim 1350\text{ cm}^{-1}$ ) used to identify the level of defects<sup>39</sup> in graphene was found to be negligible for all three spectra, implying the high quality of the transferred CVD graphene. As can be seen from **Figure 4.2(d)**, the 2D band for my CVD-grown bilayer graphene is almost symmetrical and can be fitted as one Lorentzian peak, which is consistent with other reported results.<sup>16,17</sup> It indicates that most of the areas in the synthesized bilayer graphene film exhibit weak interlayer coupling<sup>33</sup> likely due to turbostratic stacking, which is different from AB Bernal stacking nearly always obtained from mechanically exfoliated bilayer graphene.<sup>39</sup>



**Figure 4.2. Characterization of graphene grown on Cu situated in a ceramic boat and then transferred to Si substrate with 300 nm oxide layer.** (a) SEM image of the continuous graphene film transferred from copper foil onto Si substrate with a 300 nm thick layer of SiO<sub>2</sub> showing grain boundaries, wrinkles as well as few layers of graphene areas. Scale bar: 5  $\mu\text{m}$ . (b) Optical image of the graphene samples on SiO<sub>2</sub>/Si. Scale bar: 20  $\mu\text{m}$ . (c) Raman spectra of the marked spots with corresponding coloured crosses showing the existence of bi-, tri- and few-layer graphene. Blue line: bilayer graphene. Red line: ~trilayer graphene. Green line: few-layer graphene. (d) Lorentzian fitting of the 2D band in the Raman spectrum of bilayer graphene. Histogram (e) and spatial distribution (f) of sheet resistance of the graphene samples transferred onto SiO<sub>2</sub>/Si. The black box indicates that the graphene sample there was broken after transfer.

**Figure 4.2(e)** presents the histogram of graphene sheet resistance, the mean and the standard deviation of which is  $559.7 \Omega/\square$  and  $171.9 \Omega/\square$ , respectively, similar to other reported values.<sup>21,41</sup> **Figure 4.2(f)** shows a more straight-forward way to understand the distribution of the quality of transferred graphene on SiO<sub>2</sub>/Si in terms of sheet resistance. According to the sheet resistance results, it can be determined that the thickness of the graphene grown at the corners of the ceramic boat is thinner and more likely to be broken than that of the others during the transfer process. This was reflected by the relatively higher sheet resistance values at the corners and was thought to be caused by the comparatively lower methane concentration. The black box highlighted indicates an area damaged during the transfer process.

The turbostratic stacking revealed by Raman spectroscopy in **Figure 4.2(d)**, was further explored using AC-TEM to directly image the atomic structure of the bilayer graphene films. Rotational stacking faults manifest themselves as Moire patterns in the lattice images of few layer graphene films.<sup>42</sup> Most of the transferred films showed bilayer regions with turbostratic ordering. However, during the transfer of the bilayer graphene film, some areas were degraded and it was found that these regions contained a boundary of monolayer-bilayer interface. This allowed me to study the bilayer in more detail and also show that it is only 2 layers thick. **Figure 4.3(a)** shows an area of the sample containing a monolayer-bilayer interface. The yellow box in **Figure 4.3(a)** contains the interface region and is shown in higher magnification in **Figure 4.3(b)**. The fast Fourier transforms (FFTs) from the red and yellow boxes in **Figure 4.3(b)** are from the monolayer and bilayer regions, respectively, and show the misorientation angle of  $13^\circ$  between the two layers. An atomic model of a turbostratic bilayer with  $\sim 13^\circ$  angle is presented in **Figure 4.3(e)** to show how the Moire pattern forms from the overlapping positions of the carbon atoms in each layer, where each layer is given a different colour.

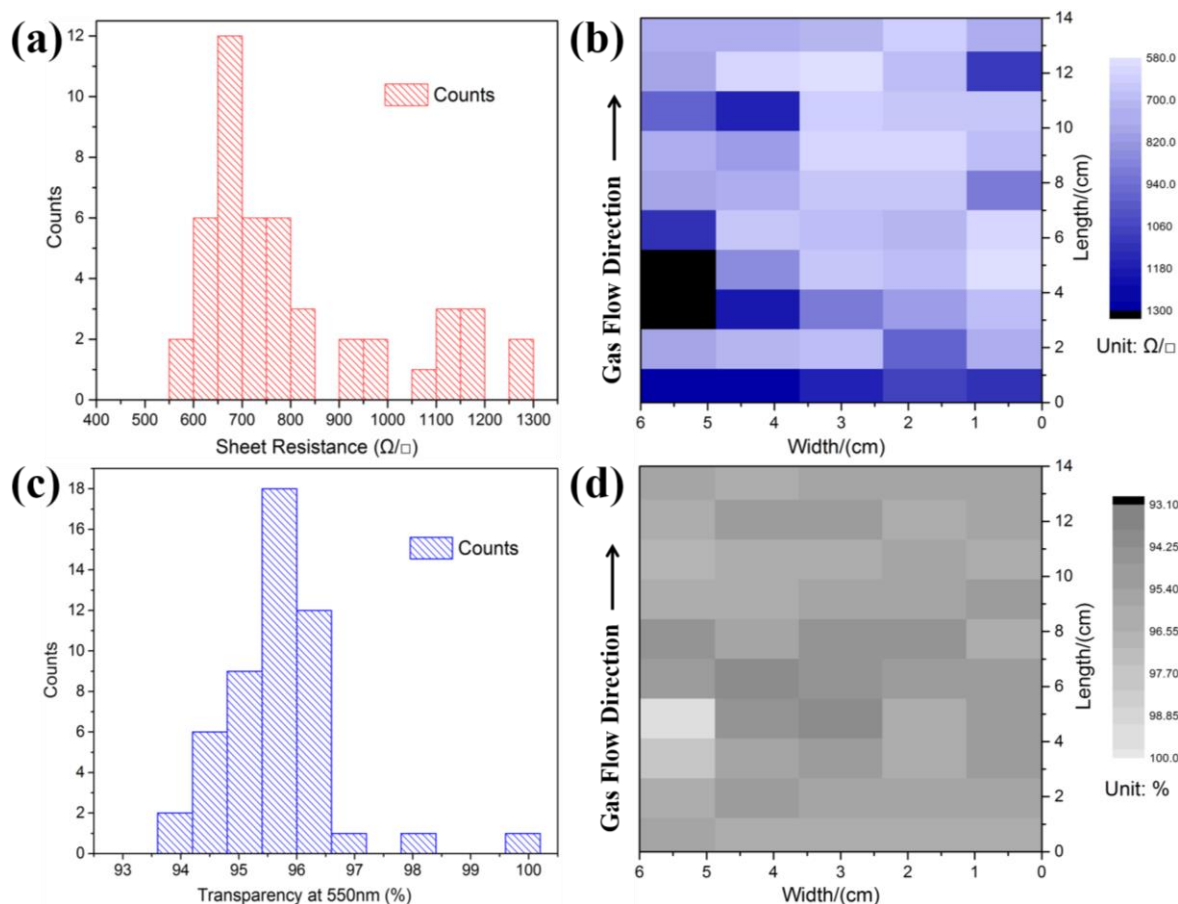


**Figure 4.3. Atomic resolution imaging of bilayer graphene by AC-TEM.** (a) AC-TEM image of a region where a monolayer-bilayer interface is found. Scale bar: 5  $\mu\text{m}$ . (b) AC-TEM image from the region indicated with the yellow dashed box in (a) showing the monolayer-bilayer interface. Scale bar: 2  $\mu\text{m}$ . (c) Fast Fourier transform (FFT) from the region indicated with the red box in (b) corresponding to the single monolayer region. (d) FFT from the region indicated with the yellow box in (b) corresponding to the turbostratic bilayer region. Angle between spots is  $\sim 13^\circ$ . (e) Atomic model of two graphene sheets with rotational angle of  $\sim 13^\circ$  to create a Moire pattern similar to those directly imaged in (b). (f) AC-TEM image of the region indicated by the red box in (a), corresponding to the edge of the monolayer graphene sheet near a hole. Scale bar: 2  $\mu\text{m}$ . (g) AC-TEM image of the large area of turbostratic bilayer graphene showing Moire pattern. Scale bar: 5  $\mu\text{m}$ . Inset shows the FFT from the entire image. (h) AC-TEM image of the area indicated by the yellow box in (g). Scale bar: 1  $\mu\text{m}$ .

I notice that the region indicated by the red box in **Figure 4.3(b)** is monolayer and not AB Bernal stacked multilayers because I followed this structure across to a region next to a hole in the film, indicated by the red box in **Figure 4.3(a)**. This region shows a single monolayer reaching the vacuum at the hole, **Figure 4.3(f)**, confirming monolayer thickness and subsequently confirming the turbostratic region as being bilayer. **Figure 4.3(g)** shows a large area region of the turbostratic bilayer graphene with a higher magnification image in **Figure**

4.3(h), revealing the details of the Moire pattern. These results confirm the findings of the Raman spectroscopy that the bilayer graphene is predominantly turbostratic and not AB Bernal stacked.

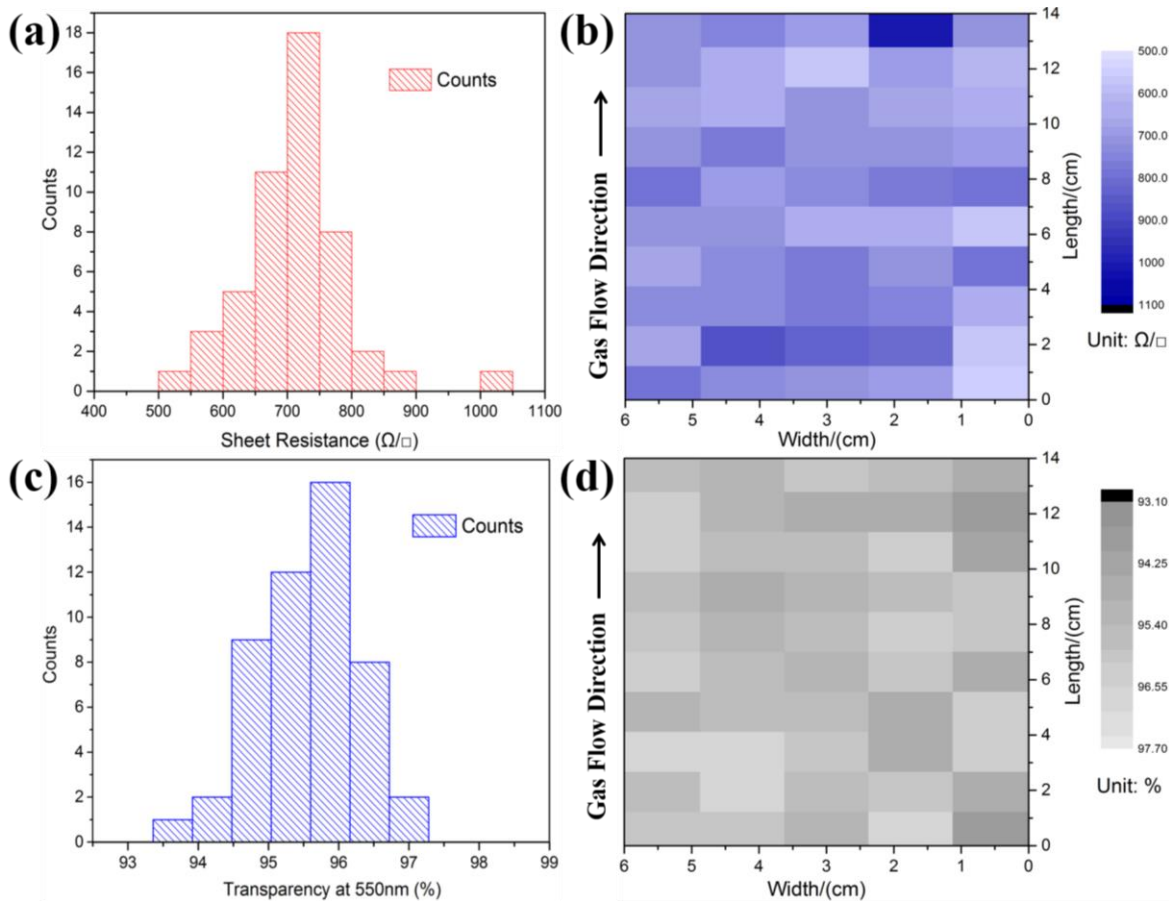
To further characterize the graphene fabricated when the copper was supported within a ceramic boat, I transferred another graphene sheet onto PET substrates and measured its combined sheet resistance and optical transmittance properties. It was reported that the theoretical value of optical transmittance of the single-layer graphene is about 97.7% and will be decreased by  $\sim 2.3\%$  when adding another layer.<sup>5,43,44</sup> For bilayer graphene, the optical transparency should be around 95.4%. **Figure 4.4(c)** and **(d)** show the histogram and spatial distribution of the large-area graphene in terms of optical transmittance at 550 nm, respectively. It shows a mean value of 95.7% with a standard deviation of 0.9%, which implies the graphene film is mostly bilayer. I also measured the sheet resistance of each graphene samples. **Figure 4.4(a)** shows the histogram of sheet resistance of all the graphene samples transferred onto PET, the average value of which is  $808.2 \Omega/\square$  with a standard deviation  $197.5 \Omega/\square$ . **Figure 4.4(b)** presents the sheet resistance mapping of the graphene, showing that the quality of the samples in first row is not as homogeneous as the others, which indicates the possibility of producing more uniform graphene if the quality of graphene in the first row can be improved.



**Figure 4.4. Characterization of graphene grown on Cu situated in a ceramic boat and then transferred to PET substrate.** (a) Histograms and (b) spatial distribution of sheet resistance of the whole graphene sheet on PET. The two black boxes indicate that the graphene samples there were broken after transfer. (c) Histogram and (d) spatial distribution of optical transmittance of the large-area graphene at 550 nm.

The ceramic boat used to support the copper during CVD growth of graphene is likely to introduce some form of non-uniformity in the gas flow around its edges which affects the quality of the graphene in terms of thickness and uniformity at the edges of the copper. To contrast this, I replaced the ceramic boat with a flat ceramic plate and kept all other conditions the same during CVD growth of graphene. The flat ceramic plate will ideally provide more uniform gas flow conditions and deliver constant precursor to the entire copper sheet. Again, I prepared a piece of graphene film using the CVD system shown in **Figure 4.1(a)** with the same growth parameters and transferred the graphene onto PET substrates,

followed by measuring its optical and electronic properties. **Figure 4.5(c)** and (d) present the histogram and optical transmittance mapping of the transferred graphene film on PET, respectively. The transparency rate at 550 nm mostly ranges from 94.9% to 96.3%. The average value is about 95.6%, which is closer to the theoretical value of bilayer graphene, with standard deviation is 0.7%, indicating a more uniform film. **Figure 4.5(a)** and (b) show the histogram and spatial distribution of sheet resistance of the graphene samples transferred, respectively. The sheet resistance is mostly between 634.1 to 792.7  $\Omega/\square$  with an average value of 713.4  $\Omega/\square$ . The standard deviation is  $\sim 79.3 \Omega/\square$ , which is half of the one grown with a ceramic boat, indicating higher uniformity for the graphene film.

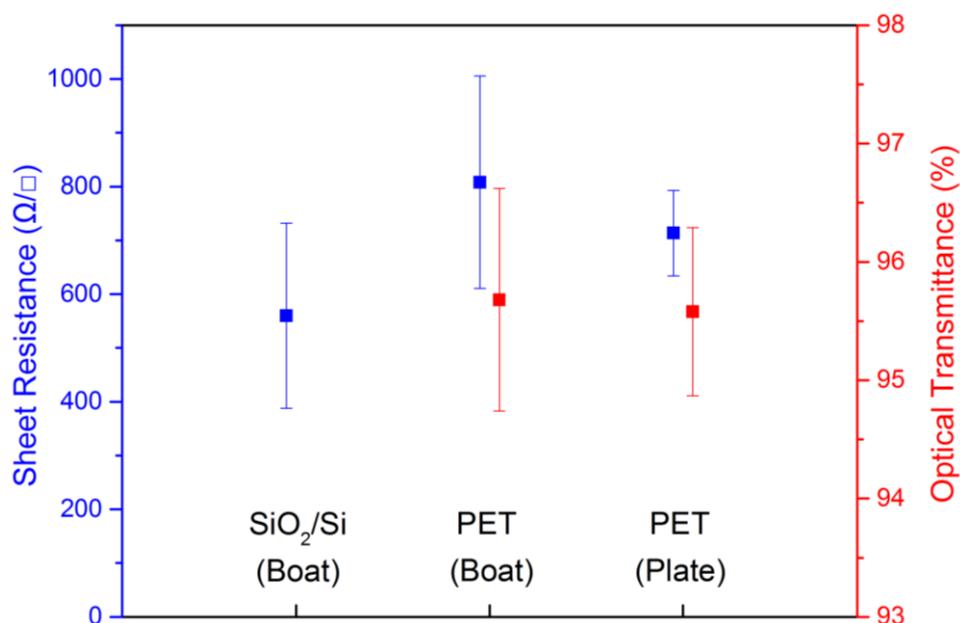


**Figure 4.5. Characterization of graphene grown on Cu situated in a flat ceramic plate and then transferred to PET.** (a) Histogram and (b) spatial distribution of the sheet resistance of the graphene on PET. (c) Histogram and (d) mapping of optical transmittance of the graphene samples on PET at 550 nm.

**Figure 4.6** presents the comparison of graphene films on different substrates in terms of sheet resistance and optical transparency at 550 nm. The average sheet resistance of graphene films transferred on SiO<sub>2</sub>/Si is lower than the ones transferred on PET. This is likely due to the higher level of doping from the SiO<sub>2</sub>/Si substrates compared to the PET.<sup>45</sup> The standard deviation of the sheet resistance for the two graphene films grown in the boat is similar, but much larger than the one grown on the plate, indicating the more uniform graphene film when using the plate during growth. The average transparency value at 550 nm for the graphene film grown on the plate is slightly closer to the theoretical value of bilayer graphene, compared with the one prepared in the boat. Similar to the sheet resistance case, the standard deviation of the transparency values for the samples grown on the plate is smaller than those fabricated in the boat, further confirming the conclusion that the uniformity of the graphene grown on the flat plate is better.

The local gas flow dynamics above the sample during growth are thought to be the main factor that affects the uniformity of the large-area graphene films fabricated here. The stability of the gas flow depends on the tube diameter ( $d$ ) and can be estimated by the Reynolds number  $Re = \rho vd/\gamma$ , where  $\rho$  is the density,  $v$  is the speed, and  $\gamma$  is the coefficient of viscosity.<sup>46</sup> Laminar flows with lower Reynolds numbers is more preferred during the conventional CVD growth in a quartz tube. In my case, the Reynolds number is estimated to be 20, which is near the lower limit of conventional laminar flow ranges (below 2100).<sup>45</sup> For the growth with a flat plate, a smoother streamline is likely to form above the copper sheet. However, for the growth with a boat, the flow is disrupted by the irregular shape of the boat, which is more likely to result in nanoscale turbulent flows above the sample. The introduced turbulent flows can cause pressure fluctuations over short areas and vortices may form at edges and corners, which corresponds to a higher Reynolds number and may influence the local growth environment for graphene synthesis. This leads to the growth of non-uniform

graphene films with poorer electrical properties. In addition, the more even surface of the ceramic plate leads to a copper sheet with a flatter surface after annealing, resulting in a more homogeneous film.<sup>47</sup>



**Figure 4.6. Correlated optical transmission at 550 nm and sheet resistance values of graphene films on different substrates and grown with either the ceramic boat or flat plate.** Blue dots: the average sheet resistance of graphene films on SiO<sub>2</sub>/Si and PET. Red dots: the average optical transmittance values at 550 nm of graphene samples on PET. Two of the graphene films were prepared in a ceramic boat and the other one was grown on a plate.

### 4.3 Conclusion

In summary, I prepared bilayer graphene sheets with areas up to 14 cm × 6 cm and studied the uniformity across the sample. The morphology and optoelectronic properties of the graphene films were characterized by SEM, AC-TEM, Raman spectroscopy, sheet resistance and optical transmittance measurements, confirming that the graphene film is mostly bilayer with turbostratic stacking configurations. In particular, I examined how different supporting substrates for the copper catalyst impacted the final graphene films. Since both supports

(boat and flat plate) have the same length, there is no difference in the temperature variation between them inside the CVD system. Both the flat support and the boat shaped support will have identical temperature profiles. The only difference between the two supports is their shape, which will influence the gas flow dynamics. Therefore the poor growth of graphene at the edge of the films when using the boat is purely due to the turbulence of the gas flow, which is not present for the even support. For the graphene films grown under turbulent local gas conditions (ceramic boat), it is found that the quality in the centre is better than the edges and corners in terms of uniformity and continuity. The graphene film grown under more uniform local gas flow (ceramic plate) and is found to be much more homogeneous according to sheet resistance and transparency measurements. It is anticipated that this study will facilitate the development of preparing large-area uniform bilayer graphene films and allow the mass-production of TCEs for commercial applications in flexible and wearable electronics.

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## Chapter 5

### *Hydrogen Addition for Centimetre-Sized Monolayer Tungsten Disulphide Continuous Films by Chemical Vapour Deposition*

After realising the synthesis of bilayer graphene films and having insights into some key parameters on the material quality, my next target is to establish practical growth strategies for the production of large area, high quality monolayer  $WS_2$  continuous films. Hydrogen gas is newly brought to the double-furnace system and the film quality is then evaluated by fabricating a  $WS_2$  field effect transistor (FET).

