

Characterisation of Atomically-Thin Transition Metal Dichalcogenides

by

Paweł Jan Palczyński

A thesis submitted in partial fulfilment of the requirements for the award of the degree

Doctor of Philosophy

from

Imperial College London

Faculty of Engineering, Department of Materials

February 24, 2020

Declaration of originality

I hereby declare that this thesis is the result of my own work unless otherwise referenced or acknowledged. This document is submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy in the Department of Materials, Imperial College London and it has not been submitted to any other academic institution awarding qualifications.

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Acknowledgements

I would like to thank my supervisor Dr. Cecilia Mattevi for enormous amount of help, guidance, support and patience throughout my entire time in her group.

I would also like to acknowledge the examiners, Prof. Alexander Tartakovskii and Dr Peter Petrov for reviewing this thesis.

Thank you to Dr Francesco Reale for all the talks, both serious and lighthearted, and for providing me with all the CVD samples, XRD, SEM and AFM measurements and analysis.

Thank you to Ms Maria Sokolikova for the enlightening conversations and cheering me on to finish this thesis, and for all the colloidal synthesis samples, TEM imaging and analysis.

Thank you to Dr Peter Sherrell, Dr Federico Pesci and Dr Sharda Kanudha for all the guidance and help with setting up experiments and support, and for heterostructure samples, SEM imaging, electrical measurements and analysis.

I would like to acknowledge the help from collaborators, Dr. Iddo Amit, Prof. Monica F. Craciun and Prof. Saverio Russo for performing the electrical measurements.

Thank you to all the lab and office mates, Chiara Grotta, Cong Lu, Aleksandra Krajewska, Julian Buchinger, Jerome Nicolas, Nikesh Patel, Elisa Burbaum, Jeremy Tan, Mauro Och, Apostolos Panagiotopoulos, Gang Cheng, Giulia Zemignani, Stefano Tagliaferri, Gianmaria Matrone, David Poussin, Shengyang Chen, Luca Occhi, Francesco Salerno, Bartosz Barzdajn for all the interactions, talks and support that made this PhD journey complete.

And finally a thank you to my family, mamie, tacie, bratu i bratowej, for all the love and support, dziękuję.

Publications

1. **P. Palczynski**, F. Reale, P. Sherrell, M. Sokolikova, C. Mattevi. In-doping of mono and few-layered WS_2 . Submitted.
2. Peter C. Sherrell+, **Pawel Palczynski**+ (equally contributed), Maria S. Sokolikova, Francesco Reale, Federico M. Pesci, Mauro Och, Cecilia Mattevi. Large-Area CVD MoS_2/WS_2 Heterojunctions as a Photoelectrocatalyst for Salt Water Oxidation. ACS Applied Energy Materials, 2019. Just accepted.
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List of abbreviations

TMDC - Transition metal dichalcogenide

CVD - Chemical vapour deposition

PL - Photoluminescence

SEM - Scanning electron microscopy

TEM - Transmission electron microscopy

AFM - Atomic force microscopy

XRD - X-ray diffraction

XPS - X-ray photoelectron spectroscopy

VBM - Valence band maximum

CBM - Conduction band minimum

DFT - Density functional theory

EDS - Energy dispersive x-ray spectroscopy

LPE - Liquid phase exfoliation

FWHM - Full width half maximum

MEX - Mechanically exfoliated

OM - Optical microscopy

Abstract

Transition metal dichalcogenides (TMDC) are a class of materials that has become increasingly popular in the recent years in the wake of discovery of graphene and its surprising properties. Despite being known for decades and being used in their bulk form as a sold lubricant or catalysts their mono and few layer form remained largely unexplored. Indeed when TMDCs are only one or few layers thick their unique optical and electronic properties emerge. In particular group VI TMDCs such as MoS_2 or WS_2 , as their numbers of layers decreases, turn from an indirect to direct bandgap semiconductor with possible applications in visible range optoelectronic and electronic devices. Moreover unique quantum effects such as quantum spin Hall effect, strong spin orbit interactions or topological insulators can be observed in these thin films.

One of the major hurdles standing in the path of further development of those materials is its synthesis. The commonly used methods successfully optimise one of the many desired parameters and therefore new techniques must be developed to provide an improvement across all aspects of the material quality. In order to properly asses those new growths methods metrological studies must equally contribute to the capabilities of rapid assessment of large area flakes and films. To that effect the commonly used Raman and PL are heavily employed throughout in mapping the as grown as well as transferred flakes on multiple different substrates. In a similar fashion the x-ray spectroscopy is utilised to gain insight into the samples chemistry, layer thickness and crystal structure. This triple role of XPS allowed for initial studies of 1T' WSe_2 which combined with Raman and PL spectroscopy with supplement of other characterisation techniques provided valuable introspective into its structure and properties.

The overarching goal of the thesis is to develop synthesis techniques for growth of TMDCs primarily via CVD as well as colloidal synthesis in order to reliably produce thin layers with controllable thickness and lateral size. This work focuses on characterisation of the as grown materials using Raman, PL and XPS techniques to assess the quality and reproducibility of the developed synthesis methods.

Additionally in this work the novel synthesis routes for growth of WS_2 large area monolayers have been assessed. The as grown samples on top of exhibiting strong PL response showed remarkable, record high electron mobility in mono and bilayer form. A certain degree of optical and electrical properties tunability is also presented in In doped WS_2 layers. By combining the growth of monolayers the heterostructures of MoS_2/WS_2

are successfully grown on multiple substrates and their quality and structure is carefully investigated.

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Chapter 1

Thesis introduction

The recently popular group of materials called Transition Metal Dichalcogenides (TMDCs) have attracted a great deal of attention following the discovery of graphene. Many of the materials belonging to that group, such as WS_2 or MoS_2 , are semiconducting in nature. As one of the manifestations of this property is a very strong photoluminescence (PL) response observed across many monolayers of the TMDCs. Despite extensive studies into the nature of this photoluminescence response the full understanding remains elusive. The PL spectrum of many of those monolayers is complex and can be a result of many contributions from different phenomena and particles. Besides the main peak resulting from recombination of excitons, other quasi particles such as trions or bi-excitons can contribute to the spectrum at room temperature. Additionally the interactions between the material and the substrate as well as any surface effects, including adparticles, vacancies, defects or strain can alter the observable spectrum. Due to its 2D nature TMDCs are especially influenced by the surface effects.

TMDCs can also exhibit different polytype structures with most common being 2H and 1T phases. An interesting phenomena can be observed in regards to those polytypes where different phases can change from semiconducting to metallic. Those phases together with structural defects and strain can also affect the electronic structure of the TMDCs and thus influence the formation of many of the photogenerated particles. Many of these interactions are however still at the early stages of understanding.

There has been many attempts at simulating the electronic structures using computational methods such as DFT. The results however are not always compatible with the observed phenomena and show even great discrepancies between different approaches.

One of the polytypes, the 1T' phase, shows interesting properties such as that of

topological insulator. It has however remained understudied, partially due to difficulty in synthesis. There still remains many TMDCs for which 1T' phase has not been demonstrated.

Because the 2D materials inherently lack much volume or mass, many standard characterisation techniques are insufficient and can either result in insufficient resolution or signal to noise ratio or can not be applied at all. Due to this a limited set of characterisation techniques remains viable. Among those, the most useful methods which can enable metrological characterisation are Raman spectroscopy, photoluminescence (PL) spectroscopy and X-ray Photoelectron Spectroscopy (XPS). Those techniques can provide information over large sample areas in relatively short times. In particular Raman and PL spectroscopy allows for relatively fast mapping, in comparison to other surface sensitive methods such as XPS or SEM, of areas in the order of tens of square millimetre in air without the need of any sample preparation and could potentially extract information about crystallographic phases, strain, density defects, number of layers and interaction between the layers. Raman and PL studies of mono and few-layered TMDCs have been conducted for few years and numerous discoveries have been made in this time for some of the TMDCs. As the synthesis methods however improve new and better materials can be produced and investigated. Both of these characterization techniques can enable relatively fast (compared to other surface sensitive methods like XPS or SEM) scanning rate of large surface areas (mm and cm scale). XPS can be further used to learn about stoichiometry, oxidation states, defects, doping or alloying and it can be correlated with Raman and PL features. The combined physical and chemical characterisation can therefore help to provide insight into the fundamental properties of those materials.

In this thesis some initial work on the interpretation of PL and Raman spectra in CVD grown WS_2 , doped WS_2 , MoS_2/WS_2 heterostructures has been performed. This work aims at contributing to the ultimate goal of establishing a correlation system between characterisation and materials properties for wafer scale grown mono and few-layered TMDCs in the 2H and 1T/1T' polytypes. The two most common methods of producing TMDC monolayers for purpose of research is mechanical exfoliation and chemical vapour deposition (CVD). While the former in many cases tends to provide higher quality flakes it does not scale in terms of size and therefore has to be replaced by different, scalable methods. The most popular such method is CVD, with which continuous layers on at least cm scales have been demonstrated. Due to variety of used precursors and synthesis paths the quality and composition of resulting flakes varies and therefore requires an

understanding of its effects on the material properties.

Using this understanding similar techniques have been applied to MoS_2 and MoS_2/WSe_2 vertical heterostructure. This allowed to contribute to greater body of knowledge about the interactions between the layers in heterojunctions and its effect on the opto-electronic properties. Furthermore, we have studied by PL, Raman spectroscopy and XPS the 2H phase of WSe_2 and by Raman spectroscopy and XPS the 1T' phase of WSe_2 .

Using colloidal synthesis unique formations of atomically thin 1T' WSe_2 flakes have been observed for the first time. They have been characterised using Raman spectroscopy and XPS to provide some of the first studies of those phases to correlate structural properties and W 4f bonding energy and Raman active vibrational modes.

Chapter 2

The state-of-the-art of group VI transition metal disulphides and diselenides

Following the discovery and characterisation of graphene in last decade the focus has been put on other 2D materials. Similar to graphene other bulk layered materials can exist in a monolayer or few layer form. Furthermore these thin layers also exhibit a significant change of properties when number of layers decreases from bulk all the way to monolayer. One of the most popular groups of these materials are transition metal dichalcogenides (TMDC). Their general form is MX_2 where M is a transition metal, and X is a chalcogen atom.

2.1 Properties of TMDCs

TMDCs in their layered form have been known, studied and utilised for a long time. They can be found commonly in use as stolid-state lubricants or catalysts. About 60 different TMDCs have been studied and characterised with a general formula of X-M-X where a plane of metal atoms (M) is sandwiched between two chalcogen planes (X) [1]. Out of those 40 can be considered layered materials where individual layers are strongly bonded in-plane and weakly bonded out-of-plane in between layers. These weak, interlayer, Van der Waals interactions allow to form a bulk material. These bonds are also what allows for those layers to slide on top of one another similarly to other layered materials like graphite [2].

TMDCs consist of two transition metal and single chalcogen atoms covalently bonded. They can be found in 3 distinct structural polytypes: 1T (tetragonal symmetry, octahedral coordination) with single layer per repeat unit, 2H (hexagonal symmetry, trigonal prismatic coordination) with 2 layers per repeat unit and 3R (rhombohedral symmetry, trigonal prismatic coordination) with 3 layers per repeat unit [3][2][?] as can be seen in Figure 2.1.

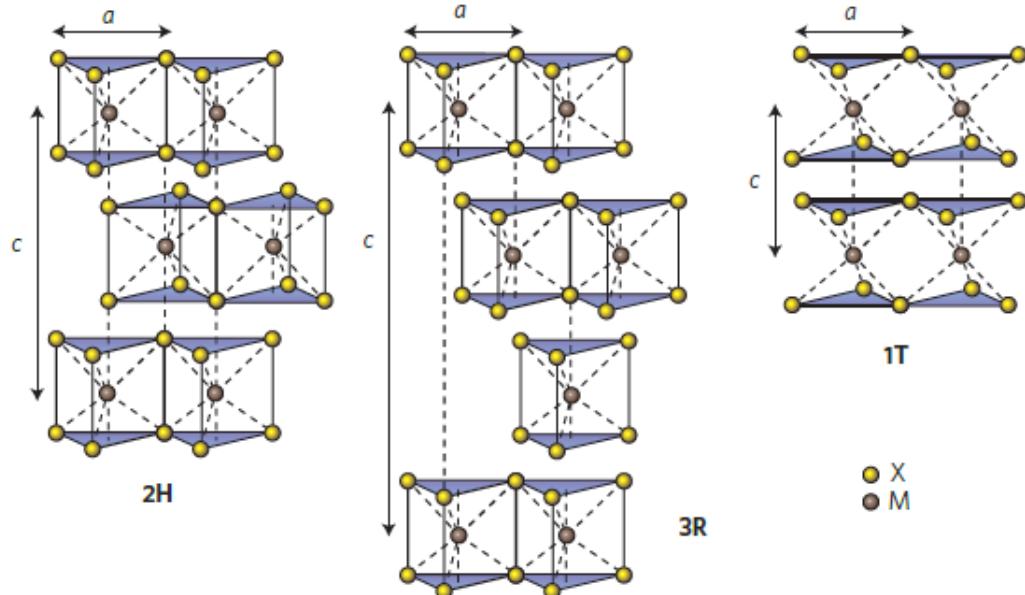


Figure 2.1: Schematics of the structural polytypes: 2H (hexagonal symmetry, two layers per repeat unit, trigonal prismatic coordination), 3R (rhombohedral symmetry, three layers per repeat unit, trigonal prismatic coordination) and 1T (tetragonal symmetry, one layer per repeat unit, octahedral coordination). The chalcogen atoms (X) are yellow and the metal atoms (M) are grey. The lattice constants a are in the range 3.1 to 3.7 Å for different materials. Adopted from [3]

Since graphene have proven to be difficult to work with in the fields of semiconductors due to its lack of natural finite electronic band gap its role as a successor in electronic and opto-electronic devices remains to be seen [?]. However the techniques learned and effects observed during its characterisation were easily transferred to other layered compounds such as TMDCs. In particular the semiconducting, group VI-based TMDCs, containing sulphur and selenium as chalcogen atoms have proven to be more readily potentially useful as an active material in electronic and opto-electronic devices. This is due to their inherent electronic and optical bandgap in visible-near IR range [3].

As the number of layers changes from bulk to monolayer the properties of the TMDC

undergo a significant change. In most TMDCs the bandgap changes from indirect to a larger direct one [3].

2.1.1 Electronic properties

One of the most interesting features that the layered TMDC materials exhibit is the shift in the bandstructure with the changing number of layers. Several studies have shown in simulations and experimentally that TMDCs have very similar electronic band structure as seen in example of WS_2 in Figure 2.2. In quadlayer WS_2 the maximum of the valence band (VBM) at Γ point and the minimum of the conduction band (CBM) at Λ (midpoint between K and Γ) form an indirect bandgap. As the number of the layers decreases the CBM at Λ point as well as VBM at K point increases causing the band gap to widen. Finally in a WS_2 monolayer the VBM at K point as well as entire conduction band increases to form a new greater direct band gap at K point. This means that WS_2 bandgap changes from 1.3 eV indirect bandgap in bulk to 2.1 eV direct bandgap in monolayer . Additionally for each of these cases there is a split in valence band which results in an additional level at K point. This split is caused by spin orbit interaction and results in two levels with opposite spins separated by about 0.4 eV [4].

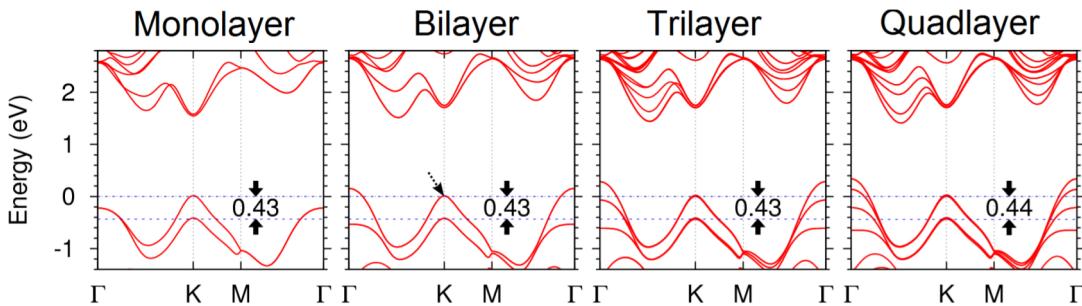


Figure 2.2: Band structures of 1,2,3 and 4 layer WS_2 , from ab initio calculations. Adopted from [4]

Like WS_2 other Mo and W based TMDC undergo similar transitions as seen in Table 2.1. In all cases the smaller indirect bandgap changes to greater direct bandgap with monolayer bandgap ranging from 1.1 eV to about 2.1 eV. Moreover the VBM at K points exhibits the orbit-spin band splitting at the K point of about 400 meV. This direct bandgap leads to presence of A and B excitons generated by transition between CBM and two VBM at the K point. The conduction band as well as the valence band are dominated by the d-electron orbitals of the transition metal atoms and at the VBM

and CBM they hybridize with the p-electron orbitals of the chalcogenide atoms. Because the hybridization happens mostly at the Γ point and the chalcogenide atoms are at the surface of the TMDC layer it leads to strong interactions between the layers. This leads to significant change in the band structure at the Γ and rise of the indirect bandgap as a result of increased number of layers. On the other hand at the K point the d-orbitals of the transition metals remain mostly unaffected due to them being positioned in the middle of the layer [5] [6]

Table 2.1: Mo and W based TMDC bandgaps comparison. Adopted from [3]

M\X	$-S_2$	$-Se_2$	$-Te_2$
Mo	Semiconducting	Semiconducting	Semiconducting
	1L: 1.8 eV	1L: 1.5 eV	1L: 1.1 eV
	Bulk: 1.2 eV	Bulk: 1.1 eV	Bulk: 1.0 eV
W	Semiconducting	Semiconducting	Semiconducting
	1L: 2.1 eV	1L: 1.7 eV	1L: 1.1 eV
	Bulk: 1.4 eV	Bulk: 1.2 eV	

2.1.2 Optical properties

TMDCs exhibit a wide array of opto-electronic effects due to their strong light-matter effects. These effects are mostly caused by the abundant presence of excitons, bi-excitons, trions or bound excitons. As a result the change in layer thickness from bulk to monolayer alters the photoluminescence, photoconductivity and absorption in the visible to infrared range.

The primary and most common quasi-particle that forms in such system is an exciton, which is a pair of a negatively charged electron and a positively charged hole bound together by Coulomb forces to form a structure similar to that of hydrogen atom. Such pair is electrically neutral and is of size exceeding size of single cell which makes it a Wannier–Mott exciton [7]. The recombination of these excitons results in a photon emission which can be easily observed during photoluminescence characterisation. On top of excitons other quasi-particles such as trions, bi-excitons or bound excitons can be found [?]. A trion is a group of 2 electrons and a hole or 2 holes and an electron, or otherwise described as a charged exciton. The exact nature of the trion depends usually on the type of intrinsic doping of the TMDC. A bi-exciton is a pair of excitons which is usually only

observed in quantum dot systems but can be also seen in excitonically dense systems such as TMDCs. A bound exciton is similar to the free exciton but is trapped by a defect. In a typical photoluminescence spectrum several peaks can be observed depending on specific type of TMDC characterised. In WS_2 monolayer for instance as seen in Figure 2.3 the strongest peak (often labelled as an A peak) at about 1.97 eV is caused by the direct transition of the electron following a generation of an exciton. At room temperature slightly redshifted by about 30 meV from the A peak a generally weaker peak caused by the trion recombination can be found. At lower energies another peak can be observed due to the presence of bi-excitons. At around the 1.3 eV a much weaker peak (I) can be seen (Figure 2.3) caused by the indirect transition, present in 2 or more layers. As the number of layers increases from 2 to bulk the peak becomes more intense. Additionally a B peak can be observed blueshifted from the A peak which is caused by valley splitting as discussed in chapter 2.1.1. As seen in Figure 2.3 as the number of layers increases the main A peak becomes dramatically weaker due to lack of direct transition and slightly blueshifted following the pattern discussed in chapter 2.1.1. At the same time the I peak becomes relatively stronger and eventually dominates the bulk material.

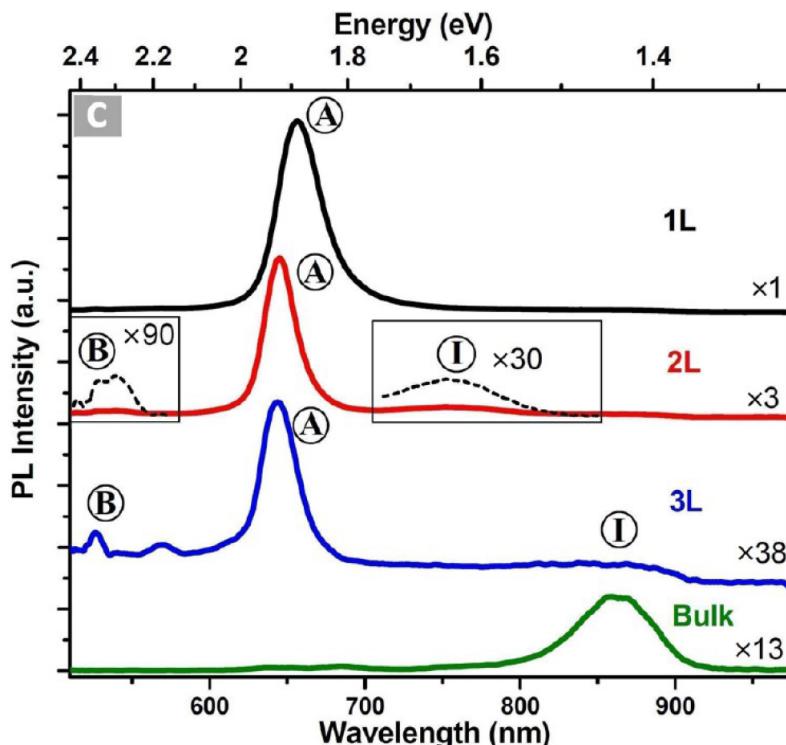


Figure 2.3: Typical PL spectrum of WS_2 showing the influence of the number of layers. Adopted from [8].

Similarly the photoconductivity of the TMDCs is strongly reliant on the number of

layers and incident photon energy. The MoS_2 for instance shows 3 times stronger photoconductivity in monolayer around 1.8 eV, where the direct transition is located, than in 2L MoS_2 around 1.6 eV. Additionally the photoconductivity appears to increase in steps with relation to the photon energy following the direct and indirect transitions. [3].

The sunlight absorption in TMDCs has been shown to be significantly more intense than in commonly used solar cell materials, at about 5-10% which is an order of magnitude greater compared to similar thickness of Si or GaAs. It is also stronger compared to 2-3% of sunlight absorption of graphene. As a result an excitonic solar cell based on MoS_2/WS_2 bilayer shows about 1% power efficiency, about 3 times greater than that of typical ultrathin solar cells [9].

Due to spin orbit interactions the valence band as well as conduction band can become split, particularly at the K point where the direct transition generally happens in TMDCs. As a result a subband with spin in one direction is above or below the subband with the opposite spin. This means that the ground state of the exciton can be such that the electron at CBM and hole at VBM have opposite spins and therefore cannot recombine optically to emit a photon. Depending on the direction of the split some ground states can be therefore "bright" (like MoS_2) while other can be "dark" (like WS_2 , WSe_2 or $MoSe_2$). However at room temperature the additional energy allows the holes in VBM to occupy the excited "bright" state and therefore be able to recombine optically. [10]. One way to observe dark excitons is to use two photon excitation. Due to two photon selection rule the single photon excitation can be excluded and the dark excitonic states can be observed. In WS_2 the PL from dark excitons recombination result in two peaks at 2.28 eV and 2.48 eV. [7] Additionally a magnetic field can be applied in the plane of the layer allows for enhancement of PL from dark excitons at low temperatures [10].

Defect engineering allows to tune the number of charge carriers. In MoS_2 or WS_2 the sulfur vacancies lead to increased number of electrons in the material. Because of that by increasing the number of defects in those materials the level of n-doping can be changed. An easy way to observe the presence of those defects and subsequent quenching of them is to expose the material to varying amounts of oxygen, nitrogen or water. Those species attract the electrons locally and therefore the electron population in the material decreases. This in turn leads to smaller trion population since trions require an extra electron to form. This then can be observed in PL as a more narrow direct peak, with especially smaller redshifted shoulder. The effect can also be of course reversed by decreasing the amount of oxygen, nitrogen or water in the environment since those exist

in already in ambient conditions [11].

In order to introduce and control the amount of vacancies in the TMDC different method have to be explored. One of the ways of achieving that in already grown material is the use of oxygen plasma. It has been shown that the number of defects can be controlled by limiting the plasma exposure. During the process the oxygen also chemically bonds to the MoS_2 at the defect sites and therefore partially negates the effect of defects on the optical properties. The PL can also be seen to increase in intensity with increasing number of defects with oxygen adsorbed due to the increased yield of bound excitons localised at these defects [12].

Similar effect has been shown using the 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ), 7,7,8,8-tetracyanoquinodimethane ($TCNQ$) and (nicotinamide adenine dinucleotide) $NADH$ for chemical doping. Both F_4TCNQ and $TCNQ$ are p-type dopants while $NADH$ is a n-type dopant. By exposing the surface of MoS_2 to these compounds the change in PL intensity and FWHM have been observed. Similar to doping with O_2 , N_2 or H_2O , all of which are p-type dopants, the intensity of PL has increased in presence of F_4TCNQ and $TCNQ$. The effect has been similarly ascribed to lowering the number of defects and therefore the lowering the trion population and subsequently increasing the exciton population increasing the yield. The opposite observation has been made with use of $NADH$ with PL intensity decreasing. Similarly the increase in trion population with lower PL yield is ascribed to the lower PL intensity. [13]

It has also been shown that alloying can be used to fine tune the PL by varying the concentration of alloying material. In monolayer $Mo_{1-x}W_xS_2$ the PL peak position initially decreases from 1.575 eV (PL peak position of pure MoS_2) to 1.56 eV at $x=0.21$ and then increases up to 1.65 eV (PL peak position of WSe_2) at $x = 1$. This effect could be attributed to the linearity of VB and non-linearity of CB with regards to change in W composition. The PL position can therefore be engineered on a monotonic range from 1.56 eV to 1.65 eV. In bilayer $Mo_{1-x}W_xSe_2$ alloy the position of both direct and indirect transition PL peaks increases monotonically from about 1.49 eV and 1.53 eV for pure $MoSe_2$ to 1.56 eV and 1.62 eV for pure WSe_2 as the W amount is increased. This opens another relatively easy way of engineering PL position [14].

Another effect that has been demonstrated that allows for certain degree of control of PL in TMDCs is relation between the helicity of incident light and valley population. It has been shown that by exciting the monolayer MoS_2 with right-polarised light the resulting excitons will fill primarily the VB at K point. Similarly by exciting the MoS_2

with left-polarised light the excitons will fill the VB at K' point. After recombination the resulting photons will exhibit the same circular polarity as the photons that excited the electrons in the first place. [15][16]

The temperature effect on TMDCs has also been investigated. In WSe_2 monolayer it has been shown that as the temperature of the sample increases from room temperature to about 400K the position of the direct transition PL peak redshifts from about 1.65 eV to about 1.58 eV. When the temperature is decreased from room temperature to about 5K the same peak blueshifts to about 1.7 eV. Between 100K and 50K as well 20K and 5K the position of the PL peak does not change. Additionally around 120K another peak appears and as the temperature is lowered it also blueshifts although less than the RT peak. The peak only present at RT is attributed to free excitons whereas the peak appearing at 120K is ascribed to bound excitons. As bound exciton peak appears its intensity increases with lower temperature while the intensity of the free exiton peak decreases. This indicates that the population of free excitons decreases while the population of the bound excitons increases with decreasing temperature [17]

There has been many reports on the spatial distribution of PL in the TMDCs. One of the observed patterns in WS_2 and MoS_2 has been that of much stronger PL intensity at the edges of the flakes. That effect has been primarily observed in small flakes of about $5 \mu m$ [8]. It has recently been shown that the edge enhancement of the PL in WS_2 flakes is caused by oxygen chemisorption. Due to presence of oxygen at the edges the electrons move towards the edges which results in greatly increased population of trions and subsequent increase in PL intensity [18].

Direct band-to-band transitions in two-dimensional system are characterized by a step-function-like spectrum originated from the energy-independent joint-density-of-states and transition matrix elements near parabolic band edges [19] (dashed blue line in Figure 2.4). However, TMDCs are dominated by excitonic effects as exemplified by experimental absorption spectrum with sharp resonance features [6] (solid green line in Figure 2.4). These excitonic effects are enabled by the very large exciton binding energies E_B (0.2–1 eV, corresponding to an exciton Bohr radius $a_B \approx 1nm$) at room temperature which has been predicted theoretically and measured experimentally using optical spectroscopy and scanning tunnelling spectroscopy [20][21]. Some discrepancies in the estimated value are still present but overall theory and experiment broadly agree. In addition to excitons, higher-order excitonic quasiparticles have also been observed in 2D TMDs (Figure 2.5). Trions, which are bound states of two electrons and one hole, or two holes and one electron,

have been observed in intrinsically doped monolayer TMDCs [15][22]. Bi-excitons (bound states of two excitons) have been reported in monolayer TMDCs under pulsed optical excitations [23][24] and the quinton (the five-particle negatively charged biexciton) [25].

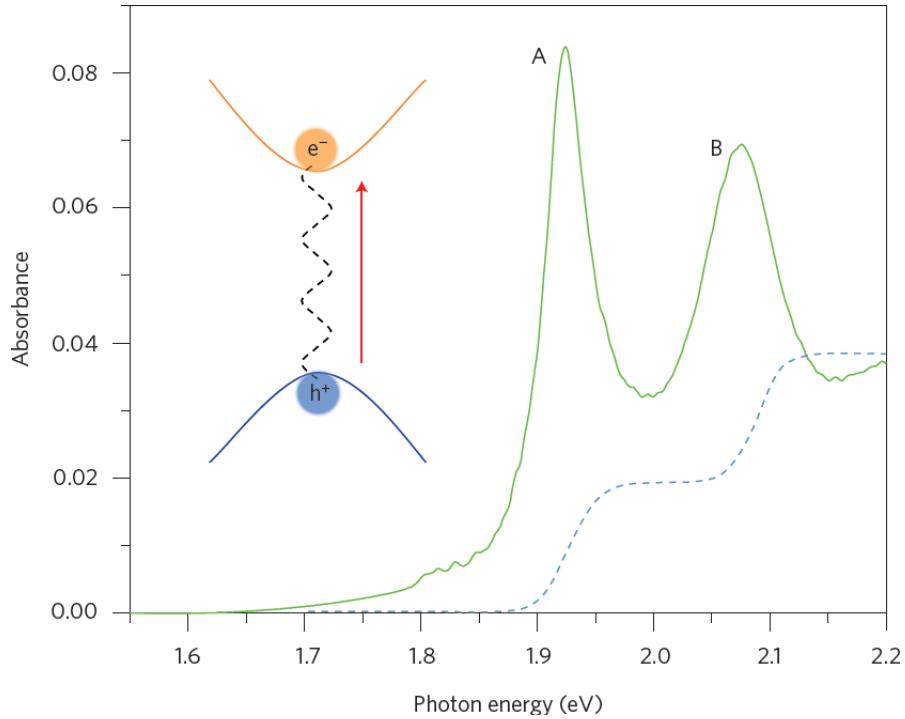


Figure 2.4: Absorption spectrum of monolayer MoS_2 at 10 K in green. A and B peaks correspond to two spin-split valence to the conduction bands transition. Blue dashed line - absorbance in absence of excitonic effects. Inset - Coulomb attraction between an optically generated electron–hole pair which forms a bound exciton. Reproduced from [26]

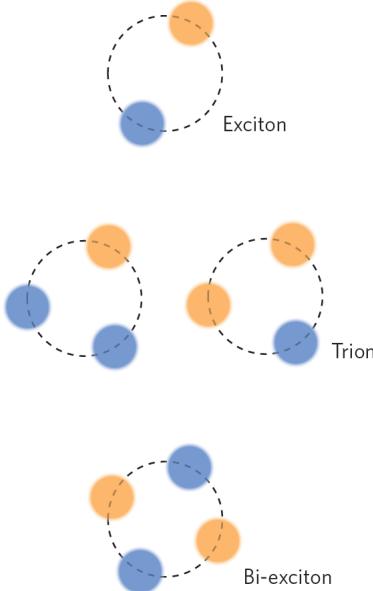


Figure 2.5: An exciton and other excitonic complexes: a neutral exciton, a trion and a bi-exciton. Reproduced from [26]

2.1.3 Optoelectronics applications

Here I summarize the main developments in optoelectronic devices based on 2D TMDs, in particular photodetectors, excitonic light-emitting devices (LEDs) and optical generation of spin-valley currents.

Photodetectors

TMDC photodetectors are still at the early stages of development and they have been used and demonstrated in the same operational wavelengths as silicon. 2D TMDCs, however present intrinsic advantages over silicon which are the mechanical flexibility and electronically highly tunability. 2D TMDC photodetectors operate mostly on the basis of the photovoltaic effect and exhibit low dark currents and high responsivity while the operation speed remain limited. Significant improvements should be possible given the short exciton lifetimes in these materials (10–100 ps)[27][28][29]. The operation modes of photodetection based on the photovoltaic effect can be divided [30] into two categories: photoconduction, and photocurrent. Photoconduction is based on photoexcited carriers which increase the device's conductance, while the photocurrent, in which photoexcited carriers are converted into current with the help of a built-in electric field originated from a symmetry-lowering element such as a junction (p-n junction). Experimental demon-

stration of photodetectors are based on both in-plane and out-of-plane structures of 2D TMDCs (Figure 2.6 and Figure 2.7). In-plane devices allows to control the material's properties through electrostatic gating which offers a better accuracy than the out-of-plane devices. However the latter can support a much higher bias field (up to 1 V nm^{-1}) which can enable a more efficient exciton dissociation. Indeed exciton dissociation in TMDCs is key due to the very high binding energy and in case of tunnelling ionization of excitons the process becomes inefficient when a bias electric field is small compared with $E_B/(ea_B) \approx 0.2 \text{ V nm}^{-1}$ [19] while excitons dissociation is effectively achieved by electric fields (either built-in or externally applied) [26].