#### 5.1 Introduction

The monolayer transition metal dichalcogenides (TMDs) with the formula  $MX_2$  ( $M = W, Mo$ ;  $X = S, Se$ ) consist of a metal layer ( $Mo, W$ , etc.) sandwiched by two planes of chalcogen atoms ( $S, Se$  or  $Te$ ).<sup>1</sup> Unlike semi-metallic graphene<sup>2-7</sup> and insulating hexagonal boron nitride,<sup>8-11</sup> atomically thin two-dimensional (2D) TMDs are semiconductors bonded to neighbouring layers via weak van der Waals force with desirable direct band gaps that transition from 1 to 2 eV when their thickness is reduced from bulk to a single layer. This makes monolayer TMDs promising for applications in electronics, optoelectronics and valleytronics.<sup>12-21</sup>

Two typical members of the TMD family, tungsten disulphide ( $WS_2$ ) and molybdenum disulphide ( $MoS_2$ ), have been the focus of many studies in recent years.<sup>22-24</sup> Because of this, many methods have been explored to prepare ultrathin 2D  $WS_2$ , including mechanical exfoliation,<sup>25-27</sup> chemically assisted exfoliation<sup>28</sup>, pulsed laser deposition<sup>13</sup> and chemical vapour deposition (CVD).<sup>29,30</sup> The top-down exfoliation methods can normally produce high quality crystals but only allow limited control over domain size, shape and coverage. The deposition of large area  $WS_2$  films is essential for further application and commercialization. Therefore, the bottom-up growth of  $WS_2$  samples via the CVD approach has drawn great attention and has become the most cost effective and reliable mean to produce large-area high quality  $WS_2$  thin films.<sup>29-34</sup>

Prior work has shown that large-area  $WS_2$  sheets from single to few-layer thickness can be formed on silicon wafers that have a surface oxide layer ( $SiO_2/Si$ ) using thermal reduction-sulfurization method,<sup>30</sup> and a wavelength sensitive photodetector can be fabricated based on the few-layer  $WS_2$  films grown by the same method using a quartz substrate.<sup>34</sup> Hussain *et al.*<sup>31</sup> presented a similar preparation technique via sulfurization of a RF-sputtered tungsten oxide ( $WO_3$ ) thin film to produce continuous and wafer-scale uniform  $WS_2$  layers. The photoresponse was also investigated in the report based on few-layer samples, indicating that the photosensitivity was linearly dependent on bias voltage.<sup>31</sup> Kang *et al.*<sup>32</sup> also achieved polycrystalline  $WS_2$  monolayer up to  $mm^2$  using two stacked substrates facing each other, one for the tungsten source and the other for growth. They also studied the effect of hydrogen ( $H_2$ ) concentration on the growth results, including crystal size, nucleation density and growth formation.<sup>32</sup> The methods described above are appropriate for growing large-area continuous  $WS_2$  films. However, the grain size of the film is mostly limited to nanoscale, which will result in poor device performance. In addition, all the reactions were carried out under vacuum or low pressure condition with a growth duration of  $\sim 30$  min, which hindered

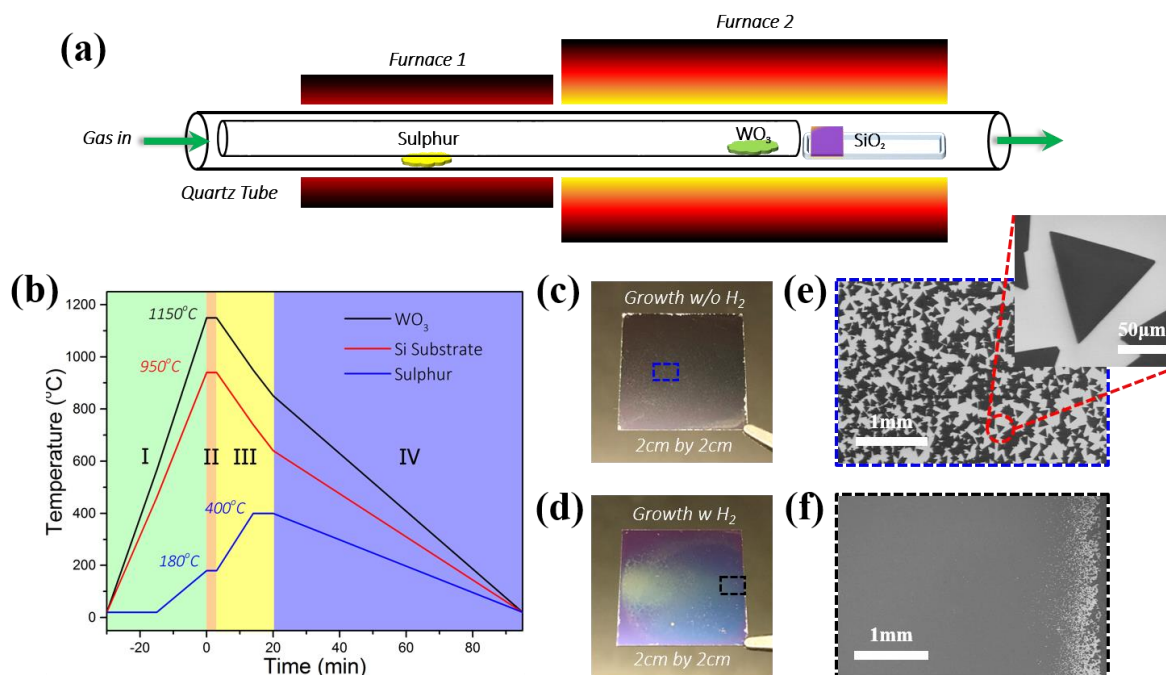
the viability of these processes for mass-production of  $WS_2$ . To increase grain size, shorten the growth time, and alleviate the difficulty of CVD setup, perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) has been introduced to grow large-area ( $\sim mm^2$ ) monolayer  $WS_2$  films in 10 min by ambient pressure chemical vapour deposition (APCVD).<sup>33,35</sup> However, the seeding promoter may produce impurities on the surface, and it is challenging to achieve full coverage without multilayer regions. Another approach demonstrated by Yun *et al.*<sup>12</sup> is to use an Au substrate instead of an insulating substrate. It has been reported that centimetre-sized  $WS_2$  film can be grown on Au in 15 min via APCVD; however, special treatment is required for preparing Au substrates, and the compulsory transfer of the film after growth may generate cracks, which will slow and hinder device fabrication.<sup>12,36</sup>

In this work, I demonstrate how hydrogen addition can be used to improve growth conditions within APCVD to achieve monolayer  $WS_2$  continuous films exhibiting  $cm^2$  coverage, grown on insulating substrates ( $SiO_2/Si$ ) using separately introduced solid powder precursors (S and  $WO_3$ ) by APCVD. By using a two-furnace system, I am able to separately control the S and  $WO_3$  precursor introduction and fine-tune reaction parameters with incorporated  $H_2$  gas flow to achieve uniform thin monolayer films. The quality and uniformity of the fully covered continuous films were then characterized by optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), photoluminescence (PL) spectroscopy and Raman spectroscopy. Moreover, I demonstrated the fabrication and performance of a  $WS_2$  field effect transistor (FET).

## 5.2 Results and Discussion

**Figure 5.1(a)** shows a schematic illustration of the standard experimental setup for growing monolayer  $WS_2$  samples.<sup>37-39</sup> The growth was conducted within a 1 inch diameter quartz tube under ambient pressure with a mixed flow of  $H_2$  and Ar. Sulphur powders was loaded

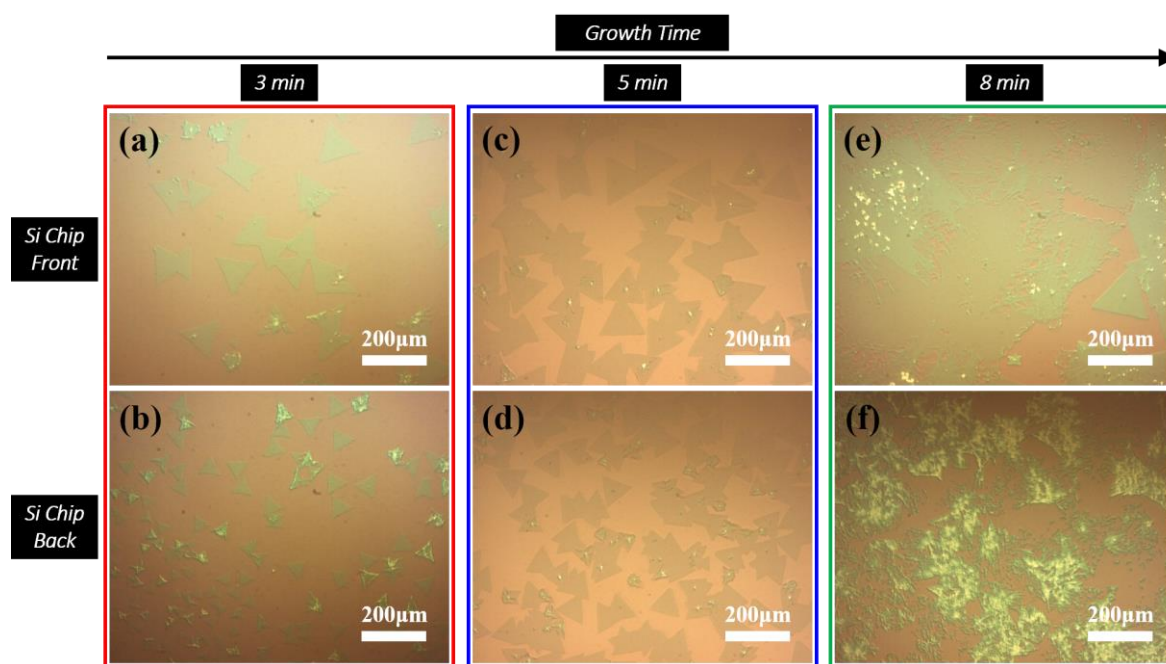
at the centre of low temperature furnace (furnace 1) in the outer 1 inch quartz tube, while  $WO_3$  powders were placed at the centre of high temperature furnace (furnace 2), in an inner quartz tube with a smaller diameter of 1 cm. The 2 cm  $\times$  2 cm substrate was then placed downstream in furnace 2, about 8.5 cm away from  $WO_3$  powder. **Figure 5.1(b)** presents the temperature profiles employed for the formation of  $WS_2$  on the  $SiO_2/Si$  substrate with four steps, including ramping, growth, and sulphur purging and fast cooling. The whole system was first flushed with argon gas for 30 min, followed by a pre-introduction of S by heating the S powder up to 180 °C, which built an S-rich environment both before and during the synthesis of  $WS_2$  monolayers. The second furnace was then heated up to 1150 °C with a ramping rate of 40 °C/min. The reaction was conducted once the temperature reached 1150 °C for a short period of time with a mixed gas flow. After the abundant sulphur was purged away from the system, a fast cooling process was then applied when furnace 2 reached 850 °C. By optimizing the reaction parameters, such as the growth time, the growth temperature, the amounts of the precursors, the position of the substrate, and hydrogen to argon ( $H_2/Ar$ ) ratio, I was able to produce either monocrystalline monolayer  $WS_2$  domains or large-area continuous polycrystalline monolayer  $WS_2$  films for different purposes. **Figure 5.1(c)** and (d) present the photos of monolayer  $WS_2$  samples after growth with and without  $H_2$  addition, respectively. **Figure 5.1(e)** presents the SEM image of the blue rectangular dashed area in **Figure 5.1(c)**, showing that large triangular  $WS_2$  crystals with domain size of over 150  $\mu m$  can be deposited on  $SiO_2/Si$  substrate with optimized growth variables without the addition of  $H_2$ . As can be seen from **Figure 5.1(f)**, the SEM image of the black rectangular dashed region in **Figure 5.1(d)**, centimetre-sized continuous  $WS_2$  films can be formed when the appropriate  $H_2/Ar$  ratio was used.



**Figure 5.1. Atmospheric pressure CVD synthesis of large-area  $WS_2$  films and domains on the  $SiO_2/Si$  substrate.** (a) Schematic illustration of the CVD setup for the synthesis of  $WS_2$ . Sulphur (S) and  $WO_3$  powder were placed in a 1 inch quartz tube running through two furnace systems to provide two heating zones. (b) Temperature profiles of the substrate,  $WO_3$  and S. The growth can be divided into four steps, including (I) heating stage, (II) growth stage, (III) slow cooling and sulphur purging, followed by (IV) fast cooling. (c,d) Photos showing contrast difference between 2 cm  $\times$  2 cm  $SiO_2/Si$  substrates after CVD processes without and with  $H_2$  addition. (e) SEM image of large triangular  $WS_2$  crystals deposited on a  $SiO_2/Si$  substrate. Scale bar: 1 mm. The zoomed-in SEM image indicates that the size of a typical crystal is around 150  $\mu m$ . Inset scale bar: 50  $\mu m$ . (f) SEM image of a millimetre-sized  $WS_2$  film on  $SiO_2/Si$ . Scale bar: 1 mm.

To explore continuous  $WS_2$  films growth by APCVD, I first investigated whether it would be viable to simply extend the growth time for the previously reported synthesis procedure one of my colleagues developed for large monolayer domain growth of  $WS_2$ .<sup>37</sup> **Figure 5.2** shows the optical images of the samples on both the front and the back regions of the  $SiO_2/Si$  substrates produced using different growth times (3, 5 and 8 min). For each growth time, the  $WS_2$  domain size on the front side of the substrate is slightly larger than that on the back, and the back region was more likely to form multilayer  $WS_2$  flakes. If grown for 3 min,

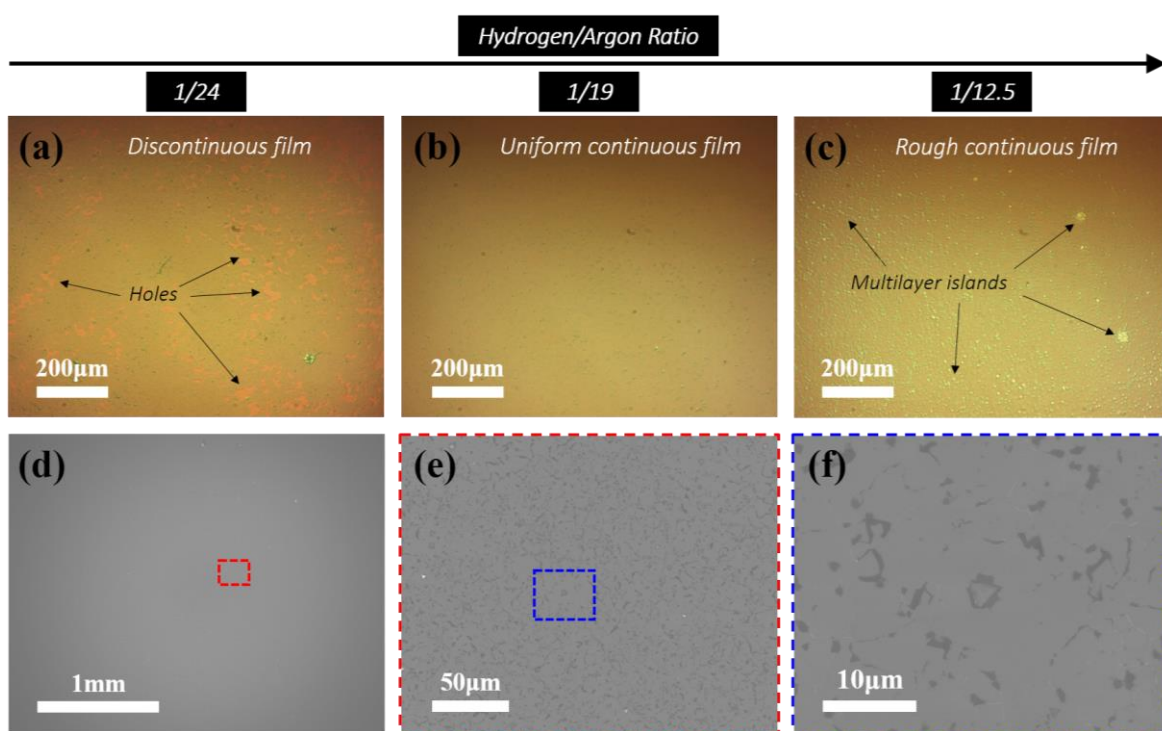
**Figure 5.2(a)** and (b), the typical domain size was about 100  $\mu m$  on the front region of the substrate and around 50  $\mu m$  on the back region. When the growth time was increased to 5 min, higher surface coverage was obtained, **Figure 5.2(c)** and (d), with larger domain size and higher nucleation density. However, increasing the growth time to 8 min led to multilayer  $WS_2$  crystals instead of a fully continuous monolayer film, **Figure 5.2(e)** and (f).



**Figure 5.2.** Optical images showing the CVD growth results as a function of growth time when **no hydrogen is used**. (a-f) Optical images of the  $WS_2$  on both the front and back side of the  $SiO_2/Si$  substrate after growth times of 3, 5 and 8 min, respectively. Scale bar: 200  $\mu m$ . The substrate used for 5 min growth has an oxide layer of 90 nm thickness, while the other two have 300 nm oxide layers, causing the difference in contrast.

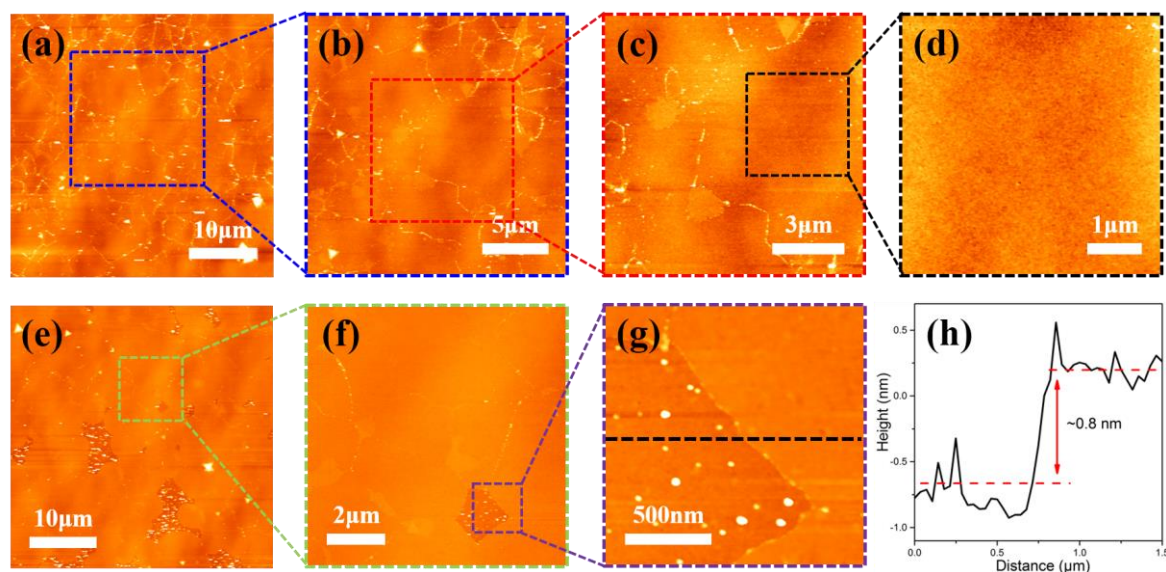
**Figure 5.3** shows the impact adding  $H_2$  has on the APCVD growth of  $WS_2$ . The role of  $H_2$  during the reaction is to increase the reaction speed and reduce damage from oxidization. The growth time was set to 3 min for all growths involving  $H_2$ . **Figure 5.3(a-c)** show the change in morphology of  $WS_2$  films produced using different  $H_2/Ar$  ratios (1:24, 1:19, 1:12.5). A semi-continuous  $WS_2$  film with holes, **Figure 5.3(a)**, can be produced with less

$H_2$  added, while a rougher continuous film with several multilayer islands (**Figure 5.3(c)**) is fabricated when the flow of  $H_2$  is increased during the growth. The optimized  $H_2/Ar$  ratio ( $\sim 1:19$ ) was between these values, leading to fully continuous  $WS_2$  films of high uniformity, **Figure 5.3(b)**. **Figure 5.3(d)** presents the SEM image of a typical region of the sample grown with a  $H_2/Ar$  ratio of 1:19, which indicates full coverage and high uniformity. **Figure 5.3(e)** and (f) show the magnified high-resolution SEM images of the red dashed rectangle in **Figure 5.3(d)** and the blue dashed rectangle in **Figure 5.3(e)**, respectively. The  $WS_2$  film is highly uniform over the whole area under SEM observation with up to 95% monolayer and only a small amount of multilayer regions.



**Figure 5.3. Surface morphology of  $WS_2$  films with different  $H_2/Ar$  flow rate during the 3 min growth.** (a-c) Optical images showing the result of growths using different  $H_2/Ar$  ratios, showing a semi-continuous film, a uniform continuous film and a rough continuous film, respectively. Scale bar: 200  $\mu m$ . (d) SEM images of an as-grown  $WS_2$  film with a  $H_2/Ar$  ratio of 1:19 during growth. Scale bar: 1 mm. (e,f) Zoomed-in SEM images chosen from the selected area, red dashed region in (d) and blue dashed region in (e), respectively, showing a continuous film with small multilayer islands. Scale bar represents 50  $\mu m$  in (e) and 10  $\mu m$  in (f).

The roughness and thickness of the fabricated continuous  $WS_2$  films were characterized by AFM. **Figure 5.4(a)** shows the surface morphology of a typical continuous region and **Figure 5.4(b)** and (c) are the zoomed-in images chosen from the selected areas, which show grain boundaries and some nucleation sites on the surface. The further zoomed-in image, **Figure 5.4(d)**, shows a uniform monolayer thickness and small surface roughness of  $\sim 0.2$  nm. At the edge of the sample, some discontinuous regions can be found. **Figure 5.4(e-g)** show AFM image of a typical area near the edge and the zoomed-in images obtained from the corresponding regions. Besides grain boundaries and nucleation sites, some holes in the  $WS_2$  film were present. **Figure 5.4(h)** presents the height profile of the black dashed line in **Figure 5.4(g)**, which shows that the height difference between the film and the substrate is about 0.8 nm, which confirms monolayer  $WS_2$ .<sup>40</sup>

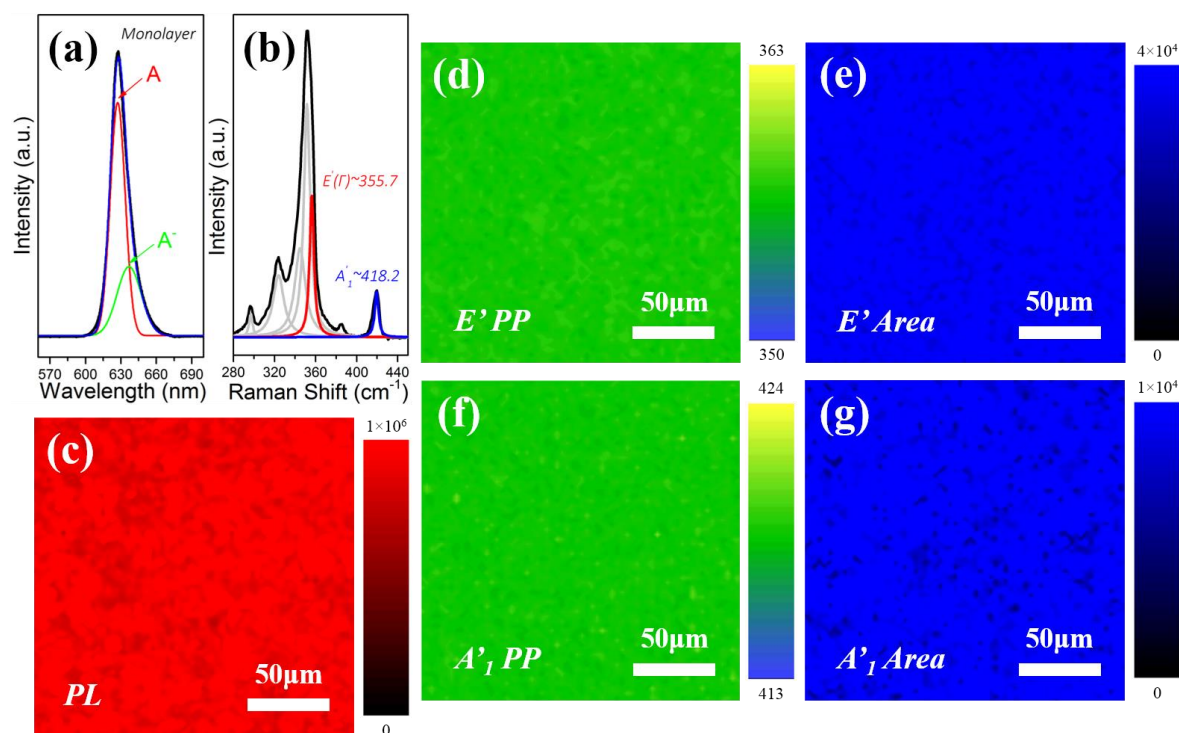


**Figure 5.4. AFM measurement of as-grown  $WS_2$  films on  $SiO_2/Si$ .** (a-d) AFM image in topological mode of a fully merged  $WS_2$  region and zoomed-in images chosen from the selected area, showing very uniform surface. Scale bar represents 10  $\mu m$  in (a), 5  $\mu m$  in (b), 3  $\mu m$  in (c), and 1  $\mu m$  in (d). (e-g) AFM image of a typical growth region near the edge of substrate and zoomed-in images obtained from the same area, showing some holes and wrinkles. Scale bar represents 10  $\mu m$  in (e), 2  $\mu m$  in (f) and 500 nm in (g). (h) Height profile taken from the black dashed line in (g), showing that the thickness of  $WS_2$  film is about 0.8 nm.

The continuous CVD  $WS_2$  film was further investigated using PL and Raman spectroscopy with a 532 nm excitation to determine the layer number and quality. **Figure 5.5(a)** shows a strong PL peak between 560 and 700 nm, typical for a CVD grown monolayer  $WS_2$  sample. The PL signal was then deconvoluted into two separate peaks by fitting Gaussian curves, which correspond to the exciton emission (A) and negative trion emission ( $A^-$ ). The peak position for A is 627.3 nm, a direct band gap of  $\sim 1.98$  eV, which falls in the range of reported PL peak positions for monolayer  $WS_2$  samples with strain from the CVD cooling process.<sup>27,39</sup> The peak position for  $A^-$  is 636.9 nm, leading to a binding energy of  $\sim 30$  meV for my continuous  $WS_2$  film, which is also in agreement with the values ranging from 20–40 meV reported previously.<sup>41,42</sup> The integrated PL intensity ratio of exciton to trion ( $A/A^-$ ) was used to determine the doping level of the  $WS_2$ , and was measured to be 2.1, indicative of high quality material. Raman spectroscopy was also used to examine the quality of the  $WS_2$  film. A Raman spectrum taken from a typical spot on my continuous monolayer  $WS_2$  film was fitted by multiple Lorentzian peaks, **Figure 5.5(b)**, with the peak positions for in-plane ( $E'$ ) and out-of-plane ( $A'_1$ ) vibration modes at 355.7 and 418.2  $cm^{-1}$ , respectively. The frequency difference between  $E'$  and  $A'_1$  mode is shown to be  $\sim 62.5$   $cm^{-1}$ , which agrees with the previous reports.<sup>29,43-45</sup>

In addition, PL and Raman mappings were used to evaluate the areal uniformity, **Figure 5.5(c-g)**. **Figure 5.5(c)** presents the PL integrated intensity mapping of a typical region of the sample with area of  $200\ \mu m \times 200\ \mu m$ , which indicates a high uniformity of the monolayer  $WS_2$  film. **Figure 5.5(d-g)** show the Raman mappings obtained from the same region as the PL mapping, including peak position and integrated intensity of the  $WS_2$   $E'$  and  $A'_1$  modes. After fitted with Lorentzian curves, Raman spectra ranging between 280 to 440  $cm^{-1}$  can be deconvoluted into six separate peaks, two of which correspond to  $WS_2$   $E'$  and  $A'_1$  modes. As shown in **Figure 5.5(d)** and (f), the average peak positions for  $E'$  and  $A'_1$

modes are  $357.0$  and  $418.7\text{ cm}^{-1}$ , respectively, which indicate high quality and uniformity of the film produced. In addition, **Figure 5.5**(e) and (g) show the Raman maps for the integrated intensity of  $E'$  and  $A'_1$  modes, respectively, which also confirm a homogeneous monolayer.



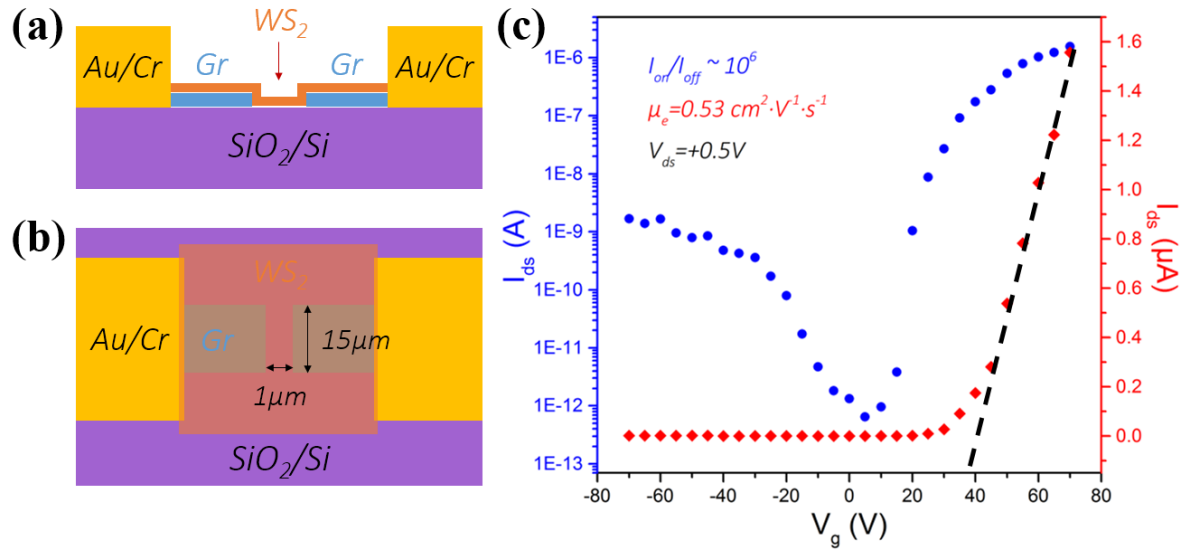
**Figure 5.5. Raman and PL measurements of as-grown  $WS_2$  films on  $SiO_2/Si$ .** (a) PL and (b) Raman spectrum of the as-grown sample, which confirm monolayer  $WS_2$ . (c-g) PL and Raman maps of a typical area ( $200\mu m \times 200\mu m$ ) of the  $WS_2$  continuous film, showing (c) PL integrated intensity, (d)  $E'$  peak position and (e) integrated intensity as well as (f)  $A'_1$  peak position and (g) integrated intensity, indicating high uniformity. Scale bar:  $50\mu m$ .

To evaluate the electrical properties of my monolayer  $WS_2$  continuous film, field effect transistors were fabricated by the transfer of polycrystalline monolayer  $WS_2$  film onto the  $300\text{ nm } SiO_2/Si$  substrate prepatterned with graphene electrodes. **Figure 5.6**(a) and (b) illustrate the side and top views of the FET based on my monolayer  $WS_2$  continuous film, showing a channel length of  $1\mu m$  and a channel width of  $15\mu m$ . The electrical properties of the  $WS_2$  FET were measured in air under ambient pressure within a  $\pm 70\text{ V}$  gate bias,

which was applied through a heavily p-doped silicon underneath the 300 nm SiO<sub>2</sub> dielectric. A typical gate sweep measurement, the red curve in **Figure 5-6(c)**, shows a well-defined N-typed transistor with a threshold voltage ( $V_{th}$ ) of  $\sim 35$  V. Then the field-effect electron mobility ( $\mu_{FE}$ ) can be extracted using **Equation 5.1**.

$$\mu_{FE} = \frac{dI_{ds}}{dV_g} \cdot \frac{L}{w} \cdot \frac{1}{V_{ds}} \cdot \frac{1}{C_{ox}}, \quad \text{Equation 5.1}$$

where  $\frac{dI_{ds}}{dV_g}$  is the transconductance,  $L$  is the channel length,  $w$  is the channel width,  $V_{ds}$  is the applied drain bias and  $C_{ox}$  is the gate capacitance.<sup>40,46</sup>



**Figure 5.6. Electrical properties of monolayer WS<sub>2</sub> continuous film.** (a) Schematic side view of a FET based on monolayer WS<sub>2</sub> continuous film with graphene electrodes. (b) Schematic top view of the WS<sub>2</sub> FET with a channel length of 1 μm and a channel width of 15 μm. (c) Field effect characteristics of the as-grown monolayer WS<sub>2</sub> FET.  $I_{ds}$ - $V_g$  (red curve) shows the N-type characteristics of the device with a threshold voltage  $V_{th}$  of  $\sim 35$  V. The on/off ratio of output current (blue curve) is  $\sim 10^6$  at room temperature.

This WS<sub>2</sub> FET shows a FET mobility of  $0.53 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at room temperature, which is amongst the best reported for CVD-grown polycrystalline WS<sub>2</sub> monolayers measured using

similar back gated doped Si electrodes on  $SiO_2$  surfaces,<sup>47,48</sup> but still falls behind those FETs based on single crystalline monolayer domains or few-layer samples.<sup>12,49,50</sup> In addition, at an applied drain bias of 0.5 V, an on/off ratio of  $\sim 10^6$  and an subthreshold swing of 2.05 V per decade were obtained, which also agree with the previous works.<sup>48-55</sup>

**Figure 5.1–5.5** indicate that the introduction of  $H_2$  to the double-furnace system produces substantially different growth morphologies compared to the isolated  $WS_2$  flakes synthesized using the same experimental conditions but without  $H_2$ . Without  $H_2$  addition, multilayer  $WS_2$  islands form before a fully-merged continuous monolayer film is complete. The addition of  $H_2$  during synthesis may reduce the  $WO_3$  precursor more effectively, leading to a higher nucleation density and faster completion of the continuous films before secondary layers begin to form.<sup>33,56</sup> It is worth mentioning that the growth with  $H_2$  usually results in a smaller domain size than that without  $H_2$ , resulting in an increased number of grain boundaries on the surface. This is similar to a prior report, where domain size decreased with  $H_2$  addition.<sup>50</sup> The electrical properties of the FET devices based on the continuous films, **Figure 5.6**, are slightly better than those obtained using the isolated  $WS_2$  domains.<sup>51</sup> This indicates that  $H_2$  addition may also aid in removing carbonaceous species and reducing the amount of  $WS_2$  oxidation during growth, and therefore lead to better quality  $WS_2$ .<sup>32,50</sup>

### 5.3 Conclusion

In summary, I present a scalable, rapid, and bottom-up approach for growing large-area monolayer  $WS_2$  continuous films using APCVD. Without introducing  $H_2$  to the double-furnace system, I am able to grow separately distributed  $WS_2$  flakes on  $SiO_2/Si$  with domain sizes of at least 150  $\mu m$  when the growth time was increased from 3 to 5 min. Further, increasing the growth time to 8 min led to vertical growth by fabricating multilayers instead of a fully merged monolayer film. The introduction of  $H_2$  allows the rapid formation of  $WS_2$

continuous films before the emergence of multilayer islands. With an optimized  $H_2/Ar$  ratio and short growth time (3 min), centimetre-scale continuous  $WS_2$  films can be directly grown on silicon wafers with an oxide surface, indicating high efficiency of this APCVD system. The results from optical microscopy, SEM, AFM, PL spectroscopy, Raman spectroscopy and FETs measurements have confirmed its high quality and uniformity. This rapid APCVD growth method utilizing simple and frequently used powder precursors will facilitate the further development of wafer scale optoelectronic devices based on all CVD-grown 2D materials.

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## Chapter 6

### *Photoluminescence Segmentation within Individual Hexagonal Monolayer Tungsten Disulphide Domains Grown by Chemical Vapour Deposition*

Following the success of producing either monolayer WS<sub>2</sub> continuous films or separately distributed large domains, I further investigate the optical and vibrational properties of this novel material using Raman and photoluminescence (PL) spectroscopies. An interesting and unusual fact come into my view that hexagonal domains of monolayer WS<sub>2</sub> have discrete segmentation in their PL emission intensity, forming symmetric patterns with alternating bright and dark regions. A wide range of characterisation tools are used in order to draw a possible mechanism behind it.

#### 6.1 Introduction

With the rapid development of two dimensional (2D) materials such as metallic graphene<sup>1-3</sup> and insulating hexagonal boron nitride,<sup>4-7</sup> 2D transition metal dichalcogenides (TMDs) have recently attracted interest because of their unique semiconducting properties.<sup>8-15</sup> Monolayer tungsten disulphide (WS<sub>2</sub>) and molybdenum disulphide (MoS<sub>2</sub>) are TMDs with

a direct band gap in the red spectral region, which can significantly expand the potential of optoelectronic devices comprising all 2D materials.<sup>16-23</sup>

Recently, the properties of monolayer MoS<sub>2</sub> have been studied in mechanically exfoliated, chemically derived, physical vapour deposition grown, and chemical vapour deposition (CVD) grown samples.<sup>24-28</sup> In terms of electronic properties, high carrier mobilities ( $\sim 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and large excitonic binding energies can give rise to photoluminescence (PL) spectra that are sensitive to many-body interactions.<sup>29-31</sup> The PL of MoS<sub>2</sub> can be dramatically affected by surface functionalization using physical adsorbates or solvents, substitutional doping, and electrical gating.<sup>32-34</sup> It is noteworthy that monolayer WS<sub>2</sub> has a significantly stronger PL signal than single-layer MoS<sub>2</sub>, indicative of better prospects for optoelectronic applications.<sup>35-38</sup>

Mechanically exfoliated monolayer WS<sub>2</sub> from synthetic bulk crystals typically has uniform PL across the sample.<sup>36,37</sup> In addition to the mechanical exfoliation method, many groups around the world have been working on the synthesis of monolayer WS<sub>2</sub> by powder vaporization or chemical vapour transport. Prior work has shown that monolayer WS<sub>2</sub> triangles grown by vaporizing sulphur powders on WO<sub>x</sub> thin films can exhibit non-uniform and uniform PL.<sup>38-40</sup> Gutierrez *et al.*<sup>38</sup> showed that the edges of WS<sub>2</sub> monolayers exhibited PL signals with higher intensity, around 25 times stronger than that at the platelet centre. The structure and chemical composition of the platelet edges were thought to be critical for PL enhancement.<sup>38</sup> Peimyoo *et al.*<sup>39</sup> also found the same phenomenon and claimed that the darkening and the blue-shift of PL are caused by the as-grown structural defects and the defect-induced negative doping. Kim *et al.*<sup>40</sup> recently reported that the intense PL emission and the preferential formation of biexcitons at the edges and grain boundaries of monolayer WS<sub>2</sub> were attributed to larger population of charge carriers caused by the excessive

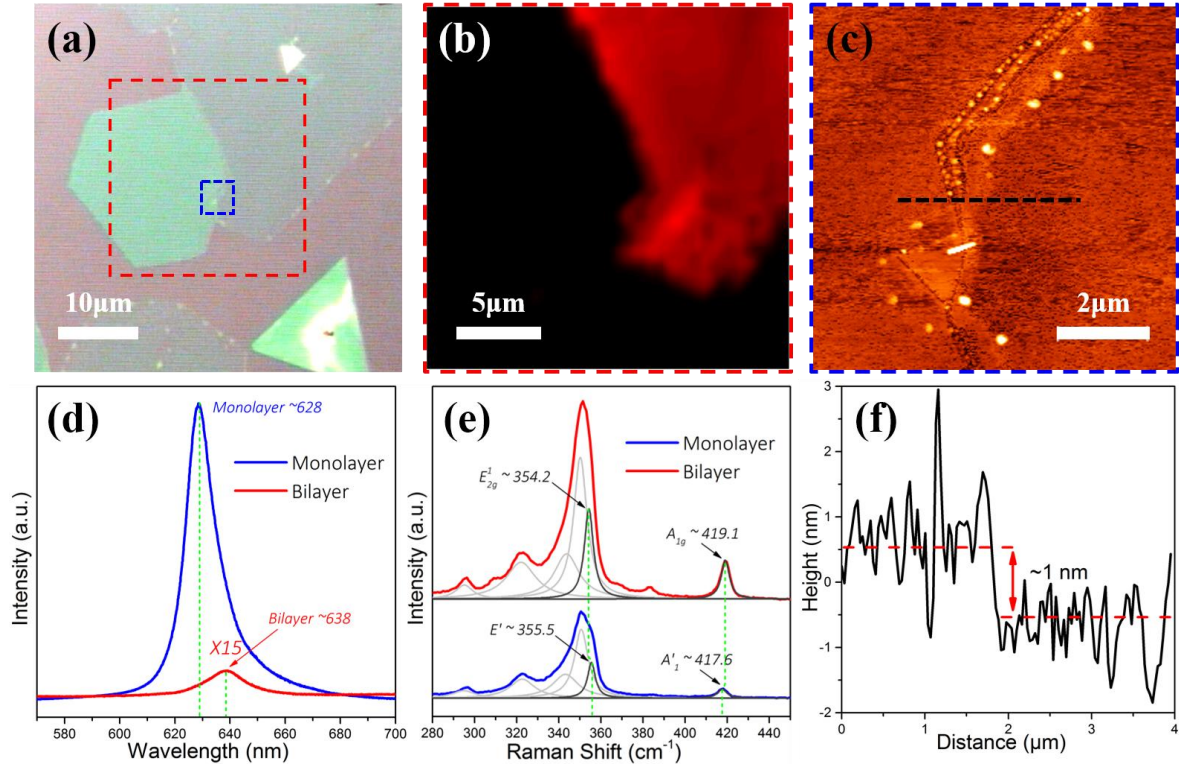
incorporation of growth promoters during CVD. Zhang *et al.*<sup>41</sup> recently reported a symmetric structure in vapour deposition fabricated MoS<sub>2</sub> monolayers with symmetrical local bilayer stacking. Raman spectroscopy indicated that the uniaxial intralayer strain originated from finite boundary and lattice deformation. These results show that uniformity in the PL properties of synthetic grown TMDs varies and needs to be understood further to ensure its role in opto-electronics is adequately described.

Here, I study 2D spatial variations of PL within CVD grown hexagonal monolayer WS<sub>2</sub> crystals grown on silicon substrates with a 300nm oxide layer (SiO<sub>2</sub>/Si) using powder precursors.<sup>42,43</sup> Interestingly, the PL emission in the hexagonal domains of WS<sub>2</sub> exhibits segmented variations associated with symmetrically distributed structural variations arising during growth. Optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), PL spectroscopy, Raman spectroscopy, and energy dispersive X-ray spectroscopy (EDX) were all used to characterize the WS<sub>2</sub> monolayers with various shapes in order to elucidate the connection between the structure and PL.

## 6.2 Results and Discussion

Monolayer and bilayer WS<sub>2</sub> can be distinguished not only by using PL and Raman spectroscopy but also by the contrast difference observed under an optical microscope, **Figure 6.1**. **Figure 6.1(a)** presents a region covered by both bilayer and monolayer WS<sub>2</sub>. **Figure 6.1(c)** and (f) show the AFM measurement of the blue dashed region in **Figure 6.1(a)**, demonstrating the thickness between monolayer and bilayer WS<sub>2</sub> is ~1.0 nm, indicating the capability of thickness measurement in nanoscale. As can be seen from **Figure 6.1(d)**, under the same excitation laser power and CCD acquisition time, the PL intensity from the monolayer is about 150 times stronger than that from the bilayer region, due to the emergence of indirect band gap transitions in bilayer WS<sub>2</sub> and the direct band gap transition

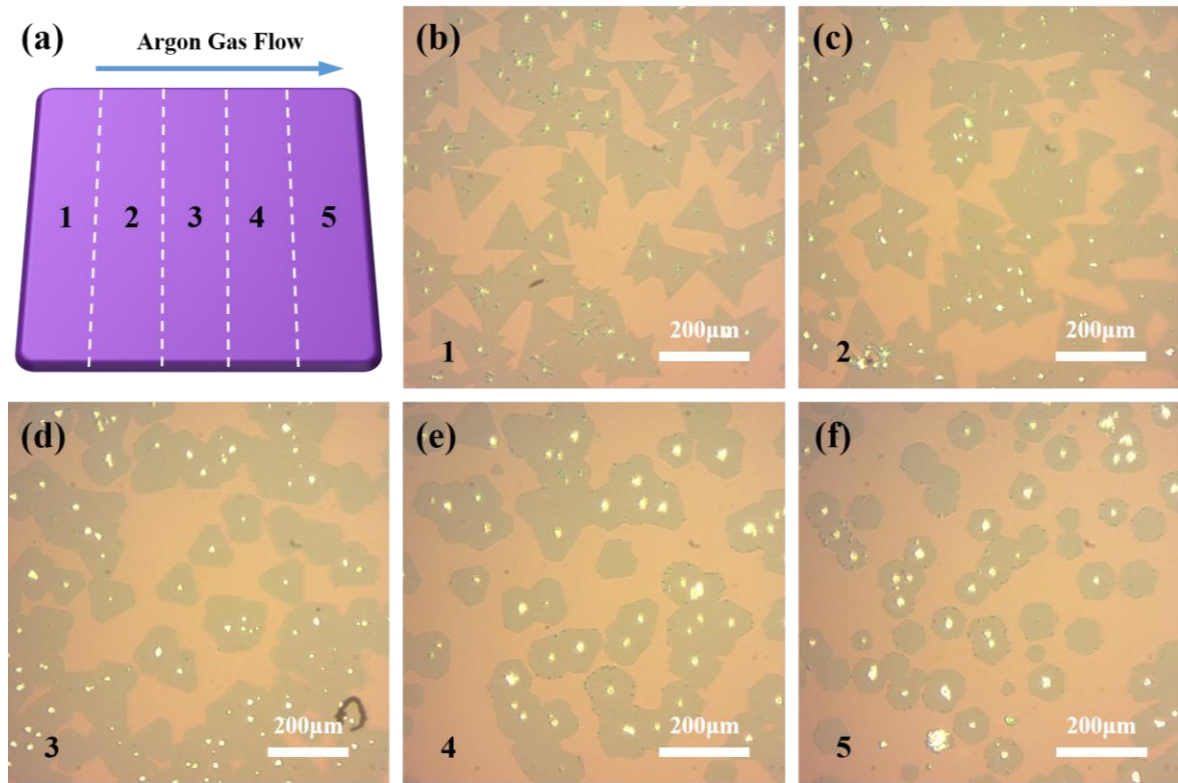
for monolayer WS<sub>2</sub>. There is a 10 nm redshift of the PL Peak position found for bilayer WS<sub>2</sub> compared with monolayer sample, which is in agreement with other literature results.<sup>36-38</sup>



**Figure 6.1. Identification of monolayer and bilayer WS<sub>2</sub>.** (a) Optical image of an area covered with both bilayer and monolayer WS<sub>2</sub>. Light pink is the bare substrate and light green represents monolayer WS<sub>2</sub>. Scale bar: 10 μm. (b) PL mapping obtained from the red dashed region in (a). Scale bar: 5 μm. (c) AFM topological mapping of the blue dashed square in (a). Scale bar: 2 μm. (d) PL and (e) Raman spectra of monolayer (blue line) and bilayer (red line) WS<sub>2</sub> on SiO<sub>2</sub>/Si, respectively. (f) Corresponding height profile taken across the black dashed line in (c).