There has been many successful attempts in making photodetectors based on photoconductivity and utilising TMDCs as an active material. Monolayer MoS_2 has been used for a transistor achieving responsivity of 880 AW^{-1} with a bandwidth of $\sim 0.1 \text{ Hz}$ (Figure 2.6) [31]. A much better bandwidth ($> 10 \text{ kHz}$) and therefore a faster device has been achieved, but with a smaller responsivity of $\sim 1 \text{ AW}^{-1}$ [32]. The large photogain is associated with the trapped carrier at the interface states [33]. The devices conductivity tends to be modified primarily by the doping as well as trapped states [32][34][26].

Similarly devices based on photocurrent for photodetection have been achieved. These can be made by creating a junction both out of plane [35][36] as well as in plane [37][38]. WSe_2 has been used to make an in plane p-n junction with a depletion region of up to 500 nm and a resulting field of 0.02 V nm^{-1} . In such a device a responsivity of $\sim 1 \text{ mAW}^{-1}$ and $\sim 200 \text{ mA W}^{-1}$ was demonstrated under zero bias and a forward bias respectively [39]. Due to large diffusion length of excitons it is difficult to achieve both wide depletion area as well as a strong built in field to dissociate strongly bound excitons. On the other hand the out of plane heterojunctions made out of one n-type (e.g. MoS_2) and one p-type (e.g. WSe_2) layers can rectify these issues. Such built device can achieve very high in built electric fields of $\sim 1 \text{ V nm}^{-1}$ and a zero bias responsivity of $\sim 0.1 \text{ AW}^{-1}$ [36][40].

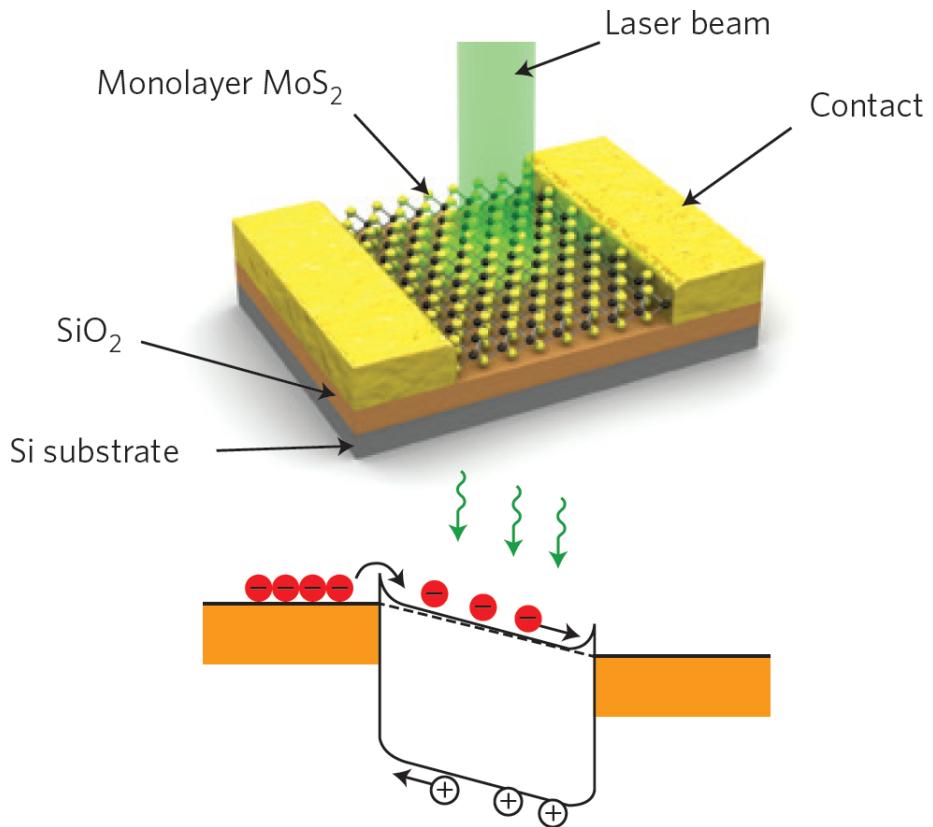


Figure 2.6: Top: Monolayer MoS_2 lateral photoconductor. Bottom: Band diagram of the monolayer MoS_2 photodetector. Reproduced from [26]

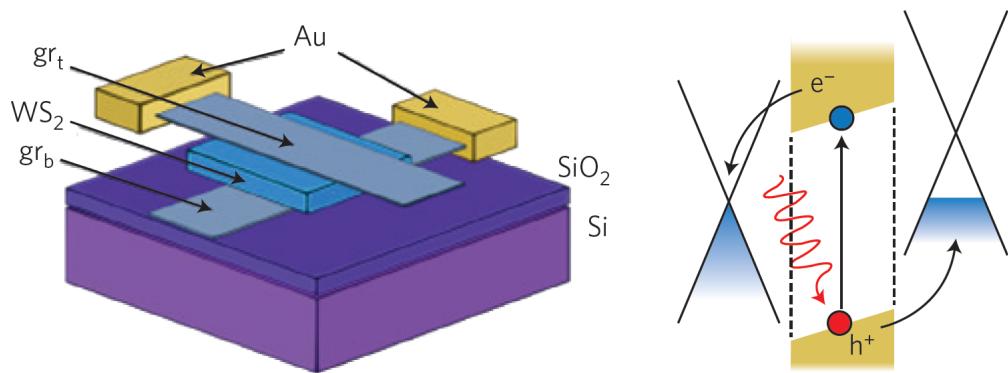


Figure 2.7: Left: WS_2 vertical photoconductor with graphene deposited on top (g_{rt}) and back (g_{rb}) electrodes. Right: Band diagram of a graphene/ WS_2 /graphene heterostructure with a built-in electric field. Reproduced from [26]

Table 2.2: Comparison of performances of graphene and 2D TMD photodetectors. Adopted from [26]

	Device type	Responsivity	Bandwidth	Quantum efficiency
Near-infrared to visible gap	Photoconduction			
Strong exciton binding	In-plane	$\sim 1 - 10^3 AW^{-1}$	0.1 Hz to > 10 kHz	$\sim 50\%$ (E)
Mainly based on photovoltaic effect	Out-of-plane	$\sim 0.1 AW^{-1}$	≤ 200 GHz	
Low dark current	Heterojunction			
	In-plane	$1mAW^{-1}$ (zero bias)	-	$\sim 2\%$ (I) (zero bias)
	Out-of-plane	$\sim 100mAW^{-1}$ (zero bias)	-	$\sim 10-30\%$ (E) (zero bias)

I and E are internal and external quantum efficiencies, respectively. LT, low temperature; RT, room temperature.

LED

The light emitting diodes (LED) and other devices utilising the electroluminescence in layered TMDCs have been realised. A variety of junctions can be formed to allow for the electron-hole recombination and therefore light emission, like Schottky junction [41], p-n junciton [37][36][42] or vertical tunnel junctions [35]. Very low current on the order of nanoamps has successfully produced light emission in the in plane junction and efficiency of $\sim 1\%$ has been demonstrated for the WSe_2 LED [37][42]. It has also been shown that by controlling the injection bias the population of excitons and trions can be manipulated [37][35][26]. It has also been shown that the chirality of the emitted light can be controlled. By applying a strong electric field a p-n junction can spontaneously form and circularly polarised light is emitted. By reversing the direction of the applied field the resulting polarisation of the light also reverses [43]. Wu et al. has demonstrated a laser based on WSe_2 and utilising nanocavities [44]. Similarly by using a disk resonator a WS_2 based laser was made [45] as well as MoS_2 based one [46].

Photoinduced valley currents

Due to an extra degree of freedom of electrons found in layered TMDCs there has been attempts to utilise it for applications. It has been shown that by illuminating a monolayer of MoS_2 with circularly polarised light an anomalous Hall effect has been observed, indicated by valley-polarised current. The observed voltage sign can be changed by reversing the polarisation of the incoming light[47]. Similarly Yuan et al. has shown that a circularly polarised light when illuminating an electric double layer transistor based on WSe_2 produces valley current. The direction and magnitude of as generated current depends on the polarisation of the light and can be further altered by an external electric field [48].

This area of optoelectronics in regards to layered TMDCs remains still largely unexplored and the exact mechanism of the effects observed is not fully understood. The possible application of the photo induced valley currents however can prove to be interesting, especially as medium for information.

2.2 Phonon dispersion

The vibrational and phononic characteristics of TMDCs have been investigated at length by both theoretical simulations as well as experimental studies. The $2H - MX_2$ crystal structure of the TMDCs belongs to D_{6h}^4 point group and there are 18 lattice dynamical modes at the Γ point. Phonons belonging to these modes can be represented as Eq. 2.1 [49]:

$$\Gamma = A_{1g} + 2A_{2u} + B_{1u} + 2B_{2g} + E_{1g} + 2E_{1u} + E_{2u} + 2E_{2g} \quad (2.1)$$

In TMDCs 4 active Raman modes can be observed $E_{1g}, E_{2g}^1, E_{2g}^2, A_{1g}$. These can be seen in Figure 2.8. The E_{2g}^2 is a shear mode that involves 2 layers vibrating against each other. The E_{1g} is an in-plane vibration of chalcogen atoms but is forbidden in the back-scattering configuration. For monolayers therefore it leaves primarily the E_{2g}^1 which is an in-plane mode involving vibration of both metal and chalcogen atoms as well as A_{1g} which is an out-of-plane mode involving only chalcogen atoms.

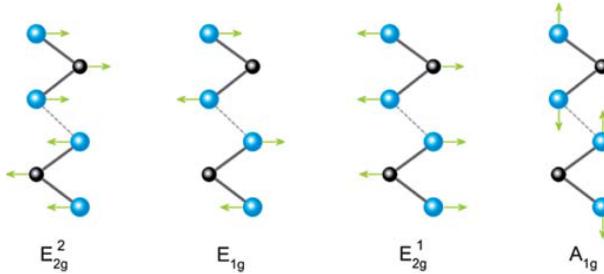


Figure 2.8: 4 active Raman modes in TMDCs. Metal atoms and chalcogen atoms are black and blue respectively. Adopted from [49]

These two peaks tend to dominate the spectrum of any TMDCs, whether monolayer or few-layer or bulk. The shear mode E_{2g}^2 appears at low Raman shift frequencies and is therefore difficult to observe but can be used to differentiate monolayer from few-layer material. Since E_{2g}^1 is an in-plane mode it tends to be unaffected by the number of layers due to weak van der Waals forces between the layers but can be seen to be slightly redshifted as the number of layers increases. As seen in Figure 2.9 the E_{2g}^1 peak at about 352 cm^{-1} is overlapping with another stronger peak, a 2LA(M) peak at 350 cm^{-1} which is a longitudinal acoustic mode caused by in-plane collective oscillations of W and S atoms. The second strongest peak at around 416 cm^{-1} is an A_{1g} peak, caused by out of plane vibrations. Because of that it is much more sensitive to the number of layers and is seen

to become blueshifted as the number of layers increases. This has been attributed to the restorative forces as well as increase in dielectric screening of the Coulomb forces. Combining both of these shifts in frequency with the changing number of layers the difference between these two peak position can be used to identify the number of layers in TMDCs as seen in Figure 2.10

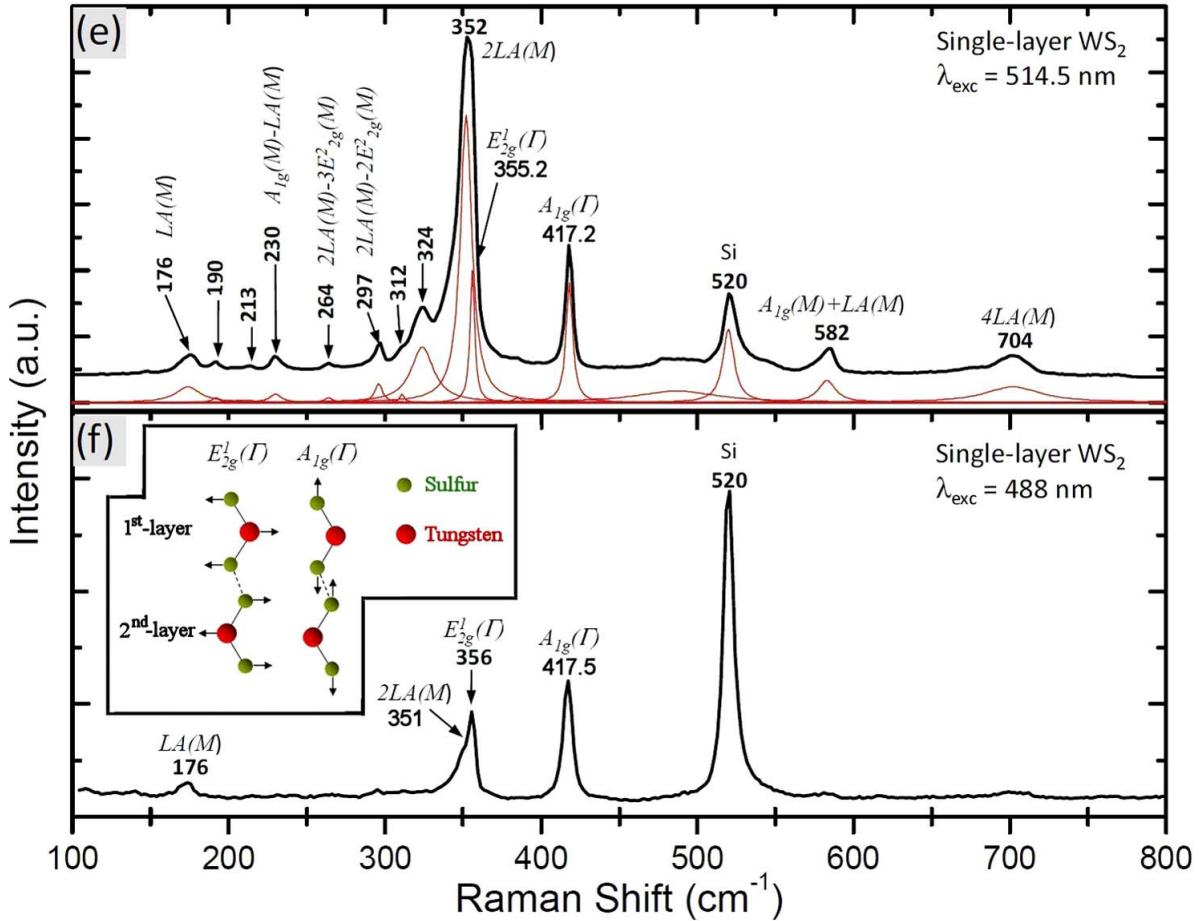


Figure 2.9: Raman spectrum of WS_2 with characteristic peaks indicated. Adopted from [50].

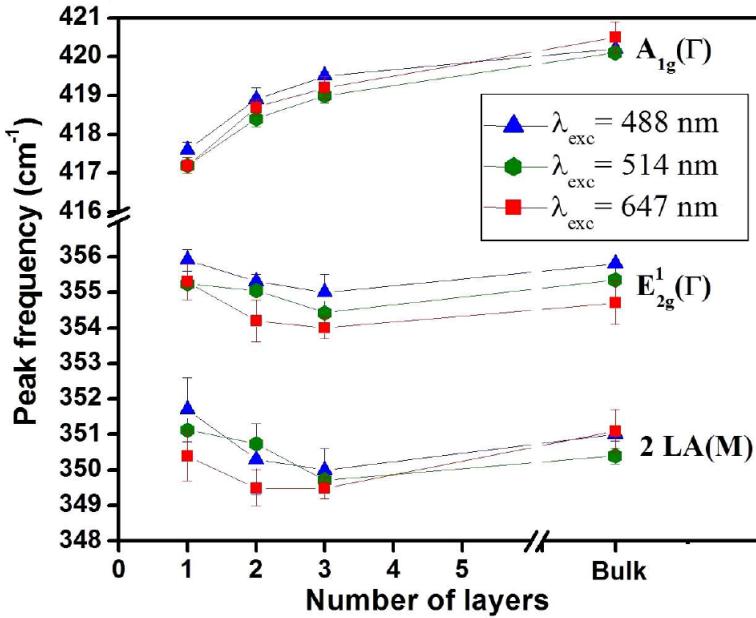


Figure 2.10: Identification of number of layers by the difference in position of A_{1g} and E_{2g}^1 peaks. Adopted from [50].

Similarly in MoS_2 the E_{2g}^1 and A_{1g} peaks can be observed easily using Raman spectroscopy. The position of the monolayer E_{2g}^1 and A_{1g} peaks are found to be about 385cm^{-1} and 403cm^{-1} respectively. Unlike the WS_2 and especially in monolayer form the E_{2g}^1 does not overlap with the 2LA peak which helps greatly with resolving and peak fitting individual peaks. Similarly to the WS_2 the peak position of those two peaks changes with the number of layers in a same manner. As the number of layers increases from monolayer to bulk the E_{2g}^1 shifts a small amount to the red being largely unaffected since that vibrational mode exists in plane and is therefore not influenced by the layer above or below. The A_{1g} on the other hand, similarly to the WS_2 A_{1g} peak blueshifts by relatively larger amount due to out of plane vibrations which are affected by the number of layers. The separation between those two peaks can be used therefore as an indicator of the number of layers similarly to the WS_2 .

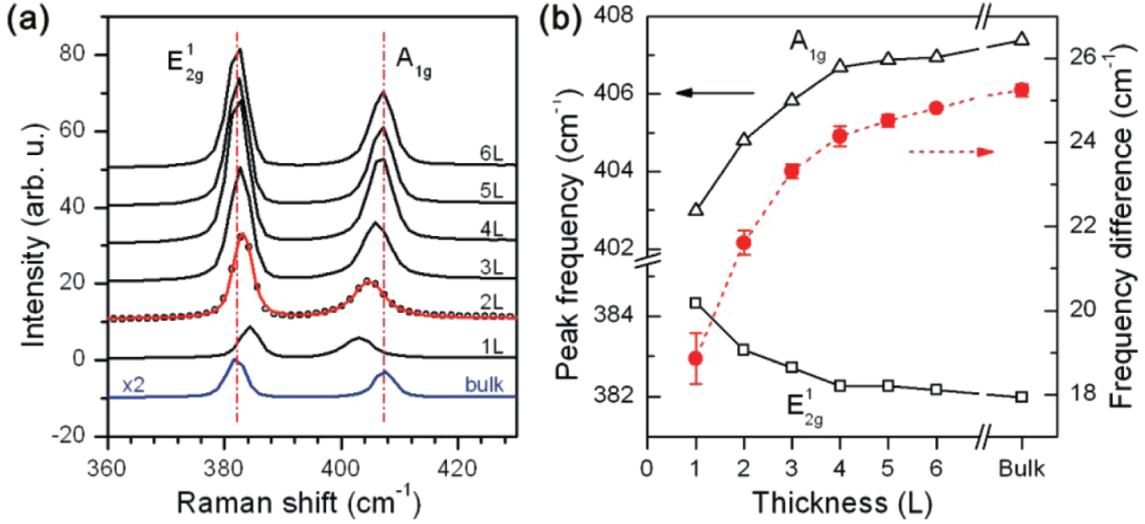


Figure 2.11: a) Raman spectra with of mono and few layers and bulk WS_2 with indicated characteristic peaks b) Characteristic Raman peak position and difference between them as a function of number of layers. Adopted from [51].

The mono and few layers of WSe_2 has not received nearly as much attention as MoS_2 or WS_2 . The monolayer of WSe_2 shows a bandgap of about 1.7 eV [52] and ~ 1 eV for bulk and therefore allows for application in electronic and optoelectronic devices operating in near infrared range. As seen in Figure 2.12 the Raman spectrum of WSe_2 shows the 2 main peaks E_{2g}^1 and A_{1g} at around 249 cm^{-1} with a 2LA peak at around 260 cm^{-1} . Because of such proximity between those two peaks the proper peak fitting is made difficult and the peak position separation between E_{2g}^1 and A_{1g} to determine the number of layers as used for WS_2 and MoS_2 cannot be easily utilised. There is however a breathing mode peak at around 320 cm^{-1} which is absent from monolayer and present in few layers of WSe_2 and can therefore be used to easily differentiate between mono and few layers of WSe_2 .

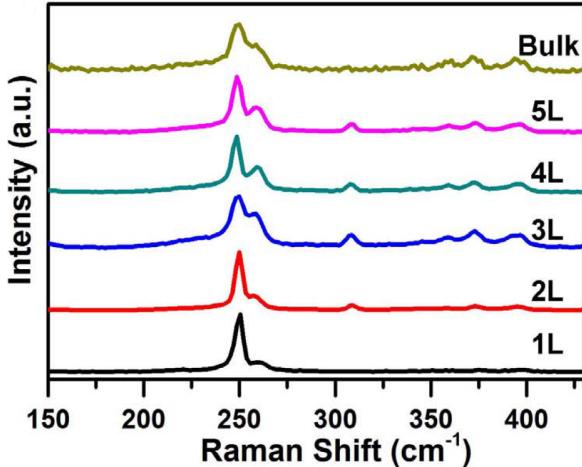


Figure 2.12: Raman spectra of mono and few-layer WSe_2 . Adopted from [53].

2.3 Conclusions

In this chapter we have presented and discuss the electronic and vibrational properties on group VI TMDs with a specific focus on WS_2 and MoS_2 . We have summarized the current state of the art which involves experimental and simulation studies. In conclusion mono- and few layer TMDCs have become an important class of materials to study in recent years. Despite their knowledge and usage in bulk forms for many more years their atomically thin form remained largely unexplored. Their particularly interesting properties arise most strikingly when the number of layers is very small. The sulphides and selenides of group VI transition metals (Mo and W) exhibit an indirect to direct bandgap placed in visible to infrared range, high electronic mobilities of $10^3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, FET switch ratio of $> 10^7$ and strain rates up to 20%. Those materials provide therefore a great potential for many applications in electronic and optoelectronic devices for light detection, emission and harvesting. One of the limiting factors in future development of material synthesis and devices is understanding of the TMDCs properties and ability to characterise them easily.

Chapter 3

Methodology

3.1 Introduction

In order to characterise the synthesised materials and acquire information about the chemistry, crystallinity, morphology as well as its optical and electrical properties a suite of state of the art techniques has to be utilised. An overview of those techniques has been provided in theory and experimental setup.

3.2 Raman spectroscopy

Raman spectroscopy is one of the most useful and versatile characterisation techniques for 2D TMDCs due to its non destructive and ease of use. The lack of need to extensively prepare the sample like in some other techniques allows for relatively fast measurements of a large number of samples. Additionally the lack of transfer required results in minimal changes to the material itself as well as allows for easier tracking of specific areas of the sample across different techniques. Raman spectroscopy can be used to measure as grown by CVD samples on *Si/SiO₂* substrate or any other solid substrate as well as liquid solution samples produced by liquid exfoliation.

The Raman spectroscopy can be used to extract information about the chemistry of the material as well as the crystal structure, the number of layers of 2D TMDCs or the strain within the layers.

When a material is irradiated with light the photons generally scatter at different angle but same wavelength. However certain small part of the incident photons (about 1 in 10 million) is scattered at different wavelength than the incident one. This is known as the

Raman effect and the photons that are scattered at wavelengths greater than the incident ones are due to Stokes scattering, while the ones emitted at wavelengths smaller than the incident one are due to anti-Stokes scattering. In the Stokes scattering phenomena the phonon is emitted while during the anti-Stokes scattering the phonon is absorbed as seen in Figure 3.1. In order for the Raman effect to take place a transition between two resonant states must occur. The probability of transition from lower to higher energy state depends on the population of the states. In a thermodynamically stable system the lower energy states are more occupied than the higher energy and therefore the transition from lower to higher is more likely to occur (Stokes scattering). The spectrum of photons scattered as a result of Raman scattering forms what is known as Raman spectrum, where the number of photons scattered is plotted against the photon frequency difference between the incident and the scattered photons. The spectrum is symmetrical around the spectrum origin in regards to the frequency but not in terms of intensity. Because of that only the Stokes part is generally used as a Raman spectrum.

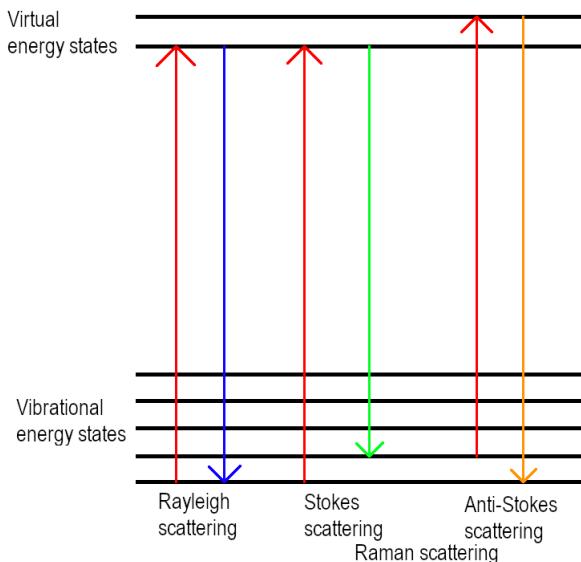


Figure 3.1: An energy diagram comparing elastic and inelastic scattering.

The phonons that are emitted or absorbed during the transitions between the virtual states in the Raman effect are phonons of the vibrational modes in the material. For any solid state crystalline material the point group can be defined. Using the point group the available vibrational modes can be found. In order for Raman scattering to occur a change in polarisability must occur in a given vibration mode. Similarly if the vibrational mode results in change in dipole moment it results in an IR active mode. As a result a set of available Raman active modes can be found. The Raman spectrum can be therefore

used to identify the vibrational modes and therefore gain insight about various factors that influence those vibrational modes.

A typical Raman spectroscope setup involves a monochromatic light source, generally a laser, which is focused on a sample. As a result some of the light is scattered elastically (Rayleigh scattering) while even smaller part is scattered inelastically (Raman scattering). The scattered light is then passed through a filter to remove the elastically scattered light at the wavelength equal to that of the incident photons. The remaining Raman scattered light is passed through a monochromator and then onto a CCD detector. A diagram of a Raman spectroscope can be seen in Figure 3.2.

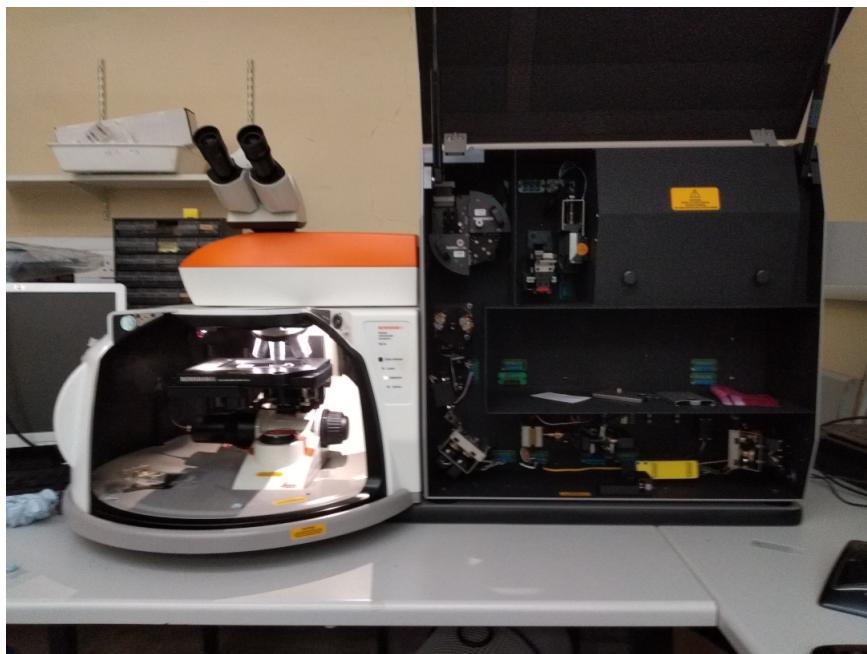


Figure 3.2: The Raman spectroscope setup used for measurements.

A Raman spectrometer used in this work is a Renishaw Raman spectrometer. The 532nm laser was used as a light source in a backscattering geometry. Unless otherwise specified the measurements were taken at room temperature and ambient pressure. An objective lens of 100x with 0.9 numerical aperture was used as the focusing lens. The laser power was set to be 1.6mW with 0.1s acquisition time for mapping and 1s acquisition time for single spectra. The grating of 1800 lines/mm was used resulting in a resolution of about 1.5 cm^{-1} . For calibration purposes a silicon sample was used with a peak at 520 cm^{-1} . All data analysis was performed using MATLAB software as described in chapter 3.10.

3.3 Photoluminescence spectroscopy

The photoluminescence spectroscopy (PL) is an another versatile non-destructive characterisation technique. When applied to the 2D TMDCs it can provide great insight into the crystal stricture, electronic structure of the material as well as some direct information about its optical properties. One of the great advantages of PL spectroscopy is shared with the Raman spectroscopy in that the sample preparation and handling is very easy and quick allowing for high throughput of characterisation. Unlike Raman spectroscopy a substrate choice might become more important for PL measurements owing to the fact that the conductive substrate might result in PL quenching. Since the bandgap of many of the 2D TMDCs lies within the optical range of the spectrum or near to it a single laser at 532 nm can be used to excite the samples.

Photoluminescence is a type of luminescence where an excitation is provided by the incident light. In a semiconducting material like many of the 2D 2H TMDCs the electron from valence band is excited to the conduction band. Following the excitation the electron and resulting hole relax in both energy and momentum to the edge of the conduction and valence band respectively. Thus they form an exciton, a quasi particle that contains no net charge and can move across the material. An exciton in TMDCs can approach large sizes (Wannier-Mott exciton) due to great value of dielectric constant and resulting screening between the electron and the hole. Such exciton can also interact with the material by getting pinned by defect sites. After very short lifetime the exciton recombines emitting the photon at the same time. The photons emitted by the recombining exciton can be then collected. A plot of the photon count versus the energy of the detected photon forms the PL spectrum.

Therefore the PL spectrum can be used to directly infer the optical bandgap which is the electronic band gap of the material minus the binding energy of the exciton. In TMDCs on top of excitons additional type of quasi particle like trions or biexcitons can be found. Those particles exhibit varying level of binding energy and sometimes require special conditions to become excited. The PL spectrum can be therefore used to infer about the presence of those particles and therefore gain insight into the structure of the material. An energy diagram representing the photoluminescence process can be seen in Figure 3.3.

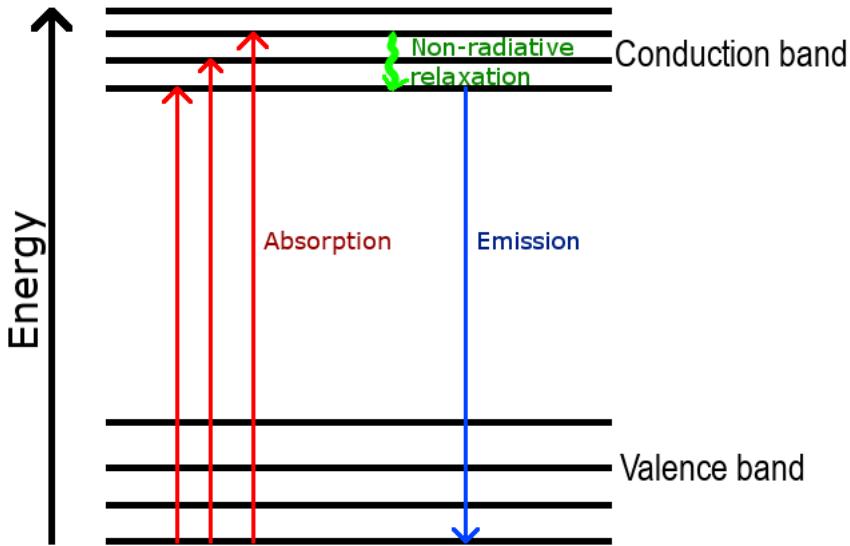


Figure 3.3: The photoluminescence process.

The PL signal becomes broadened due to variety of factors. One of the most important contributors is temperature which results in Gaussian broadening. At room temperature there is a constant peak broadening of about 25 meV. Because that broadening is relatively close to the binding energy of the trion (\sim 30 meV). Therefore at room temperature the trion peak which is generally weaker than the exciton peak cannot be easily resolved. In order to be able to resolve those peaks a PL measurement at lower temperature can be performed.

A photoluminescence setup can look very similar to that of the Raman setup as seen in Figure 3.2. A monochromatic light source e.g. a laser illuminates the sample at the energy greater than that of the materials bandgap. As a result of that the photons emitted from the material together with the inelastically (Raman) and elastically (Rayleigh) scattered photons pass through a filter to remove the latter. The remaining light is then passed through monochromator and detected at the CCD detector. As a result the PL and Raman spectra can be observed in the same spectrum, provided that the sample material can produce both of those signals.

For low temperature (77K) measurements an environmental stage, Linkam THMS-350V. A pump was used to lower the pressure in the chamber down to about 2×10^{-3} mbar. The liquid nitrogen was used to cool down the stage down to 77K. The stage was placed in Renishaw Raman spectrometer to capture PL spectra.