**Figure 6.1(b)** is the PL mapping of the red dashed area in **Figure 6.1(a)**, confirming that integrated intensity of monolayer WS<sub>2</sub> is much stronger than that obtained from bilayer. Raman spectroscopy can also help in determining monolayer from bilayer, as shown in **Figure 6.1(e)**. The blue line represents the Raman spectrum from monolayer WS<sub>2</sub>. Curve fitting using multiple Lorentzian distributions was performed to extract the peak positions at 355.5 and 417.6 cm<sup>-1</sup> in single-layer WS<sub>2</sub> for in-plane (E') and out-of-plane vibration mode

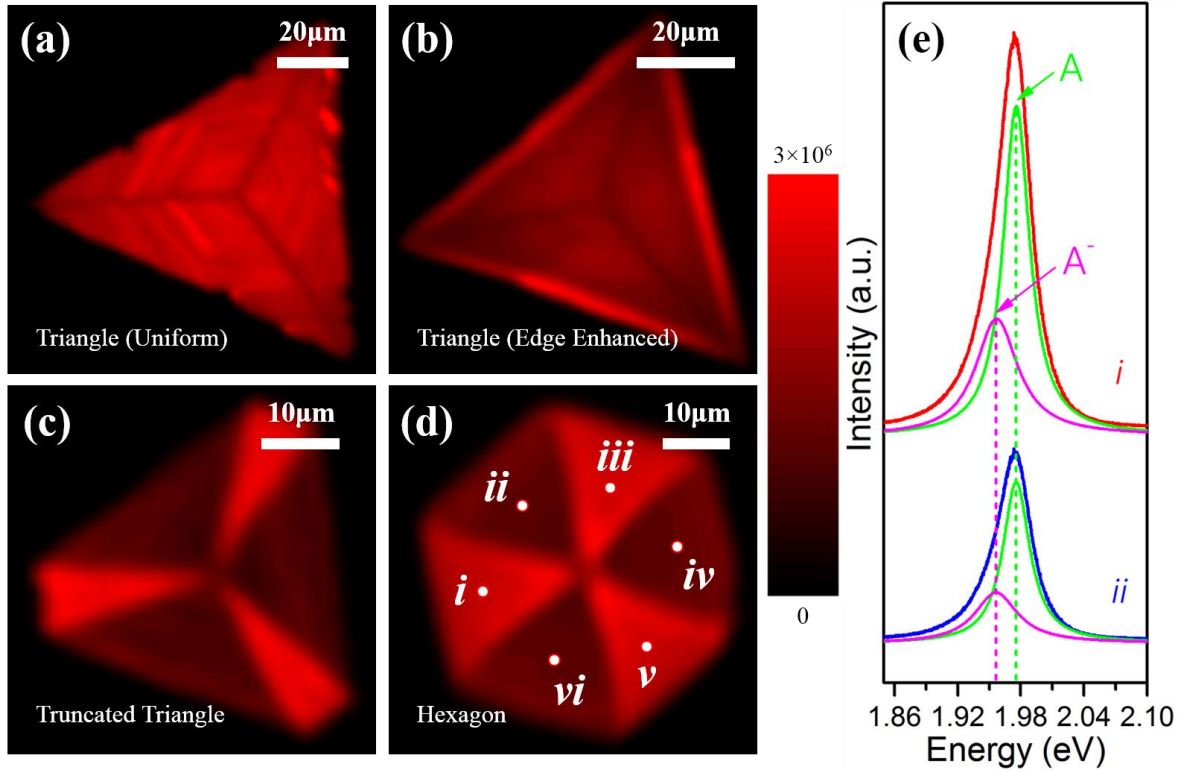
(A<sub>1</sub>') modes, respectively. Bilayer WS<sub>2</sub> has a slightly different Raman spectrum (red line), with in-plane vibration mode (E<sub>2g</sub><sup>1</sup>) blue-shifting to 354.2 cm<sup>-1</sup> and out-of-plane vibration mode (A<sub>1g</sub>) red-shifting to 419.1 cm<sup>-1</sup>, consistent with the previously reported literatures.<sup>15</sup> Prior work on MoS<sub>2</sub> monolayers grown by CVD has shown that the shape variation from triangular to hexagon is driven by the relative stoichiometry.<sup>28,44</sup> Similar shape evolution has been found in my CVD-grown WS<sub>2</sub> samples, changing from triangles to hexagons along the gas flow direction, **Figure 6.2**.



**Figure 6.2. Optical images of WS<sub>2</sub> shape distribution.** (a) Schematic illustration showing the spatial sectioning of the growth substrate into five sections along the gas flow direction. The size of the substrate is 2 × 2 cm. (b-f) The corresponding optical images from the centre of each section, respectively. Each section of sections 2–4 has a width of 2–3 mm, while sections 1 and 5 have a width of ~5 mm. Scale bar: 200 μm.

**Figure 6.3** shows the maps of the integrated PL signal for monolayer WS<sub>2</sub> with different geometrical shapes. For monolayer WS<sub>2</sub> triangles, two different PL spatial patterns have

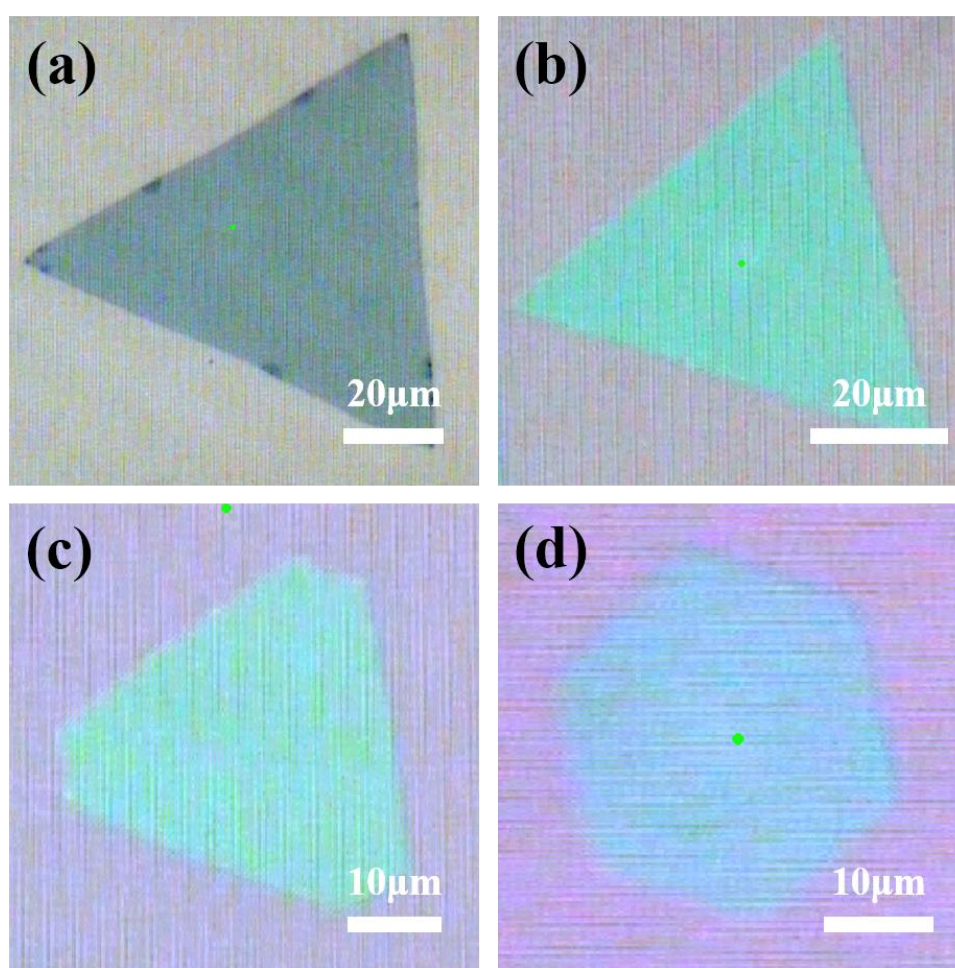
been previously reported, one with uniform PL distribution and the other with edge-enhanced PL.<sup>38-40</sup> The reduction in PL intensity and its blue-shift in spectral position were associated with as-grown structural defects and defect-induced negatively charged doping.<sup>39</sup>



**Figure 6.3. Maps of the integrated PL signals for monolayer WS<sub>2</sub> crystals with different geometric shapes.** PL mappings of (a) uniform triangular, (b) edge-enhanced triangular, (c) truncated triangular, and (d) hexagonal monolayer WS<sub>2</sub> domains. Scale bar: 20  $\mu\text{m}$  in (a,b) and 10  $\mu\text{m}$  in (c,d). (e) Corresponding PL spectra of the designated regions in (d). The two representative spectra were fitted with two Lorentzian peaks representing exciton emission (green) and negative trion emission (magenta).

**Figure 6.3(a)** and **(b)** show that these two types of triangles are also found in my WS<sub>2</sub> samples. The edges of WS<sub>2</sub> monolayers exhibit PL signals with higher intensity, around 2.5 times stronger than that at the centre. According to the previous report, PL enhancement is due to the different structure and chemical composition of the platelet edges relative to the centre.<sup>38</sup> For non-triangular WS<sub>2</sub> domains, I observed patterns inside of the monocystal, as

shown in **Figure 6.3(c)** and (d). Because of the low local concentration of sulphur during the growth, some of the WS<sub>2</sub> crystals in the centre of the substrate were truncated or hexagonal in shape. Examination using optical microscopy shows that they have the same monolayer contrast, indicating that the PL change is not from an increase in the layer number, **Figure 6.4**. **Figure 6.4** presents the optical images of monolayer WS<sub>2</sub> in different shapes. They all look very uniform under optical microscope and the contrast indicates monolayer WS<sub>2</sub> according to PL measurement.



**Figure 6.4. Optical images of monolayer WS<sub>2</sub> in different shapes.** (a) Triangle (uniform). Scale bar: 20 μm. (b) Triangle (edge enhanced). Scale bar: 20 μm. (c) Truncated triangle. Scale bar: 10 μm. (d) Hexagon. Scale bar: 10 μm. Two of them were grown on Si substrate with 90 nm SiO<sub>2</sub>, while the other two were grown on 300 nm SiO<sub>2</sub>.

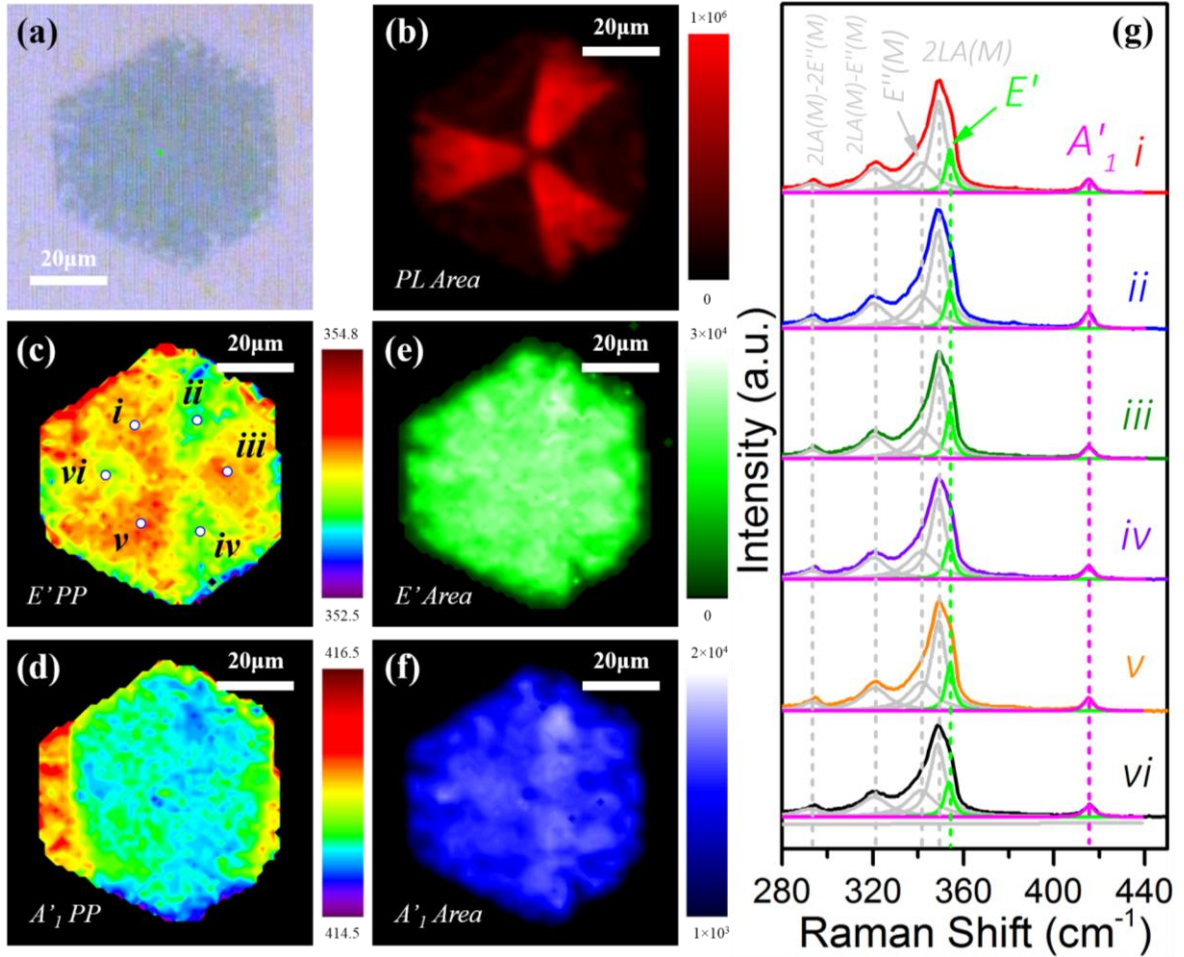
The two representative PL spectra from the marked spots in a hexagonal monolayer WS<sub>2</sub> domain in **Figure 6.3(d)** are compared in **Figure 6.3(e)**. The PL intensity in the bright areas (marked as i, iii and v in **Figure 6.3(d)**) is twice that in the dark areas (designated as ii, iv and vi in **Figure 6.3(d)**). The WS<sub>2</sub> PL signal was then deconvoluted into separate peaks by fitting two Lorentzian curves, attributed to exciton emission (A) and negative trion emission (A<sup>-</sup>).<sup>45,46</sup> The corresponding average photon energies for A and A<sup>-</sup> in the bright region are 1.976 and 1.957 eV, respectively, whereas the related average photon energies in the dark region are 1.975 and 1.956 eV, respectively, showing a difference of ~1 meV in band gap between two regions, which indicates that the bright areas have slightly more strain introduced during growth than the dark areas.<sup>47</sup> In addition, the fitting results show differences in the integrated PL intensity ratio of exciton to trion (A/A<sup>-</sup>) with an average value of 1.72 for bright area and 1.95 for dark area, indicating a higher level of doping in the bright regions of the hexagonal monolayer of WS<sub>2</sub>, **Table 6.1**.

**Table 6.1. Lorentzian curve fitting results of the PL spectra taken from the six marked spots in a hexagonal monolayer WS<sub>2</sub> as shown in Figure 6.3(d).**

| Region               | Exciton (A) |             | Trion (A <sup>-</sup> ) |             | A/A <sup>-</sup> |
|----------------------|-------------|-------------|-------------------------|-------------|------------------|
|                      | PP (eV)     | Area (a.u.) | PP (eV)                 | Area (a.u.) |                  |
| i                    | 1.976       | 239763.9    | 1.957                   | 138133.6    | 1.74             |
| ii                   | 1.975       | 115114.5    | 1.956                   | 60897.5     | 1.89             |
| iii                  | 1.976       | 238423.7    | 1.957                   | 140323.2    | 1.70             |
| iv                   | 1.975       | 106245.1    | 1.956                   | 52738.5     | 2.01             |
| v                    | 1.976       | 236639.7    | 1.957                   | 137155.7    | 1.73             |
| vi                   | 1.976       | 118042.0    | 1.956                   | 60706.5     | 1.94             |
| Average (i, iii, v)  | 1.976       | 238275.8    | 1.957                   | 138537.5    | 1.72             |
| Stdev (i, iii, v)    | 0.000       | 1567.4      | 0.000                   | 1621.9      | 0.02             |
| Average (ii, iv, vi) | 1.975       | 113133.9    | 1.956                   | 58114.2     | 1.95             |
| Stdev (ii, iv, vi)   | 0.000       | 6142.8      | 0.000                   | 4656.5      | 0.06             |

In Raman spectroscopy of monolayer WS<sub>2</sub>, the E' mode is associated with the in-plane vibration mode for WS<sub>2</sub>, whereas the A'<sub>1</sub> mode is associated with an out-of-plane vibration.

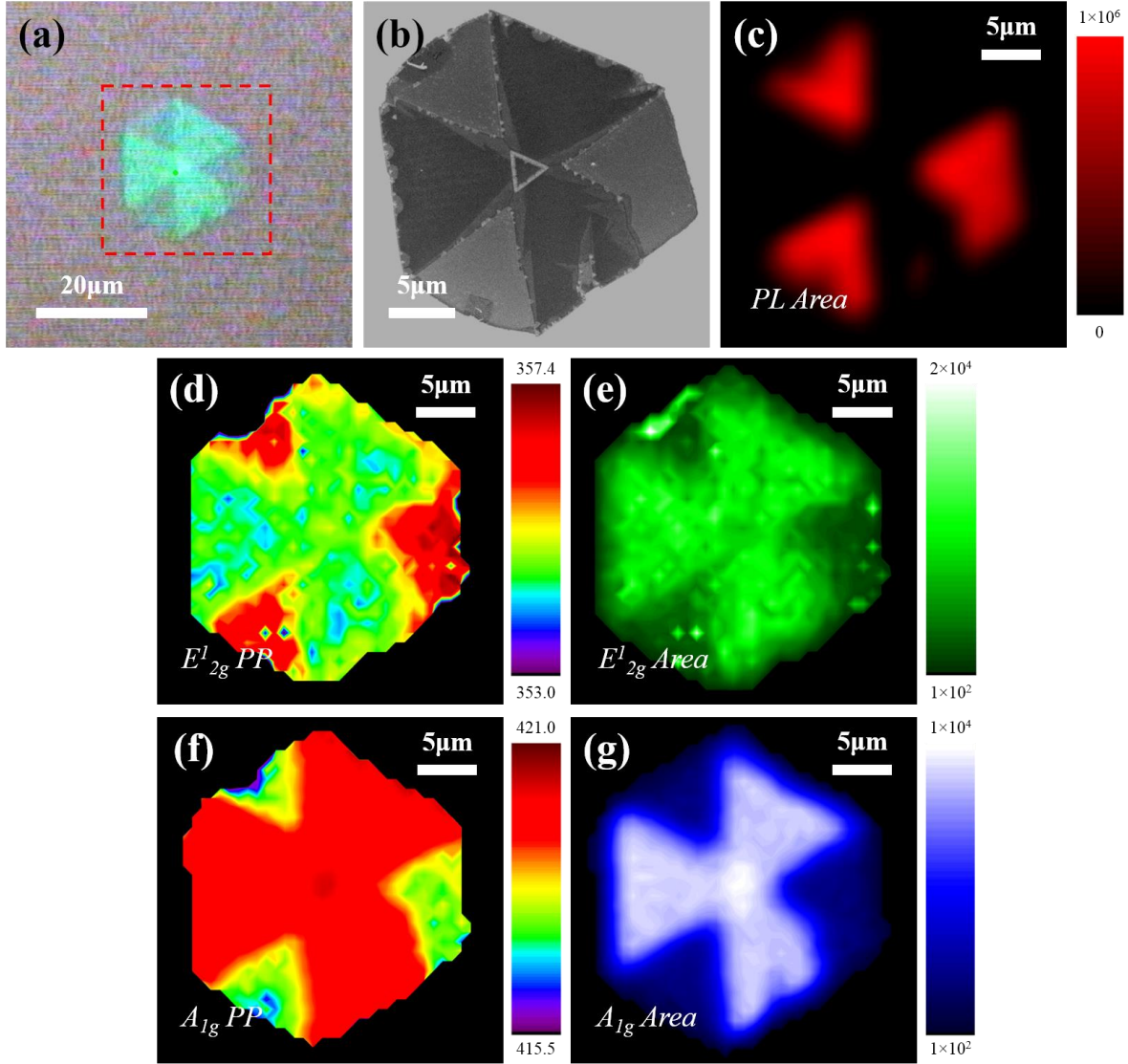
**Figure 6.5(a)** presents the optical image of a typical hexagonal monolayer WS<sub>2</sub> crystal. PL integrated intensity mapping, **Figure 6.5(b)**, shows a pattern similar to that seen in **Figure 6.3(d)**.



**Figure 6.5. Raman and PL mapping of a hexagonal monolayer WS<sub>2</sub> domain.** (a) Optical image of a hexagonal monolayer WS<sub>2</sub> crystal used for Raman mapping. The scale bar is 20  $\mu\text{m}$ . (b-f) PL and Raman mapping obtained from the hexagonal crystal shown in (a), showing (b) PL integrated intensity, (c) E' peak position and (e) integrated intensity, as well as (d) A'<sub>1</sub> peak position and (f) integrated intensity. Scale bar: 20  $\mu\text{m}$ . (g) Corresponding Raman spectra of the marked regions in (c). All spectra are fitted with six Lorentzian peaks and two peaks are highlighted, representing E' (green) and A'<sub>1</sub> (magenta) modes.

**Figure 6.5(c-f)** show the Raman mappings obtained from the same WS<sub>2</sub> domain, indicating the peak position and the integrated intensity of the WS<sub>2</sub> E' and A'<sub>1</sub> modes. As can be seen

from the Raman mappings, a small blue-shift of  $\sim 0.3 \text{ cm}^{-1}$  for the peak position of E' mode was found from the PL bright areas compared with the PL dark regions, and very small variations were found in both A'<sub>1</sub> integrated intensity and peak position mapping.



**Figure 6.6. Raman and PL mapping of hexagonal monolayer WS<sub>2</sub> with symmetric multilayer stacking.** (a) Optical image of hexagonal monolayer WS<sub>2</sub> crystal with multilayer stacking. Scale bar: 20 μm. (b) SEM image of the same crystal in (a). Scale bar: 5 μm. (c-g) PL and Raman mapping obtained from the red dashed square shown in (a), showing (c) PL integrated intensity, (d) E'<sub>2g</sub> peak position and (e) integrated intensity as well as (f) A'<sub>1g</sub> peak position and (g) integrated intensity respectively, indicating obvious distinction between monolayer and few-layer WS<sub>2</sub>. Scale bar: 5 μm.

These mappings are totally different from the Raman mappings taken from monolayer WS<sub>2</sub> with symmetric multilayer stacking, which show an obvious distinction between monolayer and few-layer WS<sub>2</sub>, **Figure 6.6**. Again, six Raman spectra were taken from the marked spots in hexagonal monolayer WS<sub>2</sub>, **Figure 6.5(c)**, for further discussion. As shown in **Figure 6.5(g)**, no obvious difference can be observed from the overall spectra. Using a Lorentzian fitting, Raman signals ranging from 280 to 440 cm<sup>-1</sup> can be deconvolved into six separate peaks, two of which can be attributed to WS<sub>2</sub> E' and A'<sub>1</sub> vibration modes.<sup>35</sup> The corresponding peak position for the A'<sub>1</sub> mode is approximately 415.2 cm<sup>-1</sup> on average for both bright and dark regions, confirming that there is no observable distinction in A'<sub>1</sub> peak positions, corresponding to the effect of inhomogeneous external electrostatic doping between PL of the bright and dark regions. In addition, the corresponding E' mode peak position is 354.0 cm<sup>-1</sup> on average for the area with lower PL intensity (marked as i, iii and v in **Figure 6.5(c)**) and 353.7 cm<sup>-1</sup> for that with higher PL intensity (designated as ii, iv and vi in **Figure 6.5(c)**), **Table 6.2**.

**Table 6.2. Lorentzian curve fitting results of the Raman spectra taken from the six marked spots in a hexagonal monolayer WS<sub>2</sub> as shown in Figure 6.5(c).**

| Region               | E'                     |             | A' <sub>1</sub>        |             |
|----------------------|------------------------|-------------|------------------------|-------------|
|                      | PP (cm <sup>-1</sup> ) | Area (a.u.) | PP (cm <sup>-1</sup> ) | Area (a.u.) |
| i                    | 354.1                  | 27638.2     | 415.1                  | 10159.3     |
| ii                   | 353.8                  | 26223.6     | 415.0                  | 12213.4     |
| iii                  | 353.9                  | 31013.5     | 415.2                  | 9808.1      |
| iv                   | 353.7                  | 25980.8     | 415.0                  | 9721.1      |
| v                    | 354.0                  | 30174.4     | 415.2                  | 9825.7      |
| vi                   | 353.6                  | 23899.0     | 415.5                  | 9998.0      |
| Average (i, iii, v)  | 354.0                  | 29608.7     | 415.2                  | 9931.0      |
| Stdev (i, iii, v)    | 0.1                    | 1757.3      | 0.0                    | 197.9       |
| Average (ii, iv, vi) | 353.7                  | 25367.8     | 415.2                  | 10644.2     |
| Stdev (ii, iv, vi)   | 0.1                    | 1277.8      | 0.3                    | 1366.0      |

To investigate if strain is the dominant mechanism in the symmetric PL segmentation, I mapped the PL of the sample before and after transferring to another SiO<sub>2</sub>/Si chip. Strain from rapid cooling during growth is released when transferred to a new substrate. No baking process was involved during the transfer process to prevent the strain being generated because of the different thermal expansion coefficients of WS<sub>2</sub> and the substrate. **Figure 6.7(a)** presents the PL integrated mapping of a typical as-grown hexagonal monolayer WS<sub>2</sub> domain. The PL intensity ratio of bright to dark area differs from sample to sample, ranging from 2 to 3. After transferring the WS<sub>2</sub> from the growth substrate to another SiO<sub>2</sub>/Si substrate, I observed an overall reduction of the PL intensity both from the bright region and the dark region. The larger reduction of PL intensity occurred for the bright region, decreasing by a factor of ~10.5, whereas the reduction was only by a factor of ~6.5 for the dark region. Although the release of the strain during the transfer process introduced impurities to the sample and degraded the quantum yield of the direct transition within monolayer WS<sub>2</sub>, I still observed the PL patterns from the mapping results, with a PL intensity ratio of ~1.2, **Figure 6.7(b)**.

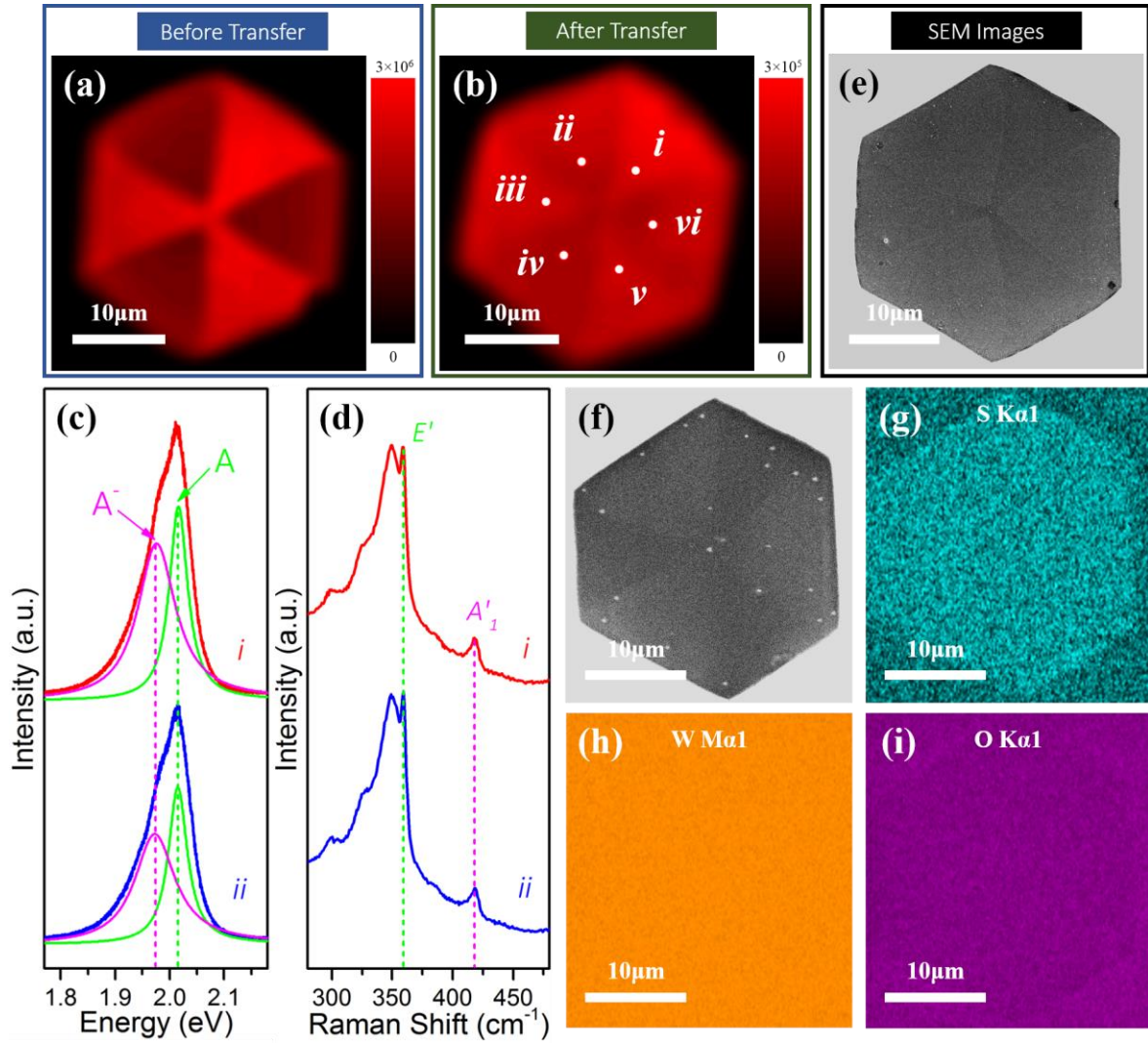
**Figure 6.7(d)** depicts the two representative Raman spectra taken from the designated points in **Figure 6.7(b)**. The peak positions of E' and A'<sub>1</sub> modes for both regions are the same, with values of 358.3 and 418.0 cm<sup>-1</sup>, respectively. The PL spectra from the six marked spots in **Figure 6.7(b)** were also plotted for further comparison. **Figure 6.7(c)** shows the two representative PL spectra, fitted with two Lorentzian peaks, correlating with A and A<sup>-</sup> respectively. The corresponding average peak positions for A and A<sup>-</sup> in the bright area (noted as i, iii and v in **Figure 6.7(b)**) are 2.015 and 1.974 eV, respectively, similar to the peak positions in the dark area (noted as ii, iv and vi in **Figure 6.7(b)**). The variation between the two regions in the peak positions for both Raman and PL spectra is negligible, confirming

that strain has been successfully released. However, the strain-free hexagonal sample still shows a difference in the  $A/A^-$  ratio, **Table 6.3**.

**Table 6.3. Lorentzian curve fitting results of the PL spectra taken from the six marked spots in a transferred hexagonal monolayer WS<sub>2</sub> as shown in Figure 6.7(b).**

| Region               | Exciton (A) |             | Trion (A <sup>-</sup> ) |             | $A/A^-$ |
|----------------------|-------------|-------------|-------------------------|-------------|---------|
|                      | PP (eV)     | Area (a.u.) | PP (eV)                 | Area (a.u.) |         |
| i                    | 2.016       | 46887.3     | 1.976                   | 81016.8     | 0.58    |
| ii                   | 2.016       | 43113.6     | 1.976                   | 65163.0     | 0.66    |
| iii                  | 2.014       | 45577.3     | 1.974                   | 79973.7     | 0.57    |
| iv                   | 2.014       | 47783.4     | 1.974                   | 61335.7     | 0.78    |
| v                    | 2.016       | 47494.3     | 1.973                   | 73174.7     | 0.65    |
| vi                   | 2.015       | 39161.9     | 1.973                   | 60900.1     | 0.64    |
| Average (i, iii, v)  | 2.015       | 46653.0     | 1.974                   | 78055.1     | 0.60    |
| Stdev (i, iii, v)    | 0.001       | 979.8       | 0.001                   | 4258.6      | 0.04    |
| Average (ii, iv, vi) | 2.015       | 43352.9     | 1.974                   | 62466.3     | 0.69    |
| Stdev (ii, iv, vi)   | 0.001       | 4315.7      | 0.002                   | 2345.6      | 0.07    |

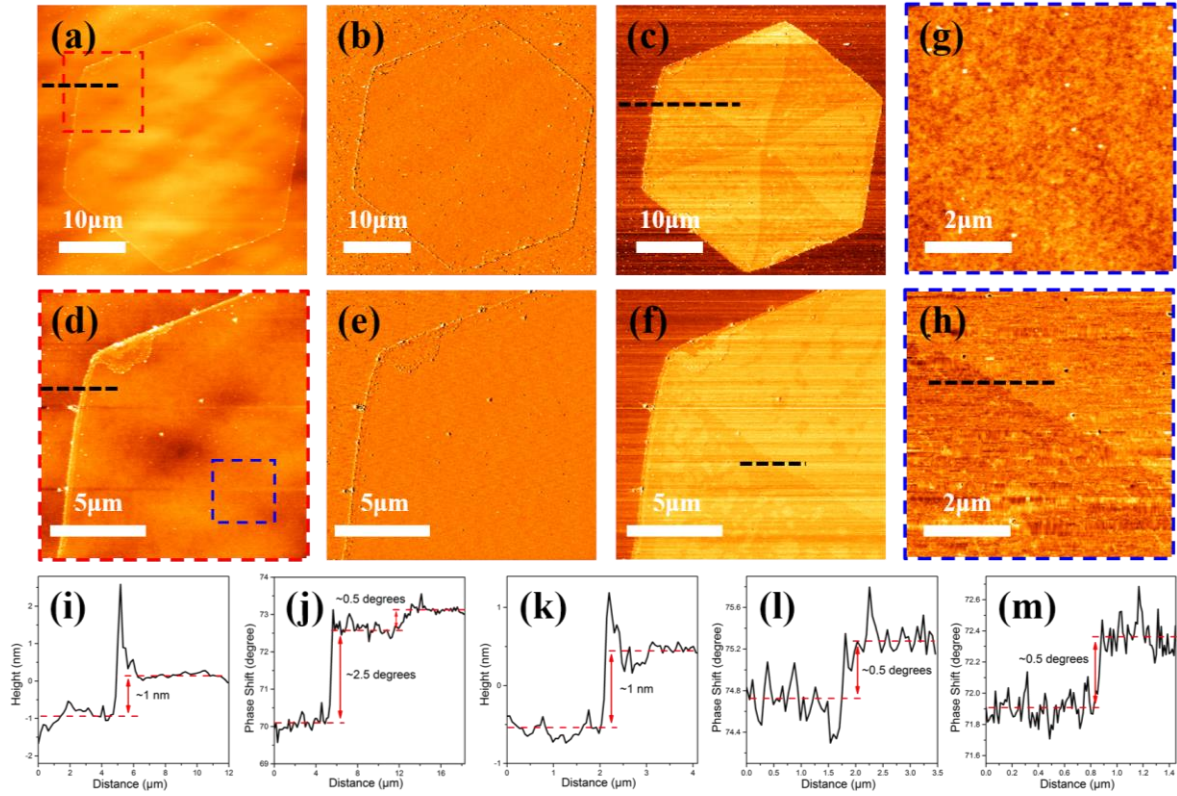
The ratio in the bright area is smaller than that in the dark area, the trend of which is similar to the as-grown sample. It implies that strain might not be the dominant factor causing the symmetric PL pattern. **Figure 6.7(e)** shows the high-resolution SEM image of a typical hexagonal WS<sub>2</sub> domain. It is not as obvious as in the as-grown sample, but a similar pattern can be observed, which implies that it might be caused by structural imperfections or physical adsorbates. The EDX results, **Figure 6.7(g-i)**, show no measureable spatial patterns for a typical as-grown hexagonal monolayer WS<sub>2</sub> domain, the SEM image of which can be seen in **Figure 6.7(f)**. This might be due to the ultrathin nature of the material, making it difficult to detect subtle variations using EDX.



**Figure 6.7. Characterization of hexagonal monolayer WS<sub>2</sub> before and after transfer.** (a,b) Typical PL integrated mapping of (a) as-grown and (b) transferred WS<sub>2</sub> domains on SiO<sub>2</sub>/Si. Scale bar: 10  $\mu$ m. (c,d) Corresponding (c) PL and (d) Raman spectra of the marked regions in (b). The two representative PL spectra were fitted with two Lorentzian peaks representing exciton emission (green) and negative trion emission (magenta). (e) SEM image of a typical as-grown hexagonal WS<sub>2</sub> crystal on SiO<sub>2</sub>/Si, showing a similar symmetric pattern. Scale bar: 10  $\mu$ m. (f-i) EDX elemental mappings of a pristine hexagonal monolayer WS<sub>2</sub> domain shown in (f), indicating the distribution of (g) sulphur, (h) tungsten and (i) oxygen. Scale bar: 10  $\mu$ m.

AFM was then used to probe changes in the WS<sub>2</sub> domains across the regions of differing PL by assessing the maps produced from topography, amplitude and phase measurements, **Figure 6.8**. As can be seen from the surface morphology shown in **Figure 6.8**(a, d, g), the

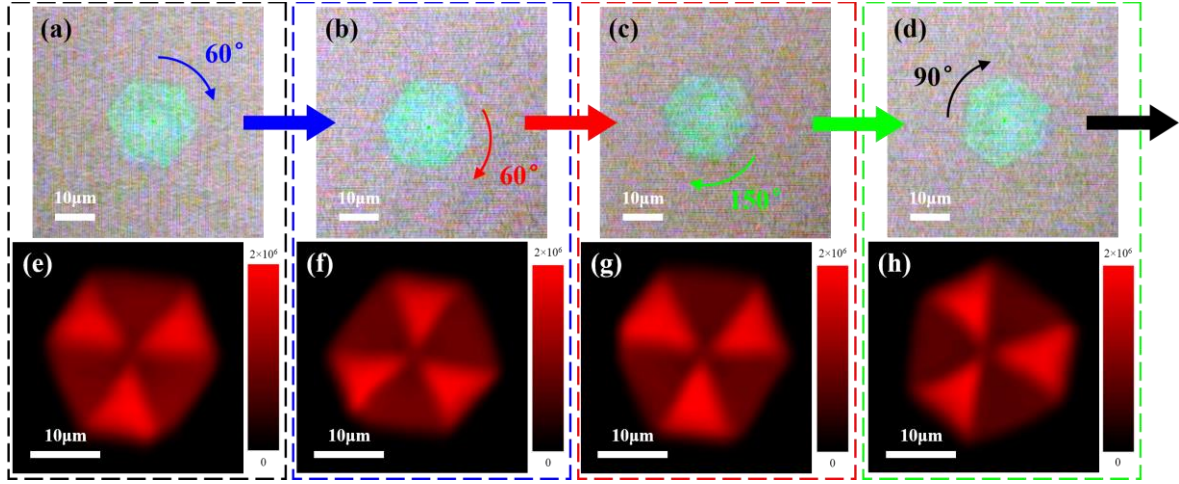
topography is quite uniform and no similar pattern is found in the crystal, which is in agreement with the optical microscope images, **Figure 6.4**. From **Figure 6.8(i)** and (k), the height difference between the crystal and the substrate is measured to be around 1nm, indicative of monolayer WS<sub>2</sub>. **Figure 6.8(g)** is the further magnified image of the blue dashed square in **Figure 6.8(d)**, indicating no topography difference at the edge of two areas with different PL intensities. AFM images in amplitude mode, **Figure 6.8(b)** and (e), showed a uniform distribution pattern. Therefore, variation in surface adsorbates can be ruled out for the non-uniform PL pattern because they would be detected as a variation in the height maps. The phase mode map is shown in **Figure 6.8(c)** with differences between the WS<sub>2</sub> and SiO<sub>2</sub> seen and associated with the elasticity changes of the two materials. The phase profile in **Figure 6.8(j)** shows that the phase change of the AFM tip vibration is  $\sim 2.5^\circ$  when moving from the surface of SiO<sub>2</sub> to monolayer WS<sub>2</sub>. Within the WS<sub>2</sub> domain, a spatial pattern in the phase map is seen, **Figure 6.8(c)**, with a phase change of  $\sim 0.5^\circ$  between the two areas, and this correlates with the same pattern observed in the maps of the PL intensities, **Figure 6.8(d)**. The phase profiles in **Figure 6.8(j, l, m)** indicate that the regions with different PL intensities may have variations in surface stiffness/softness and adhesion between the tip and surface, which can be attributed to the slight difference in structure between the two areas.



**Figure 6.8. Atomic Force Microscopy measurements of a monolayer hexagonal WS<sub>2</sub> crystal.** (a-c) AFM images of (a) topography, (b) amplitude and (c) phase modes for a typical monolayer hexagonal WS<sub>2</sub> crystal. The scale bars is 10 μm. (d-f) Zoomed-in AFM maps of the red dashed square in (a), showing (d) height, (e) amplitude and (f) phase modes. Scale bar: 5 μm. (g,h) Further zoomed-in images of the blue dashed region in (d), presenting (g) topology and (h) phase modes. Scale bar: 2 μm. (i) Height and (j) phase profiles taken from the black dashed line in (a) and (c). (k) Height and (l) phase profiles taken across the black dashed line in (d) and (f). (m) Corresponding phase profile taken from black dashed line in (h).

The characterization results shown in **Figure 6.1–6.8** reveal that neither physical adsorbates nor doping from the dielectric environment contribute to the observed difference in PL intensity mapping. The 2D monolayer WS<sub>2</sub> crystal is anisotropic and the laser used for PL and Raman spectroscopy is polarized, but no change was found when rotating the stage during measurements, indicating the symmetric pattern is not related to the polarized incident light, **Figure 6.9**. The relative spatial variations in strain within the WS<sub>2</sub> upon cooling after growth may impact the distribution of defects in the material, and defects in a

2D semiconductor can trap free charge carriers and localize excitons, which leads to a change in the intrinsic PL.<sup>48-50</sup>



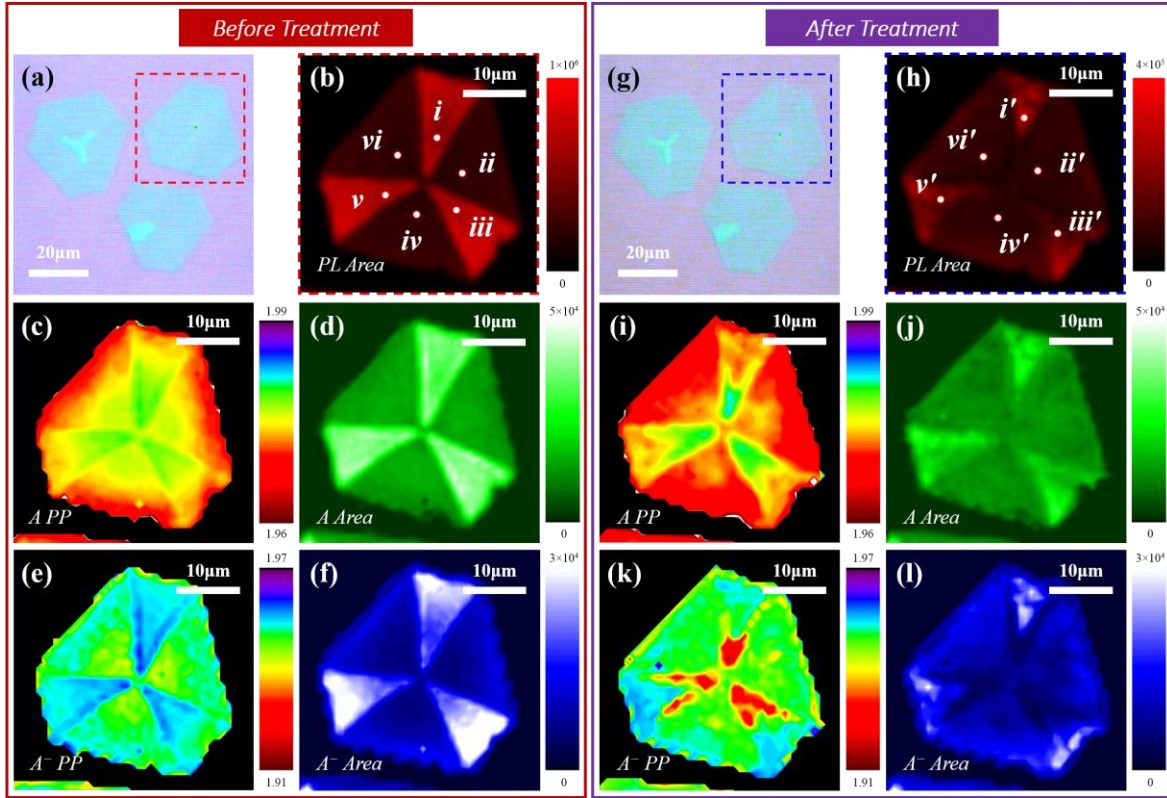
**Figure 6.9.** PL mappings and optical images of one typical monolayer hexagonal WS<sub>2</sub> at different rotation angles. (a-d) Optical images of one typical monolayer hexagonal WS<sub>2</sub> domain at rotation angles of 0° (blue), 60° (red), 120° (green) and 270° (black), respectively. Scale bar: 10 μm. (e-h) Corresponding PL mappings of the same hexagonal WS<sub>2</sub> crystal, showing the same symmetric patterns at different rotation angles. Scale bar: 10 μm.

Defective regions of WS<sub>2</sub> should be more sensitive to oxidization, and to probe this, I exposed the sample to a higher power laser to accelerate the oxidative decomposition of the sample. **Figure 6.10(a)** shows the optical image of three WS<sub>2</sub> domains; the contrast difference indicates different thicknesses of the WS<sub>2</sub> grown by powder vaporization. **Figure 6.10(b)** presents the PL integrated intensity mapping of the region highlighted with red dashed line in **Figure 6.10(a)**. **Figure 6.10(c-f)** present the PL fitting results of the same crystal, showing obvious variation in the mappings of A peak position, A integrated intensity, A<sup>-</sup> peak position and A<sup>-</sup> integrated intensity. I took six spots from each side of the pristine hexagonal monolayer WS<sub>2</sub>, **Figure 6.10(b)**, for further discussion. It was found that, before treatment, the dark areas (designated as ii, iv and vi in **Figure 6.10(b)**) had only about one-third of PL intensity obtained from the bright areas (marked as i, iii and v in **Figure**

**6.10(b)).** After Lorentzian curve fitting, the average peak positions for A and A<sup>-</sup> are 1.977 and 1.958 eV in bright region and 1.976 and 1.951 eV in dark region, respectively. The fitting results, **Table 6.4**, show a difference in A/A<sup>-</sup> ratio with an average value of 1.94 for bright areas and 2.89 for dark areas, the trend of which is consistent with the previous untreated PL data.