The PL spectrometer used in this work is a Renishaw Raman spectrometer. The 532nm green laser with objective lens of 100x with 0.9 numerical aperture was used and

the data was recorded in backscattering configuration. The laser power used was 0.32mW with 0.1s exposition time for maps and up to 5s exposition time for a single extended spectrum. The 1800 lines/mm grating was used resulting in a resolution of about 0.2 meV. The spectrum was calibrated using silicon Raman peak at 520 cm^{-1} . All data analysis was carried out was done using MATLAB software as described in chapter 3.10.

3.4 X-ray photoelectron spectroscopy

One of the most useful characterisation techniques for study of 2D TMDCs is X-ray photoelectron spectroscopy. It is a non-destructive method which allows to gain information about the chemical composition of the studied material. It is a very surface sensitive method that allows for obtaining signals from about 10 nm of the sample depth. In order to perform the XPS measurement the sample must be placed in high vacuum (about 10^{-8} mbar). It is therefore necessary that the sample contains no liquids or adsorbed gasses which would increase the pressure inside the analysis chamber.

When a sample is irradiated with a beam of x-ray photons some of those photons get absorbed by the electrons in the sample. Because the energy of the incident photons is relatively large the electrons have enough energy to leave the atoms and travel towards the detector. At the detector their kinetic energy is measured. Because the energy of the incident x-ray photons is known and the kinetic energy of the photoelectrons is measured the remaining energy can be calculated using Equation 3.1:

$$E_{binding} = E_{photon} - (E_{kinetic} + \Phi) \quad (3.1)$$

If the Φ which is a instrumental correction factor is known then the $E_{binding}$ can be found. This binding energy depends on the specific atoms from which the electron as well as the specific atomic configuration. Because of that the chemical composition of a given sample surface can be determined. Additionally the number of detected electrons is directly correlated to the concentration of the atoms in the given sample the specific atomic percentages within the scanned area can be calculated. The number of detected electrons can be then plotted against the calculated corresponding binding energy of the electrons to form an XPS spectrum. A diagram of the XPS physics can be seen in Figure 3.4.

In TMDCs the XPS can be used to determine the stoichiometric composition of the as grown material as well as detect any traces of unintentional doping from alkali or halogen

atoms or intentional doping by e.g. In atoms. Additionally the amount of oxides as well as the presence of 2H or 1T phases can be quantitatively determined.

The XPS spectra were collected using the Thermo Scientific K-Alpha XPS system. The Al K_{α} emission line was used as the x-ray source. The pass energy of 20 eV and the energy step of 0.1 eV were used. The XPS spectra were collected at room temperature and pressure of about 3×10^{-8} mbar. The acquired data was analysed using Avantage software.

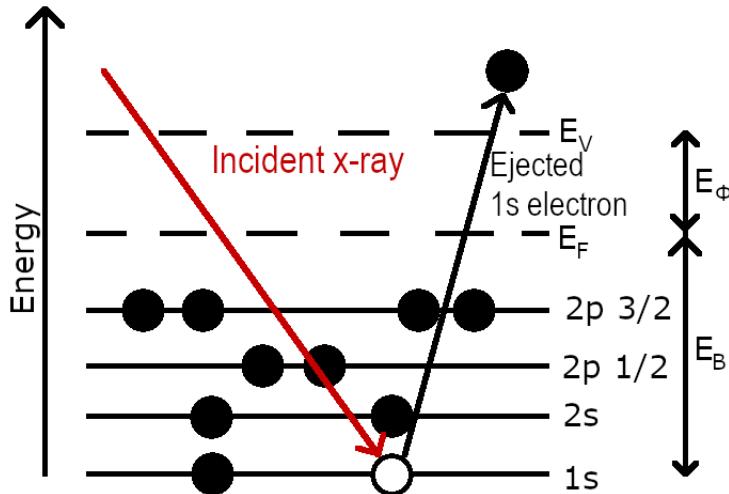


Figure 3.4: Photoelectron effect energy diagram present during XPS.

3.5 Transfer

Due to the nature of the 2D materials, the 2D TMDCs are generally always deposited on some substrate and cannot be used independently of it. Depending on the manufacturing method different substrates can be used to initially synthesise or deposit the material. In general however the initially used substrate is different to that which can be used for either characterisation or specific application. The samples synthesised by CVD are grown generally on Si/SiO_2 at very high temperature and as such cannot be readily used in electronic applications due to Si deterioration at high temperature. To that effect the as grown samples are required to be transferred to a new substrate.

In this work the wet transfer method has been utilised to transfer CVD grown samples from Si/SiO_2 to another Si/SiO_2 , Au or TEM grid substrate. In this method the sample is first spin-coated with a thin layer of PMMA at 3000 RPM for 60 s. After that the sample is dried and heated up to about 50 °C for about 1 hour to ensure full polymerisation. Following that the substrate with the sample is then placed in a bath of 8% KOH solution

for about 45 min or until the *Si* under the SiO_2 has completely sank to the bottom of the beaker. The thin layer of PMMA with the sample at the bottom is then scooped up with a glass slide and transferred to a DI water to remove the KOH. The sample is held in a water bath for about 30 min and the step is repeated 2-3 more times. After the last dilution step the sample is scooped onto a target substrate. The sample is then gently dried using compressed nitrogen or air to drive any water from between the PMMA and the substrate. The substrate is then heated up to about 50 °C for about an 1h to completely dry the sample of any water and ensure better adhesion to the substrate. The substrate is then placed in a bath of acetone and isopropanol heated up to 60 °C for about an 1h to remove the PMMA layer. After all PMMA has been removed the sample is heated again on a hot plate up to 100 °C to remove any traces of PMMA.

3.6 Device fabrication

The devices were prepared by collaborators from Exeter University: Iddo Amit, Gareth F. Jones, Jake D. Mehew, Agnes Bacon. In order to measure the electric properties of the as-grown materials the material can be used to make a field effect transistor (FET) device. For that purpose the as grown mono- and bi-layer WS_2 was transferred onto a *Si*/ SiO_2 substrate with the SiO_2 layer of 285 nm in thickness. The *Si*, which is highly p-doped, then acts as a global gate electrode while the SiO_2 is a gate dielectric. On top of the deposited contacts for source and drain electrodes additional probes were used in each of the FET devices to eliminate any voltage contributions from the contacts and thus allow for correct measurement of the channel conductance. The drain and source drains as well as the voltage drains were deposited using electron beam lithography. The contacts as well as the probes were made using 50 nm thick Au, while the rest of the leads were made using 5nm thick Ti and 50 nm thick Au. Following the contacts and leads deposition the FET devices were annealed at 200 °C fpr 2h under H_2/Ar (10/90) flow at 1 bar to remove any remaining PMMA from the lithographic process. The sample was then annealed at 115 °C for 60 h under high vacuum (10^{-6} mbar) to remove any remaining water.

Following the FET preparation the samples were then characterised in a vacuum chamber in high vacuum (10^{-6} mbar). A low noise source-meter was used to bias the drain electrode with source being grounded. Additionally another source was used to bias the gate electrode. The current across the channel I_{ds}) was measured using ammeter while the voltage V_{A-B} across the voltage probes was measured with a voltmeter. The gate

bias was applied until the measured current reached linear regime where it is described by Equation 3.2 [54]:

$$I_d = \mu_n C_{Ox} \frac{W}{L} (V_{gs} - V_{th}) V_{ds} \quad (3.2)$$

where μ_n is electron field effect mobility, C_{Ox} is the SiO_2 capacitance, W, L are the channel width and length, V_{th} is the threshold voltage, V_{ds} and V_{gs} are the drain-source voltage and gain-source voltage respectively. From the measurement of the current the field-effect mobility for the mono- and bi-layer of the WS_2 can be calculated using the linear part of the plot from Equation 3.3:

$$\mu_n = C_{Ox}^{-1} \frac{d\sigma}{dV_{gs}} \quad (3.3)$$

where σ is the channel conductivity which can be calculated from Equation 3.4:

$$\sigma = \frac{LI_{ds}}{WV_{A-B}} \quad (3.4)$$

and the oxide capacitance C_{Ox} was calculated to be $115\mu Fm^{-2}$ using Equation 3.5:

$$C_{Ox} = \frac{\epsilon_0 \epsilon_r}{d_{Ox}} \quad (3.5)$$

where ϵ_0 and ϵ_r are the vacuum and relative permittivity of SiO_2 respectively and d_{Ox} is the oxide thickness [54].

Additionally the the resistance vs temperature measurements were performed flakes were contacted using two wires configuration. The contacts were deposited using standard photolithographic method by applying the photo resist mask (AZ 5214E) followed by evaporation of Ti (5 nm) and Au (30 nm) using thermal evaporation and sputtering respectively. The measurements were then performed using six arm cryogenic probe station. The measurements were taken at high vacuum of 10^{-5} mbar and liquid nitrogen temperature. Following the measurements the conductivity was calculated from $\sigma = \frac{L}{RA}$, where L is the distance between contacts ($\sim 3 \mu m$), R is the resistance while A is the flake cross section (0.9 nm - $40\mu m$). The Keithley 2410 source measure unit as well as Lakeshor temperature controller were used for the measurement.

3.7 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a versatile technique that allows for high resolution imaging of the sample surface. The fundamental operation of the SEM is based on a high energy (1 - 30 keV) electron beam which is rastered across the surface sample under high vacuum ($< 10^{-5}$ mbar). The incident beam then is scattered by the atoms producing backscattered electrons, secondary electrons, Auger electrons, characteristic x-rays, fluorescent x-rays and continuum x-ray. The backscattered electrons (BSE) are those electrons that undergo elastic scattering during the process and are then measured by the detector. Similarly the secondary electrons (SE) are those electrons that undergo the inelastic scattering and can then, using a different detector to the BSE, be detected and counted. The depth from which the BSE are detected ranges up to ~ 100 nm while that of the SE is limited to ~ 10 nm.

The SEM images were produced using field emission gun SEM (FEG-SEM, Gemini 1525) with an In-Lens SE detector. The FEG-SEM allows for narrower spot size ($< 5\text{nm}$) and a higher signal to noise ratio compared to the conventional thermionic emitters utilised in SEM [55]. Due to the thickness of the WS_2 the SE were primarily used for imaging. Due to the position of the In-Lens SE detector in the electron column with a rotational symmetry around the optical axis it allows for use of low energy ($\sim 1 - 5$ keV) for acceleration and close distance. Because of that the contrast between different number of layers can be achieved for some 2D materials [56]. However in order to maintain good signal to noise ratio a slightly higher energy (5 - 10 keV) was utilised.

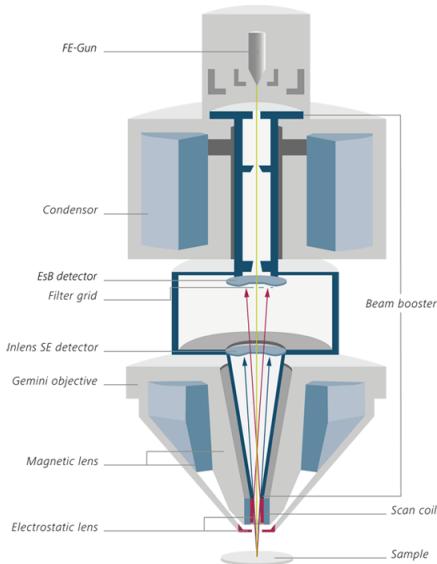


Figure 3.5: Cross section of the SEM optical column. Reproduced from zeiss.com

3.8 Atomic force microscopy (AFM)

The atomic force microscopy (AFM) is one of scanning probe microscopy methods that allows for imaging surface morphology below the nm range as well as manipulation and force measurement. As seen in Figure 3.6 the AFM operates by touching and following the sample surface. The probe, which is a very sharply ended tip made of silicon or silicon nitride and a tip radius in the range of nanometers, is mounted on a cantilever. That cantilever is then controlled by a piezoelectric actuator which adjust the position based on the feedback from the laser measuring the actual cantilever deflection. The tip itself when brought close to the surface of the sample experiences a number of possible forces such as van der Waals forces, electrostatic forces, magnetic forces, chemical bond forces or mechanical contact forces which leads to a deflection one way or the other.

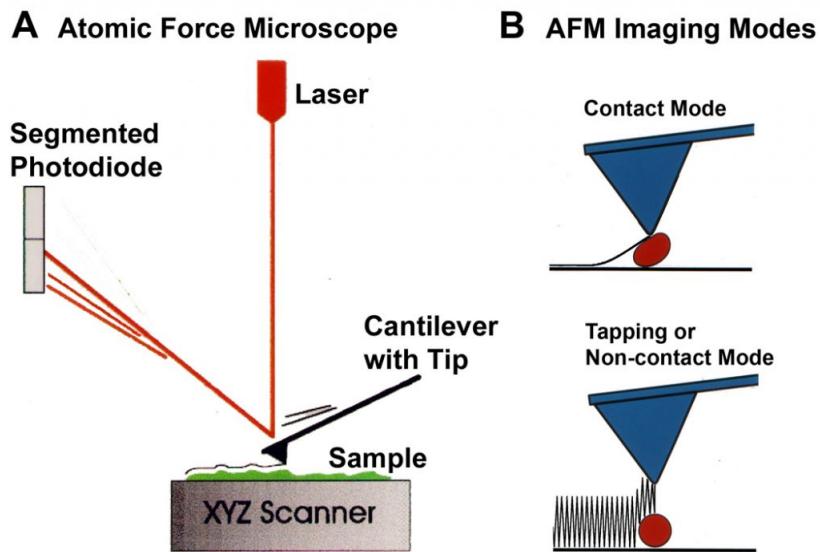


Figure 3.6: Diagram of AFM setup and operating basics. Reproduced from ccem.mcmaster.ca

The measurement can be performed in different modes as seen in Figure 3.6. In contact mode the tip is dragged along the surface and either a tip deflection is directly measured or a constant height is maintained while the deflection required to maintain it is recorded [57]. Alternatively in a tapping mode the tip is oscillated at a resonant frequency and a constant amplitude is maintained. As the tip gets closer to the surface the forces act stronger and therefore the required correction is recorded and surface morphology and force can be determined. A tapping mode tends to be more useful for characterisation of 2D materials as it avoids damage to them but it is slower and may result in some artefacts

[58].

When using tip with radius of <5 nm of curvature a lateral resolution of ~ 5 nm and a vertical resolution of few Å can be achieved. With a contaminated surface the resolution can quickly become bigger and therefore the thickness measurement of the 2D materials can become overestimated. In this work the measurements were carried out using AFM Asylum MFP 3D in a tapping mode with a probe tip made of silicon nitride and a radius of ~ 8 nm on a PPP-NCHR 20 Nanosensors cantilever.

3.9 TEM

Transmission electron microscopy (TEM) is a microscopy technique in which a high energy (60-300 kV) electron beam is directed at a very thin (<100 nm) sample. As a result an image of the sample can be produced at resolution much greater than that achieved with optical microscopy due to much smaller wavelength of the electrons compared to the visible photons. As the electron beam passes through the sample it carries information about its electron density, periodicity and phase and can then form an image on a fluorescent screen. The resulting bright field image shows contrast due to variation in thickness across the sample, and as the magnification increases the interaction between the electron beam and the sample becomes more complex giving rise to different types of contrast.

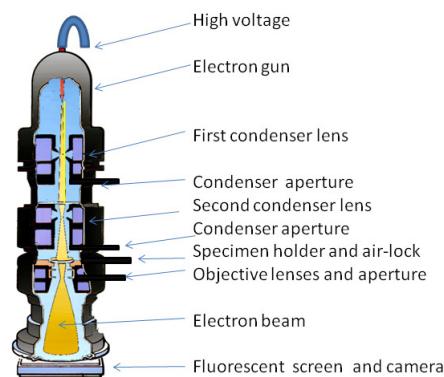


Figure 3.7: Crossection of a TEM column. Reproduced from ccber.ucsb.edu

Because the wavelength of the high energy electrons is much smaller than the distance between the atoms in a crystal lattice, the sample can act as a diffraction grating for the incident beam. By shifting the back focal plane instead of the image plane onto the imaging screen and inserting an aperture the diffraction pattern from selected area

(SADP) can be achieved. This allows to gain information about the crystal structure and defects within much smaller area than what is possible with x-ray diffraction.

In this work the TEM used was a FEI Titan 80-300 S/TEM at 80kV with a monochromator and C_s aberration image corrector. The focal series images were produced using different objective lens focus values ($C_s = -4\mu m$). Exit wave reconstruction was achieved using TrueImage (FEI).

3.10 MATLAB Script

In order to analyse the PL and Raman spectra, both individual and maps, the MATLAB software was utilised. The spectra were exported from the Wire software used for Renishaw Raman spectrometer and they were then imported into MATLAB. Using "peakfit.m" script from "<https://terpconnect.umd.edu/toh/spectrum/peakfit.m>" the peaks were fitted with required number of peaks. For peak fitting the Voigt peakshape was used. Several scripts were developed for the purpose of automating data import, analysis and peak fitting of PL and Raman maps.

Chapter 4

WS_2 CVD state of the art

4.1 Introduction

After extensive attention was provided to MoS_2 and its synthesis as well as properties WS_2 has quickly become one of the most studied TMDCs. As a semiconductor its optical bandgap of about 2 eV for monolayer and 1.3 eV in bulk form makes it an interesting material for any electronic and optoelectronic applications. In an atomically thin form its n type semiconductor [8][23][59] and its light emission at room temperature has been shown to be 50 times that of the MoS_2 [60]. It has also been shown that the valley splitting caused by spin orbit interaction is up to 0.45 eV in WS_2 [61]. Another interesting properties observed strongly in WS_2 is the valley index, referring to the confinement of electrons of the same energy but different momentum to local minima [3]. These and other properties mentioned in Chapter 2 make WS_2 an important material to study. One of the major development hurdles in the field of the TMDCs is the lack of scalable and reproducible method of producing large area samples of TMDCs. Therefore it is imperative to develop a reproducible and scalable method of growing high quality atomically thin TMDCs. This is an overview of latest developments in the field of WS_2 CVD synthesis.

4.2 The state of the art

4.2.1 Bulk crystals

One of the most popular method of obtaining samples, especially for the purposes of further research, has been mechanical exfoliation from bulk crystals to single or few layer TMDCs. Said bulk crystals can be found naturally or synthesised using a chemical vapour

transport (CVT) method. In this method the precursors are kept in a closed system together with carrier gas and the target substrate and the temperature gradient is applied across the system. The precursor powder (a mixture of metal and chalcogenide precursors) evaporates with the assist of the transport agent to then deposit on the target substrate over the course of days to weeks [62][63]. Utilising this method it has been shown that single bulk crystals of WS_2 , MoS_2 , WTe_2 , $MoSe_2$, $MoTe_2$ can be grown [62][63][64][65][66][67][68][66]. Such grown crystals are then used to produced single and few layer TMDCs by micromechanical exfoliation and deposition onto a desired substrate. While as produced thin layers show good optical and electronic properties their size, thickness and distribution are not easily controllable.

4.2.2 Thin films of W

Because of that a different method of direct synthesis of thin layers of TMDCs has been used. For the synthesis of WS_2 thin films several different W precursors has been considered. The most common W precursor used is a WO_3 which tends to produce WS_2 samples with very low number of impurities. At the same time however it requires the high temperature (~ 1000 °C) to evaporate and sulfurise. As an alternative with much lower evaporation temperature (~ 300 °C) and high volatility the tungsten hexacarbonyl (WC_6) can be used. The downside of that precursor however is the potential contamination of the sample with carbon and oxygen. Finally the tungsten halides can form films of high purity, but at the same time their usage results in release of highly corrosive byproducts [62]. As an alternative to regular CVD the metal organic chemical vapour deposition (MOCVD) has been used to produce uniform WS_2 films of ~ 65 nm thickness using WC_6 and H_2S as precursors [69].

4.2.3 WO_3 based CVD of WS_2

One of the methods of producing WS_2 thin films is a two step process where a thin film of W or WO_3 is first deposited onto the substrate and subsequently sulphurised. Those thin films of tungsten can be first deposited using electron beam evaporation or magnetron sputtering. In order to produce thin film of WO_3 the as produced W film can be then thermally oxidised. Those thin films of W or WO_3 are then placed in a tubular furnace, like the one used in CVD, heated up to ~ 800 °C and exposed to chalcogen atmosphere. As grown WS_2 films of up to ~ 200 nm in lateral size from W films retain the distribution

and shape of the W films. The WS_2 films produced from WO_3 films showed triangular growths of up to micrometers in size. This suggests that in case of the sulphurisation of the thin layers of WO_3 the W and S species diffuse on the substrate nucleating WS_2 triangles and growing. They can further coalesce with other islands resulting in a wide size and density distribution of WS_2 domains [70][62].

4.2.4 CVD growth of mono and few layer WS_2

The CVD approach to growing atomically thin layers of TMDCs have been mostly a single step growth process using metal oxide and chalcogenide powders as precursors [62][60][71][72][73][74][75][76][77][78][79]. For WS_2 growth one of the main challenges in this process is a significant difference of vapour pressure between the W and S precursors. It is therefore crucial to carefully control the evaporation rate of both of the precursors to allow for a degree of reproducibility. In order to do that the usual precursors, WO_3 and S powders, are placed in separate crucibles in a quart tube in a CVD tubular furnace [80][81]. Because of great difference in evaporation temperature of S (100-150°) and WO_3 (800 - 1070°) two separate furnaces are generally used. The growth is generally performed under inert atmosphere of Ar or N_2 owing to high reactivity of S when reducing the WO_3 . The H_2 can be introduced into the process to promote the reduction of WO_3 which can help regulate the shape of the grown samples from jagged edges to smooth triangles [82]. The synthesis of WS_2 can be achieved at both atmospheric pressure as well as low pressure [80][81]. The low pressure growth condition allows for greater volatility of precursors as well as keeps the substrate free of particulates thus leading to more uniform nucleation. The atmospheric growth can however produce good quality WS_2 using metal halides for promoting growth [83]. Thanks to reaction between the metal halides and tungsten oxide species and the subsequent formation of tungsten-oxyhalide species the growth temperature can be brought down to 850 °C [83]. In order to improve the substrate coverage and produce more flakes on the substrate nucleation promoters have been used. By dropping a solution of perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt (PTAS) onto the substrate and drying it prior to growth of WS_2 a number of PTAS nuclei are formed across the substrate. This promotes the subsequent CVD synthesis of WS_2 via heterogeneous nucleation. It also allows for CVD synthesis on a variety of surfaces (sapphire, quartz, silicon) with different surface corrugation [84]. The growth temperature has also been shown to have great effect on the flake size with a change from 880 °C to 900 °C resulting

in later size of flakes increasing from $\sim 5\mu m$ to $\sim 50\mu m$ [82]. Different approaches to heating the precursors as well as precursor and substrate placement have also been proposed. By placing both WO_3 and S precursors in the same furnace, with WO_3 in the centre and S at the edge small triangles with anisotropic PL signal across the flake have been observed. The variation in PL has been attributed to S deficiencies resulting from premature evaporation of the S precursor [60]. It has also been shown that by spreading WO_3 powder onto one Si wafer positioned in the centre of the furnace and placing target substrate above it and facing it with S precursor in a separate heating element a successful growth can be achieved. The resulting flakes however showed a wide range of both lateral sizes as well as thickness with monolayer flakes showing uniform PL signal across the flake [71]. A CVD synthesis was performed on a hBN substrate using WCl_6 as a tungsten precursor with flakes up to $3\mu m$ and narrow PL emission (26 meV) centred around 2.01 eV [85]. In order to grow large area monolayer flakes WS_2 Rong et al. has shown that by controlling the S evaporation time and therefore presulphurising the WO_3 powders by 10 min flakes of up to $370\mu m$ were grown [72].

At the same time the CVD growth of WSe_2 has proven to be much more difficult. The most common strategy involves the use of H_2Se as the Se source which is a corrosive and extremely toxic gas. Because of that there is need to find substitutes to limit any possible exposure. There has been some successful growths using Se powders but the growth is often limited by low reactivity of Se, especially compared to S [86][87][83]. The resulting flakes therefore tend to be on the size order of 20-30 μm . There is therefore room for further study and improvements to achieve bigger flakes with better substrate coverage.

4.3 Conclusions

In conclusion there has been a tremendous push in the area of CVD growth of mono and few layer TMDCs. Especially in case of MoS_2 and WS_2 many discoveries have been made regarding the mechanism responsible for the nucleation, growth, precursors evaporation and transport. Many strategies however manage often to optimise one parameter at cost of others and therefore no one of those methods can be easily utilised for scalable production for future applications. In case of less popular TMDCs like WSe_2 there is even more that needs to be discovered to achieve parity with the established techniques for more common TMDCs.

Chapter 5

The state-of-the-art of heterostructures and heterobilayers of MoS_2/WS_2

5.1 Introduction

As two-dimensional TMDCs have emerged as promising candidate materials for next-generation electronic and optoelectronic technologies with valley functionalities it has become apparent the need of enhancing some of their properties in view of their applications. For instance, creating band offsets between different monolayer TMDCs would enable efficient separation of charge carriers and rectification of charge flow. This would offer a mechanism for designing devices made by entirely van der Waals atomically thin materials. Furthermore, the semiconducting monolayer TMDCs — MoS_2 , $MoSe_2$, WS_2 and WSe_2 — are also interesting because they possess direct bandgap in the visible region at energy degenerate band edges (valleys), spin–valley coupling and valley-contrasting electronic and excitonic properties. The valley physics of TMDC excitons have been intensely studied in the past few years, with recent advances including the optical generation and control of exciton valley coherence. However, as the valley degree of freedom is affected by very fast recombination time (picosecond timescale) would impede any possible exploitation of the valley-functional optoelectronic devices based on valley excitons in monolayer TMDCs in practical applications. The fabrication of bilayered van der Waals (vdW) heterostructures would enable to fully exploit the potential of TMDC in electronic, opto and valleytronic applications.

5.2 Properties of bilayer heterostructures

As it has been explained in Chapter 2, TMDCs undergo a crossover from indirect bandgap in the bulk to direct bandgap in the monolayer form. As a consequence of this direct band gap, monolayers absorb and emit light rather efficiently. The band structure changes as a function of the number of layers due to the strong interlayer coupling, which results in different shifts in the conduction and valence band edges at various symmetry points in the Brillouin zone as a function of the layer number [5]. Vertical TMDCs heterostructures formed by stacking up different monolayers offer a rich collection of physics and functionalities. Theory predicts that any stacked MX_2 heterostructures form type II semiconductor heterojunctions and thus it facilitate efficient electron–hole separation [88]. This would be particularly beneficial for light harvesting and light detection applications. It has been further demonstrated that the charge separation can occurs over ultra fast time scales, such as femtosecond [89]. In type II semiconductor heterojunctions, the conduction band minimum and valence band maximum are found in two separate materials. If electrons and holes are photoexcited they will then prefer to stay in different materials. The alignment of electronic bands of MoS_2 and WS_2 monolayers as predicted [90] is reported in Figure 5.1. It shows that monolayer MoS_2 and WS_2 have bandgaps of 2.39 eV and 2.31 eV, respectively, and the MoS_2 valence band maximum is 350 meV lower than that of WS_2 and the conduction band level is also lower. Thus in this material system, the conduction band minimum resides in MoS_2 and the valence band maximum in WS_2 . This heterojunction structure can lead to efficient charge transfer upon optical excitation with separated electrons and holes residing in two layers. Hong et al has demonstrated that the electron-hole separation occurs in 50 fs [89]. The fast separation can be particular beneficial in solar-driven applications such as photoelectron catalysis and solar cells as it reduces the chances of immediate recombination of the charges. We have demonstrated that the formation of this type of heterojunction of chemically exfoliated MoS_2/WS_2 and assembled in a form of thin films can be beneficial for photoelectrochemical water splitting. In Chapter 10 we discuss the formation of MoS_2/WS_2 heterostructures in the form of thin films via CVD and their identification via physical characterization. The same structures have been used for photoelectrochemical water splitting. In general, the most studied bilayer heterostructures is formed by MoS_2 and WS_2 monolayers. This is due to the fact that synthesis of these materials via CVD is better established as compared to the selenides materials.

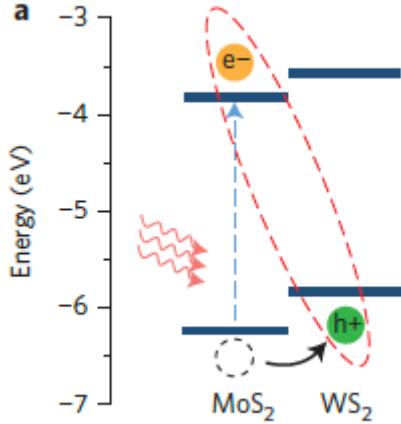


Figure 5.1: Charge separation across heterojunction following photoabsorption. Adopted from [89]

5.3 Fabrication of bilayer heterostructures

The first studies of heterostructures of TMDCs have been based on CVD materials. Two different approaches have been adopted. The first strategy was based on the transfer of two monolayers priorly synthesized independently. While the second approach, which has not seen nearly any further work on, was based on the direct synthesis of heterostructures via CVD.

Approach based on transfer

WS₂/MoS₂ heterostructures have been prepared from conventional PDMS stamping method from CVD grown monolayers [91]. In the first report about this [92], *MoS₂* and *WS₂* monolayers have been grown by high-pressure CVD technique onto *SiO₂/Si* substrates. The CVD *MoS₂* monolayers were continuous over 1mm with large, single-domain crystals reaching up to 75 microns while the CVD *WS₂* monolayers were in the form of individual triangle islands of 5-50 microns in size. The fabrication process consisted in a first transfer of the *WS₂* monolayers onto PDMS substrates, followed by stamping the *WS₂* monolayers onto CVD *MoS₂* monolayers, which formed vertical heterostructures of *WS₂/MoS₂* [91]. The overlap region (approximately 40 μm) of *MoS₂* and *WS₂* monolayers show slightly darker contrast under the optical microscope and it is the region which has been characterized by Raman spectroscopy and photoluminescence and

electrical measurements.

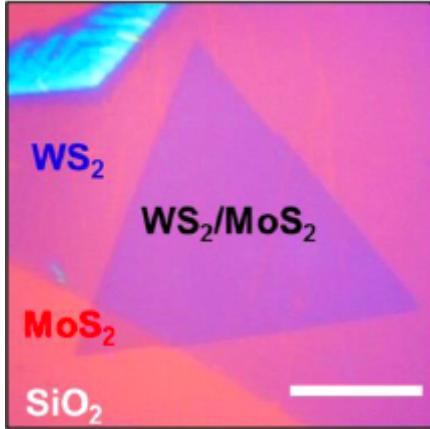


Figure 5.2: Optical micrograph of the heterostructure of WS_2/MoS_2 . Adopted from [91].

Direct synthesis of vertical heterostructures

Firstly, with the term, vertical heterostructures, we differentiate those from the lateral heterojunction created by two adjacent and consecutive layers of two different TMDs. This terminology differentiates these two different types of heterojunction which can be obtained by direct CVD synthesis. The direct synthesis of bilayer heterostructures have been obtained via CVD where molybdenum trioxide (MoO_3) powder was placed in front of a bare SiO_2/Si wafer for the growth of MoS_2 in a tubular furnace. A mixed powder of tungsten and tellurium was scattered on the wafer for the growth of WS_2 . A small amount of tellurium was used to accelerate the melting of tungsten powder during the growth [92]. Upstream in a low-temperature zone, the sulphur powder was placed. The furnace was heated up to the temperature range of 650-850 °C and argon gas was used as a carrier gas to protect the system from oxygen and carry sulphur vapour from the upstream of the tube during the reaction. The difference in the nucleation and growth rates of MoS_2 and WS_2 and the chosen growth temperature favours the sequential growth of MoS_2 and WS_2 , instead of the formation of their ternary alloy ($Mo_xW_{1-x}S_2$ alloy). Vertically stacked bilayers were found to grow preferentially at temperature of 850 °C, whereas in-plane lateral heterojunctions were found at 650 °C. The CVD synthesis can lead to clean interfaces [92][our paper submitted] between the two monolayer components, in contrast with mechanical transfer of layers or assembly from liquid phase. A typical optical, SEM and atomic force microscopy (AFM) images of the layers are shown in Figure 5.3. The bilayers can be easily distinguished from monolayers via optical contrast (Figure

5.3), with MoS_2 monolayers showing a light purple colour and the bilayer regions a much darker purple.

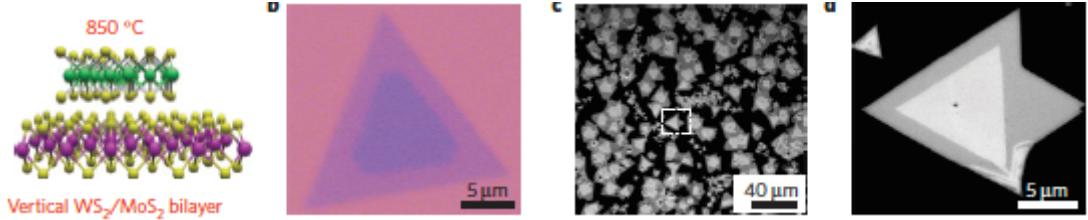


Figure 5.3: Heterostructure imaging. Adopted from [92].