**Table 6.4.** Lorentzian curve fitting results of the PL spectra taken from the marked spots in a typical hexagonal 2D WS<sub>2</sub> crystal before and after treatment as shown in Figure 6.10(b) and (h), respectively.

| <i>Before Treatment</i> |             |             |                         |             |                  |
|-------------------------|-------------|-------------|-------------------------|-------------|------------------|
| Region                  | Exciton (A) |             | Trion (A <sup>-</sup> ) |             | A/A <sup>-</sup> |
|                         | PP (eV)     | Area (a.u.) | PP (eV)                 | Area (a.u.) |                  |
| i                       | 1.978       | 38840.0     | 1.960                   | 18800.0     | 2.07             |
| ii                      | 1.976       | 14356.0     | 1.951                   | 5193.4      | 2.76             |
| iii                     | 1.977       | 37117.0     | 1.957                   | 20273.0     | 1.83             |
| iv                      | 1.975       | 14939.0     | 1.951                   | 5068.0      | 2.95             |
| v                       | 1.977       | 28999.0     | 1.956                   | 15184.0     | 1.91             |
| vi                      | 1.976       | 14330.0     | 1.950                   | 4838.9      | 2.96             |
| Average (i, iii, v)     | 1.977       | 34985.3     | 1.958                   | 18085.7     | 1.94             |
| Stdev (i, iii, v)       | 0.001       | 5255.4      | 0.002                   | 2618.6      | 0.12             |
| Average (ii, iv, vi)    | 1.976       | 14541.7     | 1.951                   | 5033.4      | 2.89             |
| Stdev (ii, iv, vi)      | 0.001       | 344.3       | 0.001                   | 179.8       | 0.11             |
| <i>After Treatment</i>  |             |             |                         |             |                  |
| i'                      | 1.973       | 20566.0     | 1.958                   | 15297.0     | 1.34             |
| ii'                     | 1.969       | 12098.0     | 1.950                   | 7668.7      | 1.58             |
| iii'                    | 1.973       | 15907.0     | 1.957                   | 11472.0     | 1.39             |
| iv'                     | 1.970       | 11867.0     | 1.951                   | 6847.7      | 1.73             |
| v'                      | 1.972       | 17681.0     | 1.953                   | 12757.0     | 1.39             |
| vi'                     | 1.968       | 11642.0     | 1.949                   | 7301.2      | 1.59             |
| Average (i', iii', v')  | 1.973       | 18051.3     | 1.956                   | 13175.3     | 1.37             |
| Stdev (i', iii', v')    | 0.001       | 2351.5      | 0.003                   | 1946.5      | 0.02             |
| Average (ii', iv', vi') | 1.969       | 11869.0     | 1.950                   | 7272.5      | 1.64             |
| Stdev (ii', iv', vi')   | 0.001       | 228.0       | 0.001                   | 411.3       | 0.09             |

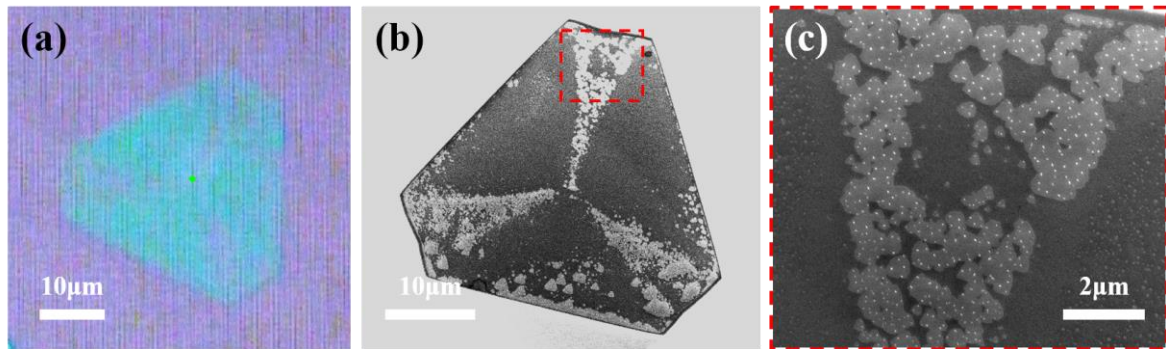


**Figure 6.10. Characterization of as-grown WS<sub>2</sub> domain before and after degradation.** (a) Optical image of WS<sub>2</sub> domains before high-power laser exposure. The red dashed square indicates the region for PL mapping. Scale bar: 20  $\mu\text{m}$ . (b) PL integrated intensity mapping of the corresponding WS<sub>2</sub> crystal before treatment. Scale bar: 10  $\mu\text{m}$ . (c-f) PL mappings of the same WS<sub>2</sub> crystal, showing spatial distributions of (c) A peak position, (d) A integrated intensity, (e) A<sup>-</sup> peak position, and (f) A<sup>-</sup> integrated intensity. Scale bar: 10  $\mu\text{m}$ . (g) Optical images of WS<sub>2</sub> domains after high-power laser exposure. Scale bar: 20  $\mu\text{m}$ . (h) PL mapping of the corresponding WS<sub>2</sub> crystal highlighted with blue dashed square in (g). Scale bar: 10  $\mu\text{m}$ . (i-l) PL mappings of the same WS<sub>2</sub> crystal after treatment, showing spatial distributions of (i) A peak position, (j) A integrated intensity, (k) A<sup>-</sup> peak position and (l) A<sup>-</sup> integrated intensity respectively. Scale bar: 10  $\mu\text{m}$ .

After higher-power laser exposure, the area with higher PL integrated intensity degrades, leaving a pattern similar to that shown previously by PL mapping, **Figure 6.10(g)**. As can be seen from **Figure 6.10(h)**, the intensity of the degraded area is significantly quenched, so that it is even lower than the dark areas on the untreated sample (noted as ii, iv and vi in **Figure 6.10(b)**). **Figure 6.10(i-l)** show the corresponding PL maps of the treated sample. The difference can be clearly seen in comparison with the untreated PL maps, **Figure 6.10(c-**

f). The corresponding peak positions for A and A<sup>-</sup> of the dark regions (designated as ii', iv' and vi' in **Figure 6.10(h)**) red-shifted to 1.969 and 1.950 eV, respectively. A similar phenomenon can also be found in the bright areas (noted as i', iii' and v' in **Figure 6.10(h)**), with A and A<sup>-</sup> peaks red-shifting to 1.973 and 1.956 eV, respectively.

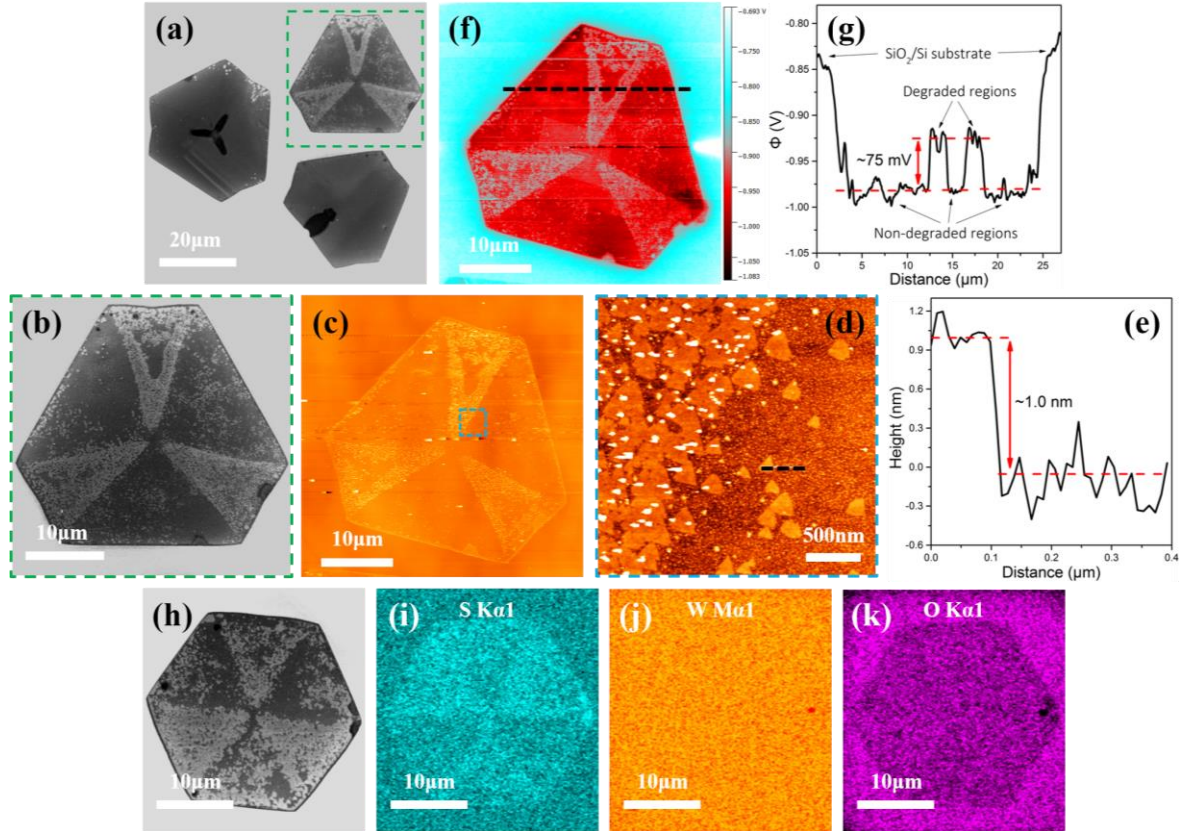
**Figure 6.12(a)** shows the optical image of the same area as in **Figure 6.10**, after high power laser exposure. The contrast difference between monolayer and multilayer WS<sub>2</sub> seen from the optical image, **Figure 6.10(a)**, can also be observed under SEM. **Figure 6.12(b)** is the magnified SEM image of the green dashed region in **Figure 6.12(a)**. **Figure 6.12(c)** and (f) show the AFM surface morphology and KPM images of the degraded WS<sub>2</sub> crystal, respectively. As can be seen from **Figure 6.12(d)**, the degraded area is formed of small triangles, which is in agreement with SEM images, **Figure 6.11**.



**Figure 6.11. Morphology of degraded WS<sub>2</sub>.** (a,b) Optical and SEM images of the degraded WS<sub>2</sub> crystal on SiO<sub>2</sub>/Si substrate. Scale bar: 10 μm. (c) Zoomed-in SEM image of the red dashed area in (b). Scale bar: 2 μm.

The height difference between the brighter triangle and the monolayer WS<sub>2</sub> is approximately 1 nm, **Figure 6.12(e)**. In addition, as shown in **Figure 6.12(g)**, the work function increased by 75 mV after degradation, and the work function of the degraded areas is closer to the SiO<sub>2</sub>/Si substrate compared with that of non-degraded areas, indicating that the degraded part might be oxidized into an insulating material. **Figure 6.12(g-k)** present the EDX

elemental mapping (S, W, and O) of a degraded hexagonal WS<sub>2</sub> crystal shown in **Figure 6.12(h)**. As can be seen from **Figure 6.12(i)** and (k), the degraded area corresponds to the region with less sulphur and more oxygen elements, confirming that the oxidation has taken place during degradation.



**Figure 6.12. Characterization of the preferentially degraded WS<sub>2</sub> after high-power laser exposure.** (a) SEM image of the degraded WS<sub>2</sub> on SiO<sub>2</sub>/Si. Scale bar: 20  $\mu\text{m}$ . (b) Zoomed-in SEM image of the green dashed area in (a). Scale bar: 10  $\mu\text{m}$ . (c) AFM topological mapping of the green dashed highlighted region in (a). Scale bar: 10  $\mu\text{m}$ . (d) Zoomed-in AFM image of the selected area marked in cyan dashed square in (c). Scale bar: 500 nm. (e) Corresponding height profile taken across the black dashed line in (d), showing the height difference between degraded and non-degraded areas as approximately 1 nm. (f,g) AFM image in Kelvin probe microscopy (KPM) mode, and the corresponding profile taken from the black dashed line in (f), showing the work function difference between two areas as approximately 75 mV. Scale bar: 10  $\mu\text{m}$ . (h) SEM image of a degraded hexagonal WS<sub>2</sub> on SiO<sub>2</sub>/Si. Scale bar: 10  $\mu\text{m}$ . (i-k) EDX elemental mapping of the same crystal in (h), indicating the distribution of (i) sulphur, (j) tungsten, and (k) oxygen. Scale bar: 10  $\mu\text{m}$ .

## 6.3 Conclusion

In summary, I found that the discrete symmetric segmented PL patterns from hexagonal monolayer WS<sub>2</sub> are associated with structural variations, and not surface adsorbates or secondary layers of WS<sub>2</sub>. Only slight changes in peak positions from PL and Raman spectra are observed, suggesting that the strain introduced during the growth might be a minor factor and that doping from the dielectric environment owing to different adhesion to the substrate can be discounted. In addition, AFM images in topology mode show no height difference between the two areas with different PL intensities, which can help me rule out physical adsorbates. A difference in the A/A<sup>+</sup> ratio for both the as-grown sample and the strain-free sample was found, implying that the structural imperfections may play a major role in the PL spatial distribution. The segmentation of defects might be caused during the CVD cooling process and these findings can give insights into the PL properties of hexagonal monolayer WS<sub>2</sub>, which could expand the application of this semiconducting material in the future.

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## Chapter 7

### *Mixed Multi-layered 2D Heterostructures Utilizing Strained Monolayer Tungsten Disulphide*

Subsequent to the CVD synthesis and characterisation of bilayer graphene and monolayer WS<sub>2</sub>, my project then turned to the formation and optical properties of the heterostructures based on these two materials. A novel non-aqueous sliding transfer method is developed for the layer by layer van der Waals reassembly. Mixed vertical heterostructures with different stacking sequences are fabricated and then spectroscopically examined.

#### **7.1 Introduction**

The van der Waals heterostructures based on TMDs<sup>1-10</sup> and other 2D materials, such as graphene and hexagonal boron nitride (h-BN), are believed to be the fundamental platform for many important future device applications including field-effect transistors, solar cells, light-emitting diodes and lasers.<sup>11-26</sup> These 2D heterostructures can be achieved either through transfer<sup>13-23</sup> or direct growth.<sup>24-27</sup> As for the transfer approach, the dry transfer method, such as the Polydimethylsiloxane (PDMS) stamping technique, is often used by research groups.<sup>16-21</sup> By using the dry transfer method, one 2D material can be transferred

onto another 2D material, which was either grown or exfoliated on a Silicon chip with a layer of Silicon dioxide on top (SiO<sub>2</sub>/Si), for device fabrication.

The development of transfer methods is essential for the layer by layer van der Waals reassembly.<sup>11</sup> Schneider *et al.*<sup>28</sup> reported a transfer method in 2010, which occurs through the intercalation of a layer of water between a hydrophilic substrate and a hydrophobic nanostructure (for example, graphene and carbon nanotubes) locked within a hydrophobic polymer thin film. This led to a so-called surface energy assisted perfect transfer.<sup>29</sup> They successfully detached the Polystyrene (PS)/MoS<sub>2</sub> film (hydrophobic) from a sapphire substrate (hydrophilic) by water penetration. A similar transfer technique was demonstrated by Xu *et al.*<sup>30</sup> and they delaminated WS<sub>2</sub> from sapphire substrates via capillary force in water. Recent studies also reported using polydimethylsiloxane (PDMS) (as the carrier polymer) and cold water to lift off the synthesized MoS<sub>2</sub> films from the SiO<sub>2</sub>/Si substrate.<sup>31</sup> However, this requires the presence of a water-soluble layer beneath the as-grown films, which is not typical in the synthetic approaches for TMDs.

Recent reports show that water can easily detach TMDs from a hydrophilic substrate, such as SiO<sub>2</sub>, making it difficult to transfer other 2D materials on top of as-grown TMDs by the standard wet transfer method that is widely used for graphene.<sup>32–34</sup> A dry transfer method (PDMS)<sup>16–21</sup> can be used to form a heterostructure based on TMDs. Limited success has been achieved for monolayer TMD films on sapphire using a wet transfer method to build the 2D heterostructures, but this approach does not work consistently with SiO<sub>2</sub> surfaces.<sup>22</sup> It might be the case that the synthesized monolayer film adhered better to the growth substrate, which then hinders the water penetration and allows it to remain undamaged on the surface.<sup>29</sup>

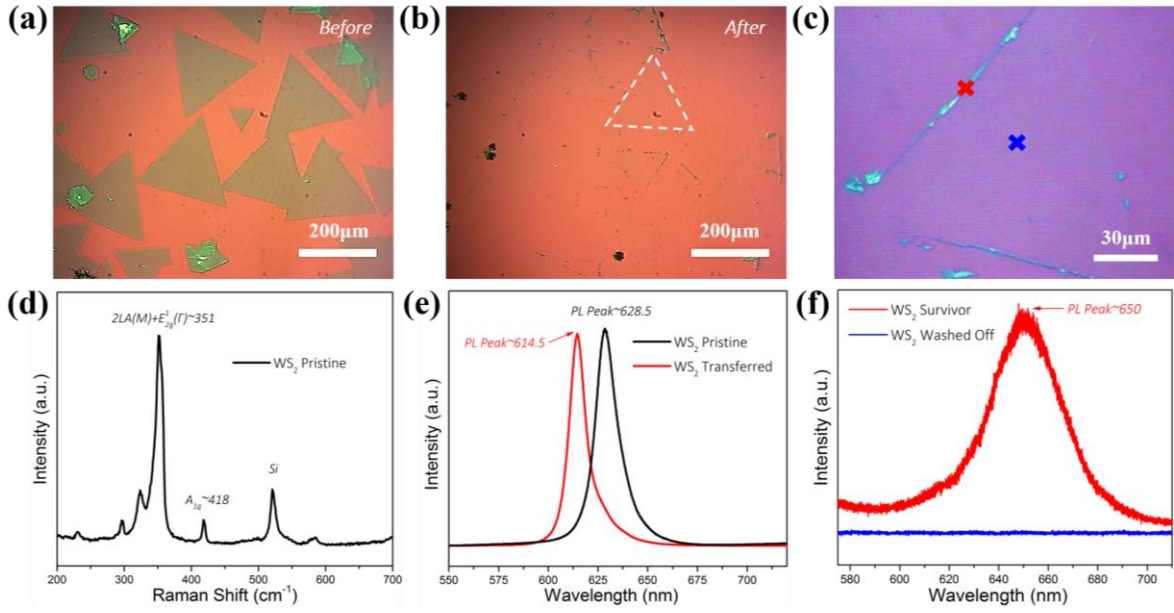
One important aspect of atomically thin TMDs is their flexibility, which is better suited for strain engineering compared with other bulk semiconductors.<sup>35,36</sup> It was reported that the local strain in as-grown TMD samples normally arises from the CVD growth procedures that end with a fast-cooling process due to the difference in the coefficient of thermal expansion between the substrate and as-prepared material, and the tensile strain can be released by a transfer process to another substrate.<sup>37</sup> Tuning the band structure and carrier transport properties by applying a strain through bending of materials on flexible substrates or through lattice mismatch between substrates and samples has been explored recently, and it can be used to significantly improve their optical and electronic properties.<sup>16,35–40</sup> It has been predicted that tunable photonic devices and solar cells with better energy band matching can be realized by building multilayer 2D heterostructures based on strained TMDs.<sup>38,41</sup> Building layer-by-layer 2D vertical heterostructures containing a strained TMD layer has been challenging due to the standard aqueous based transfer processes washing off the TMDs from the growth substrate. It is important to develop a non-aqueous transfer approach that allows other 2D crystals to be achieved on top of the strained TMDs to build multi-layered vertical heterostructures.

Here, I introduce a novel alcohol-based approach to the transfer of 2D materials, such as h-BN and graphene, on top of WS<sub>2</sub> directly grown on a Si substrate with SiO<sub>2</sub> surface. Using isopropanol (IPA) instead of water enables layer-by-layer transfer of 2D material onto CVD grown strained TMDs on hydrophilic substrates, such as sapphire and SiO<sub>2</sub>/Si without using PDMS. The non-aqueous transfer method is also suitable for transferring monolayer WS<sub>2</sub> from its growth substrate to other substrates, releasing the strain and building vertical 2D heterostructures with different stacking order. Optical microscopy, scanning electron microscopy (SEM), Raman spectroscopy and Photoluminescence (PL) spectroscopy was used to characterize the h-BN/WS<sub>2</sub>, graphene/h-BN/WS<sub>2</sub> and WS<sub>2</sub>/graphene stacks prepared

by both the standard aqueous-based wet transfer method and the non-aqueous sliding transfer approach.

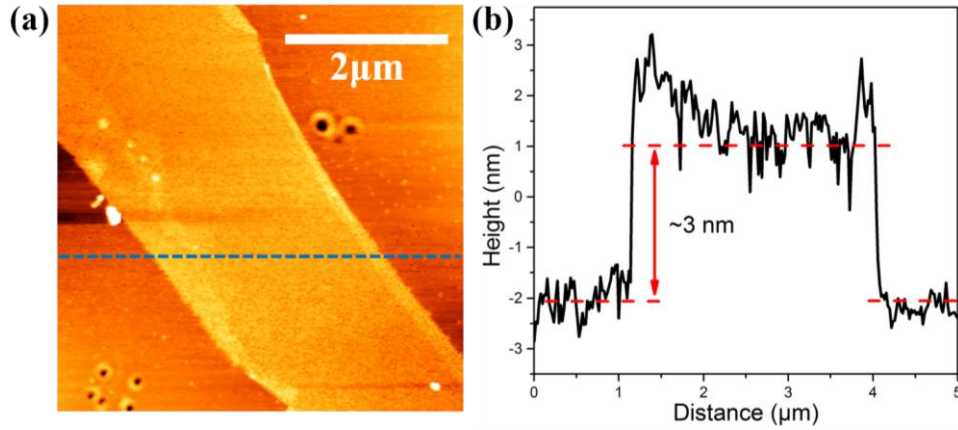
## 7.2 Results and Discussion

All 2D materials used in this study were grown by CVD. **Figure 7.1(a)** presents the optical image of my as-grown monolayer WS<sub>2</sub> crystals on SiO<sub>2</sub>/Si. **Figure 7.1(d)** shows the Raman spectra of the monolayer WS<sub>2</sub> domain on SiO<sub>2</sub>/Si. A peak at 351 cm<sup>-1</sup> was observed and assigned to the 2LA+E<sub>2g</sub><sup>1</sup> mode for monolayer WS<sub>2</sub>, while the peak at 418 cm<sup>-1</sup> corresponds to the A<sub>1g</sub> mode, consistent with the previous reports.<sup>42-44</sup> **Figure 7.1(e)** compares the PL spectra of as-grown (~628.5 nm) and transferred (~614.5 nm) monolayer WS<sub>2</sub> on SiO<sub>2</sub>/Si. A blue shift of 14 nm was observed after transfer, which is thought to be mostly caused by the released strain. The 2D vertical heterostructure was first prepared by transferring a layer of 2D material using a standard wet transfer approach<sup>32</sup> onto another layer that was grown directly on SiO<sub>2</sub>/Si. During the transfer process, it was found that most of the WS<sub>2</sub> crystals were washed away after being immersed in deionized (DI) water, leaving traces of some WS<sub>2</sub> triangles and hexagons on the surface. **Figure 7.1(a)** and (b) show the optical images of WS<sub>2</sub> domains before and after being submerged in DI water. The white dashed triangle indicates where a WS<sub>2</sub> domain used to be. **Figure 7.1(c)** shows the zoomed-in optical image of the outline of some WS<sub>2</sub> crystals left after transfer. From the PL spectra as shown in **Figure 7.1(f)**, it can be confirmed that most of the monolayer WS<sub>2</sub> was detached from the substrate.



**Figure 7.1. Removal of monolayer WS<sub>2</sub> crystals from the substrate by immersion in DI water.** Optical images of WS<sub>2</sub> (a) before and (b) after submerged in DI water. The white dashed area shows where a WS<sub>2</sub> triangle used to be. The Scale bar: 200 $\mu$ m. (c) Zoomed-in optical image of WS<sub>2</sub> residues on SiO<sub>2</sub>/Si after being in contact with DI water. Scale bar: 30 $\mu$ m. (d) Raman spectrum of as-grown monolayer WS<sub>2</sub> on SiO<sub>2</sub>/Si. (e) PL spectra of as-grown monolayer WS<sub>2</sub> (black line) and transferred WS<sub>2</sub> (red line) on SiO<sub>2</sub>/Si, respectively. (f) PL spectra of the marked spots with corresponding coloured crosses in (c), showing that the material left on the surface is not monolayer, but multilayer WS<sub>2</sub>.

The low PL intensity and peak position ( $\sim 650$  nm) of the WS<sub>2</sub> residue near the edge indicates that the material left on the surface is not monolayer, but multilayer WS<sub>2</sub>, **Figure 7.2**, possibly formed by back folding of some monolayer regions. **Figure 7.2(a)** presents an AFM topological map of the WS<sub>2</sub> residues on SiO<sub>2</sub>/Si after transferring a layer of h-BN using the standard wet transfer method. The line profile, **Figure 7.2(b)**, for the blue dashed line in **Figure 7.2(a)** shows that the thickness of the surviving WS<sub>2</sub> is  $\sim 3$  nm after standard wet transfer, indicating the material left on the surface is multilayer WS<sub>2</sub>.

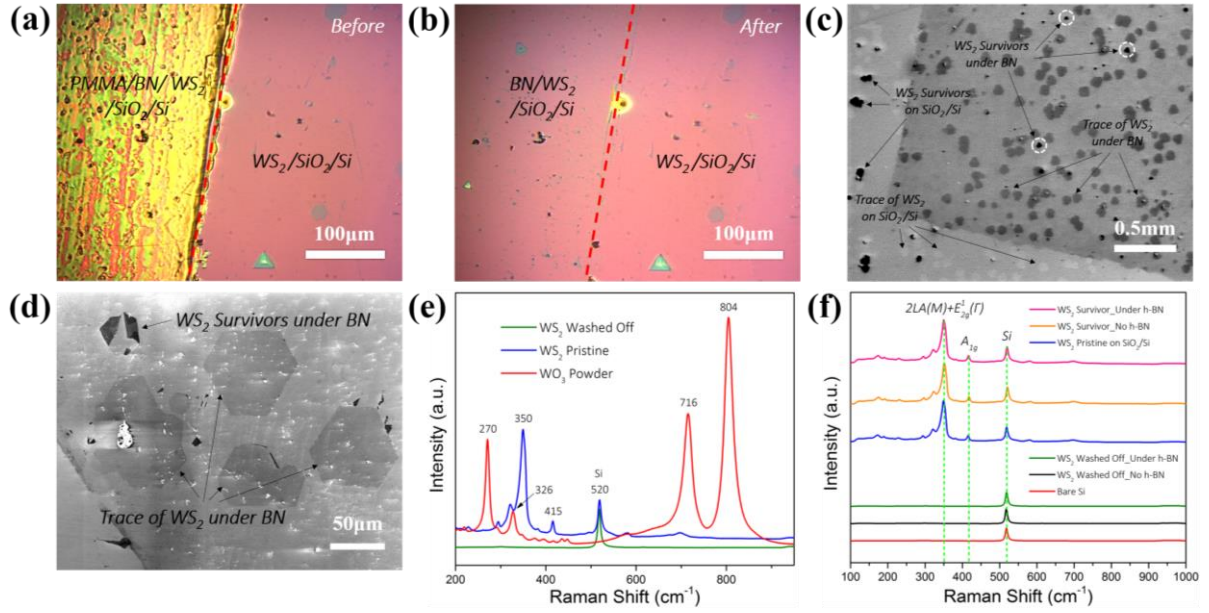


**Figure 7.2. AFM characterization of WS<sub>2</sub> residues.** (a) AFM topological mapping of the WS<sub>2</sub> residues on SiO<sub>2</sub>/Si after being in contact with DI water. Scale bar: 2μm. (b) Corresponding line profile for the blue dashed line in (a).

**Figure 7.3(a)** shows the optical image of WS<sub>2</sub> with a PMMA/h-BN stack on top. After soaking in acetone at 45 °C for 2 hours to remove PMMA, **Figure 7.3(b)**, it was found that PMMA, which sits on top of h-BN, can be well removed during this process and the WS<sub>2</sub> will not be removed from the substrate by the acetone. The small optical contrast from the h-BN film on SiO<sub>2</sub> is attributed to its negligible opacity in the visible spectrum arising from its large band gap (>5 eV), making it hard to detect. The high transparency of the h-BN makes it easy to find WS<sub>2</sub> survivors and the traces of WS<sub>2</sub> crystals using an optical microscope even when it is covered with a layer of h-BN film. According to the optical images, it seems that there is still some residue of the material lying at locations where the WS<sub>2</sub> triangles or hexagons used to be before exposure to DI water. If WS<sub>2</sub> was changed to some other material, which has a large band gap, it might be transparent under optical microscope. So it is necessary to examine the samples under SEM to see whether there is anything left on the surface. From the SEM images, **Figure 7.3(c)** and (d), it was confirmed that just a very small number of WS<sub>2</sub> domains were left on the surface after transferring a layer of h-BN using the standard wet transfer method. The trace of WS<sub>2</sub> under h-BN on top

(darker in contrast) and without h-BN (brighter in contrast) can be easily found in **Figure 7.3(c)**. The water might be oxidizing the WS<sub>2</sub> and changing it to WO<sub>3</sub> or other W-oxides during the transfer process. So it is necessary to check the darker and brighter areas using Raman spectroscopy in order to confirm whether the disappearance of WS<sub>2</sub> leads to a rise of 2D W-oxides.

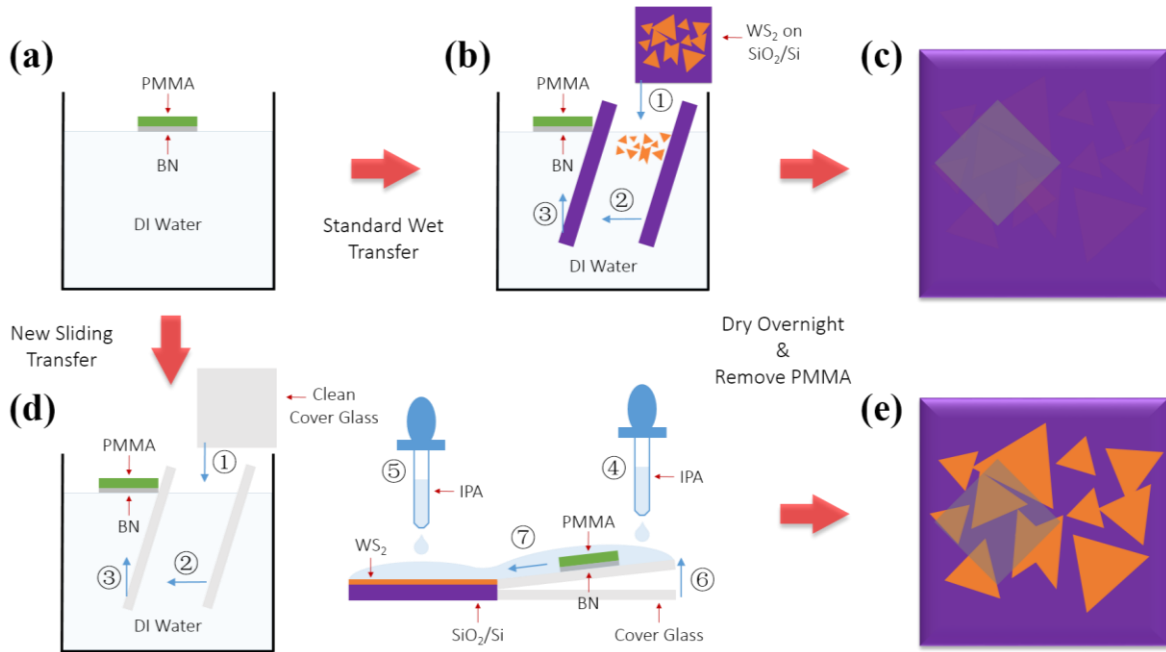
It was reported by Xu *et al.*<sup>45</sup> that Raman peaks centred at 272, 326, 717 and 807 cm<sup>-1</sup> can be found from WO<sub>3</sub>, the first two are induced by W-O-W bending mode vibration and the other two correspond to W-O-W stretching vibration mode. As can be seen in **Figure 7.3(e)**, peaks in the Raman spectrum at similar positions (270, 326, 716 and 804 cm<sup>-1</sup>) were found for pure WO<sub>3</sub> powder deposited onto the sample for the measurement, which is the same as the precursor used to grow monolayer WS<sub>2</sub> by CVD. There is no difference between the spectra of washed off WS<sub>2</sub> without h-BN on top and bare Si, indicating that the WS<sub>2</sub> was completely washed off and no W-oxides were left on the surface after exposure to water. The Raman spectra of pristine WS<sub>2</sub> on SiO<sub>2</sub>/Si, surviving WS<sub>2</sub> with and without h-BN on top after exposure to DI water were compared and show almost the same peak positions, but with slightly different peak intensity. Although the contrast for washed off WS<sub>2</sub> under SEM is brighter on SiO<sub>2</sub>/Si and darker under h-BN, **Figure 7.3(c)**, that their Raman spectra are almost the same, **Figure 7.3(f)**, showing only one peak centred at 520 cm<sup>-1</sup>, which corresponds to bare Si. The contrast in both SEM and optical microscopy can be attributed to the concave surface left by the detachment of WS<sub>2</sub>, most likely formed during the initial growth of WS<sub>2</sub> on the SiO<sub>2</sub> surface by CVD at high temperatures.



**Figure 7.3. Probing WO<sub>3</sub> or W-oxide formation after transferring a layer of h-BN onto as-grown WS<sub>2</sub> using the standard wet transfer method.** Optical images of WS<sub>2</sub> with a layer of h-BN on top (a) before and (b) after PMMA removal. Scale bar: 100 μm. (c) SEM image of the trace of the WS<sub>2</sub> crystals on SiO<sub>2</sub>/Si with and without h-BN on top. Scale bar: 0.5 mm. (d) Zoomed-in SEM image of the trace of surviving WS<sub>2</sub> and surviving WS<sub>2</sub> under h-BN. Scale bar: 50 μm. (e) Raman spectra of washed off WS<sub>2</sub>, pristine WS<sub>2</sub> and WO<sub>3</sub> powder measured using 532 nm excitation. (f) Comparison of Raman spectra among pristine WS<sub>2</sub> on SiO<sub>2</sub>/Si, surviving WS<sub>2</sub> with and without h-BN on top after exposure to water, bare Si, washed off WS<sub>2</sub> with and without h-BN on top.

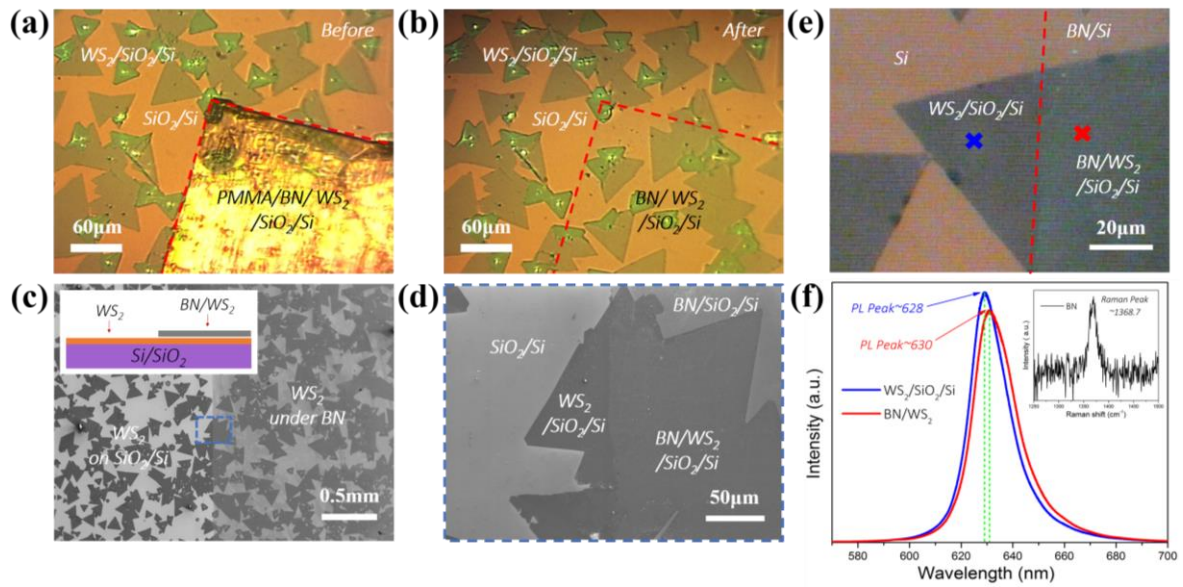
**Figure 7.4** shows the schematic illustration of standard aqueous wet transfer process and non-aqueous sliding transfer method. Taking h-BN/WS<sub>2</sub> as an example, after etching the Cu away and removing the etchant via several cleaning steps, the PMMA/h-BN stack was transferred to DI water, as shown in **Figure 7.4(a)**. As can be seen from **Figure 7.4(b)**, the standard wet transfer method involves DI water when scooping the PMMA/h-BN stack onto WS<sub>2</sub>/SiO<sub>2</sub>/Si substrate, and most of the WS<sub>2</sub> crystals were found to be washed off after this process, **Figure 7.4(c)**. Therefore, a new transfer process has been introduced here in order to solve this problem. **Figure 7.4(d)** shows the schematic illustration of the non-aqueous sliding transfer approach that eliminates the need to bring WS<sub>2</sub> monolayers in contact with water. First, a thin cover-glass slide was used to collect the PMMA/h-BN stack after all the

cleaning process. Then some IPA is added to surface of the cover glass, allowing the solution to draw away the DI water between the cover glass and the stack. In the meantime, some IPA is dropped onto the WS<sub>2</sub>/SiO<sub>2</sub>/Si, which is kept horizontal on the desk. With one side of the cover glass resting on the edge of the Si chip, the other end of the cover glass is lifted up so that the PMMA/h-BN stack slides across to the Si chip slowly. Then the whole stack is left to dry in a fume hood overnight and is then baked at 150 °C for 15 minutes. All the WS<sub>2</sub> crystals remain intact after the PMMA removal by acetone, **Figure 7.4(e)**.



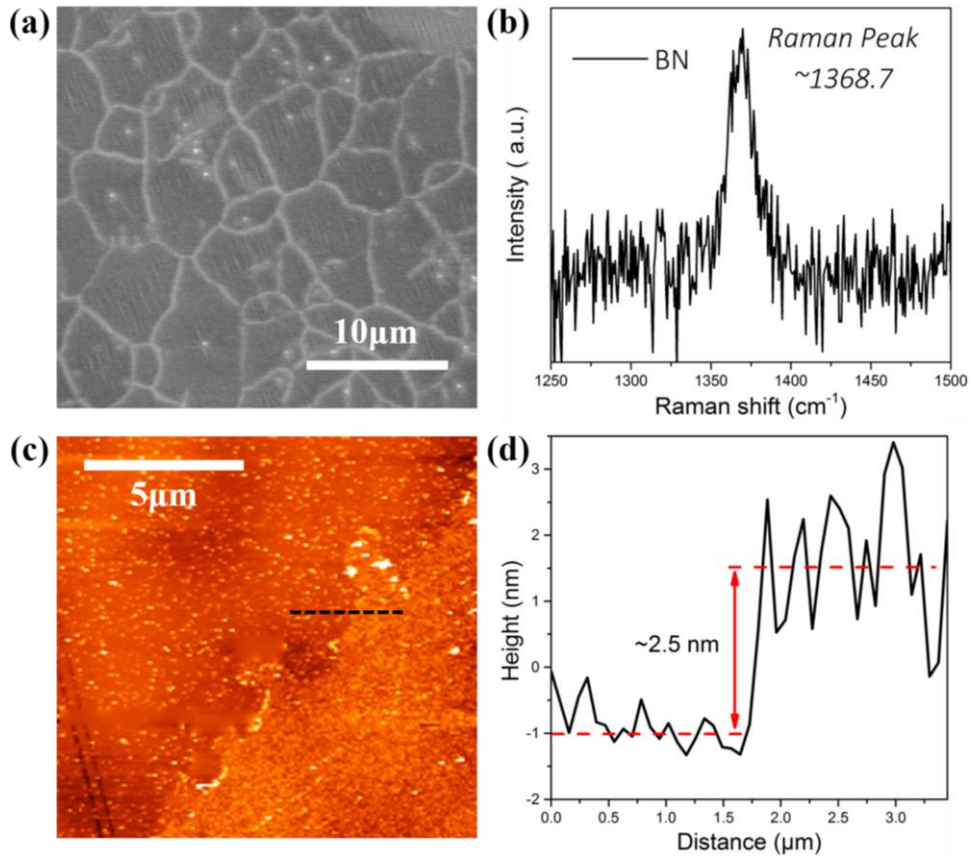
**Figure 7.4. Schematic illustration of the non-aqueous sliding transfer method and the standard aqueous wet transfer process.** (a) After all the cleaning processes, the PMMA/h-BN stack was floating on DI water. (b) The standard wet transfer involves (1) suspending the WS<sub>2</sub>/SiO<sub>2</sub>/Si chip in the DI water, (2) pushing it towards the stack and (3) scooping the stack onto the WS<sub>2</sub>/SiO<sub>2</sub>/Si chip. (c) It was found that most of the WS<sub>2</sub> crystals were washed off when soaked in DI water. (d) The sliding transfer process includes (1) dipping a piece of clean cover glass into DI water, (2) pushing it towards the stack, (3) scooping the stack onto the cover glass, (4) wetting the cover glass with some IPA, (5) dropping IPA onto the WS<sub>2</sub>/SiO<sub>2</sub>/Si chip and keeping it horizontal on the desk, (6) resting one side of the cover glass on the edge of the chip and lifting the other side up slightly and (7) allowing the stack to slide down very slowly. (e) All the WS<sub>2</sub> crystals remain intact after removing PMMA.

**Figure 7.5(a)** shows the optical image of WS<sub>2</sub> samples before removing PMMA using acetone, with the PMMA/h-BN stack indicated by a red dashed line. As can be seen from **Figure 7.5(b)**, all the WS<sub>2</sub> crystals remain intact after PMMA removal. Due to h-BN's high transparency, there is almost no difference in contrast between the area with BN and without BN under the optical microscope. The inset in **Figure 7.5(c)** shows a schematic of the h-BN/WS<sub>2</sub> stack. According to the SEM image shown in **Figure 7.5(c)**, it can be confirmed that a layer of h-BN was transferred onto the WS<sub>2</sub> using the sliding transfer approach. **Figure 7.5(d)** presents the SEM image of zoomed-in blue dashed area in **Figure 7.5(c)**. **Figure 7.5(e)** shows the zoomed-in optical image of WS<sub>2</sub> crystals with and without h-BN on top.



**Figure 7.5. Characterization of an h-BN/WS<sub>2</sub> stack prepared via the sliding transfer approach.** Optical images of WS<sub>2</sub> underneath h-BN (a) before and (b) after PMMA removal. The red dashed line indicates the boundary of h-BN. Scale bar: 60 μm. (c) SEM image of WS<sub>2</sub> crystals on SiO<sub>2</sub>/Si with and without h-BN on top. Scale bar: 0.5 mm. Inset shows the schematics of the h-BN/WS<sub>2</sub> stack. (d) SEM image of zoomed-in blue dashed region in (c), showing WS<sub>2</sub> domains partially under h-BN. Scale bar: 50 μm. (e) Zoomed-in optical image of WS<sub>2</sub> crystals on SiO<sub>2</sub>/Si after transferring a layer of h-BN using the new transfer method. Scale bar: 20 μm. (f) PL spectra of the marked spots with corresponding coloured crosses in (e), showing the difference in PL signal between WS<sub>2</sub> with and without h-BN on top. The inset is the Raman spectra of multilayer h-BN.

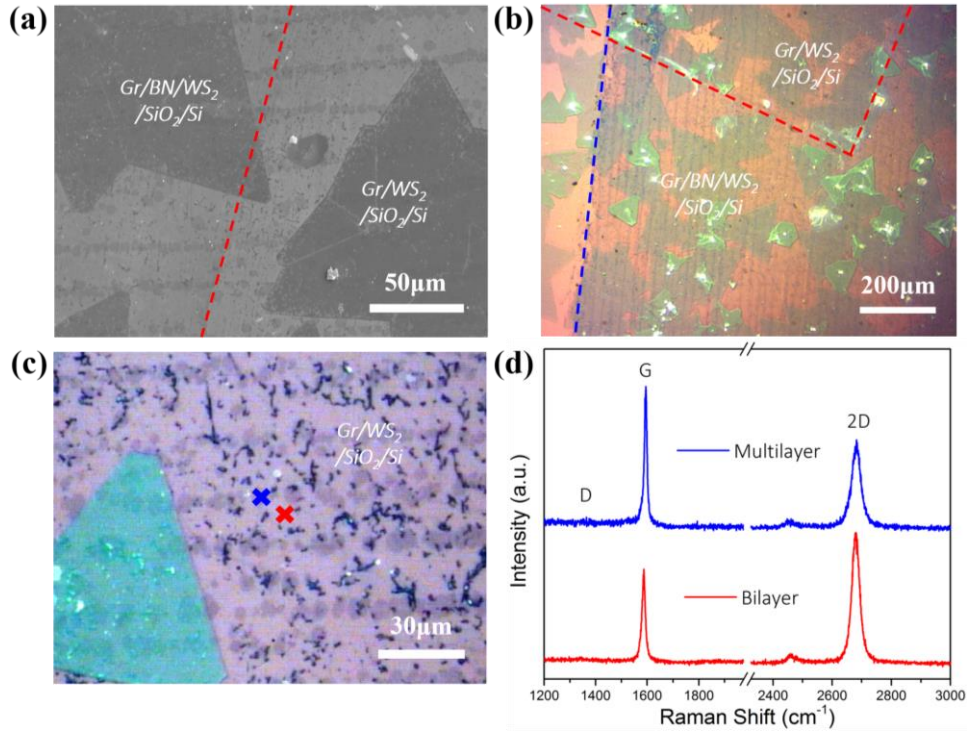
As can be seen from **Figure 7.5(f)**, the WS<sub>2</sub> underneath the h-BN has weaker PL intensity with broader full width at half maximum (FWHM) than the one on SiO<sub>2</sub>/Si. The PL peak position has barely changed with only a slight redshift from 628 nm to 630 nm after all the transfer process. The existence of an h-BN layer transferred on WS<sub>2</sub> was further confirmed by Raman spectroscopy. The inset in **Figure 7.5(f)** shows the characteristic Raman vibration mode of the h-BN film lying above the WS<sub>2</sub> domains, which was measured to be around 1368.7 cm<sup>-1</sup>, indicating multilayer h-BN, **Figure 7.6**.



**Figure 7.6. Characterization of CVD-grown multilayer h-BN.** (a) A typical SEM image of the CVD-grown multilayer h-BN film on Cu substrate. Scale bar: 10 μm. (b) Raman spectrum of the transferred h-BN film on SiO<sub>2</sub>/Si substrate. (c) AFM topological mapping of the transferred h-BN film. Scale bar: 5 μm. (d) Corresponding height profile taken across the black dashed line in (c).

**Figure 7.6(a)** presents a typical SEM image of the CVD-grown continuous h-BN film on Cu. The Raman spectrum, **Figure 7.6(b)**, shows a characteristic peak centred at  $\sim 1368.7 \text{ cm}^{-1}$ , which indicates the film thickness to be multilayer. **Figure 7.6(c)** and (d) give a typical AFM measurement, showing the thickness of the h-BN film is  $\sim 2.5 \text{ nm}$  following transfer onto a SiO<sub>2</sub>/Si substrate.

To further illustrate the flexibility of the non-aqueous transfer method in preparing mixed vertical stacked 2D heterostructures with a variety of 2D materials, a layer of graphene was then transferred onto the as-prepared h-BN/WS<sub>2</sub> stack using the non-aqueous transfer method. The graphene film is mostly bilayer with 15% area of multilayer graphene strips, **Figure 7.7**. **Figure 7.7(a)** and (b) present typical areas of the graphene/h-BN/WS<sub>2</sub> stack on SiO<sub>2</sub>/Si examined by SEM and optical microscopy, respectively. The non-uniform contrast indicates the variation of the film thickness.<sup>46</sup> The graphene film is continuous with several other thicker graphene strips. **Figure 7.7(d)** shows the Raman spectra of two marked spots with different colour in **Figure 7.7(c)**. The 2D/G intensity ratio of the spectra in red is  $\sim 1.3$ , which indicates bilayer graphene.<sup>47-50</sup> The blue spectrum with a ratio of  $\sim 0.6$  indicates that the graphene is about 2-4 layers thick.<sup>51</sup> The D peak ( $\sim 1350 \text{ cm}^{-1}$ ) used to identify the level of defects<sup>52</sup> in graphene was found to be negligible for both spectra, indicating the high quality of the transferred CVD graphene.