5.4 Characterization of bilayer heterostructures

5.4.1 Raman spectroscopy

Heterostructures fabricated by both these approaches were characterized by Raman spectroscopy. As the vibrational modes of MoS_2 and WS_2 are quite different the Raman spectrum of the heterostructure displays in-plane (E_{2g}^1) and out-of-plane (A_{1g}) modes of MoS_2 and WS_2 at the same frequencies as in their monolayers. The WS_2 E_{2g}^1 and A_{1g} modes are located at 350 cm^{-1} and 416 cm^{-1} while for MoS_2 they are at 380 cm^{-1} and 405 cm^{-1} respectively [91]. Spatial maps show consistently distinct signal from each of the two layers using both fabrication techniques (Figure 5.4). In the transferred bilayered heterostructures there is a clear difference between the Raman modes position of the as transferred materials versus an annealed heterostructure. The position of the peaks for each material in the as transferred materials is compatible with monolayers while after annealing (at the temperature of $70\text{ }^\circ\text{C}$) the peaks are affected by redshift/blueshift as it is characteristics of bilayer materials. This result suggest that as a consequence of annealing ($120\text{ }^\circ\text{C}$ at $<0.13\text{Pa}$ for 6 h) there is an increased interlayer interaction. The fact that no changes are observed in the E modes in plane can be explained with the fact that they are generally less sensitive to changes in the environment. The increased interaction has been also revealed by AFM where the step height of the bilayer heterostructure can be reduced from 1.6 nm toward the expected 0.8 nm by annealing. This can be explained with the possibility that such annealing is able to drive out trapped residual molecules, such as water. In the CVD grown materials, the A_{1g} Raman peaks appears at 418.5 cm^{-1} and 405.3 cm^{-1} respectively for WS_2 and MoS_2 . These values are compatible with a

bilayer structures of the annealed transferred samples. This suggest there is an increased interaction between the layers in CVD grown materials in line with layered bulk materials [91].

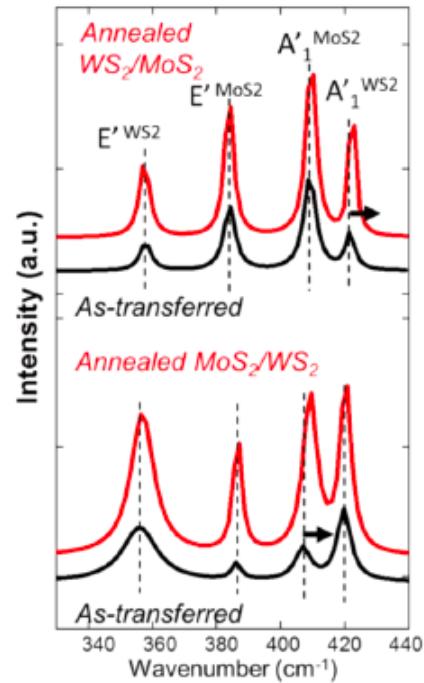


Figure 5.4: Heterostructure Raman spectrum. Adopted from [91].

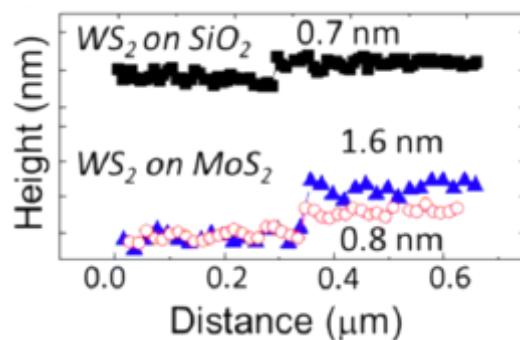


Figure 5.5: Comparison of AFM profiles of WS_2 on Si/SiO_2 and MoS_2 . Adopted from [91].

5.4.2 Photoluminescence

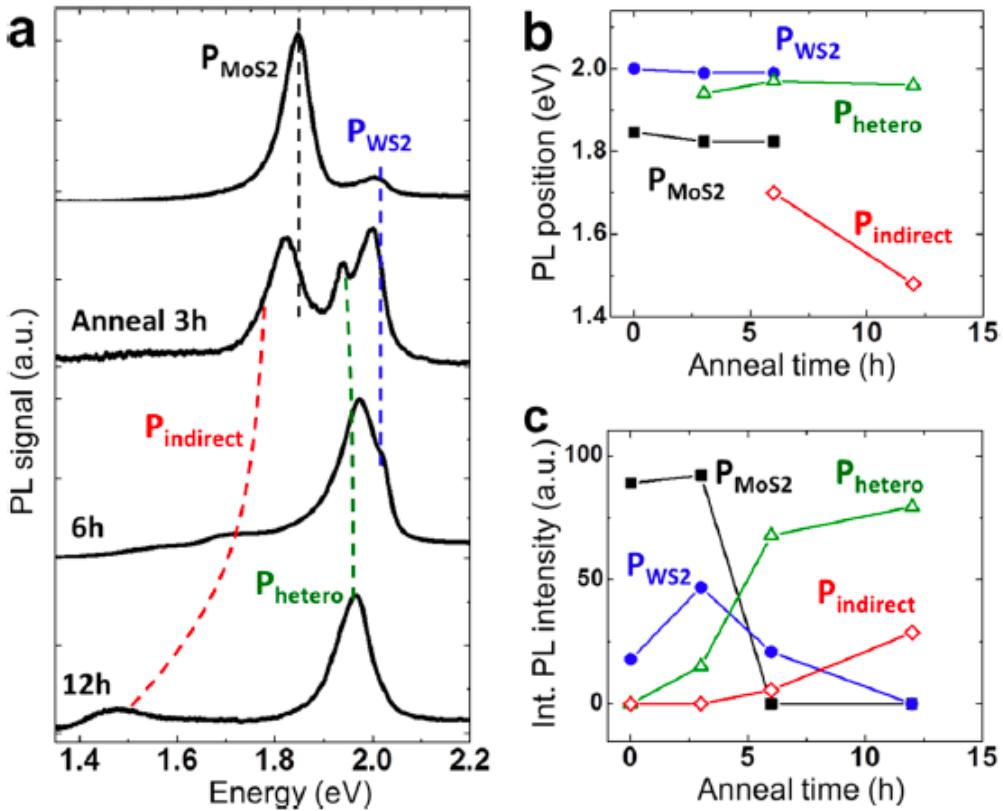


Figure 5.6: PL Spectrum of heterostructure after annealing. Adopted from [91].

The vertical heterostructures were further characterized by photoluminescence (PL) spectroscopy. The as transferred heterostructures manifest PL peak typical of MoS_2 and WS_2 . The spectrum can be defined as additive. The PL peak of MoS_2 shows intensity much higher WS_2 and this was attributed to possibly higher density of defects in WS_2 associated with its higher growth temperatures. After annealing the WS_2/MoS_2 heterostructures, the PL spectrum gradually changes. The transition as seen in Figure 5.6 from transferred to fully annealed bilayer heterostructures occur through the followings: (1) A new PL peak (P_{hetero}) appears at 1.94 eV, and its integrated intensity grows for prolonged annealing time. (2) Upon the annealing, P_{MoS_2} and P_{WS_2} gradually decrease up to the point of appearing as small features at lower and higher energy of the P_{hetero} peak (3) at the end of 12 hours of annealing, another weak emission peak ($P_{indirect}$) appears at 1.75 eV, and the peak position rapidly and eventually red-shifts to 1.5 eV [91].

The explanation for this trend has been the following. As a consequence of the transfer the two monolayers end up well separated from each other due to residual water molecules and/or impurities trapped between the sheets. This large distance has been assessed by

AFM (Figure 5.5). This system display PL peaks characteristics of isolated monolayer MoS_2 (P_{MoS_2}) and monolayer WS_2 (P_{WS_2}). After the annealing, the PL peak intensity of MoS_2 (P_{MoS_2}) and WS_2 (P_{WS_2}) decreases and two new peaks appear, called P_{hetero} and $P_{indirect}$, with the former arising from the electronic coupling between the two monolayer materials while the latter arising due to the indirect band gap formed at the interface of the heterobilayer (Figure 5.7). Because the $P_{indirect}$ peak position changes rapidly with the degree of coupling (annealing time). This has been attributed to a phonon-assisted, indirect bandgap transition, which involves the valence band maximum (VBM) at the Γ -point and the conduction band minimum (CBM) at the K-point. To prove this hypothesis, the authors have fabricated by transfer method a MoS_2/MoS_2 heterostructure and the indirect peak has similar behaviour. This suggested that the indirect peak can be associated with a similar behaviour as the bulk material. DFT calculations has supported this hypothesis [93]. The formation of a type II heterojunction led to establishing a large electric field which develops across the 1 nm thick junction. This leads to strong exciton splitting by which holes (electrons) are rapidly swept from MoS_2 to WS_2 (from WS_2 to MoS_2).

In order to understand the interlayer interactions DFT simulations have been performed. It has been observed that the twist angle between 2 layers has an effect on several properties of the TMDCs. By twisting the layers from being aligned at 0° to 30° the distance between the layers increases by about 0.3 Å. The trend then reverses with distance returning back at 60° to the same value as at the 0° . Additionally it has been predicted that as the twist angle changes from 0° to 30° the valence band at K point remains mostly unchanged while the valence band at Γ point rises. Due to this the direct transition K-K remains unchanged while the indirect K- Γ transition shows lower energy gap. As an explanation of that phenomenon it has been noted that both the valence and conduction band states at K point involve primarily Mo states that are located within the layer. The valence state at the Γ point however involves appreciable p_z content of S atoms and $Mo - d_z^2$. Because of that the overlap between those p_z states of S atoms varies significantly with the layer separation [94].

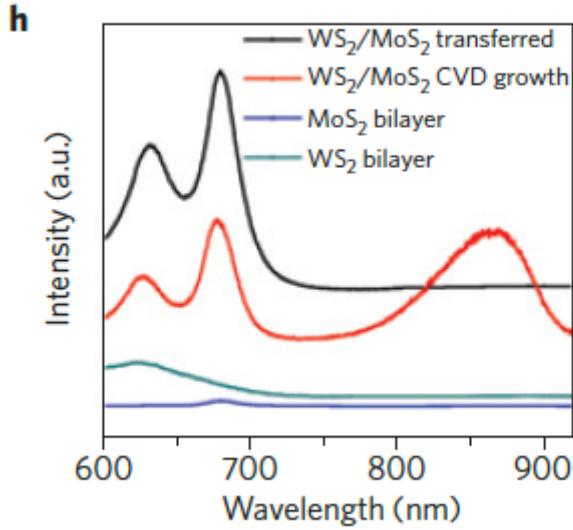


Figure 5.7: Comparison of PL spectra from hetero and homo bilayers of WS_2 and MoS_2 . Adopted from [92].

The CVD grown heterostructures shows a bandgap of 1.42 eV while at the same time separate pronounced PL peaks of MoS_2 and WS_2 can be seen (Figure ??) [92]. Subsequent studies have tremendously developed the understanding of the heterobilayer PL behaviour. The main factor which has been taken into consideration in the following studies is the mismatch angle between the lattices orientations of the two monolayers. Experimentally, it was found that the twist angle in a heterobilayer determines the photoluminescence efficiency of interlayer excitons (bound electrons and holes situated in adjacent layers) and their peak position. It has been hypothesized that twist-angle-dependent interlayer orbital hybridization can cause the variation in the photon emission energies of indirect excitons in heterobilayers (e.g. MoS_2/WSe_2) and also in MoS_2 bilayers [94]. Additional experimental work has reported similar results [95][96]. In a study by Kunstamnn [97] the heterobilayer region of MoS_2/WSe_2 shows a new PL peak that been ascribed to the indirect exciton, and labelled as interlayer exciton (ILE). This peak has been shown to vary with the twist angle while the peaks associated with monolayers remained unaffected. Very recently, Alexeev et al [98] have demonstrated that the positions of PL peaks in WSe_2/MoS_2 heterostructure vary with change in twist angle.

Chapter 6

Polymorphism in group VI transition metals dichalcogenides; a specific case of 1T' and 2H phases of WSe_2

6.1 Introduction

In contrast to other 2D materials like hBN or graphene, TMDCs exhibit structural polymorphism and as such open an additional avenue in 2D material engineering. The relation between different phases observed in TMDCs can be seen in Figure 6.1. On top of altering the electronic nature of the TMDC, semiconducting or metallic, there can also be observed a variety of superconducting states [99][100], quantum spin Hall insulators [101][102][103][104] or Weyl semimetals [105]. Interestingly the various TMDC phases can coexist at specific temperatures and pressures [106][107][108]. Those different phases can exhibit small difference in energy per formula unit MX_2 . As such a phase transition can be induced via e.g. a charge injection [109]. Overall the various phases of the TMDCs and the transitions between are of great interest and remain unexplored in full detail.

6.2 WSe_2 phases

The monolayers of TMDCs can be usually found in either 1H or 1T phase where the exact configuration depends on the thermodynamics [107][108]. In order to identify which of those phases is more favourable the crystal field theory can be applied. The number of electrons in d orbitals of transition metals needs to be counted for a given TMDC

material. For group IV TMDCs (Ti, Zr and Hf) that number is 0 (d^0) while for group 10 (Ni, Pd and Pt) the number is 10 (d^6). It can be therefore shown that the number of electrons in d orbitals correlates with the phase transitions in TMDCs as seen in Figure 6.2. The group IV TMDCs (d^0) for instance are most stable in 1T phase. However the d_{z^2} level of the 1H phase has the lowest energy and therefore the TMDCs of group V (d_1) and group VI (d_2) fill that level first and therefore, the group V TMDCs are found most stable in either 1T or 1H phase while the group VI TMDCs are most favourable in 1H. After filling the d_{z^2} level in group VI TMDCs, the additional electron in group VII TMDCs contribute to the 1T levels and results in a distorted octahedral coordination (1T') with clusterisation or Peierls distortions of the metal atoms. Furthermore the group 9 and 10 TMDCs are most stable in the regular octahedral coordination (1T).

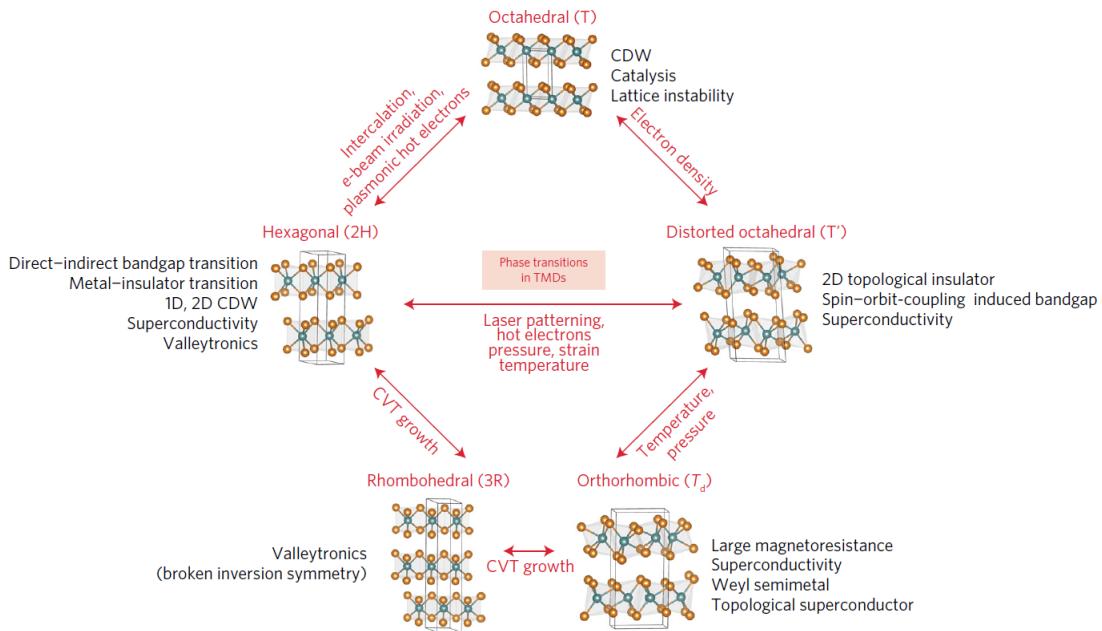


Figure 6.1: Transition and correlation between phase and physics in TMDCs. Reproduced from [110]

Recently the 1T' phase has received attention due to the predictions of potential Weyl semimetal or quantum spin Hall effects for group VI TMDCs [101][105]. Additionally the lattice distortion orientation can be affected by strain which allows for mechanical control of ferroelasticity and potential application as a shape memory material [111]. In order to achieve those effects in group VI TMDCs a phase transition from 1H to 1T' generally has to occur [2]. Such transition is usually performed via the lithium intercalation or chemical exfoliation. Following the lithiation the excess of the electrons is found in the d orbitals of the transition metals. As a result of that the electron density of those orbitals

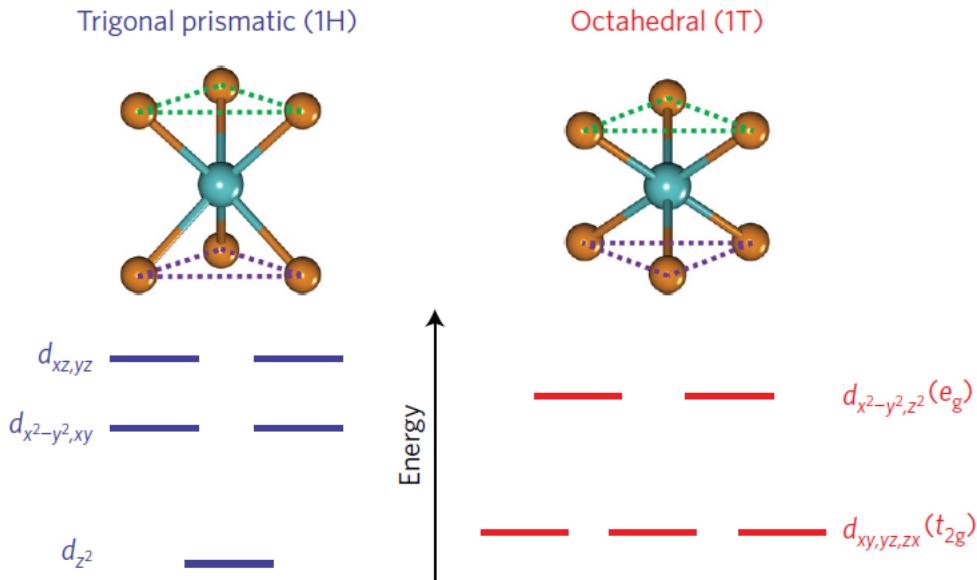


Figure 6.2: Diagrams of 1H and 1T lattices and energy levels of d-orbital electrons. Reproduced from [110].

increases from d_2 to d_{2+x} . In order for a full transition from 1H to 1T to occur the excess of the electrons must be in range of 0.2 to 0.4. However if the excess is smaller than that then the distortion of the lattice may help to accommodate the phase transition.

One of the most important characteristics of TMDCs that influences a myriad of different properties is the number of layers. Especially in case of optical and electronic properties of 2H TMDCs the number of layers strongly affects the size and the nature of the bandgap, transitioning from indirect in bulk to direct in monolayer. The number of layers is however also of crucial importance to quantum effects observed or predicted in TMDCs in that the bulk material exhibits the in-plane inversion symmetry while the monolayers break it [99][100]. Such breaking of symmetry leads to strong spin-orbit coupling as well as effective Zeeman fields in TMDCs. Additionally an out of plane spin polarisation which depends on the valley, K or -K point, has been observed when a strong anisotropic magnetic field has been applied to quench the superconductivity in 2H-*MoS*₂ [110]. There has also been observed a superconducting state in monoclinic and 1T' *MoTe*₂, and where also the Weyl semimetal and topological insulator states are expected [101][105][112].

Due to the distortion in the 1T' phase of the group VI TMDCs a band inversion near the Fermi level is observed, with chalcogen p and metal d bands. These bands result in some interesting phenomena, the Weyl state and quantum spin Hall effect. Those effects

can manifest themselves in distorted octahedral phase ($1T'$) or orthorhombic (T_d) phase. It has been shown using DFT calculations that group VI TMDC in the T' phase exhibit the band inversion resulting in the quantum spin Hall effect [101][102]. The change in number of layers results not only in inversion symmetry breaking but also affects the bandgap magnitude and as such is crucial in achieving the dissipationless spin transfer by the QSH [113][114]. It has theorised that a topological FET can be realised through the application of the external electric field which can turn the topological states on or off.

In contrast to the $1T'$ phases of group VI TMDCs, the orthorhombic T_d phase shows Weyl semimetallic states as a result of the inversion symmetry breaking. The T_d phase can be achieved via control of the defects, cooling down the T' phase below 240K or as a result of high pressure [112].

A phase transition from 2H to 1T in MoS_2 has been observed using the TEM. Several intermediate phases have been identified and the gliding planes of Mo and S atoms have been observed. It has also been shown that the electron injection in TEM can be used to pattern the phase transition, and therefore that the electron driven phase transition is possible [115]. Additionally it has been shown that local heating and the chalcogenide defects created as a result can induce an irreversible transition from hexagonal to monoclinic phase in $MoTe_2$ [108]. A laser irradiation can also cause a phase transition in MoS_2 from monoclinic to hexagonal, where the activation energy for the transition has been found to be ~ 400 meV [116]. There has also been demonstrated transition from hexagonal to monoclinic MoS_2 using plasmonic hot electrons [117]. The injected hot electrons in the 4d band of the Mo atoms result in a more stable monoclinic phase according to the crystal field theory. As one of the potential application an infrared sensor can be proposed where a phase transition is engineered by strain to occur at such low temperature that a small change in temperature can induce it [118].

A contact between the 2D TMDC layer and rest of the device is of critical importance for any electronic and energy application. The commonly used transfer method of assembling the material with the contacts is generally undesirable as it alters the structure of the TMDC material. To this effect the homojunction offers a viable alternative as it has been presented with local transition from 2H MoS_2 to 1T MoS_2 [106]. An example of it can be seen in Figure 6.3, where an in-plane homojunction between metallic 1T and semiconducting 2H phase of MoS_2 allows for a low contact resistance interface.

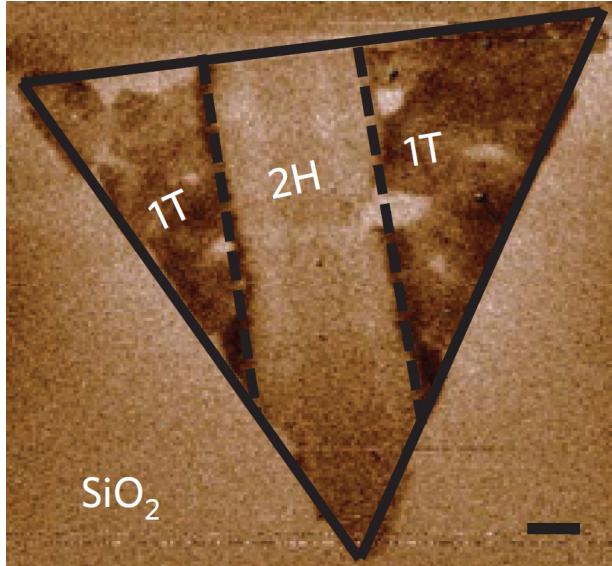


Figure 6.3: Electrostatic force microscopy phase image of a monolayered MoS_2 homojunction. Reproduced from [106]

One of the approaches to synthesis of TMDCs and which has been applied to growth of WSe_2 is colloidal synthesis. This wet synthesis method involves dissolution of precursors in solution, careful control of time and temperature of reaction and subsequent deposition of dispersed flakes onto a substrate. Using that method small 2H WSe_2 and $MoSe_2$ flakes were successfully produced [119][120]. There have been however no successful growths of 1T' TMDCs using this methods.

6.3 Conclusions

In this chapter we have summarized the fundamental differences between 2H and 1T/1T' phases of TMDCs with emphasis on the different crystalline phases and electronic properties along with different phenomena that can be enabled by the 1T' phases. Additionally, we have laid out a short summary of the synthesis methods for the metastable 1T/1T' phases.

Chapter 7

Chemical vapour deposition of mono-and-few-layer WS_2 : the role of precursors

In this chapter the CVD growth of WS_2 using different precursors is investigated. The as grown samples were characterised by Raman and PL spectroscopy as well as XPS, XRD, AFM and electrical measurements. As a result it was concluded that using $H_2WO_4 + NaCl$ at 850 °C gives best results. Such grown samples exhibit biggest flakes up to 200 μm in size as well as show the strongest and most narrow PL peak with 36 meV FWHM. The samples grown using $H_2WO_4 + NaCl$ at 950 °C show also best transistor electron mobility in monolayer CVD grown WS_2 while that grown using $WO_3 + NaCl$ at 950 °C shows best transistor electron mobility in bilayer CVD grown WS_2 .

7.1 Introduction

Monolayers of transition metal sulphides and selenides exhibit range of interesting properties such as strong light absorption in the IR and visible range [121][9][122], valley polarisation [123] [124], spin-orbit interactions [125][61], tightly bound excitons [15] or second-harmonic generation [126]. Some of these effects can be attributed to the lack of free dangling bonds and configuration of d-orbitals [1], [127].

Among these materials one of the most promising is the WS_2 . Its visible range optical bandgap of 2 eV as well as an easy and safe manufacturing route via CVD makes it one of the more interesting and studied TMDCs. The typical characterisation by

photoluminescence spectroscopy allows to probe the varying synthesis conditions, the grain boundaries or defect population [8] [60] [83] [72]. The PL efficiency in as-grown monolayer WS_2 produced via CVD growth shows $\sim 2\%$ efficiency with higher efficiency observed in mechanically exfoliated [60][128] [129]. This efficiency is caused mostly by defect-mediated non-radiative recombination centres [130]. LEDs have been successfully produced [131] showing external quantum efficiency up to 5% [132][35]. WS_2 is typically a n-type semiconductor due to the presence of sulphur vacancies [8][23][59]. In order to utilise this material in any potential future applications a reliable and scalable manufacturing method must be developed to ensure a high quality crystal on the wafer scale area. The main method for WS_2 synthesis that satisfies these conditions is Chemical Vapour Deposition (CVD) [133]. The growth of tungsten based TMDCs have been less successful than the equivalent molybdenum based TMDCs and has produced mostly isolated flakes of up to $40 \mu m$ [8] [82] [72] [70][134][135][84]. Even larger films of monolayer WS_2 have been shown, however they also exhibit low carrier mobility [136][137]. In the typical CVD synthesis process the sulphur and tungsten oxide are evaporated simultaneously in a tubular furnace with a constant flow of carrier gas like argon at temperatures of at least $900 ^\circ C$ [8][82][72][70][134][135][84]. Such growth is predicated by topotactic transformation leading to low density distribution of domains on an amorphous [8][82][70][135][84] or crystalline substrate [72][134][85] possibly due to low evaporation rates of WO_3 . Since WO_3 requires high temperatures of 950 - $1000 ^\circ C$ to evaporate while the S becomes volatile at $90 ^\circ C$ the thermodynamics of the process are difficult to control. The low growth dictated by fast evaporation of S leads to limited domain growth and lack of continuous layer. One of the proposed solutions have been to spread the WO_3 on the target substrate [60][83][137][71][138][139][92]. This has however led to low reproducibility, poor control of thickness and stoichiometry and unreacted material left on the substrate. Another approach has been to use more volatile W precursors such as WCl_6 [140] or $W(CO)_6$ [136][141] together with organic compounds as S precursors. Such method while producing a large area domains at lower temperature has led to lower crystal quality and purity.

Here we propose a different method of CVD synthesis that allows for much larger flake growth of up to $800 \mu m$ at temperature of $750 ^\circ C$. Such grown material exhibits high electron mobility in one and two layers of WS_2 , higher than other values reported in literature [138][142]. The photoluminescence peak is also very narrow at 36 meV FWHM at room temperature.

The most common method of producing the TMDCs is by CVD. During the CVD

growth the process the substrate, usually a Si/SiO_2 substrate, and the sample are heated to very high temperatures, up to 1000 °C. Because of that there is substantial thermal expansion in both substrate and sample. However due to difference in thermal expansion coefficient between those two elements there is potential build up of thermal strain. Additionally because the substrate, upon which the sample is grown, is heated to such high temperatures that it cannot be used for electrical measurements. More specifically the thermal expansion coefficients of WS_2 and SiO_2 are on the order of 10^{-3} and $10^{-7} K^{-1}$ respectively [143][144]. Therefore it is expected that during cooling down the WS_2 will come under tension due to thermal expansion coefficient difference. There has been studies showing variation in PL position and FWHM under strain [145]. Similarly Raman peaks have also been shown to become shifted under strain, especially when using polarised light source [146]. Theoretical studies have also shown the effect of the change in lattice constants on electronic band structure of TMDCs [52]. Moreover in order to use TMDCs as components in devices different layers have to arranged together either vertically or laterally. Due to aforementioned reasons there is a need to develop methods for transferring single layers of TDMCs from one substrate to another one. In this chapter a focus is put on transferring WS_2 monolayer flakes from SiO_2/Si onto other surfaces.

7.2 Experimental

Majority of growths were performed by a fellow PhD student, Francesco Reale. For the purpose of comparing the CVD synthesis method conditions several sets of precursors were used: WO_3 , $WO_3 + NaCl$ and $H_2WO_4 + NaCl$. For each of the conditions sets at least 10 different growths were performed and from each grown sample at least 3 different flakes were investigated. The standard growth procedure involves two separate crucibles placed at distance from each other in a quartz tube. Next to the crucible containing the tungsten precursor a Si/SiO_2 (285 nm SiO_2 substrate) Each of these crucibles is independently heated to ensure that the S and the W precursors evaporation rate is maximised at the same time. The vapours then are deposited on SiO_2/Si (285 nm) substrate which is placed close to the W precursor crucible. The entire process is performed under low vacuum and a supply of Ar gas. The furnace setup can be seen in Figure 7.1.

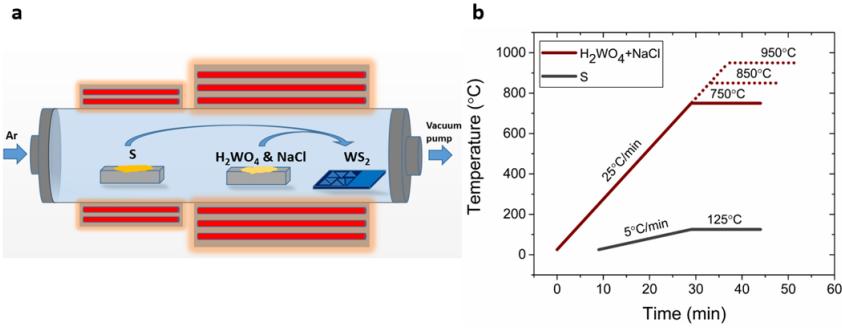


Figure 7.1: a) CVD furnace setup; b) Temperature profiles for the W and S precursors.
Adopted from [147]

The most common method of transferring flakes synthesised via CVD method is a wet transfer method utilising an intermediate substrate. In such procedure a thin layer of PMMA is first spun on top of the substrate. After drying the substrate is placed in a KOH aqueous solution (6% to 8%) heated to about 50 °C. As a result the thin layer of *SiO*₂ on top of *Si* is dissolved leaving a PMMA with the sample attached to it floating on top of the solution. The PMMA is then rinsed in water several times and scooped up onto a new substrate. Next the sample is dried and annealed to ensure good adhesion and remove wrinkles and strain. Then the PMMA is removed with a solution of acetone and IPA at about 50 °C. Any remaining PMMA can be removed by annealing the sample at about 100 °C in air.

7.3 Results

By following this synthesis method a reproducible deposition of large area flakes can be shown. As seen in Figure 7.2 the size of the flakes increases from left to right as the precursors used (*WO*₃, *WO*₃–NaCl and H₂*WO*₄–NaCl) change as well as demonstrating the lower temperature required to achieve these growths. All of these growths result in formation of triangular flakes with sharp edges and uniformity of colour throughout which suggest a high quality, pristine material across the flake. The growth using only *WO*₃ results in formation of small flakes of 10 μm at 950 °C while no growth occurs at lower temperatures (Figure 7.2). This can be explained by the high sublimation temperature of *WO*₃.

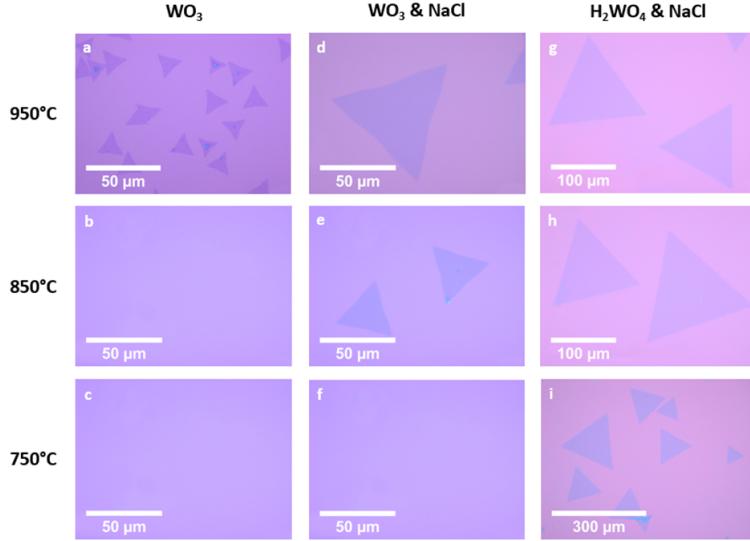


Figure 7.2: OM image of WS_2 . Adopted from [147].

The growth can also be observed using $WO_3 + NaCl$ at $950\text{ }^\circ C$ and $850\text{ }^\circ C$ with the former showing flakes of size of about $60\text{ }\mu m$ while the latter showing smaller flakes of about $30\text{ }\mu m$ in size. To explain this difference in size a Robinson & Robin model can be used which states that at higher temperatures the diffusivity of the adsorbed precursors is favourable to the expansion of the existing domains [148]. On the other hand the desorption of the adsorbed species is high which limits the supersaturation and formation of new domains. If the temperature is lowered even further to $750\text{ }^\circ C$ then no growth is observed at all, most likely due to slow evaporation of WO_3 precursor.

With the change of precursors from WO_3 to H_2WO_4 a significant change in size of flakes is observed at $850\text{ }^\circ C$ and higher temperatures with lengths exceeding $200\text{ }\mu m$. Additionally the growth has been shown to occur at $750\text{ }^\circ C$ with flakes of the size of $50\text{-}200\text{ }\mu m$. Moreover continuous monolayer areas of up to 0.8 mm in size has been shown (Figure 7.3a). By increasing the growth pressure (1.6 mbar to 13 mbar) at $950\text{ }^\circ C$ bilayer WS_2 flakes can be preferentially formed (Figure 7.3b).

To understand the facilitated synthesis of WS_2 using H_2WO_4 and $NaCl$, we conducted X-ray diffraction (XRD) analysis of the reaction products between $H_2WO_4 + NaCl$ and $WO_3 + NaCl$ systems at different temperatures ($500\text{ }^\circ C$, $650\text{ }^\circ C$ and $750\text{ }^\circ C$) to understand the chemical differences (Figure 7.4). The precursors ($H_2WO_4 + NaCl$ and $WO_3 + NaCl$) were annealed in vacuum up to several different temperatures ($500\text{ }^\circ C$, $650\text{ }^\circ C$ and $750\text{ }^\circ C$) and resulting products from each annealing procedure were characterised using XRD. XRD spectra of these products can be seen in Figure 7.4 and the peaks have been assigned

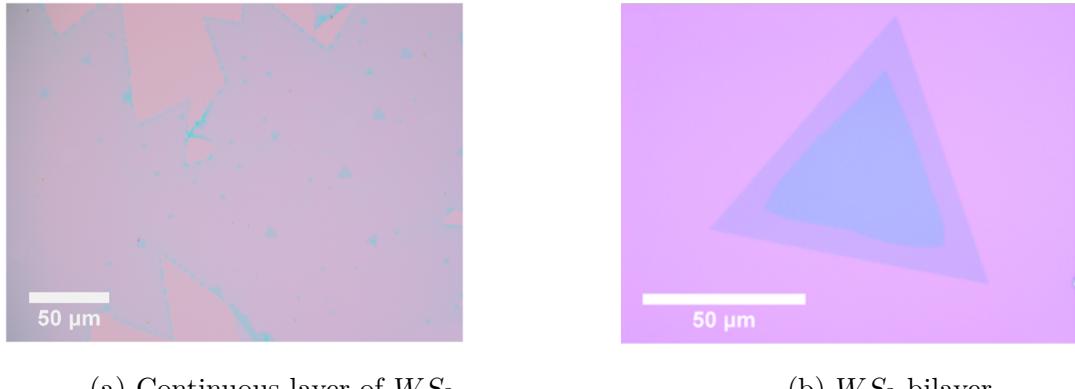


Figure 7.3: OM Images of WS_2 . Adopted from [147].

to several known compounds. We found that the main products of the reactions between $NaCl$ and H_2WO_4 are: $Na_xW_yO_z$ and tungsten oxychloride ($WClO_4$ and WO_2Cl_2). The $Na_xW_yO_z$ possesses a high evaporation temperature as it remains in the crucible after the synthesis of WS_2 is completed. Further, using this compound as precursors for a new growth of WS_2 at 950 °C did not lead to the formation of any WS_2 flakes, confirming the high evaporation temperature. On the bases of previous studies on the synthesis of bulk crystals, the formation of tungsten oxychloride species (WO_2Cl_2 and/or $WOCl_4$) is likely to occur while the formation of metal halides is less favourable (e.g. WCl_6) [149][150]. Tungsten oxychlorides are volatile already at 200 °C [151] and they can be sulfidised in vapour phase and then be deposited onto the target substrate as atomic clusters. There has been successful growths of bulk WS_2 using $WOCl_4$ as a precursor [140]. Owing to clean decomposition pathways $WOCl_4$ has proven to be an effective precursor avoiding the formation of tungsten oxysulfide. We have shown that growth of WS_2 is possible at low temperatures of 550 °C using this precursor. When the growth is attempted using only tungsten as sole precursor the role of the oxyhalide species becomes highlighted. In such a growth only small WS_2 flakes are observed with PL performance similar to that of the pure WO_3 precursor growth. By replacing the $NaCl$ by similar precursor, KCl , we further confirmed the key role of Cl in this growth.

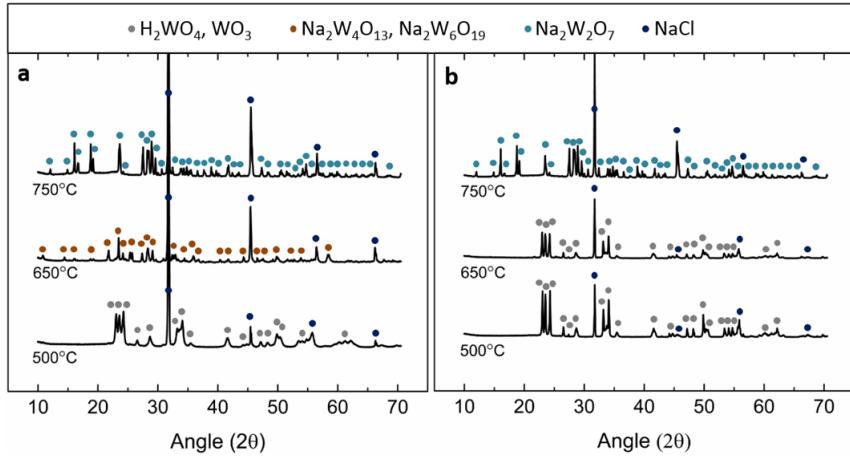


Figure 7.4: XRD spectra of residuals after annealing, a) $H_2WO_4 + NaCl$ b) $WO_3 + NaCl$. Adopted from [147].

The flakes were investigated using HRTEM (performed by fellow PhD student, Maria Sokolikova) to confirm high crystallinity of the material (Figure 7.5). The lattice constant measured in this way has been found to be 0.3 nm, which is consistent with that of 2H-WS₂ (0.318 nm). The AFM characterisation allowed to confirm the presence of monolayer (Figure 7.5) and bilayer (Figure 7.3b) flakes with the step of 0.8 nm [152][153].

The Raman spectroscopy characterisation of WS₂ flakes obtained under different growth conditions can be seen in Figure 7.5. All of these spectra exhibit the main 2 peaks at $\sim(351 \pm 0.53) \text{ cm}^{-1}$ and $\sim(417.6 \pm 1) \text{ cm}^{-1}$. The latter peak corresponds to the A_{1g} vibrational mode while the former peak can be further resolved into two peaks, one related to 2LA vibrational mode and the second to E_{2g}^1 . As seen in the Figure 7.8a and Figure 7.8c the distribution of intensity of both main peaks is uniform across the flakes. Similarly the difference between peak positions of A_{1g} and E_{2g}^1 is also uniformly distributed as seen in Figure 7.9 and is equal to $\sim(66.5 \pm 0.53) \text{ cm}^{-1}$ which is indicative of monolayer [154].

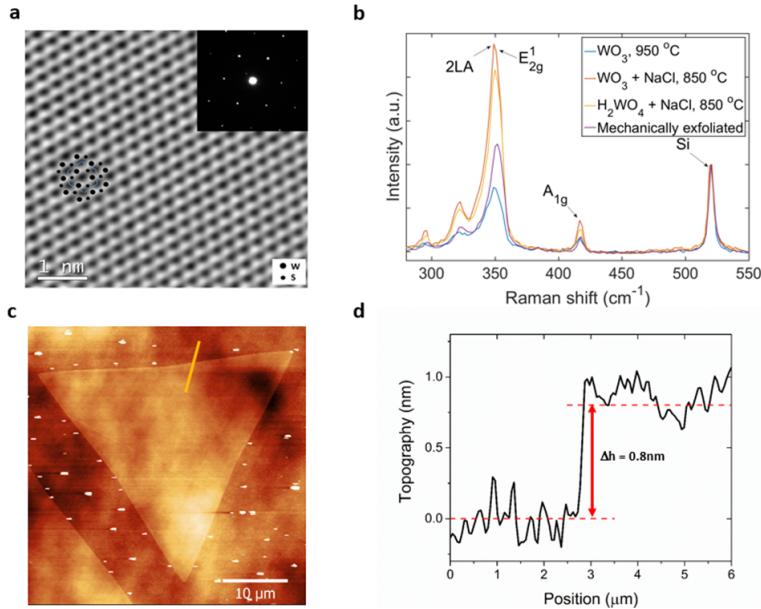


Figure 7.5: a) HRTEM image of WS_2 grown with $H_2WO_4 + NaCl$, inset shows a hexagonal diffraction pattern. b) Raman spectra taken from WS_2 grown various precursors with characteristic peaks indicated. c) AFM image and d) height profile of single layer WS_2 . Adopted from [147].

As seen in Figure 7.6 maps of PL intensity has been collected for samples grown using different growth condition. The sample grown using WO_3 at 950 °C appears to be trisected into 3 symmetrical areas. The intensity is lowest along the the trisecting lines and highest in the centre of each of the sub-triangles. As the PL peak position blueshifts the intensity the peak decreases and vice versa as seen in Figure 7.6 and Figure 7.10a. The distribution of the PL peak positions seems to be bimodal with maxima at 1.96 eV and 1.94 eV. The FWHM is distributed mostly uniformly with few small areas of greater and few of smaller FWHM (Figure 7.10b with the average value of 65 meV. These peak position and FWHM values are comparable with those reported in literature [8][72][155][156]. The PL spectra taken from one of the three smaller parts of the flake are redshifted by about 0.02 eV and are wider than average. This can be explained by the presence of defects, in particular sulfur vacancies, which effectively cause the WS_2 to be n-doped [157][158]. This in turn increases the trion population which introduces new peak, redshifted by about 30 meV, which results in overall shift and broadening of the PL peak [159][8]. Additionally such localised changes in PL peak intensity and position can be caused by local strain [160][157]. To investigate the potential effect of strain on the observed PL pattern a flake was cut using high power 532nm laser. As seen in Figure

7.11 the resulting pattern remains the same as before treatment. Therefore the observed pattern is most likely caused by the local variation in defect density [161].

By introducing the NaCl and mixing it with WO_3 precursor WS_2 samples are grown that exhibit higher energy and narrower PL peaks. The spectra are asymmetric and can be therefore deconvoluted to obtain an exciton and trion component (Figure 7.7). The spatial distribution of the PL position and width is mostly uniform throughout the flake. However the distribution of PL peak positions and FWHM across different flakes grown at the same conditions is bimodal (Figure 7.7). The PL peak position is found to be ($\sim 1.95 \pm 0.002$ eV and 1.96 ± 0.002 eV) while the FWHM is ($\sim 43 \pm 2.8$ meV and 51 ± 3 meV) which is smaller than most reported works [8][72][155][156]. This can be explained by smaller trion component in the PL spectrum which in turn means that WS_2 samples grown at these conditions contain less structural defects compared to the pure WO_3 growth. A difference in growth mechanism (topotactic or molecular conversion) which results in different defect distribution can be attributed to the differences in samples.

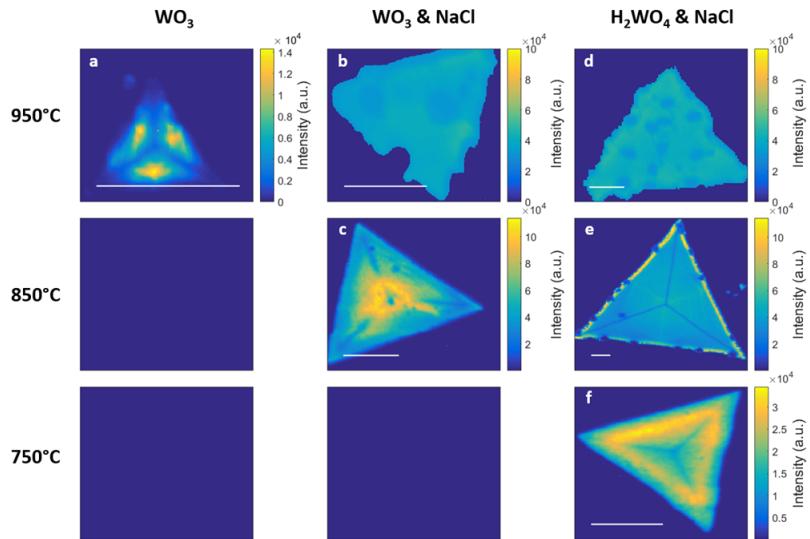


Figure 7.6: Maps of WS_2 PL intensity. The scale bar is $10\mu\text{m}$. Adopted from [147].

By changing the WO_3 precursor to the H_2WO_4 precursor a further shift in PL peak position, as well as increase in PL intensity and narrowing of the PL peak is observed as seen in Figure 7.6, Figure 7.7. The PL peak position distribution across the flake is narrow and is ($\sim 1.980 \pm 0.005$ eV) which is higher than that of the WO_3 and $WO_3 + NaCl$ systems. The FWHM is found to be ($\sim 36 \pm 3$ meV) which is also smaller than that of the WO_3 and $WO_3 + NaCl$ systems. The PL peak width is also smaller than that reported in literature for CVD grown [8][72][155][156] exfoliated WS_2 [122][23]. At the same time

it is comparable to the WS_2 grown on van der Waals substrates (Si/SiO_2) [85] as well as mechanically exfoliated WS_2 [131]. Additionally the peak position as well as FWHM variation is also smaller than that of other samples (5meV and 3 meV respectively) (Figure 7.12d). The PL peak intensity map (Figure 7.6) shows that the spatial distribution of intensity is also much more homogeneous with faint weak pattern of three trisecting lines still visible.

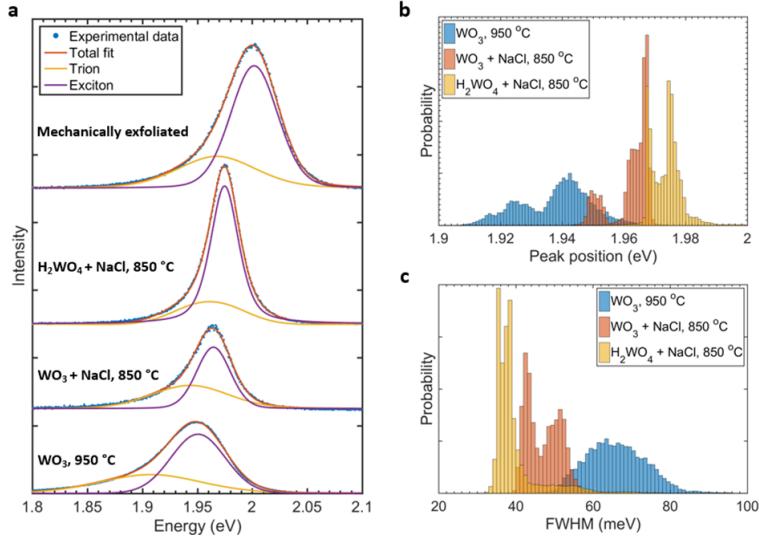


Figure 7.7: a) WS_2 PL spectra grown using various precursors b) histograms of PL peak positions c) histograms of PL peak widths. Adopted from [147].

As seen in Figure 7.8 the Raman peaks are generally uniform in both intensity and position for most samples. The irregularities in the intensity and position of both the E_{2g}^1 and A_{1g} in the sample grown at 950 °C with both $WO_3 + NaCl$ and $H_2WO_4 + NaCl$ are caused primarily by residue deposited on top of the flakes after the growth as seen in optical micrographs. Additionally as seen in Figure 7.8a the deviations from the mean value are located primarily at the edges of the sample. This suggests that the rest of flake is pristine and the deviations are associated with growth residue, such as $NaCl$ or WO_3 , located at the edges. The coefficient of variation (CV) for the intensity and position for the samples grown at 950 °C with WO_3 and at 850 °C with $WO_3 + NaCl$ and $H_2WO_4 + NaCl$ is on the order of up to 10^{-4} which indicates a very high homogeneity across the samples. This further shows that the crystal quality of the flakes is quite uniform regardless of the growth method.

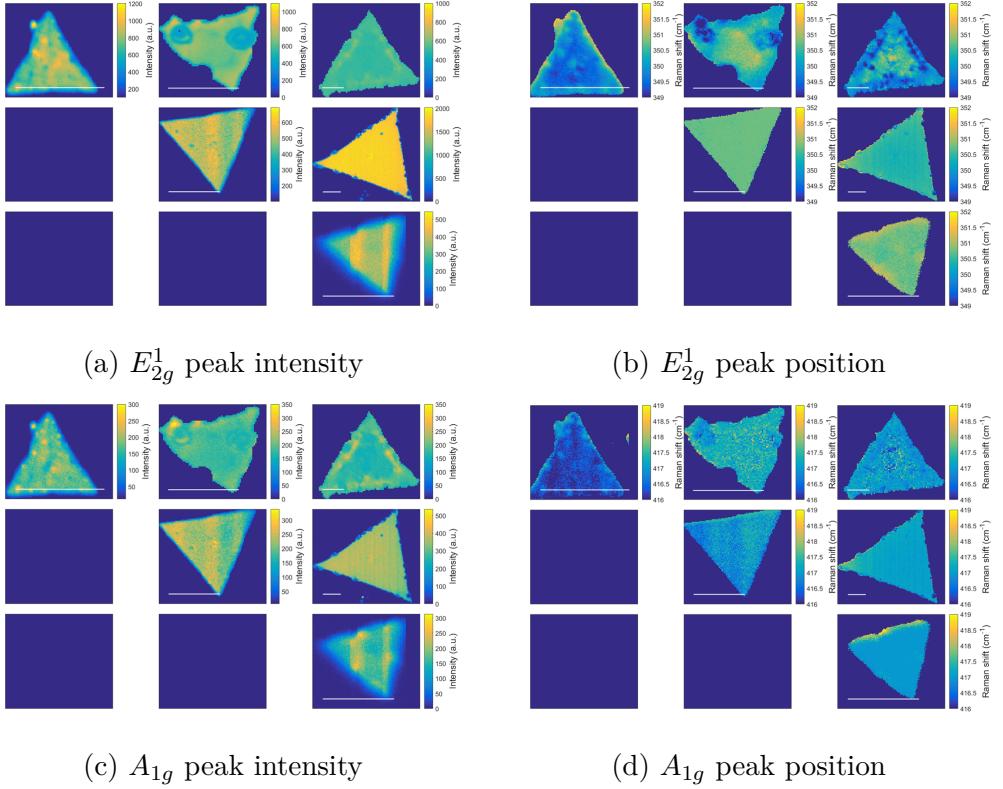


Figure 7.8: Raman peaks maps. Adopted from [147].

By looking at the difference in position between A_{1g} and E_{2g}^1 peak positions as seen in Figure 7.9 it can be further concluded that the flakes are uniformly monolayer. The deviations from the mean are heavily localised and correlated with differences in PL as well as optical images and are most likely caused by precursors residue. Additionally no trisecting lines (as seen in Figure 7.6) can be seen in the maps of Raman spectra.

The maps of PL peak positions and widths can be seen in Figure 7.10. The PL positions map of the sample grown at 950 °C using WO_3 shows some variability with spots of lower energy that loosely correlate with the PL intensity. There is still faintly visible pattern of three trisecting lines of higher energy as seen in Figure 7.6. This indicates the areas with higher intensity correlate with lower peak position, especially along the trisecting lines. The other maps, especially the ones grown at 850 °C and 750 °C with $WO_3 + NaCl$ and $H_2WO_4 + NaCl$, are more uniform in terms of PL peak position and PL peak width. The deviations are again highly localised and correlated with the deviations in Raman and PL intensity. These deviations are generally of lower PL peak position as well as greater PL peak width which generally indicates lower crystal quality.

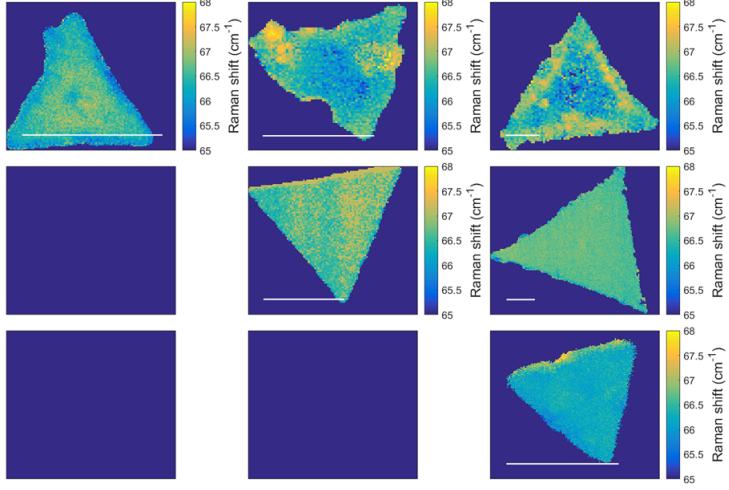


Figure 7.9: Raman peaks $2LA$, A_{1g} positions difference. Scale bar is $10 \mu\text{m}$. Adopted from [147].

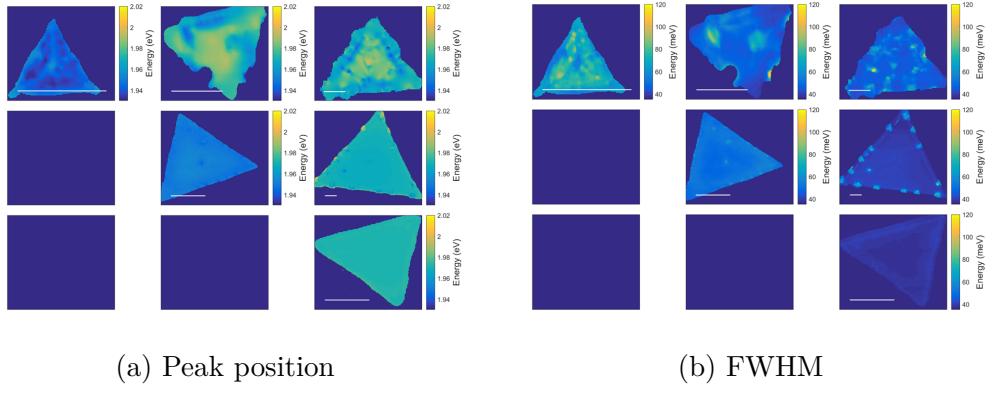


Figure 7.10: PL peak positions and FWHM maps. Adopted from [147].

One possible explanation of the pattern of trisecting lines as seen in e.g. Figure 7.6 is the thermal strain caused by difference in thermal expansion coefficient between WS_2 and the SiO_2 substrate. Since it is known that the strain in TMDCs including WS_2 can cause the change in Raman and PL spectrum [160][157] then removing a piece of the material should cause the strain to adapt to new bounding conditions. In order to investigate the trisecting pattern a flake with such pattern has been cut using 532 nm high intensity laser (50 mW). As seen in Figure 7.11 both the PL intensity maps and Raman E_{2g}^1 maps show a clear separation. The resulting PL and Raman intensity maps however do not show any significant change in the pattern. The trisecting lines as well as local maxima can still be seen in PL intensity map. The Raman shows few spots of increased intensity on one of the halves of the flake as well as a very weak increased intensity area along the cut. Since

there is no observed increased intensity along any edges before cutting the flake it does not appear that the increased intensity along the cut is a result of strain being resolved into new bounding conditions. It appears therefore that cutting the material did not alter the pattern nor alter the rest of the PL or Raman spectra maps.

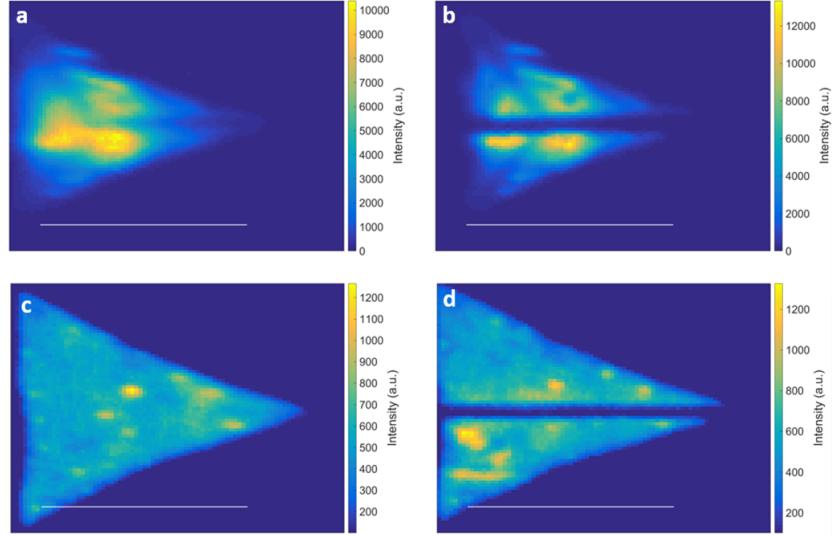
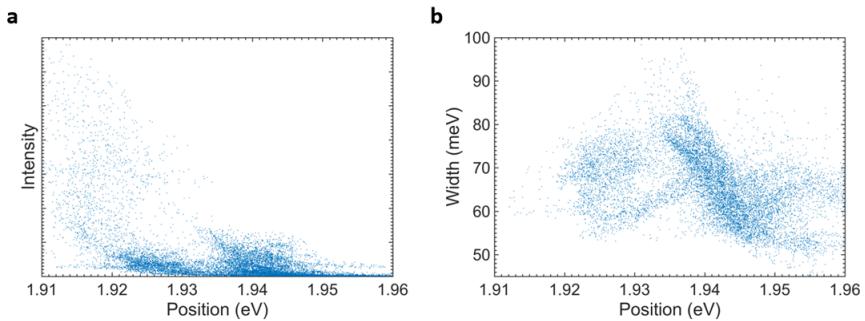
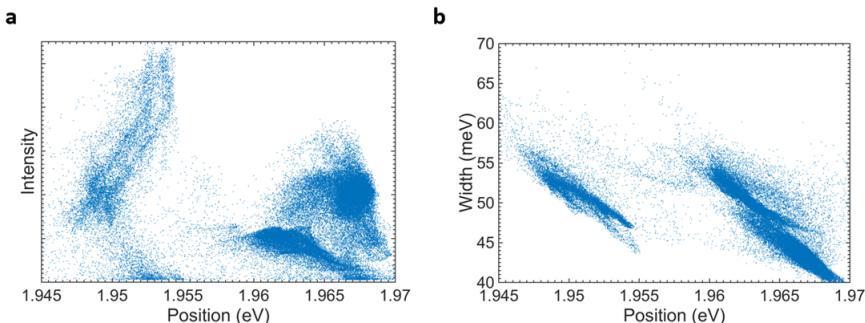


Figure 7.11: Maps of PL intensity a) before b) after performing the cut. Maps of $2LA + E_{2g}^1$ Raman peak intensity c) before d) after performing the cut. Scale bar is $10 \mu\text{m}$. Adopted from [147].

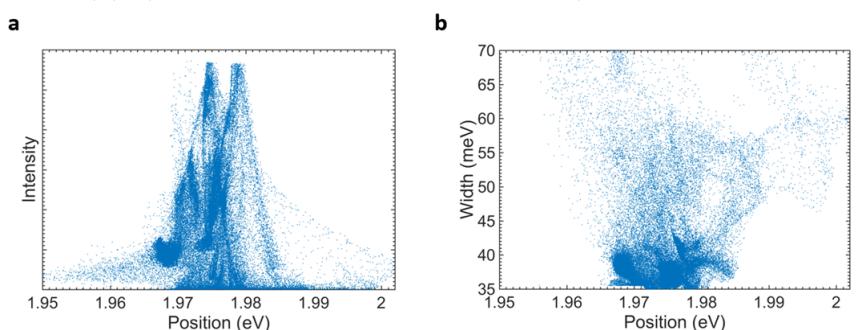
The spectral maps from different flakes grown with the same conditions were then collected and plotted as graphs of intensity or width versus position. As seen in Figure 7.12d the PL intensity seems to be largely independent of the PL position. If PL is present at given position then intensity is mostly uniformly distributed in terms of intensity. The PL width seems to be inversely related with regards to PL position. In samples grown at 850°C with $WO_3 + NaCl$ the relation seems to be the strongest. Across all the samples the values vary between around 60-80 meV at low PL energies (1.92 eV) to 40-60 meV at high PL energies (1.98 eV). This seems to be related to overall quality of the crystals, i.e. the presence of defects, stoichiometry, crystallinity, doping, adatoms. The more uniform the sample the less mechanisms for peak broadening as well as fewer added energy levels facilitating different electron recombination paths.



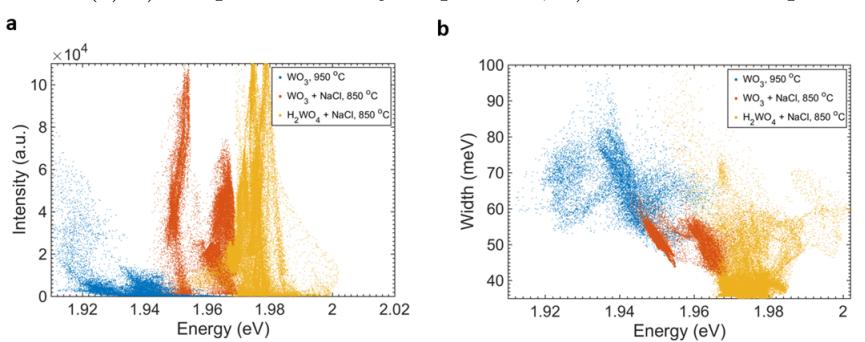
(a) a) PL peak intensity vs position, b) PL FWHM vs position



(b) a) PL peak intensity vs position, b) PL FWHM vs position



(c) a) PL peak intensity vs position, b) PL FWHM vs position



(d) a) PL peak intensity vs position, b) PL FWHM vs position

Figure 7.12: a), b) WS_2 grown using WO_3 at $950\text{ }^\circ C$; c), d) WS_2 grown using $WO_3 + NaCl$ at $850\text{ }^\circ C$; e) f) WS_2 grown using $H_2WO_4 + NaCl$ at $850\text{ }^\circ C$; g), h) WS_2 grown using $WO_3, WO_3 + NaCl, H_2WO_4 + NaCl$. Adopted from [147].

The chemical composition of the flakes grown using $H_2WO_4 + NaCl$ has been investigated using XPS. The W 4f5/2 and W 4f7/2 core levels show peak positions that of the W^{4+} in WS_2 [162][163] (32.7 eV 34.8 eV respectively) with FWHM of 1 eV (Figure 7.13, the smallest possible using Mg K α x-ray source. It means therefore that the WS_2 is of perfect stoichiometric ratio of W and S. Additionally by integrating the intensity of the W 4f and S 2p core level peaks the same result is achieved. Furthermore the S 2p1/2 and 2p3/2 core levels are also present at the expected position for WS_2 (162.3 eV and 163.4 eV respectively, Figure 7.13) and small FWHM of 1 eV [163]. Small peaks indicative of W^{6+} (W 4f5/2 and W 4f7/2 at 35.9 eV and 38.1 eV respectively, Figure 7.13) can be attributed to presence of WO_3 and which partially overlaps with W 5p core level (38.5 eV). These peaks however disappear after the flakes are transferred to another Si/SiO_2 substrate, suggesting that they can be caused by residue WO_3 given that the XPS spot size is relatively big (~ 1 mm). The FWHM of the W 4f core levels was unchanged after the transfer, indicating that the crystallinity and the quality of the flakes was preserved with no extra defects introduced.

The WS_2 samples grown using $WO_3 + NaCl$ have been characterised by XPS as well and the stoichiometric ratio of 2:1 for S:W has been found. However the W^{6+} component, caused most likely by presence of WO_3 (W 4f5/2 and W 4f7/2 at 35.9 eV and 38.1 eV respectively) is more pronounced indicating incomplete sulfurisation. Similarly to the sample grown with $H_2WO_4 + NaCl$ this component disappears entirely upon transferring the sample onto new Si/SiO_2 indicating it is present around the flakes, distributed across the substrate. The W^{4+} 4f core levels peak width is ~ 1.2 eV which indicates higher defect concentration compared to that of the sample grown using $H_2WO_4 + NaCl$. This FWHM however increases after the transfer, which is most likely caused by the increase in the concentration of the defects caused by the mechanical stress during the transfer. In conclusion the H_2WO_4 is shown to be a better precursor compared to WO_3 .

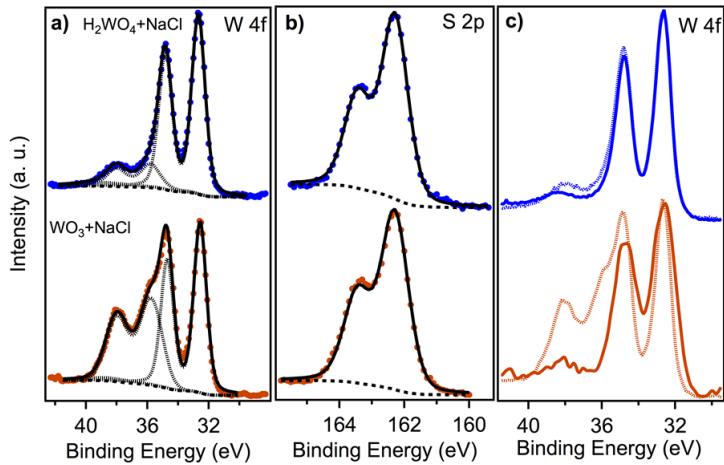


Figure 7.13: XPS spectra of the WS_2 samples. a) W 4f_{5/2}, W 4f_{7/2}, W 5p core levels of sample grown with $H_2WO_4 + NaCl$ /950 °C (top), sample grown with $WO_3 + NaCl$ /950 °C (bottom). Black dashed line - deconvolution of the peaks, black continuous line - total fit. (b) S 2p_{1/2}, 2p_{3/2} core levels for corresponding samples. (c) W 4f_{5/2} , W 4f_{7/2}, W 5p core levels taken from samples before (dashed line) and after (solid line) transfer. Adopted from [147].