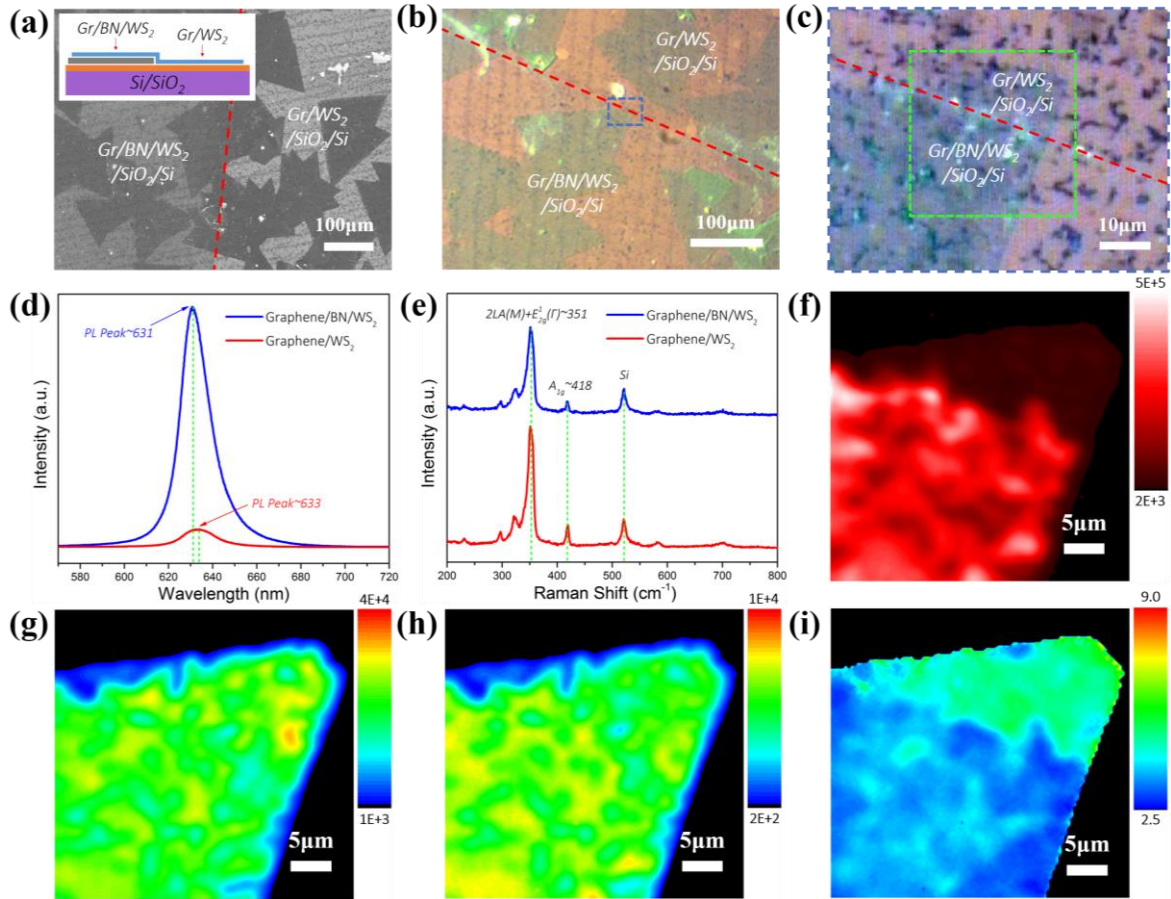


**Figure 7.7. Characterization of CVD graphene.** (a) SEM image of graphene/h-BN/WS<sub>2</sub> (left part) and graphene/WS<sub>2</sub> (right part) on SiO<sub>2</sub>/Si. Scale bar: 50 μm. (b) Optical image of the graphene/h-BN/WS<sub>2</sub> stack on SiO<sub>2</sub>/Si. The blue dashed line and the red dashed line indicate the boundary of graphene and h-BN film, respectively. Scale bar: 200 μm. (c) Optical image of the graphene/WS<sub>2</sub> stack. Scale bar: 30 μm. (d) Raman spectra of the marked spots with corresponding coloured crosses showing the existence of bi- and multi-layer graphene. Blue line: multilayer graphene. Red line: bilayer graphene.

The inset in **Figure 7.8(a)** presents a schematic diagram of the graphene/h-BN/WS<sub>2</sub> stack. The SEM image in **Figure 7.8(a)** shows WS<sub>2</sub> crystals with a layer of graphene on top. The left area indicated by the red dashed line was covered by a layer of h-BN, showing different contrast compared to the right region. **Figure 7.8(b)** shows the optical image of graphene/h-BN/WS<sub>2</sub> stack and **Figure 7.8(c)** is the zoomed-in optical image of the blue dashed area in **Figure 7.8(b)**, showing almost no difference in contrast due to h-BN's high transparency under visible light. The red dashed line indicates the boundary of h-BN. Again, Raman and PL spectroscopy were used to characterize the graphene/h-BN/WS<sub>2</sub> stack prepared by the non-aqueous transfer method. As can be seen from **Figure 7.8(d)**, under the same excitation

laser power and acquisition time, it was found that the integrated PL intensity is about 12 times stronger from the graphene/WS<sub>2</sub> stack with h-BN in between than that without the h-BN separator. The drastic PL quenching observed results from the charge transfer between WS<sub>2</sub> and graphene, which is in agreement with the literature.<sup>53</sup> **Figure 7.8(e)** shows the Raman spectra obtained from graphene/WS<sub>2</sub> and graphene/h-BN/WS<sub>2</sub>, both showing the peaks centred at 351 and 418 cm<sup>-1</sup>, which correspond to the WS<sub>2</sub> 2LA+E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> Raman modes, respectively.

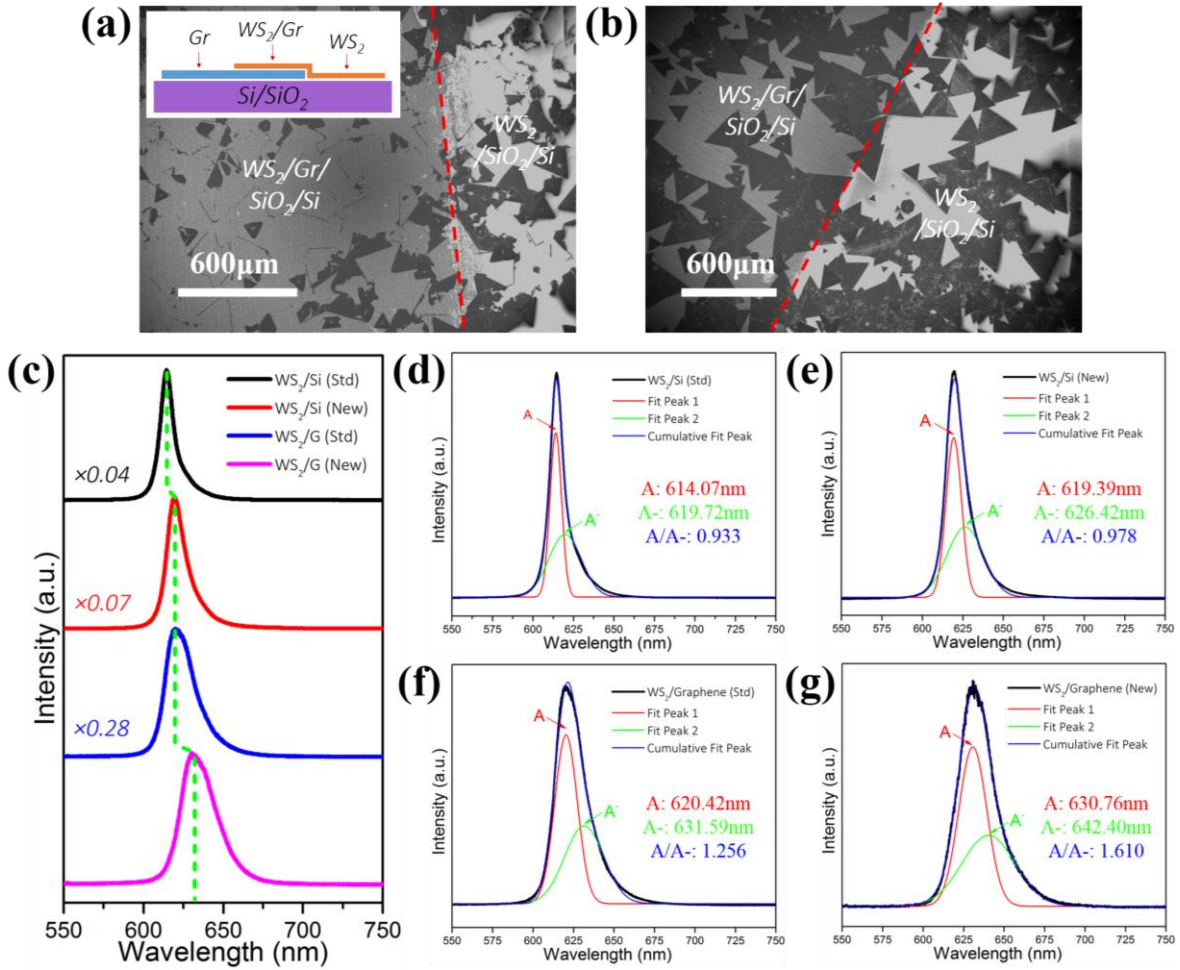
Furthermore, **Figure 7.8(f-i)** present PL and Raman intensity maps of the same region, the green dashed square in **Figure 7.8(c)**. The whole area mapped was covered by a layer of graphene on top, but only part of it has a layer of h-BN in between, which is indicated by a red dashed line. Raman mapping of the 2LA+E<sub>2g</sub><sup>1</sup> peak, **Figure 7.8(g)**, shows a relatively uniform integrated intensity over the area, while the integrated intensity of graphene/h-BN/WS<sub>2</sub> area at the A<sub>1g</sub> Raman vibrating mode, **Figure 7.8(h)**, is slightly higher than that of the graphene/WS<sub>2</sub> region, which leads to a different ratio of integrated 2LA+E<sub>2g</sub><sup>1</sup> peak intensity (330-370 cm<sup>-1</sup>)/integrated A<sub>1g</sub> peak intensity (400-430 cm<sup>-1</sup>), **Figure 7.8(i)**. The ratio is around 3 for the area with h-BN and about 5 for the region without. In addition, significant variations were seen in the PL mapping, **Figure 7.8(f)**, and it can be confirmed that the PL integrated intensity of the region without a layer of h-BN in between is much lower than the area with h-BN. The boundary of h-BN can be clearly distinguished, which means that by applying this transfer method, both h-BN and graphene can be assembled onto as-grown CVD WS<sub>2</sub> and h-BN can be an effective insulating layer which prevents interactions between WS<sub>2</sub> and graphene.



**Figure 7.8. Characterization of a graphene/h-BN/WS<sub>2</sub> stack prepared by the non-aqueous sliding transfer approach.** (a) SEM image of WS<sub>2</sub> crystals on SiO<sub>2</sub>/Si after transferring a layer of graphene on top of the h-BN/WS<sub>2</sub> stack. The left side is covered with a layer of h-BN while the right side is not. Scale bar: 100  $\mu$ m. The Inset shows a schematic of the graphene/h-BN/WS<sub>2</sub> stack. (b) Optical image of graphene/h-BN/WS<sub>2</sub> stack. The red dashed line indicates the boundary of h-BN. Scale bar: 100 $\mu$ m. (c) Optical image of zoomed-in blue dashed area in (b). The green dashed square indicates the region for PL and Raman mapping. Scale bar: 10 $\mu$ m. (d) PL spectra of graphene/WS<sub>2</sub> stack with and without h-BN in between, showing a large PL quenching when there is no h-BN in between. (e) Raman spectra obtained from graphene/h-BN/WS<sub>2</sub> stack compared with the graphene/WS<sub>2</sub> stack, with highlighted Si peak and WS<sub>2</sub> characteristic peaks, 2LA+E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub>. (f) PL mapping obtained from the green dashed region in (c). The integrated photo emission intensity from wavelengths of 600 to 660nm is shown. (g-i) Raman mapping obtained from the same graphene/h-BN/WS<sub>2</sub> region, highlighted with the green dashed line in (c), showing the integrated 2LA+E<sub>2g</sub><sup>1</sup> peak intensity from 330 to 370 cm<sup>-1</sup>, the integrated A<sub>1g</sub> peak intensity from 400 to 430cm<sup>-1</sup> and the ratio of integrated 2LA+E<sub>2g</sub><sup>1</sup> peak intensity (330 to 370 cm<sup>-1</sup>)/integrated A<sub>1g</sub> peak intensity (400 to 430 cm<sup>-1</sup>), respectively. Scale bar: 5 $\mu$ m.

The non-aqueous transfer method explored in this work is also suitable for transferring monolayer WS<sub>2</sub> from its growth substrate to other substrates, releasing the strain and also building multi-layered mixed vertical heterostructures with different stacking order. In **Figure 7.9**, I examined the properties of the transferred WS<sub>2</sub> on SiO<sub>2</sub>/Si and transferred graphene film. Both the non-aqueous sliding transfer approach and the standard wet transfer method are used for comparison. Graphene only partially covered the substrate and enables comparisons of the WS<sub>2</sub> properties for both the SiO<sub>2</sub> and the graphene region. **Figure 7.9(a)** and (b) present the SEM images of transferred WS<sub>2</sub> and WS<sub>2</sub>/graphene stack on SiO<sub>2</sub>/Si, prepared by the sliding transfer approach and the standard wet transfer method, respectively. The inset in **Figure 7.9(a)** shows a schematic of the WS<sub>2</sub>/graphene stack. It was found that some of the WS<sub>2</sub> crystals were washed off during the water-based transfer, while all the crystals can be successfully transferred onto other substrates when using the sliding transfer approach. The red dashed line indicates the boundary of the graphene film.

Following this, I investigated the PL spectra of transferred monolayer WS<sub>2</sub>, **Figure 7.9(c)**, for both transfer methods. The PL intensity of the WS<sub>2</sub> on graphene was quenched for both transfer methods, indicative of strong interactions. However, the non-aqueous transferred sample show larger quenching of the PL signal compared to the aqueous based method, **Figure 7.9(c)**, indicating stronger interlayer interactions. The peak position of the WS<sub>2</sub> on graphene transferred by the non-aqueous method is also significantly redshifted compared with the aqueous method. The larger quenching and redshift for the WS<sub>2</sub> transferred by the sliding transfer method indicates a cleaner atomic interface between the two layers and results in increased coupling between WS<sub>2</sub> and graphene.



**Figure 7.9. Characterization of WS<sub>2</sub>/graphene stacks prepared by either non-aqueous sliding transfer approach or standard wet transfer method.** SEM images of the WS<sub>2</sub>/graphene stack prepared by (a) the non-aqueous sliding transfer approach and (b) the standard wet transfer method. Scale bar: 600 μm. The inset in (a) shows a schematic diagram of the WS<sub>2</sub>/graphene stack. (c) PL spectra of the WS<sub>2</sub> on SiO<sub>2</sub>/Si and graphene transferred by either the sliding transfer method or the standard wet transfer method, respectively, which highlights the peak shape, intensity and position variation. (d-g) Gaussian fits to the PL peaks of transferred WS<sub>2</sub> on SiO<sub>2</sub>/Si and graphene using different transfer method, respectively.

As can be seen from **Figure 7.9(d-g)**, the PL peaks for the WS<sub>2</sub> under different conditions were fitted with two separate Gaussian peaks, which correspond to the neutral exciton (A) and negative trion (A<sup>-</sup>) emission. The energy difference between A and A<sup>-</sup> is about 20 meV for the WS<sub>2</sub> on graphene and 35 meV for that on SiO<sub>2</sub>/Si, which is consistent with previous reports of binding energy range 20 to 40 meV.<sup>54-56</sup> In addition, the fitting results show a

difference in integrated PL intensity ratio of exciton to trion ( $A/A^-$ ), indicating a different doping level of WS<sub>2</sub>. It was found that the WS<sub>2</sub> on graphene fabricated by the sliding transfer method has the highest  $A/A^-$ , while the WS<sub>2</sub> transferred on SiO<sub>2</sub>/Si by the standard aqueous transfer technique has the lowest. It is worth noting that, for both transfer methods, the WS<sub>2</sub> on graphene has a relative higher  $A/A^-$  than that on SiO<sub>2</sub>/Si, which confirms the higher degree of charged impurities for SiO<sub>2</sub> compared with graphene. Furthermore, for the WS<sub>2</sub> on the same substrate, the  $A/A^-$  for the sample transferred by the non-aqueous transfer method is higher than that prepared by aqueous-based one, indicating less contamination is introduced by using the IPA sliding transfer method.

### 7.3 Conclusion

In summary, an alcohol-based transfer technique was developed for transferring 2D materials onto as-grown CVD WS<sub>2</sub> to preserve the inbuilt strain produced during the CVD growth. All the h-BN/WS<sub>2</sub>, graphene/h-BN/WS<sub>2</sub> and WS<sub>2</sub>/graphene stacks prepared were characterized by optical microscopy, SEM, Raman spectroscopy and PL measurements, indicating that, by using this method, the as-grown WS<sub>2</sub> domains remain intact on the surface. Stronger interactions between WS<sub>2</sub> on graphene was found when swapping water for IPA, likely resulting from reduced contamination between the layers associated with aqueous impurities. This new method is thought to be particularly useful for fabricating devices that involves transferring one 2D material onto as-grown strained TMDs on sapphire or SiO<sub>2</sub>/Si substrates.

### 7.4 References

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## Chapter 8

### *Conclusions and Future Outlook*

#### 8.1 Thesis Summary

The novel research in this doctoral thesis has been divided into four broad sections. Each has been given a dedicated focus for one chapter. Chapter 4 investigated the methods and procedures for the growth of bilayer graphene films with areas up to  $14\text{ cm} \times 6\text{ cm}$  by copper catalysed chemical vapour deposition (CVD); Chapter 5 detailed the synthesis of monolayer tungsten disulphide ( $\text{WS}_2$ ) continuous films on insulating substrates using separately introduced solid powder precursors by ambient pressure CVD (APCVD). Chapter 6 dived into the study of photoluminescence (PL) segmentation within APCVD-grown hexagonal monolayer  $\text{WS}_2$  crystals via a wide range of characterisation tools; finally, Chapter 7 introduced a novel non-aqueous sliding transfer approach, providing for the fabrication and characterisation of various vertical stacks based on all two-dimensional (2D) materials.

#### 8.2 Conclusions

2D materials, such as graphene and  $\text{WS}_2$ , exhibit exceptional properties that hold promise for various applications, including electronics, optoelectronics, and flexible devices. Other than mechanical exfoliation, many approaches have been developed to achieve a reliable and

repeatable synthesis of large area, high quality 2D materials with large grain sizes and uniform thickness. Among these, CVD is regarded as one of the most promising ways to achieve it in a simple, easy and low cost manner.

The Graphene grown by chemical vapour deposition (CVD) on copper foils is a viable method for large area films for transparent conducting electrode (TCE) applications. The study here shows how different supporting substrates for the Cu catalyst impact the final graphene films (Chapter 4). Characterisations, including Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), confirm that the graphene films are mostly bilayers with turbostratic stacking configurations. The spatial uniformity of the bilayer films is examined on the centimetre scale when transferred onto both Si substrates with 300 nm oxide and flexible transparent polyethylene terephthalate substrates. The difference in the quality of the graphene, as measured by the sheet resistance and transparency, was found for the areas at the edges of large sheets that depend on the supports used for the CVD growth. As the only difference between the two supports is their shape, the poor growth of graphene when using the boat is entirely due to the turbulence of the gas flow, which is not present for the balanced flat support.

As one of the thinnest layer-structured semiconductor, monolayer WS<sub>2</sub> offers great prospects for use in optoelectronic devices due to its direct band gap and high PL intensity. The progress in producing CVD bilayer graphene pushed my synthesis research into the second stage, *i.e.*, establishing techniques for the growth of monolayer WS<sub>2</sub> with increased coverage, growth uniformity and continuity. I implemented this task by controlling the addition of hydrogen (H<sub>2</sub>) into the APCVD system which enabled an increase in the growth rate of WS<sub>2</sub>, resulting in fully-merged films with cm<sup>2</sup> coverage and reduced multilayer content (Chapter 5). Modifications of the reaction conditions, including growth time and H<sub>2</sub>

to argon ratio, allowed for control over the domain size, film coverage and film uniformity of the prepared WS<sub>2</sub> film. Field effect transistors were fabricated to demonstrate the WS<sub>2</sub> monolayer has high quality for electronic applications.

The high-throughput ability of this CVD synthesis provides the opportunity to produce not only monolayer WS<sub>2</sub> continuous films, but also separately distributed WS<sub>2</sub> crystals with different geometrical shapes. It allows a regular spatial-dependent shape evolution to be observed in the WS<sub>2</sub> samples, changing from triangles to hexagons along the gas flow direction. Interestingly, the PL emission in the hexagonal domains of monolayer WS<sub>2</sub> exhibits symmetric patterns which may arise during growth (Chapter 6). 2D maps of the PL reveal significant reduction within the segments associated with the longest sides of the hexagonal domains. Further analysis of the PL spectra shows differences in the exciton to trion ratio, indicating variations in doping level. Monolayers of WS<sub>2</sub> hexagonal islands transferred to new substrates still exhibit this PL segmentation, ruling out local strain regions as the dominant cause. High power laser irradiation causes preferential degradation of the bright segments by sulphur removal, a result which indicates the presence of a more defective region that is higher in oxidative reactivity. Atomic force microscopy (AFM) images of topography and amplitude show uniform thickness of the WS<sub>2</sub> domains and no signs of segmentation. However, these AFM phase maps show the same segmentation of the domain as the PL maps and indicate that this segmentation is caused by some kind of structural difference that could not clearly identified. These results reveal the spatially varying properties of these CVD-grown 2D materials, which may play an important role for their future implementation in optoelectronic products.

Following the aforementioned work on the synthesis and characterisation of individual 2D materials, namely bilayer graphene and monolayer WS<sub>2</sub>, mixed vertical 2D heterostructures

based on these materials are formed *via* layer by layer transfer. Monolayer CVD WS<sub>2</sub> can have inherent strain due to interactions with the substrate. The strain modifies the band structure and properties of monolayer WS<sub>2</sub>, and can be exploited in a wide range of applications. However, WS<sub>2</sub> monolayers grown by CVD directly on Si substrates with SiO<sub>2</sub> surface are easily washed off by water and this makes aqueous based transfer methods challenging for creating vertical stacks on the growth substrate. Therefore, a novel non-aqueous transfer technique is developed for transferring 2D materials onto as-grown CVD WS<sub>2</sub> to preserve the inbuilt strain. By using this method, stronger interactions between WS<sub>2</sub> and graphene is found, likely resulting from reduced aqueous impurities. Moreover, 2D hexagonal Boron Nitride films were used to provide an insulating layer that limits interactions with a top graphene layer and preserve the strong PL from the WS<sub>2</sub>. This transfer method is shown to be transferrable for all 2D materials grown by CVD, enabling large area vertical heterostructures to be formed.

### 8.3 Future Outlook

The experiments conducted on one 2D material are often cross-applicable to the rest of group. As to the two CVD synthesis methods mentioned in this thesis, given the lateral sizes of the continuous films (*i.e.*, bilayer graphene  $\sim 14\text{ cm} \times 6\text{ cm}$  and monolayer WS<sub>2</sub>  $\sim 1\text{ cm} \times 1\text{ cm}$ ), the process is still far from industrial or commercial application. In particular, for the growth of monolayer WS<sub>2</sub>, substituting solid precursors with liquid/gas precursors in further experiments that seek to understand the influence of gas dynamics on the uniformity of the product is the logical evolution of this work. In an effort to facilitate the future industrialization of 2D Materials, further work will involve introducing low pressure or vacuum pump into the upscale CVD system with a quartz tube of larger diameter size than the existing one. This will allow for the creation of a much more uniform 2D material film

over large areas. In addition, the symmetrically distributed PL emission within hexagonal monolayer WS<sub>2</sub> crystals could be further studied and explored. By utilising transmission electron microscopy, it would be possible to directly observe the defect structures in the two regions with different PL intensities. Further research involving electrical measurements could elucidate the connection between the PL segmentation and the growth mechanism of defect formation. Lastly, with the assistance of the aforementioned non-aqueous sliding transfer method, it would be of particular interest to the process of building more complicated and better designed 2D vertical stacks based on all 2D materials, the properties of which could later be compared with those fabricated by direct CVD growth. These results could provide a valuable insight into the relative importance of the production of large area, high quality 2D materials using CVD on next generation electronics and optoelectronics.