The samples were further characterised for their electrical properties. Bottom-gated field effect transistors were prepared as seen in Figure 7.14. The FET transfer curve indicates accumulation-type n-channel transistor, where the drain current increases with applied gate bias after a threshold is crossed. Once the current-bias curve reaches linear range it can be described by $I_d = \mu_n C_{ox} (W/L)((V_{gs} - V_{th})V_{ds})$, where μ_n is the electron field-effect mobility, C_{ox} is the oxide dielectric and V_{th} is the threshold voltage. As seen in Figure 7.14 a typical response curve for both the as grown as well as transferred samples of WS_2 grown with H_2WO_4 show an asymmetry around $V_{ds} = 0$ V due to difference in the source and drain potentials. The Schottky barrier at the source is pinned by the gate, while the barrier at the drain diminishes proportionally to the drain bias and vice versa. The contacts however become more "Ohmic", when the bands bend more at the semiconductor/metal interface while the gate bias increase, leading to more significant tunnelling current.

By looking at the linear regime of the transport graph (red-dashed line in Figure 7.14) the field-effect mobility can be calculated as $\mu_n = C_{ox}^{-1}(d\sigma/dV_{gs})$. The electron mobility calculated for WS_2 grown with $H_2WO_4 + NaCl$ is generally higher than that of WS_2 grown with $WO_3 + NaCl$ (Figure 7.14) which further indicates higher crys-

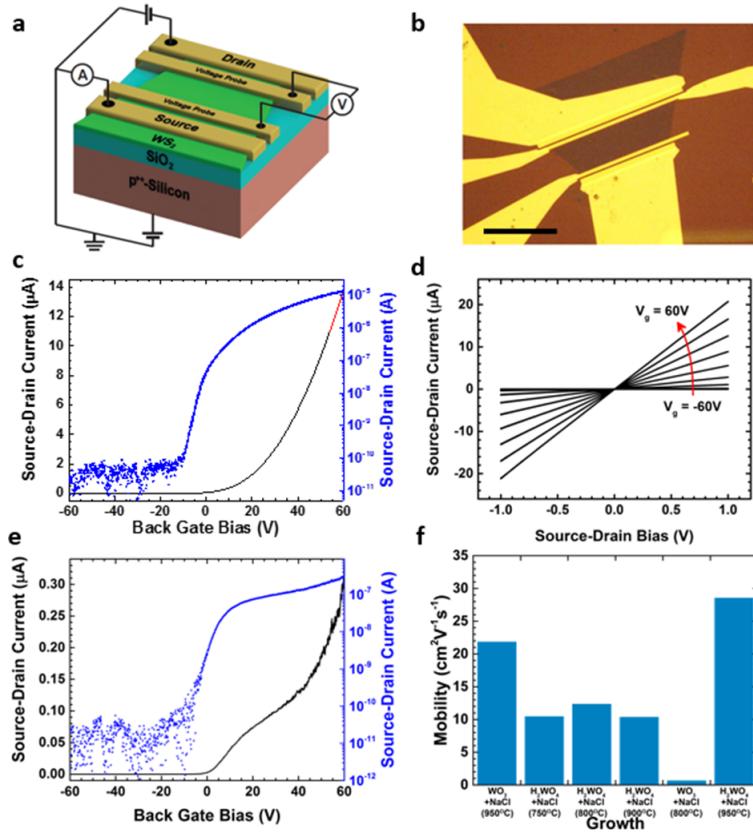


Figure 7.14: a) FET diagram; b) OM image of the FET (scale bar is $20\mu\text{m}$); c) FET transfer curve taken from the single layer sample made with $\text{H}_2\text{WO}_4 + \text{NaCl}/950\text{ }^\circ\text{C}$; d) I-V curves taken at different gate biases for sample made with $\text{H}_2\text{WO}_4 + \text{NaCl}$; e) FET transfer curve taken for single layer sample made with $\text{WO}_3 + \text{NaCl}/800\text{ }^\circ\text{C}$; f) comparison of electron mobilities of single layer WS_2 made with different precursors.

Adopted from [147].

tal quality when using H_2WO_4 . The monolayer WS_2 exhibits electron mobility of $28\text{ }cm^2\text{V}^{-1}\text{s}^{-1}$, the highest reported value for CVD grown WS_2 and transferred onto SiO_2 [83][136][137][82][134][84][138][164][165][166][167] and comparable to mechanically exfoliated WS_2 [154][168][169][142]. The highest mobilities were recorded in WS_2 grown at $950\text{ }^\circ\text{C}$, grown with either $\text{H}_2\text{WO}_4 + \text{NaCl}$ or $\text{WO}_3 + \text{NaCl}$, which indicates a role of the growth temperature in improving the quality of the WS_2 . As the temperature is lowered the difference between precursors becomes more pronounced in terms of the crystal quality. The $\text{H}_2\text{WO}_4 + \text{NaCl}$ precursor system grown WS_2 shows electron mobility of 10 to $20\text{ }cm^2\text{V}^{-1}\text{s}^{-1}$ at temperatures of $750\text{ }^\circ\text{C}$ and $850\text{ }^\circ\text{C}$. The electron mobilities of WS_2 grown using $\text{WO}_3 + \text{NaCl}$ are much lower, $\sim 2\text{ }cm^2\text{V}^{-1}\text{s}^{-1}$ at $800\text{ }^\circ\text{C}$. Bilayer WS_2 samples have overall greater electron mobility than their monolayer equivalent (between ~ 38

$cm^2V^{-1}s^{-1}$ and $52\text{ }cm^2V^{-1}s^{-1}$), similarly to the mechanically exfoliated flakes [170][142]. The electron mobility of bilayer WS_2 ($52\text{ }cm^2V^{-1}s^{-1}$) (Figure 7.16 and Figure 7.15) is also higher than that of other CVD grown WS_2 as well as mechanically exfoliated onto SiO_2 samples of WS_2 reported [59][170][142]. The highest mobility has been obtained for bilayer system using $WO_3 + NaCl$ indicating that the precursor choice is less important for electron mobility in such systems.

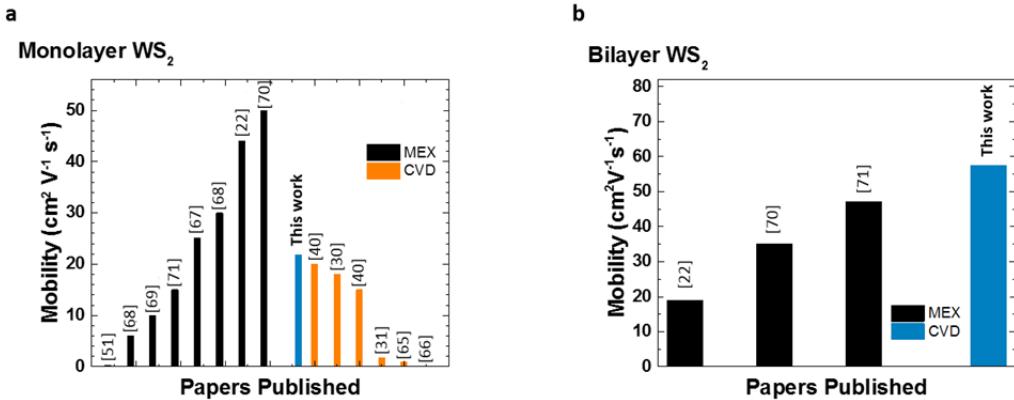


Figure 7.15: Comparison of electron mobility with literature for a) monolayer b) bilayer. Adopted from [147].

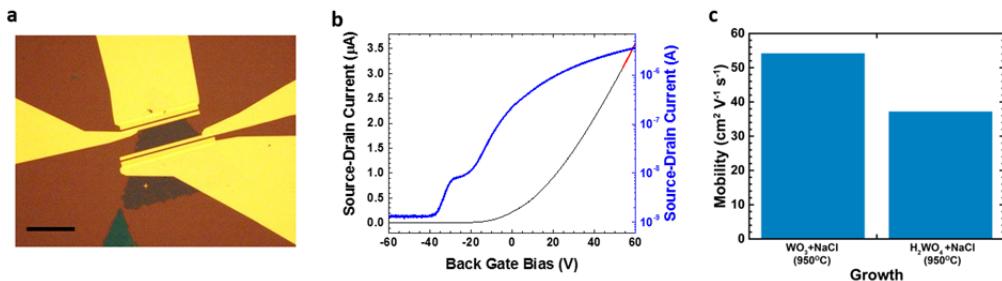


Figure 7.16: a) OM image of FET from bilayer WS_2 (scale bar is $30\mu m$); (b) FET transfer curve taken from WS_2 made with $WO_3 + NaCl/950\text{ }^\circ C$ c) electron mobility of double layer sample made with different precursors. Adopted from [147].

7.3.1 Transfer

About 10 different samples (separate growths) were investigated with 2-3 flakes per each sample. A sample has been investigated using Raman and PL spectroscopy before and after transfer. In Figure 7.17 a comparison between samples before and after transfer can be seen in PL spectra. The as grown sample shows mostly homogeneous PL intensity,

position and FWHM across the sample with the exception of the edge and trisecting lines in the middle where the PL intensity is higher and lower accordingly. In the sample after transfer the PL intensity, position and FWHM is more randomly distributed across the flake and there is a distinct lack of edge enhancement or the presence of trisecting lines.

The position of the PL peak from the as grown sample is $1.97 \pm (9.84 \times 10^{-4})$ eV, while the PL peak position from transferred sample $1.97 \pm (8.35 \times 10^{-3})$ eV. Therefore the peak position is shifted by 6.2 meV after transfer while the relative standard deviation is about 8.5 times greater in the transferred sample than in the as grown sample. The FWHM in the as grown sample is 36.37 ± 0.79 meV while in the transferred sample the FWHM is 83.27 ± 6.79 meV. The FWHM then increases by 46.90 meV while the relative standard deviation increases 3.72 times compared to the as grown sample.

The Raman E_{2g}^1 peak position in the as grown sample is 350.87 ± 0.21 cm^{-1} while in the transferred sample is 351.34 ± 0.29 cm^{-1} . The relative uncertainty is therefore 1.39 greater in the transferred sample. The position of the Raman A_{1g} peak in the as grown sample is 418.65 ± 0.28 cm^{-1} while in the transferred sample it is 417.32 ± 0.48 cm^{-1} . The relative uncertainty is therefore 1.69 times greater in the transferred sample. The position difference between these two peaks is 67.79 ± 0.24 cm^{-1} in the as grown sample while it is 66.01 ± 0.48 cm^{-1} in the transferred sample. The relative uncertainty increases therefore by 2.03 after the transfer. The intensity ratio between those peaks in the as grown sample is 5.75 ± 0.68 and after transfer it is 7.16 ± 0.89 . The relative uncertainty changes 1.58 times after transfer.

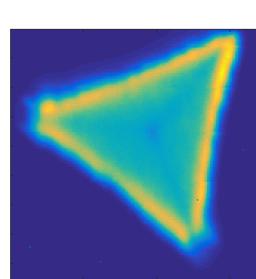
It can be therefore seen that after transfer the relative uncertainty increases for every parameter of Raman and PL spectra maps. This indicates that the sample after the transfer is much less homogeneous. Because both the position of PL as well as the position of Raman peaks is affected by the strain the inhomogeneity can indicate a relaxation or build up of strain. Since the CVD growth method involves heating up the sample and the substrate to very high temperatures, up to $850^\circ C$, there is possibility of residual thermal strain after cooling down. Since the PMMA is much more flexible than the SiO_2 , that the sample is grown on, the WS_2 can relax before being placed on a new SiO_2 substrate. On the other hand the water present in between the WS_2 and PMMA can also be a source of strain. During the water evaporation the surface tension can induce local strain leading to high inhomogeneity. The PMMA can also have varying thickness and can swell to small degree therefore contracting in size during drying. Any or all of these effects can potentially contribute to the variation in parameters observed.

Additionally the removal of PMMA following the transfer involves immersing the substrate with samples covered in PMMA in an acetone isopropanol solution at about 50 °C. This results in a relatively intensive reaction which can potentially damage the flakes. By reducing the temperature as well as the acetone concentration the reaction occurs visibly less intensively however no changes in optical microscopy, PL or Raman are observed.

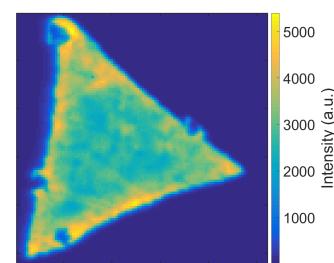
The average values of peak fitting parameters can be then compared between the two sample states to estimate the strain in the sample. The average position of $E_{2g}^1 + 2LA$ peak changes from 350.8601 cm^{-1} to 351.34 cm^{-1} , a 0.48 cm^{-1} difference. Since the position of this peak changes by $-3.1\text{ cm}^{-1}/\%$ this indicates the change in strain of -0.16% . The $E_{2g}^1 + 2LA$ peak intensity change ($\Delta I/I_0$) of 23.15% indicates a 0.23% change in strain. The average value of A_{1g} peak position changes from 418.65 cm^{-1} to 417.32 cm^{-1} , a difference of 1.33 cm^{-1} . This indicates then a strain of -4.45% . The intensity change of A_{1g} peak of 25.64% corresponds to 0.33% strain [146].

The PL peak position changes from 1.9765 eV to 1.9703 which corresponds to change from about 1% to 0.75% strain, a -0.25% change [145].

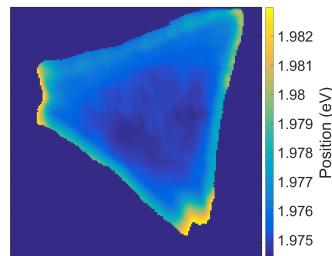
By comparing different average Raman and PL peaks fit parameters it is not clear to what extent the WS_2 is strained before or after the transfer. Neither the direction nor the extent of strain can be estimated then in the sample overall. The difference in deviation of these values however indicates that the sample after transfer is less homogeneous than before. Therefore while it cannot be said that the sample strain changes on average as a whole, there is a change in strain across the sample. While the thermal strain should result in the sample as a whole being under tension due to thermal expansion and contraction other effects could still take place like aforementioned variation in water presence, inhomogeneity of PMMA layer thickness or folds in PMMA layer.



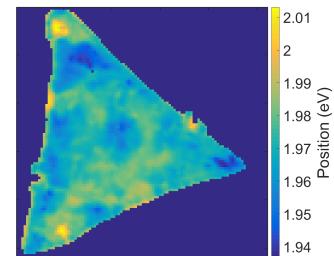
(a) PL Intensity map of as grown sample



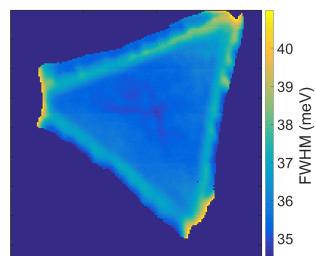
(b) PL Intensity map of transferred sample



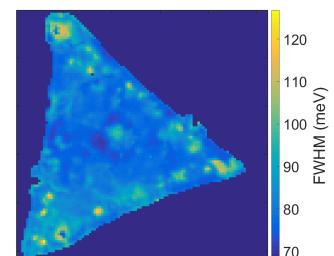
(c) PL Position map of as grown sample



(d) PL Position map of transferred sample

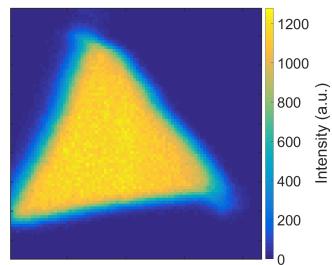


(e) PL FWHM map of as grown sample

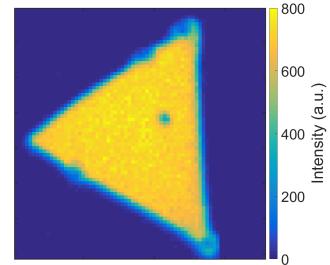


(f) PL FWHM map of transferred sample

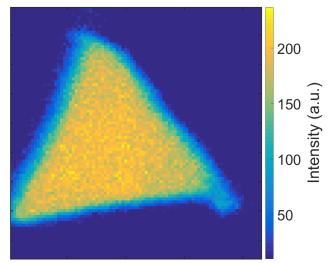
Figure 7.17: PL spectra maps of samples before and after transfer



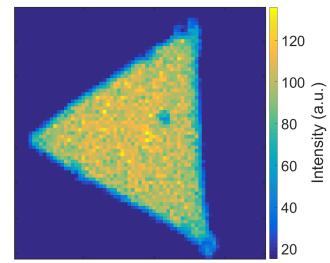
(a) Raman E_{2g}^1 intensity map of as-grown sample



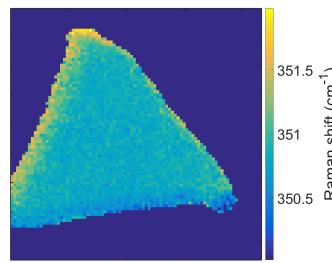
(b) Raman E_{2g}^1 intensity map of transferred sample



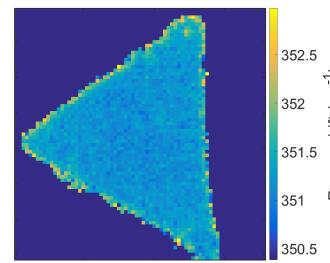
(c) Raman A_{1g} intensity map of as-grown sample



(d) Raman A_{1g} intensity map of transferred sample



(e) Raman E_{2g}^1 position map of as-grown sample



(f) Raman E_{2g}^1 position map of transferred sample

Figure 7.18: Raman spectra maps of samples before and after transfer

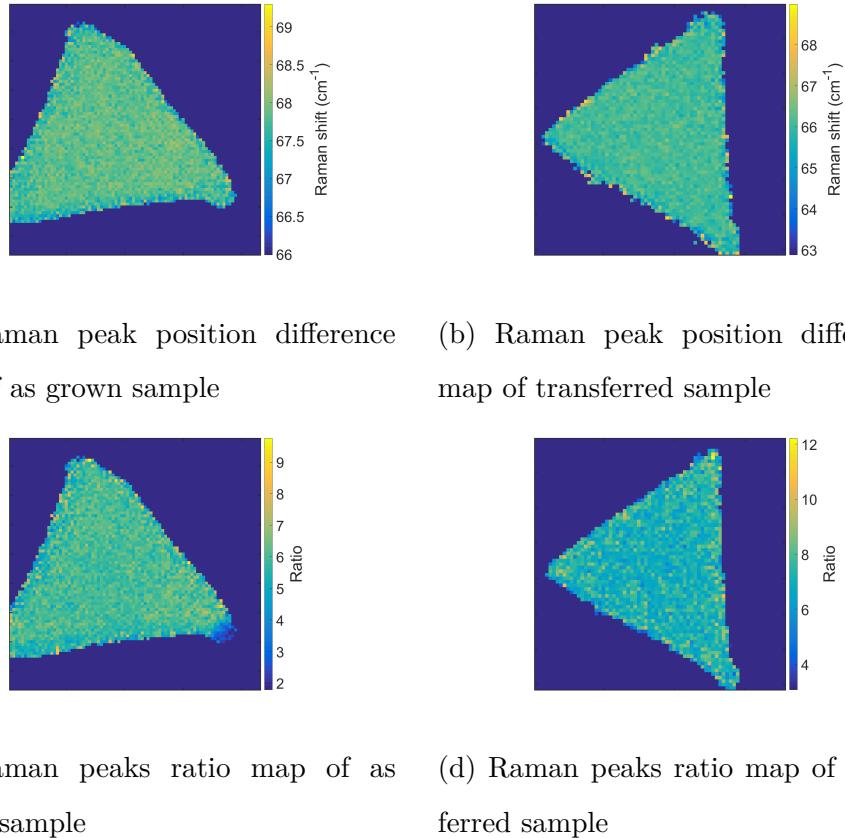


Figure 7.19: Raman spectra maps of samples before and after transfer

7.4 Conclusions

In conclusion a synthesis route has been developed that allows for high quality monolayer and bilayer WS_2 CVD growth. This quality is demonstrated by highest recorded electron FET mobility for both monolayer and bilayer CVD grown WS_2 compared to the literature and comparable to that of mechanically exfoliated ones. Additionally, the triangle flakes grown using $H_2WO_4 + NaCl$ are much larger (up to $\sim 200 - 300\mu m$) compared to ones grown using standard WO_3 . The CVD growth using H_2WO_4 has also been demonstrated to work at lower temperatures, down to 750 °C compared to more commonly used 950 °C. Finally, the PL of the WS_2 grown using H_2WO_4 is uniform throughout the flake and has very narrow FWHM (36 meV) which again points to high crystal quality and lack of defects in form of sulphur vacancies. Additionally we have presented the transfer methodology that we have developed in our own way for monolayer TMDCs. Overall the quality of the transfer material is good and the flakes are pristine in shape, in that they retain the triangular shape without visible cracking or folding. It is unclear to what

extent the CVD grown WS_2 sample is strained prior to transfer or after it. The difference in relative uncertainty of different fitting parameters of PL and Raman spectra however reveals that the sample becomes less homogeneous following the procedure. This could indicate that a certain degree of strain or damage, especially caused by aggressive PMMA etching, is introduced as a result of the transfer. This in turn could be attributed to the presence of a non uniform distribution of water molecules, non uniform thickness of PMMA layer, folds in the PMMA layer or presence of residue PMMA. These findings allow to develop further the TMDCs synthesis method of CVD and can potentially lead to industrially scalable synthesis of monolayer WS_2 or other TMDCs over large area.

Chapter 8

Post-transition metal doping of monolayer WS_2

8.1 Introduction

Single layer TMDC materials present a range of unique optical, electrical and mechanical properties and atomic doping can further extend the potential of TMDCs since it has been predicted that a number of properties can be tuned through compositional variation. Up until now doping has relied on charge transfer induced by changing the environmental conditions such as surface adsorption, metal contacts and dielectric interfaces. This approach has demonstrated to severely limit the device working conditions thus doping through stable incorporation of non-volatile metal atoms is highly preferred. Achieving controlled doping is a challenge which is aggravated by the fact that established synthesis protocols for these materials are still lacking.

Doping of monolayer WS_2 with post-transition metals has not been reported as yet. Doping of WS_2 with post-transition metals can lead to chemisorbed intercalated atoms between layers which can be regarded as analogous to deep level impurities. It can lead to an additional energy level near to the top of the valence band or, alternatively, as a modification of the energy band of the host crystal due to the interaction between the intercalate and W or S atoms [171][172]. In particular indium may generate an additional energy state at the top of the valence band which leads to a subsequent upward shift of this band [173]. A gradual increase in this shift with increasing number of intercalating atoms would lead to a linear decrease in the energy gap with increasing In content as observed in In-intercalated bulk WS_2 [173]. This led to the demonstration of higher conductivity and

photocurrent than both pure WS_2 films thus proving to be highly photo-active. Unlike their alkali and alkaline earth metal analogues, In-intercalated bulk WS_2 compounds were found to be stable against oxidation when exposed to air or chemical due to a fairly strong guest-host bonding which hinders deintercalation processes and preserving a perfect 2H crystalline phase [173][174]. Further, In has lower melting and boiling points than B, Al and Ga enabling doping via CVD or MOCVD synthesis of WS_2 at low temperatures. These characteristics make Indium a very interesting prospected dopant of WS_2 to pave the way towards applications as photoelectrodes in solar cells. Post transition metals are prone to intercalate between the layers however displaying very different effect with respect to the alkali and alkaline earth metal intercalates of WS_2 .

Here we demonstrate indium doping of monolayer WS_2 in-situ during CVD synthesis of WS_2 . The process relies on the addition of a volatile indium precursor which results in large-area In-doped WS_2 atomic layers exhibiting tunable optical properties and a semiconducting-to-metallic transition at high doping levels. We also demonstrate controlled indium content from 0 up to 45% in WS_2 maintaining a 2D morphology and atomically thin nature of the material without sacrificing the lateral extension and scalability of the synthesis process.

8.2 Results

The In doped WS_2 samples were grown by following the synthesis route developed for the monolayer WS_2 as discussed in Chapter 7 [147]. The synthesis was mostly performed by a fellow PhD student Francesco Reale. The main change was to add $In(OH)_3$ powder as an indium precursor to the same crucible as W precursor. Such mixed powders in a crucible were then placed in the centre of the furnace similarly to the established procedure.

A first indication of the effect of indium in the WS_2 is provided by the morphology of the triangular domains. SEM and OM images of WS_2 domains grown by using different $In(OH)_3/H_2WO_4$ weight ratios [$In_{0.25}WS_2$, $In_{0.5}WS_2$, $In_{0.75}WS_2$, In_1WS_2] are shown in Figure 8.1. While from the optical contrast it is possible to see that the monolayer nature of the domains is unchanged, it can be noticed how the shape of triangles progressively change. Triangles with straight edges similar to that of pristine WS_2 are displayed for low In content while convex and jagged edges appear by increasing the Indium content, which might suggest a more significant incorporation of the latter. WS_2 with high indium content can also present different morphologies and even large coverage.

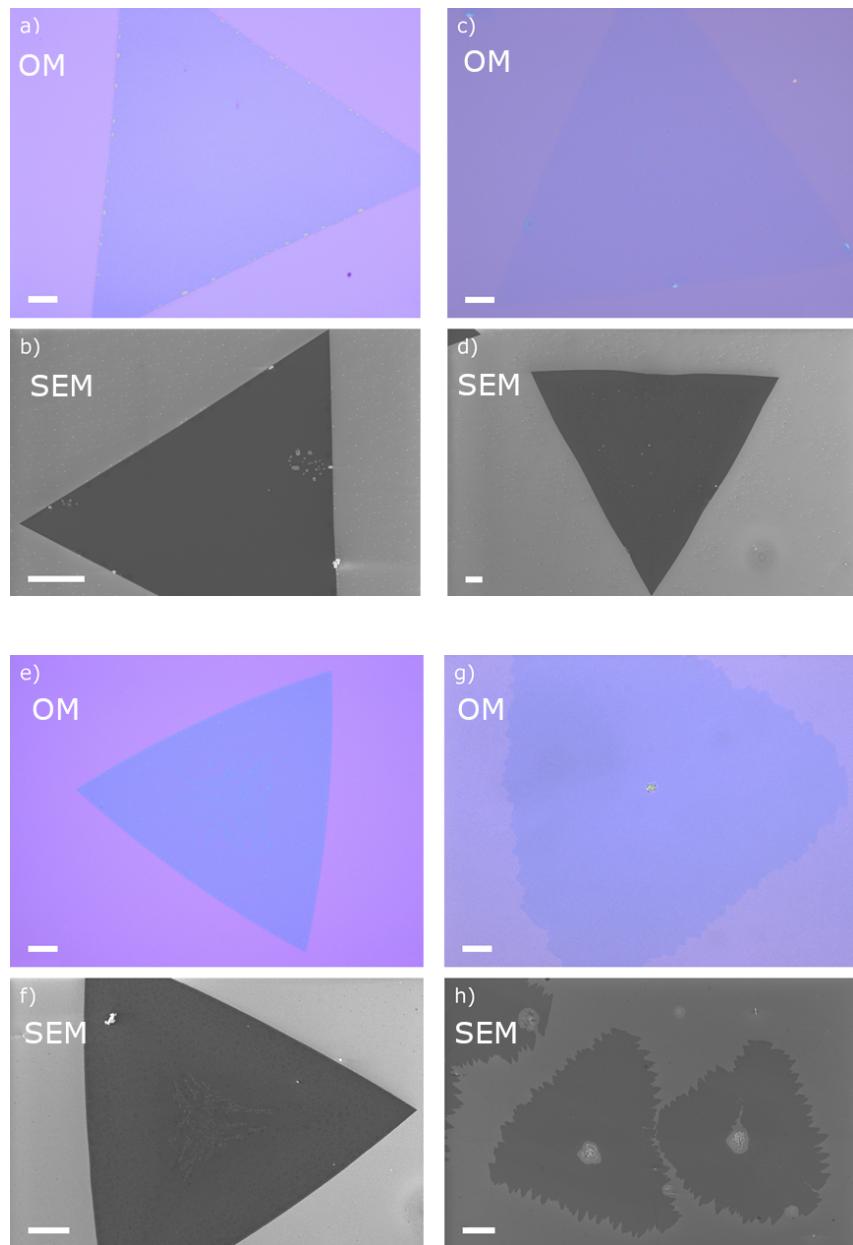
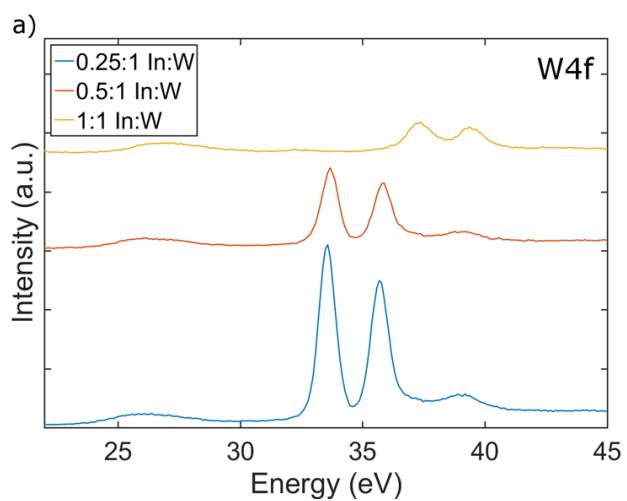
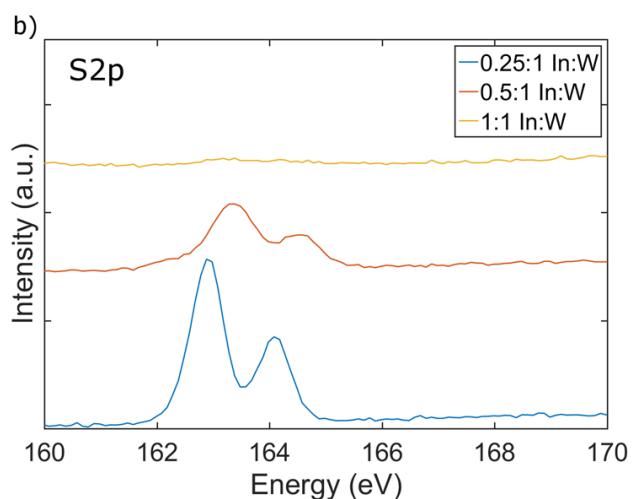


Figure 8.1: OM and SEM images of flakes grown with different $In(OH)_3/H_2WO_4$ weight ratios: (a, b) 0.25, (c, d) 0.5, (e, f) 0.75 and (g, h)=1. Scale bar is 10 μm

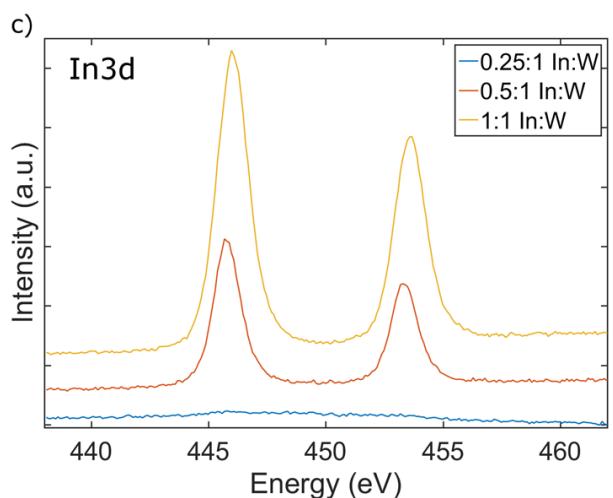
The samples were further characterised using XPS to assess the exact chemical content and therefore the level of doping.



(a) W 4f



(b) S 2p



(c) In 3d

Figure 8.2: XPS spectra comparison

Figure 8.2 shows the In 3d, W 4f and S 2p core levels XPS spectra for pure WS_2 and

In-doped WS_2 ($In/W=0.25$, $In/W=0.5$, $In/W=1$). It is immediately noticeable in Figure 8.2c that the the sample with 0.25:1 In:W precursor ratio does not exhibit any In 3d peak. At the same time the samples with 0.5:1 In:W as well as 1:1 In:W show pronounced In $3d_{5/2}$ core level peak at 445.8 eV and 446.0 eV respectively and In $3d_{3/2}$ at 453.3 eV and 453.8 eV respectively. This slight shift might be attributed to the presence of $In_xW_yS_z$ compounds [175]. The In 3d core levels for 1:1 In:W sample are also about twice as intense as the ones for the 0.5:1 In:W sample. Furthermore the W 4f core levels for the 1:1 In:W sample are significantly shifted to the blue which might indicate presence of W^{6+} in the doped sample compared to W^{4+} to pure WS_2 . This would indicate bonding between W and In atoms. The S $2p_{1/2}$ and S $2p_{3/2}$ core levels for 0.25:1 In:W ratio can be observed at 162.9 eV and 164.1 eV respectively while for the 0.5:1 In:W sample they are at 163.4 eV and 164.6 eV respectively. No significant S 2p peak can be observed for the 1:1 In:W ratio sample. There is therefore indication of interaction between the S and In atoms, with stronger S 2p core level peak shifts than those of the W 4f core levels. It is therefore possible that the In atoms became chemisorped on the surface, intercalated in between the layers or incorporated as an interstitial. The stoichiometric composition was then calculated using the concentrations of elements from peak integration of In 3d, W 4f and S 2p core levels as seen in Table 8.1.

Table 8.1: In:W and S:W ratios obtained by calculating the In, W and S concentrations from the integrated intensity of the In 3d, W 4f and S 2p core levels.

Sample	In/W	S/W
$In/W = 0.25$	0.038:1	2.32:1
$In/W = 0.5$	0.45:1	2.22:1
$In/W = 1$	1.98:1	0.27:1

The XRD diffraction patterns of all the In-doped WS_2 samples can all be indexed on a hexagonal unit cell basis (Figure 8.3a) and an analogy can drawn to the pattern of $2H - WS_2$. The set of reflections can be then used to calculate the lattice parameters in a known crystal structure. The most intense reflection is the (002) and for pure and In-doped WS_2 (Figure 8.3b) it can be seen that the FWHM decreases as the In precursor concentration increases and that a peak shift towards a larger d spacing, the height of single layer, (Table 8.2) occurs for the highest indium content. Additionally the samples with indium content of $In/W=0.5$, $In/W=0.75$ and $In/W=1$ show an additional reflection

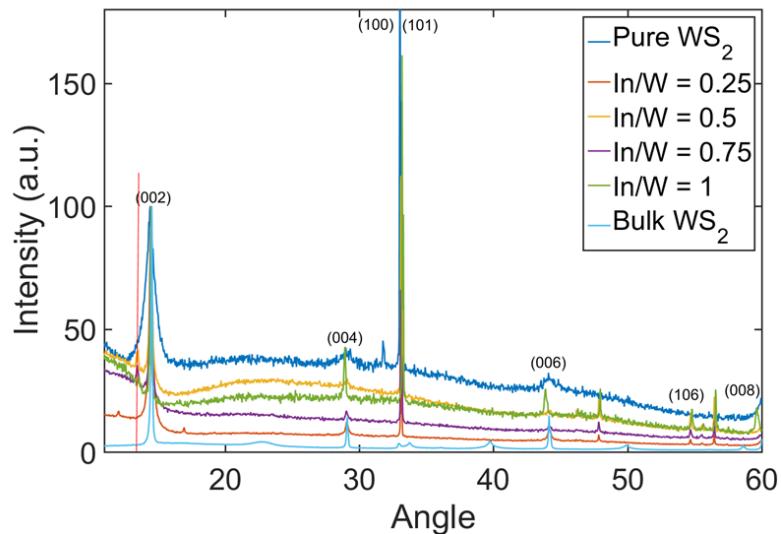
at $2\Theta = 13.44$ not belonging to WS_2 , which can be an indicator of successful incorporation of In atoms.

Table 8.2: Data for the (002) XRD peak and lattice parameters for pure WS_2 and Indium-doped WS_2 samples.

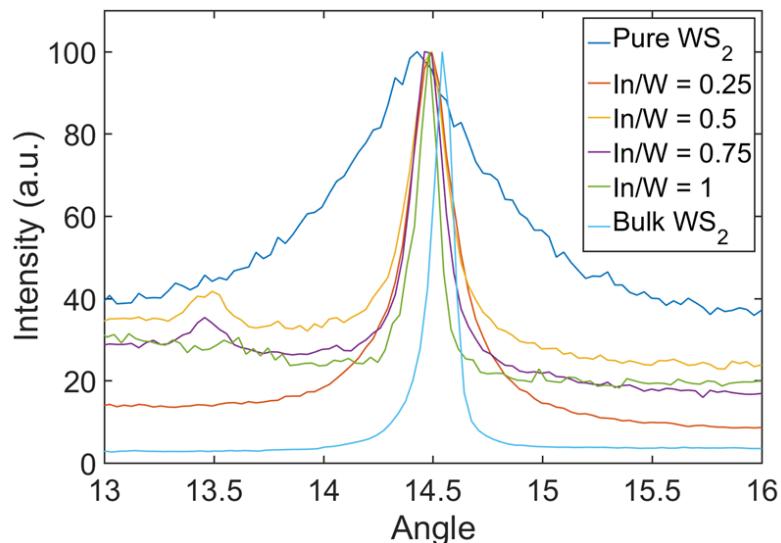
Sample	Position (2Θ)	FWHM (2Θ)	a (\AA)	c (\AA)	d (\AA)
WS_2	14.44	0.703	3.23	11.02	5.51
In/W = 0.25	14.47	0.294	3.23	11	5.50
In/W = 0.5	14.444	0.168	3.22	11.02	5.51
In/W = 0.75	14.479	0.137	3.22	11	5.50
In/W = 1	14.307	0.182	3.21	11.14	5.57

Therefore, it can be concluded that the crystal structure remains unchanged for Indium content of less than 0.038, corresponding to a precursor ratio of In/W = 0.25 as seen in Table 8.1. For large indium contents an expansion of the van der Waals gap is observed due to the large amount of indium intercalated between the layers in few-layered regions and also a small portion of indium can result incorporated in the crystal structure.

From XRD results we can see that the crystal structure remained hexagonal with small shifts in lattice parameters as the indium content increased in the sample. Our results are therefore comparable to previous reports on the In intercalation in bulk MoS_2 which showed that smaller ions can lead to a significant change in the crystallographic order [176] changing it to an octahedral coordination. It has also been shown that inclusion of the large metal ions (In, Ga) preserves the hexagonal structure [176]. The presence of d-bands in indium metal contributes additionally to the bonding stabilization.



(a) XRD patterns for CVD-grown pure WS_2 and In-doped WS_2 .



(b) (002) XRD peak for CVD-grown pure WS_2 and In-doped WS_2

Figure 8.3: XRD spectra of WS_2 samples

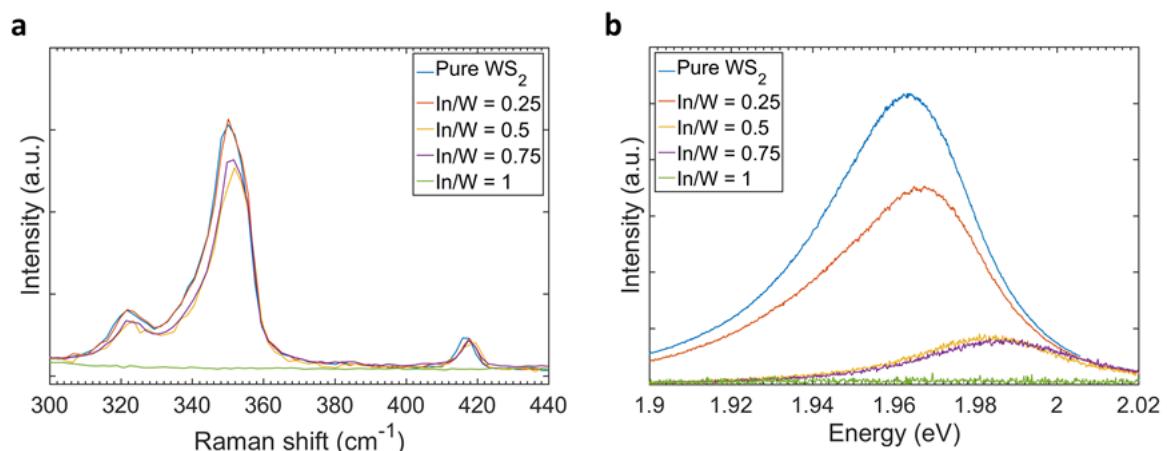


Figure 8.4: Representative a) Raman and b) PL spectra for pure WS_2 (grown by using H_2WO_4 as metal precursor) and In-doped WS_2

Further evidence of In_2S_3 can be inferred by the presence of peaks at $2\Theta = \sim 48$ and ~ 57 [177], specifically the (002) plane. This has been observed in the form of thick crystals in the centre of atomically thin flakes (Figure 8.5) and has been confirmed by Raman (Figure 8.5). The In_2S_3 have been rarely observed and can therefore be the result of secondary reaction products.

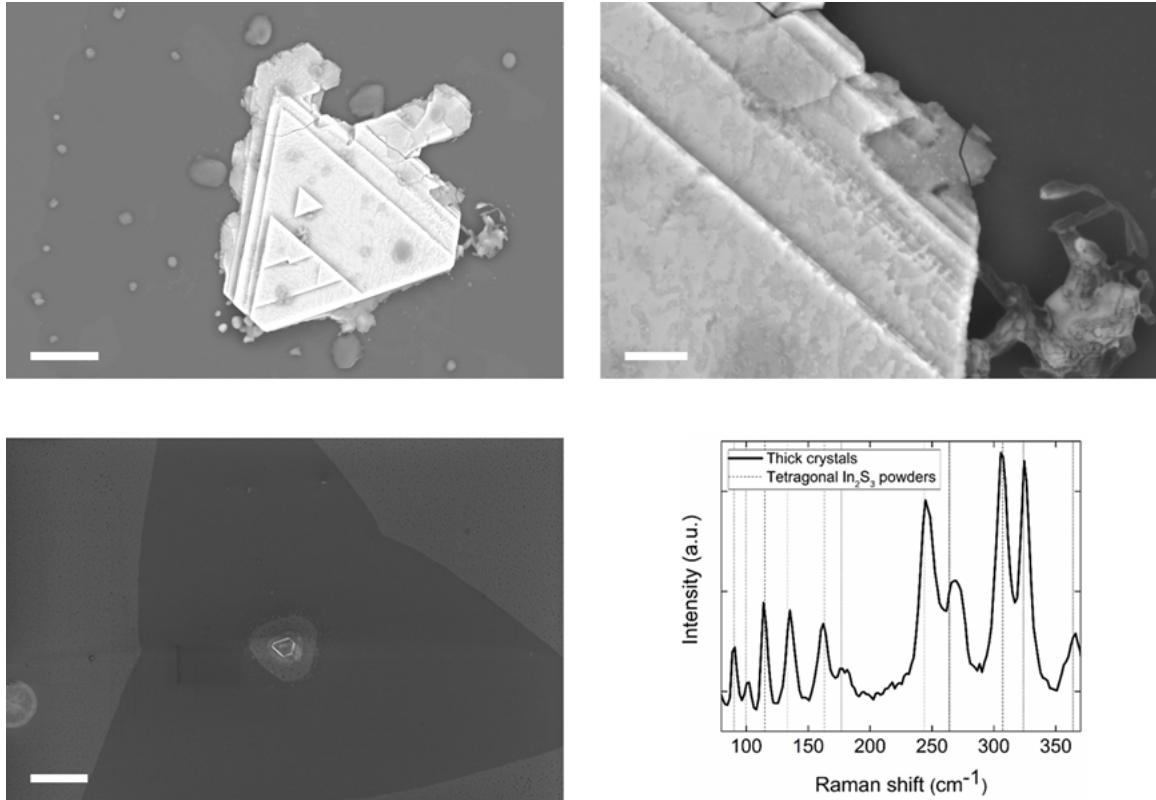


Figure 8.5: Low-magnification SEM images in (a) SE and (scalebar = $2 \mu m$) (b) BSD imaging mode of the same area of sample In/W=1 (scalebar = $10 \mu m$). High-magnification SEM images in (c) SE (scalebar = $200 nm$) and (d) Raman spectrum of the thick flake in a) and c) showing that it consists of In_2S_3

The representative Raman spectra for undoped WS_2 and In-doped WS_2 are reported in Figure 8.4 a). It can be observed that WS_2 sample with In:W ratio of 0.25:1, 0.5:1 and 0.75:1 show the characteristic in-plane $2LA - E_{2g}^1$ and out-of-plane A_{1g} vibrational Raman active modes of WS_2 , while the sample with In content of 1 is not Raman active. Similarly, WS_2 with In content between 0.038-0.45 exhibit PL while WS_2 with In content of 1 does not luminescence (Figure 8.4 b)). Therefore, a very large amount of In (equal to 1) changes the crystal lattice and properties of the base material. The E_{2g}^1 and A_{1g} Raman peaks (Figure 8.7) of the 0.25:1, 0.5:1 and 0.75:1 In-doped samples are shifted towards higher frequencies (E_{2g}^1 at $\sim 351.5 cm^{-1}$ and A_{1g} at $\sim 418 cm^{-1}$) as compared to

pure WS_2 sample. This could be due to the differences in the binding energy between W–S and (W-In)–S bonds. The shifts in Raman peak position observed in mono and few layer thick TMDCs are however not fully yet understood and further characterisations are necessary.

The excitons-to-trions ratio (Figure 8.8a) calculated for the samples that exhibit PL is lower compared to that of the undoped WS_2 , which indicates increase in n doping behaviour as the In content increases. It can be explained due to the presence of fully filled d-orbital in In atoms with an additional electron in the p-orbital in the most outer shell. These extra electrons may therefore contribute to the semiconductor to metal transition with high enough In concentration. To confirm that electrical measurements were performed. Metal contacts were patterned onto one of the flakes on the In:W=1 ratio samples. Conductivity has been measured across the flake and a direct increase in resistivity with increase in temperature has been revealed which is indicative of the metals (Figure 8.6).

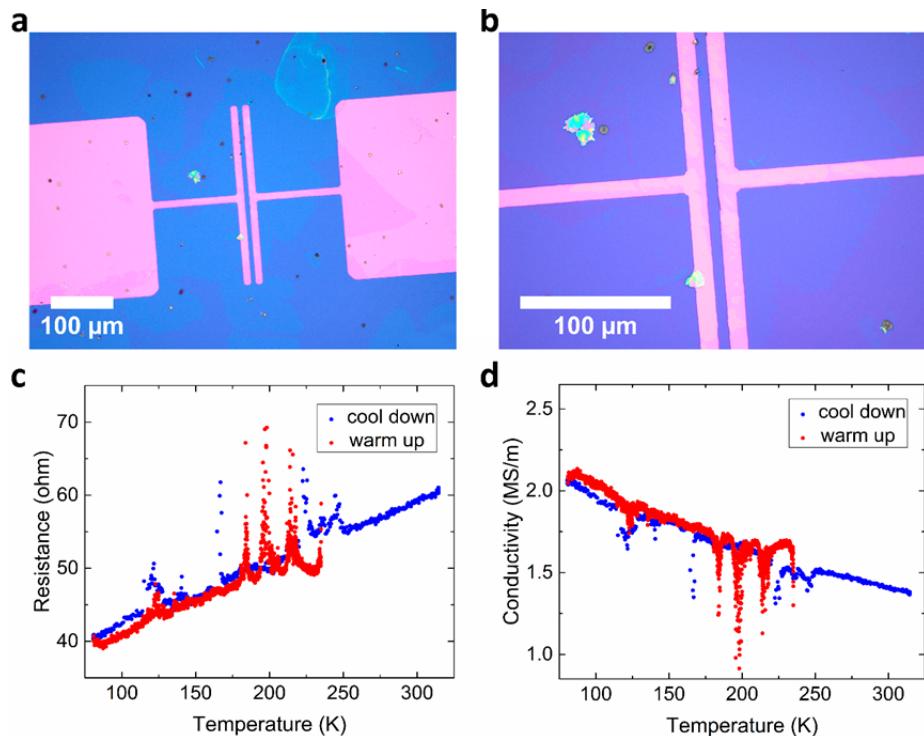


Figure 8.6: (a, b) Optical micrographs of Ti and Au contacts deposited on In/W=1 flakes. (c) Measured resistance as a function of temperature. (d) Calculated conductivity vs. temperature revealing a semi-metallic behaviour.

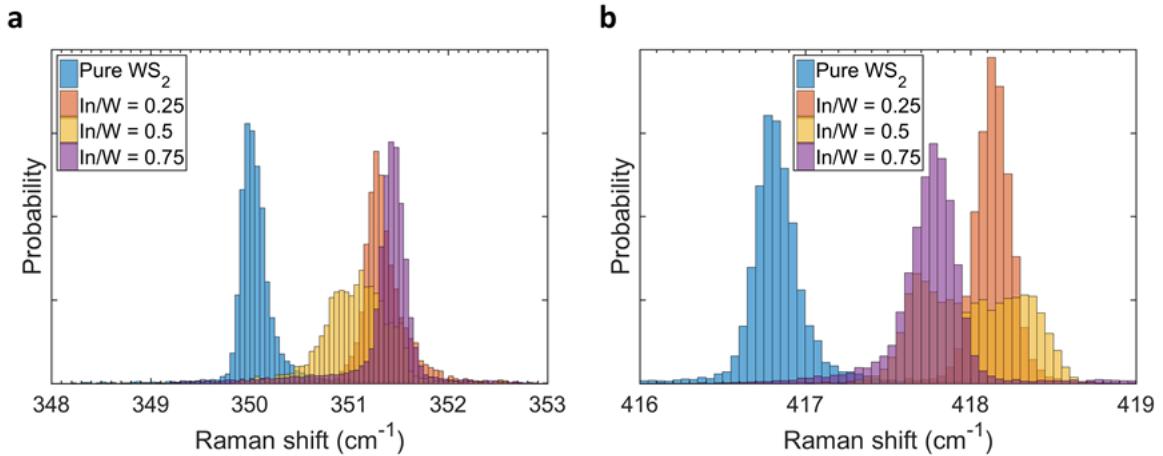
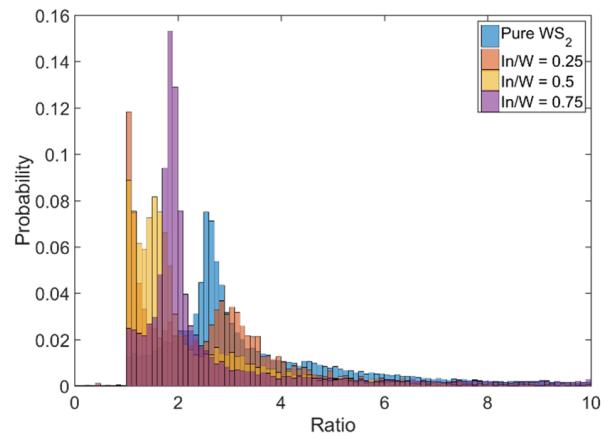
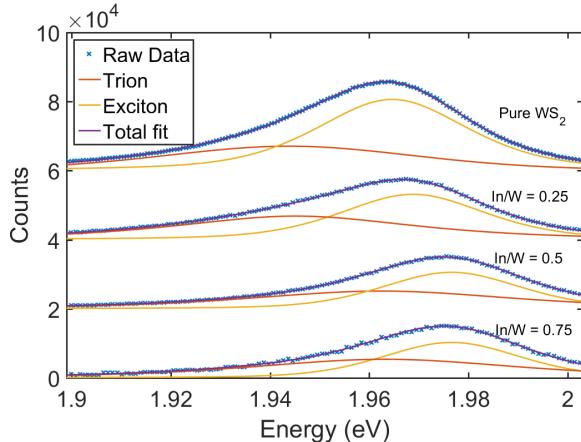


Figure 8.7: a) E_{2g}^1 and b) A_{1g} peak positions for pure WS_2 and Raman active In-doped WS_2 samples.

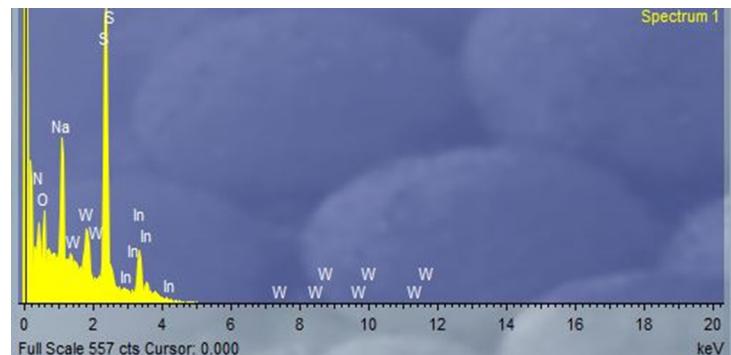


(a) Excitons-to-trions ratio for pure WS_2 and PL active In-doped WS_2 samples XPS

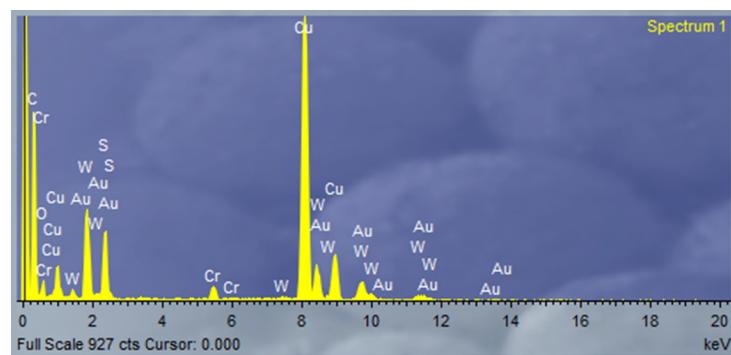


(b) PL spectra from samples of different In/W precursor ratio.

The energy dispersive x-ray spectroscopy (EDS) has been then utilised to find the chemical makeup of the sample. First the as grown sample was characterised using SEM EDS which requires no sample transfer. As seen in Figure 8.9a there are In peaks present at: $L_{\alpha 1} = 3286.94\text{eV}$; $L_{\alpha 2} = 3279.29\text{eV}$; $L_{\beta 1} = 3487.21\text{eV}$; $L_{\beta 2} = 3713.81\text{eV}$; $L_{\gamma 1} = 3920.81\text{eV}$. This indicates and further confirms in addition to the XPS results that there is some In in, on or around the WS_2 flake. There is also a visible Na peak which indicates remaining Na from $NaCl$ used during synthesis. In order to compare the as grown sample, the transferred sample was characterised using TEM EDS. As seen in Figure 8.9b there is no visible In peak. This indicates that the In is somehow removed during the transfer process. It is therefore most likely that the In is not present inside the WS_2 as a dopant, as substitution or an interstitial, or that it is located in between the layers, but that it is present on top of or around the as grown WS_2 flake.



(a) Before transfer



(b) After transfer

Figure 8.9: EDS spectra collected using TEM from WS_2 sample with $In : W = 1 : 2$

Additionally the electron diffraction (ED) measurement was performed. As seen in Figure 8.10 the present pattern correspond to the expected pattern for WS_2 . The spots are sharp and narrow indicating mostly monolayer WS_2 with no elongation or broadening expected due to the presence of irregular presence of doping element. There is also no

additional pattern that could indicate a super structure of ordered atoms of the dopant. The faint halo indicates presence of the amorphous carbon of the TEM grid. The faint signal is therefore indicative of a lack of polymer remains after the transfer. Finally the calculated lattice parameter a was found to be $a = 2.71 \text{ \AA}$ which is in agreement to the a parameter found for the un doped WS_2 from the XRD spectrum as seen in Figure 8.3 ($a = 2.71 \text{ \AA}$) as well as the one found for the bulk WS_2 ($a = 2.73 \text{ \AA}$). This indicates therefore that the transferred sample shows no change in strain after the transfer.

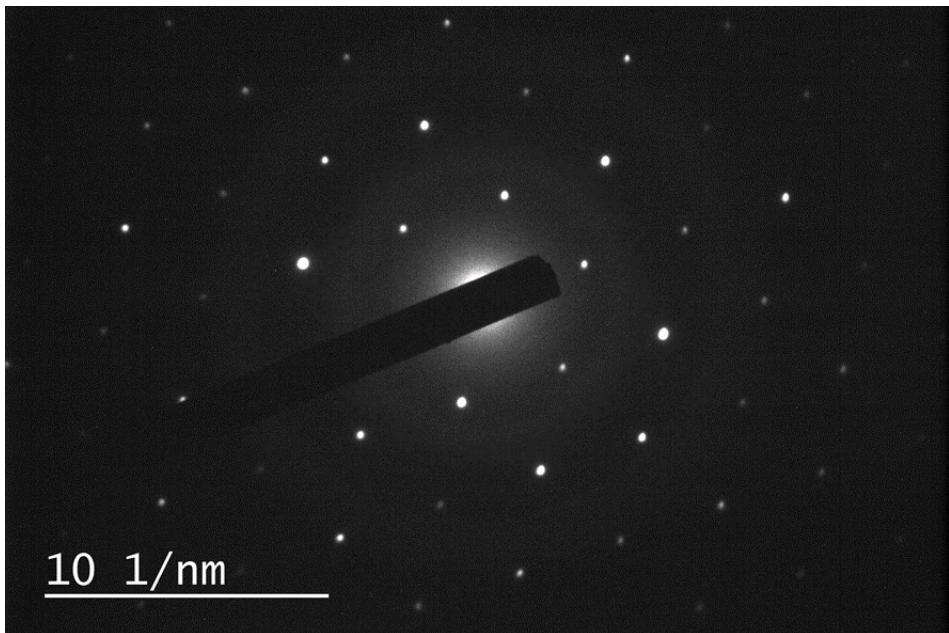


Figure 8.10: Electron diffraction pattern of WS_2 flake with $In : W = 1 : 2$

8.3 Conclusions

In summary, we have reported indium atoms doping of WS_2 atomic layers in situ during synthesis, without sacrificing the lateral extension or the reproducibility of the synthesis process. Remarkably, the In-doped WS_2 samples exhibit tunable light emission and a semiconducting-to-semimetallic transition at high doping levels. It remains unclear where the In atoms are located after the growth and to what degree are they incorporated into the base material. Moreover the range of In/W ratios from 0.25 to 0.5 needs especially further investigation as it shows a substantial change in In content in the as grown material. Therefore, the present synthesis strategy can be employed to achieve tailorabile optical and electrical characteristics of atomically-thin WS_2 through stable incorporation of non-volatile post-transition metal atoms.

Chapter 9

CVD of mono-and-few-layer 2H *WSe₂* and colloidal synthesis of 1T' and 2H *WSe₂*

9.1 Introduction

In this chapter we present our work on the characterisation of CVD monolayer and few layer *WSe₂*. The novelty of this work resides in the use of a solid state inorganic precursor of Se for the first time which replaces the commonly used toxic *H₂Se* and Se powder in presence of hydrogen gas. The purpose of the work reported here is to assess the quality of the *WSe₂* synthesized using this precursor as compared to the current literature. *WSe₂* is a TMDC material and it is similar in some important aspects like layered structure or indirect to direct bandgap transition to the *WS₂*. In its 2H semiconducting form the main difference from the point of view of optoelectronic applications between 2H *WSe₂* and *WS₂* is its optical bandgap which for monolayer is about 1.65 eV compared to 2 eV for *WS₂*. This allows for potential application in the near infrared range. Its crystal structure is the same as the other TDMCs as outlined in Chapter 2.

The 1T and 1T' phases of group VI TMDCs have only recently gained significant attention compared to the more popular semiconducting 2H and number of reports in the literature has increased. They have been found to show promise in areas of electrocatalytic water splitting and energy storage thanks to lower charge transfer resistance [178], a result of their metallic nature [179]. The 1T' phase is also predicted to be a large gap quantum spin Hall (QSH) insulator which can be useful in spintronic devices application [180]. In

contrast to 1T' WTe_2 [104] 1T' WSe_2 can be used in ambient temperatures as well as ambient atmosphere unlike other known large gap QSH insulator materials like stanene [181] or 2D In-Sb compounds [182].

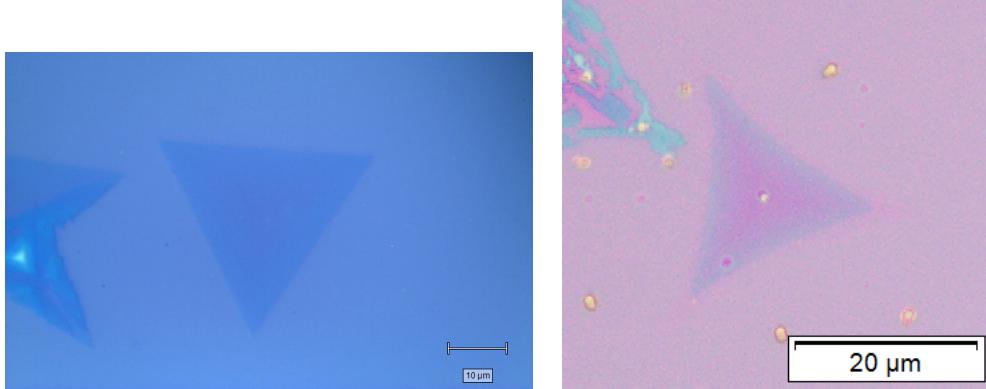
So far the synthesis of 1T and 1T' group VI sulfides and selenides (MoS_2 , WS_2 , $MoSe_2$, WSe_2) phases has proven difficult due to the metastable nature of them. Most commonly a direct synthesis via e.g. a CVD route results in more thermodynamically stable 2H phase. The difference in energy per formula unit between 1H and 1T' WSe_2 phase is only 0.27 eV which suggests that under certain reaction conditions a metastable 1T' can be synthesised.

The following work shows first time colloidal synthesis route of 1T' WSe_2 as well as Raman and XPS studies of the as grown material. The WSe_2 flakes of varying thickness has been successfully grown via the colloidal synthesis method by a fellow PhD student Maria Sokolikova.

9.2 Results

9.2.1 CVD growth of 2H WSe_2

Most of the samples were produced by fellow PhD student Francesco Reale. The WSe_2 were grown using standard growth procedure developed for growth of the WS_2 . The mix of H_2WO_4 and $NaCl$ was placed in one crucible near the target substrate while $ZnSe$ powder was placed in a separate crucible in a separate heating element. The growth was performed at 850 °C and W and S precursors were exposed to the same temperature in order to enable the evaporation. The resulting flakes as seen in Figure 9.1a are triangularly shaped similarly to the WS_2 flakes. The monolayer flakes are up to about 30 μm and are similarly distributed to the growths observed for WS_2 . Numerous smaller monolayer flakes as well as larger flakes with 2 or more layers together with the big monolayer flakes cover up to about 50 % of the substrate. Some of the WSe_2 monolayer triangles optical images also show relatively thin strip of contrast along the border as seen in Figure 9.1b.

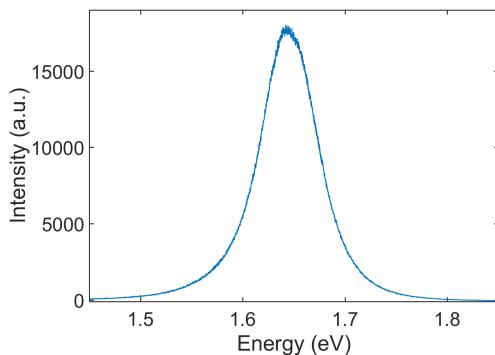


(a) A typical triangular monolayer flake

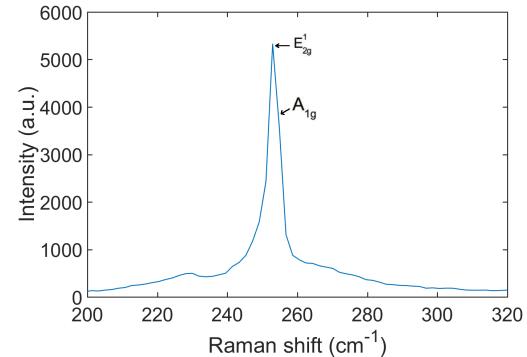
(b) Triangular flake with visible strip of contrast along the edge

Figure 9.1: Optical micrographs of WSe_2 monolayer flakes

These flakes have been characterized by PL and Raman spectroscopy (Figure 9.2). A typical PL and Raman spectrum can be seen in Figure 9.2. The peak is centred at 1.65 eV which suggests a monolayer nature of the flake (as the direct band gap of monolayer is 1.65 eV) and the peak appears mostly symmetrical with FWHM of 66 meV. The symmetry of the peak and the fact it can be fitted with a single function, suggest a negligible contribution from trions in contrast to what we observed for WS_2 flakes. The Raman peak around 250 cm^{-1} is a convolution of 2 peaks, an E_{2g}^1 and A_{1g} vibrational modes, as already observed for bulk as well as exfoliated WSe_2 .



(a) Typical PL spectrum from monolayer WSe_2



(b) Typical Raman spectrum from monolayer WSe_2

Figure 9.2: PL and Raman spectra from monolayer WSe_2

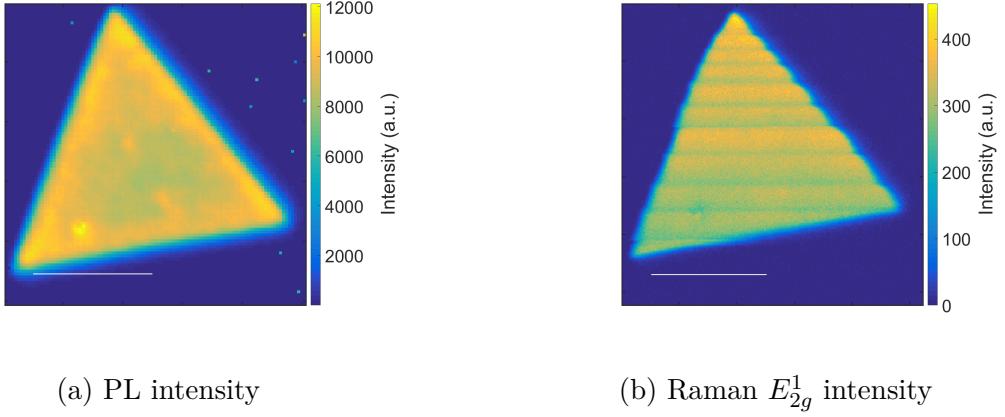


Figure 9.3: PL intensity and Raman E_{2g}^1 intensity maps

A typical map of PL intensity of a WSe_2 sample can be seen in Figure 9.3a. Compared to the WS_2 samples grown using the same procedure the PL intensity is much more homogeneous throughout the flake. In particular it does not exhibit the trisecting pattern as seen in WS_2 samples e.g. Figure 9.3a. Similarly the Raman E_{2g}^1 peak intensity map as seen in Figure 9.3b also does not show the same pattern of trisecting lines. Due to technical issues with the spectrometer the map in Figure 9.3b shows periodically repeating horizontal lines of lower intensity.

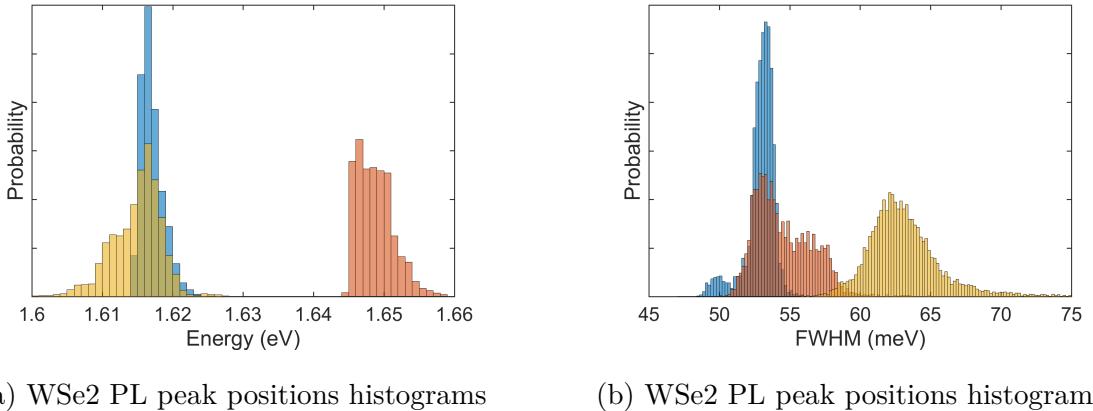


Figure 9.4: Comparison of PL peak positions and widths in different WSe_2 samples. Different colour correspond to separate growths.

A comparison of PL peak positions and widths between different samples of WSe_2 , all grown using the same conditions, can be seen in Figure 9.4.

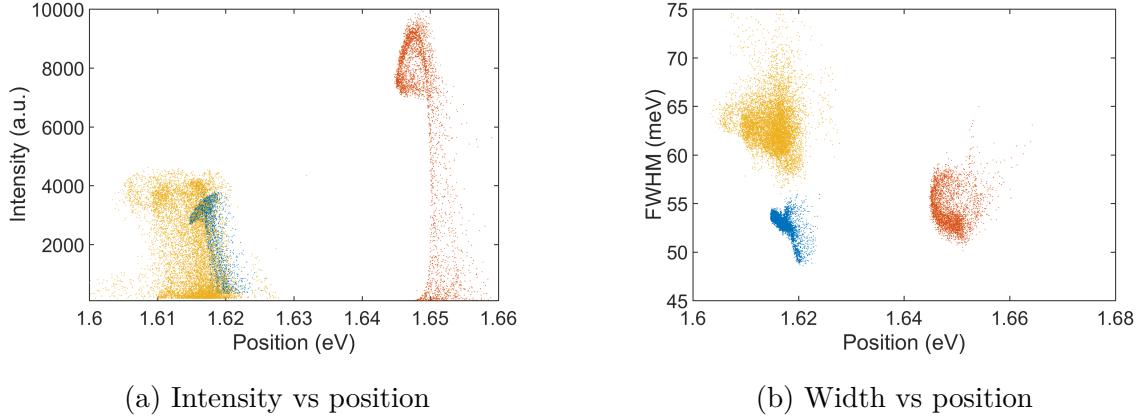


Figure 9.5: PL peak parameters distribution

By plotting the intensity and width of the PL peaks against the peak position as seen in Figure 9.5 certain patterns can be observed. The intensity is mostly grouped around maximum values and relatively narrowly spread across the position spectrum. One of the growths (in red) shows much more even distribution of intensity across the position, which combined with the wide distribution of positions results in a much more inhomogeneous sample. The PL FWHM and positions are generally well grouped with flakes with smaller FWHM having more narrow distribution than those with greater width. Also the flake with greater average PL peak position shows a smaller peak width. Overall there is no obvious relation between position and width.

For most of the TMDCs Raman can be used to identify the number of layers or strain within the layer. However in the case of WSe_2 the position of the E_{2g}^1 and A_{1g} largely overlaps and therefore it is difficult to accurately determine the difference in their position. Because of that this method of identifying the number of layers cannot be employed easily. It is however still possible to examine the strain within the layers by noting the shift of the E_{2g}^1 peak. A Raman E_{2g}^1 peak position distribution from a representative sample can be seen in Figure 9.6. The strain can be then determined from the mean position of $250.7 \pm 0.01 \text{ cm}^{-1}$ to be 2.44 % [146].

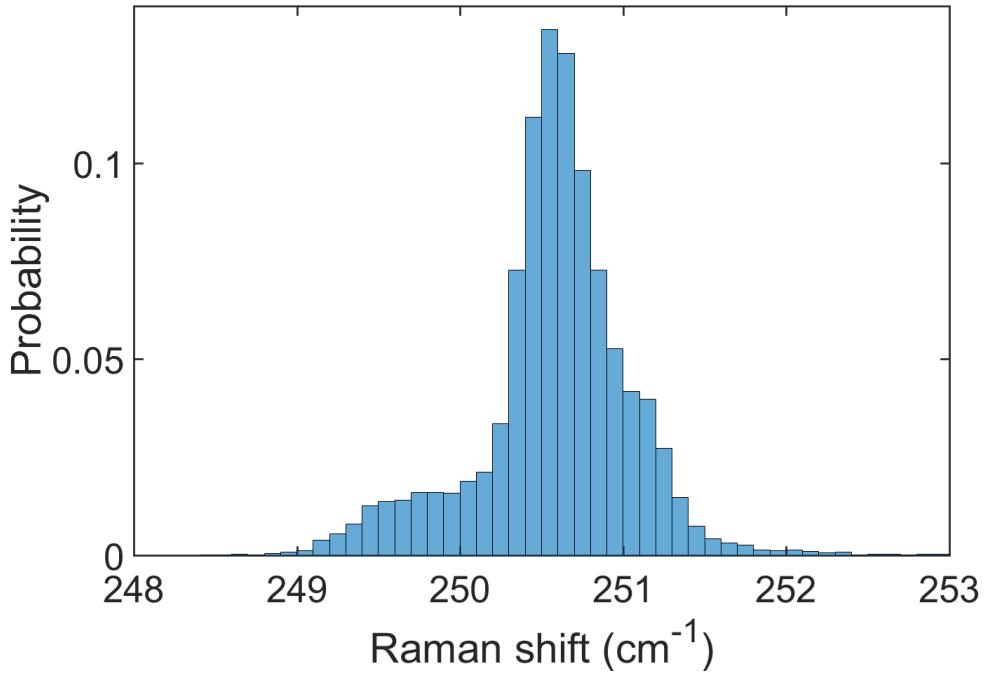


Figure 9.6: Histogram of Raman E_{2g}^1 peak position from monolayer WSe_2

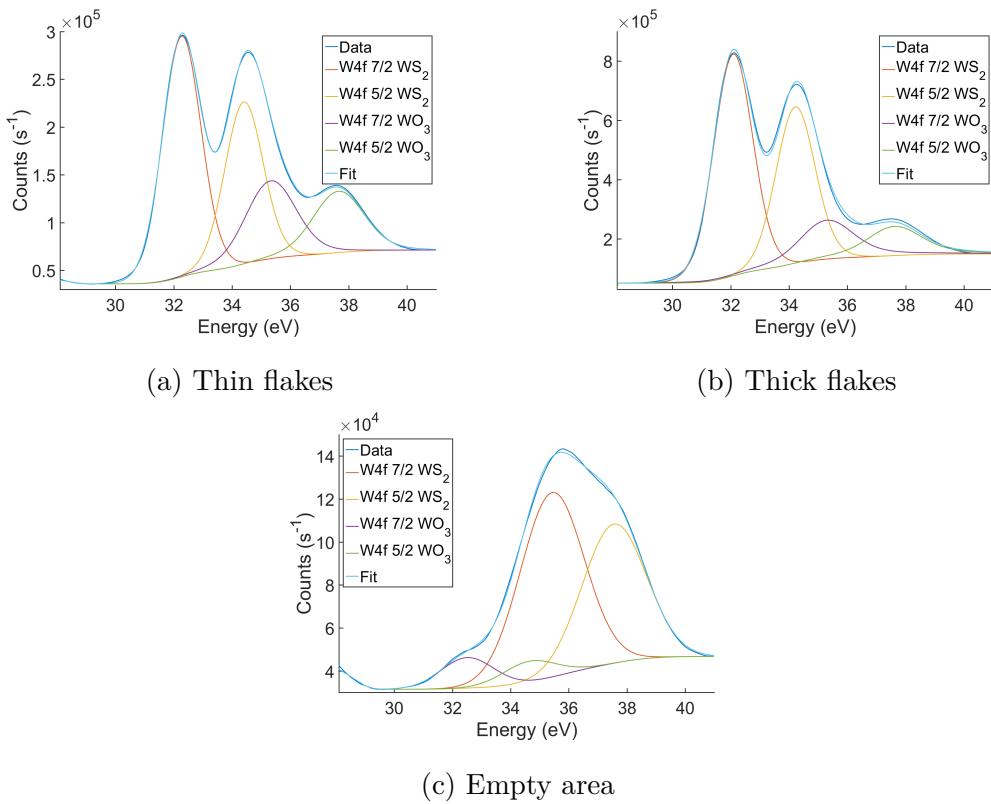


Figure 9.7: XPS spectra of W4f peaks in different areas of the sample

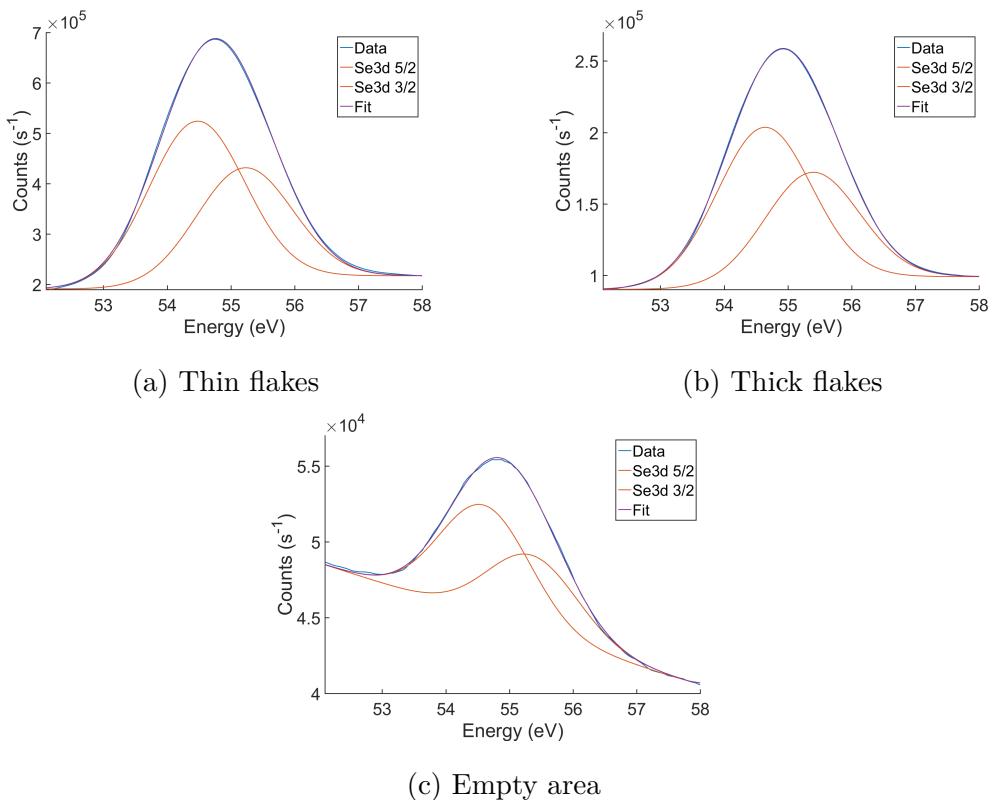


Figure 9.8: XPS spectra of Se3d peaks in different areas of the sample

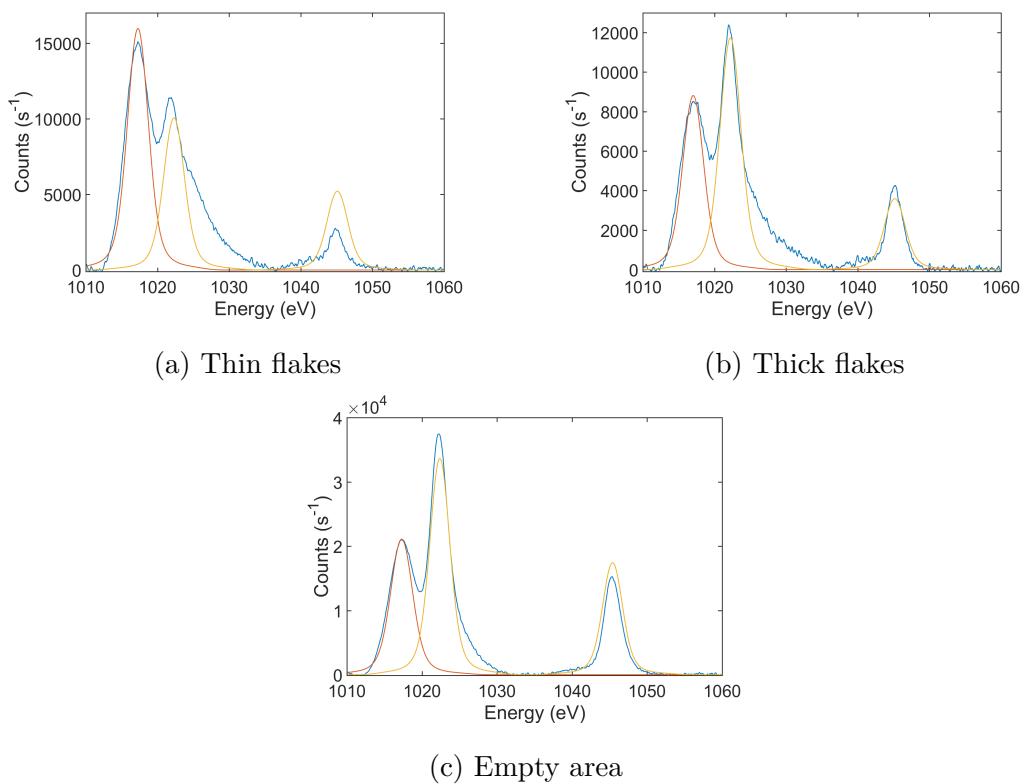


Figure 9.9: XPS spectra of Zn2p peaks in different areas of the sample

The sample has been further characterised with XPS. Three areas were selected for measurements, one with thin, mono or double layer WSe_2 , one with thick bulk WSe_2 and one with no visible WSe_2 flakes. The Figure 9.7 shows W4f core levels measured in those spots. The first area (Figure 9.7a), with thin flake shows one doublet at 32.08 eV and 34.23 eV and a second doublet at 35.33 eV and 37.68 eV. The first doublet corresponds to WSe_2 while the second one can be attributed to WO_3 . Since the spot size in the measurement covers both the flake as well as some surrounding substrate it is possible that the WO_3 is located outside of the flake. Furthermore the background indicates that the emission from WSe_2 came from the surface and therefore the WSe_2 flake is not contaminated with WO_3 . The second area with thicker flakes (Figure 9.7b) shows similarly two doublets: one at 32.28 eV and 34.43 eV and a second one at 35.38 eV and 37.63 eV. Similarly to the area with the thin flake we can ascribe the former to the WSe_2 and the latter to WO_3 . There is a small shift of 0.2 eV between WSe_2 from the thin flake and WSe_2 from the thick flake. It is possible that XPS is sensitive to the number of layers in WSe_2 and TMDCs in general since it is known that number of layers does modify the electronic structure of the material [3]. The WO_3 is found to be at the same position in both areas. The WO_3 peak is also relatively weaker in the area with the thick flake than in the area with thin flake which could be a result of the thick flake having larger surface area than the thin flake and smaller presence of WO_3 around the flake. Additionally an empty area (Figure 9.7c) with no visible flakes has been measured. Similarly two doublets, one at 32.58 eV and 34.73 eV and a second one at 35.48 eV and 37.58 eV have been fitted and their presence can be again explained by presence of WSe_2 and WO_3 . The WSe_2 peak is shifted in relation to that from the thin flake by 0.5 eV which could indicate presence of a highly defective WS_2 or very small amounts of very bulk WS_2 . The WS_2 peak is also much weaker than that of the WO_3 which is expected since there is no visible WS_2 . This result suggesting presence of residues of tungsten oxide species across the whole substrate and thus also possibly across the grown flakes of WSe_2 . This result corroborates the evidence of chemical purity of WSe_2 .

We can also look at Se3d core levels measured at the same locations. As seen in Figure 9.8a, taken from an area with the thin flake, we can fit it with one doublet corresponding to the presence of WSe_2 at 54.48 eV and 55.23 eV. Similarly in Figure 9.8b we can see Se3d peaks taken from area with the thick flake and can fit it with a doublet at 54.63 eV and 55.38 eV which also corresponds to the WSe_2 . Similar to the W4f levels there is a shift of 0.15 eV between those two flakes which can be explained by their thickness

which changes the electronic structure. The Se3d levels measured in the reference empty area also can be fitted with a doublet at 54.53 eV and 55.33 eV which can be attributed to WSe_2 . Similarly there is a shift of 0.05 eV from the peak associated with the thin flake, which is much smaller than the W4f peak shift. The Se3d peak from the empty area is about a magnitude weaker than that from either the thin or thick flake which is expected as no visible flake was observed. It does however indicate a non insignificant presence of WSe_2 , perhaps in the form of nuclei that never grew into proper flakes or flakes that shrunk or became etched and are highly defective and thinner than monolayer. The Se3d from the empty area also exhibits a steep background which indicates that the Se is covered with some layer, perhaps that of WO_3 .

Finally the Zn2p levels were measured across the same areas. As seen in Figure 9.9a a doublet can be identified at 1022.02 eV and 1045.11 eV together with a single peak at 1017.33 eV taken from a thin flake. Similarly in Figure 9.9b the doublet is located at 1022.23 eV and 1045.16 eV and a single peak at 1017.03 eV. The reference area shows a doublet at 1045.39 eV and 1022.38 eV and a single peak at 1017.29 eV. It seems therefore that the peak position of the Zn2p doublet does not change significantly from the empty reference area and the thin or thick flake. The peak intensity in the empty area is also much greater than that of the peak in the area with thin or thick flakes. It suggests then that the Zn that was used in the synthesis is therefore located mostly on a substrate and not on the WSe_2 flakes.

Table 9.1: WSe_2 W 4f and Se 3d peak position dependance on number of layers

	Thin (<3 layers)	Thick (~6 layers)
W 4f7	32.08 eV	32.28 eV
W 4f5	34.23 eV	34.43 eV
Se 3d5	54.48 eV	54.63 eV
Se 3d3	55.23 eV	55.38 eV

As seen in Table 9.1 the peak positions of W 4f and Se 3d taken from WSe_2 thin and thick flakes can be compared. The thick flake can be considered to be equivalent to a bulk form. There is a consistent shift of about 0.2 eV for all of those peaks.

9.2.2 Colloidal synthesis of 1T' and 2H WSe_2

The sample was characterised using TEM as seen in Figure 9.10. The TEM images show well defined flower shaped nanostructures with the average diameter of 200 nm. The petals stem from the central point and thin down towards the edges down to single layer. The single petals appear to be of 1T' phase while each petal is a single crystal. Additionally the structural parameters $a = 5.76 \text{ \AA}$ and $b = 3.30 \text{ \AA}$ have been identified. Reciprocal lattice created by FFT from high resolution TEM image from a single petal is rectangular and corresponding to monoclinic phase of WSe_2 .

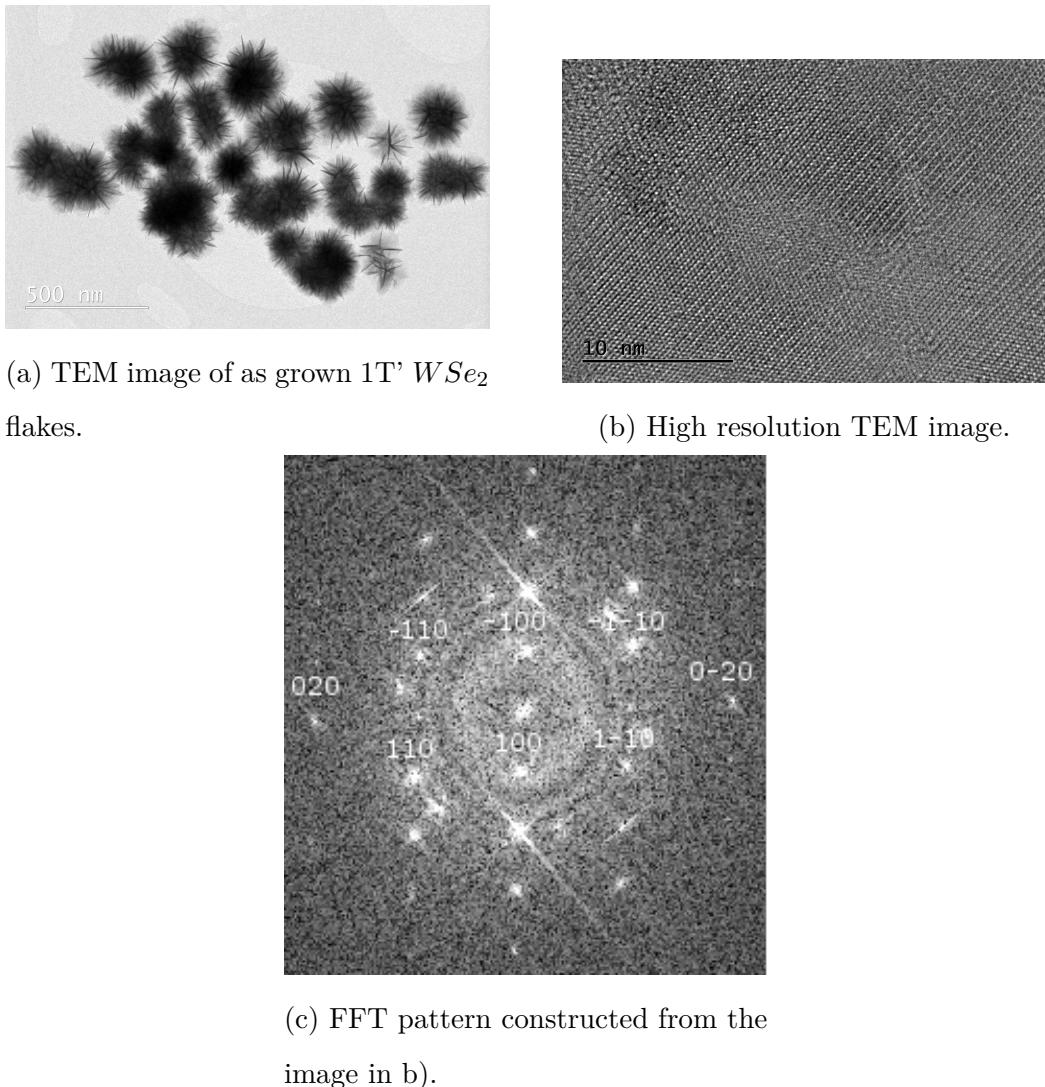


Figure 9.10: TEM characterisation of as grown 1T' flakes.

In order to ascertain the phase of the as grown WSe_2 a Raman spectrum has been taken. As seen in Figure 9.11 the spectrum of the as grown 1T' WSe_2 looks very different to the Raman spectrum of the CVD grown 2H WSe_2 as seen in e.g. Figure 9.2b. The

E_{2g}^1 and A_{1g} located around 250 cm^{-1} and are convoluted in case of the monolayer. In spectrum of the 1T' sample (Figure 9.11) the closest peaks to those are located at 248.6 and 260 cm^{-1} and can be therefore ascribed to E_{2g}^1 and A_{1g} modes respectively. Additionally the absence of the B_{2g}^1 peak suggest that the material is very thin. Furthermore there are 5 more unresolved peaks at 104.5 , 149 , 177 , 218 and 236.3 cm^{-1} . Thus far there is no published information regarding the vibrational modes of 1T' WSe_2 and therefore the peaks cannot be assigned to the modes. Similarly new peaks have been reported for 1T' MoS_2 where new peaks were labelled as J_1 , J_2 and J_3 [183].

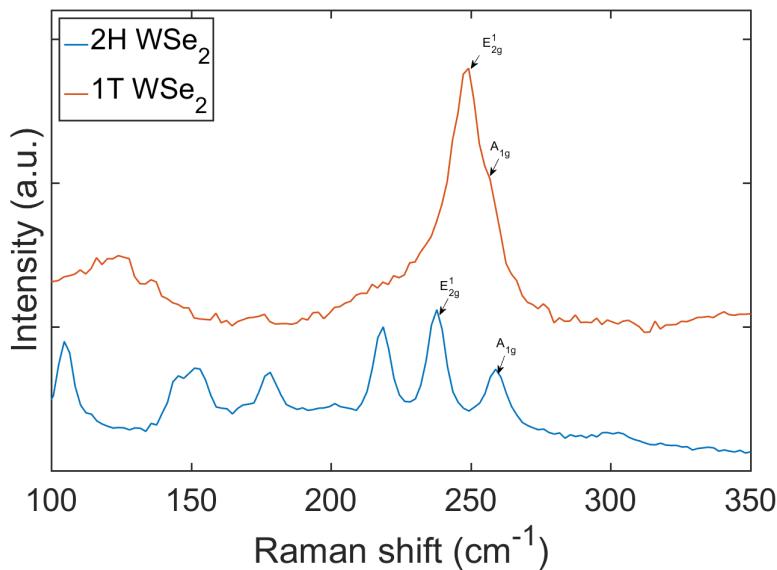
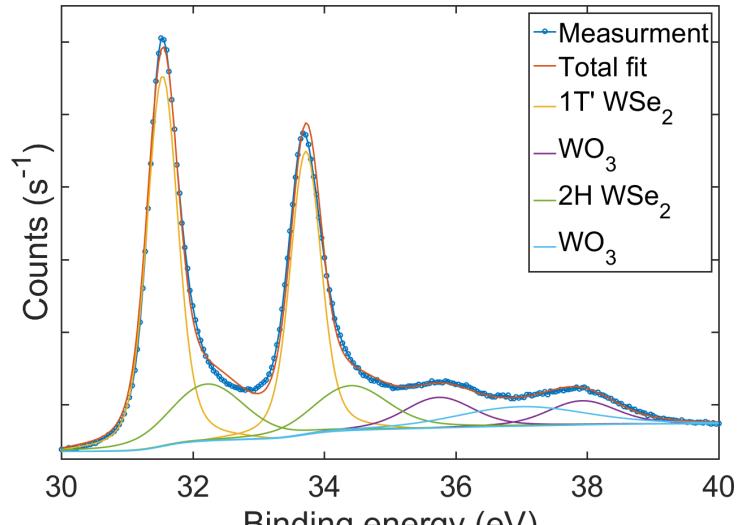


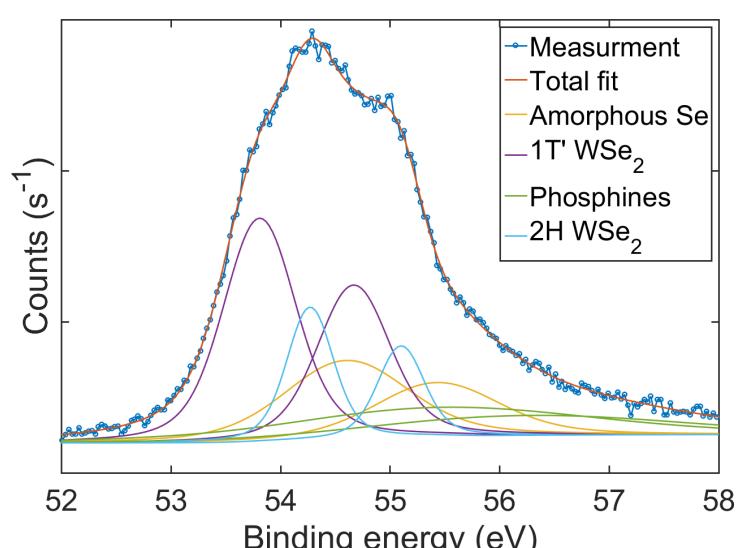
Figure 9.11: Raman spectra of 2H WSe_2 and 1T' WSe_2

Similarly, the XPS spectra were taken of the as-grown sample as seen in Figure 9.12a and Figure 9.12b. The XPS spectrum of the W 4f electron shell shows a doublet of W^{+4} 4f at 31.49 and 33.63 eV . This position varies notably from those reported for 2H WSe_2 and therefore are attributed to 1T' WSe_2 . The shift itself is most likely caused by change in coordination of the metal atom or a change in the W-Se bond length from 2.531 \AA to 2.66 \AA . On top of the 1T' phase of WSe_2 additional small contributions to the spectrum can be attributed to the 2H WSe_2 at 32.22 eV and 34.30 eV . Additionally an even smaller contribution from tungsten oxides can be identified at 35.74 eV and 37.92 eV . The Se 3d level spectrum seen in Figure 9.12b of the as-grown sample has been fitted with 4 doublets. Two of those doublets are associated with Se^{-2} atoms and are assigned to 1T' WSe_2 (53.60 eV and 54.46 eV) and 2H WSe_2 (54.26 eV and 55.1 eV). The remaining two doublets, with much lower integrated area as compared to the Se bound to W, are assigned

to amorphous Se (54.62 eV and 55.46 eV) and Se partially coordinated with phosphines (55.49 eV and 56.36 eV). The latter is remaining from the unreacted precursors of Se for the colloidal synthesis and a small component of amorphous Se is excepted as residual from the synthesis as well.

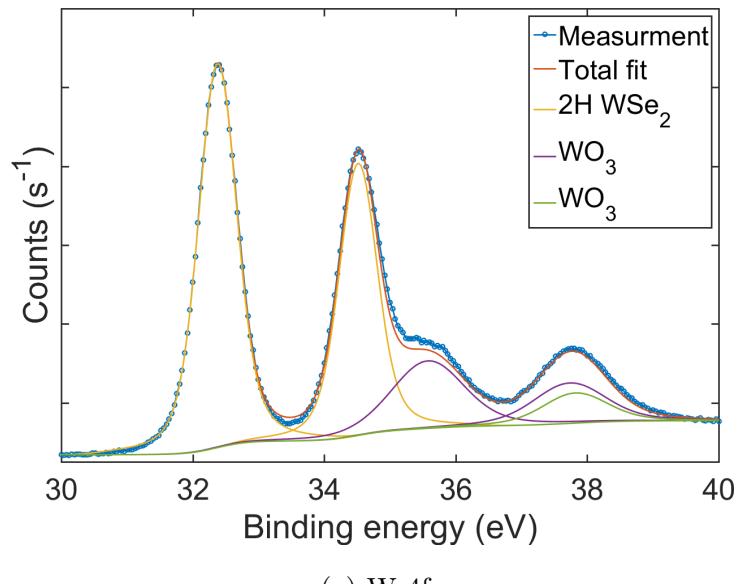


(a) W 4f

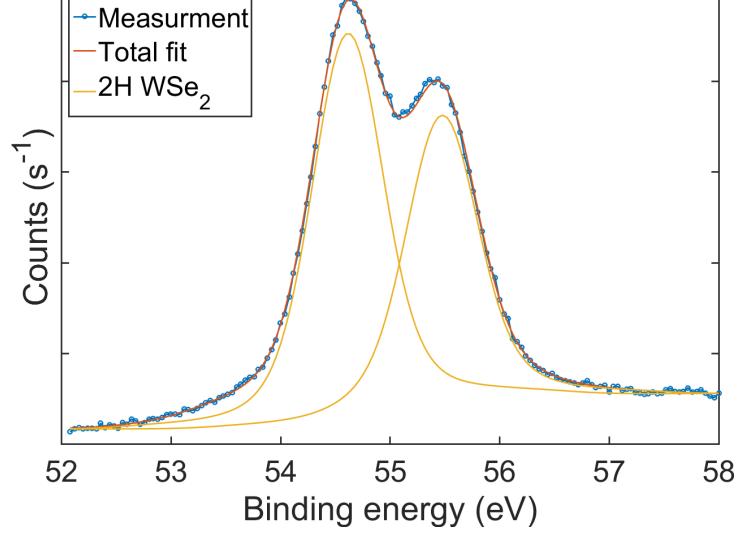


(b) Se 3d

Figure 9.12: XPS spectra of W 4f and Se 3d levels in as grown sample of WSe_2



(a) W 4f



(b) Se 3d

Figure 9.13: XPS spectra of W 4f and Se 3d levels in the annealed sample of *WSe₂*

The as-grown sample was then annealed at 400 °C in an argon atmosphere. The Raman spectrum of the annealed sample can be seen in Figure 9.11. The previously unidentified peaks are no longer present except for the two convoluted peaks at around 250 cm^{-1} . This is indicative of 2H *WSe₂* and suggests that the entirety of the 1T' phase has been converted to the 2H phase. Additionally the XPS spectra of the annealed sample can be seen in Figure 9.13. The presence of 4f W^{4+} peaks 32.40 eV and 34.58 eV and an almost complete absence of the 1T' 4f *WSe₂* indicates that the sample is primarily a 2H *WSe₂*. It is worth noting that after annealing the oxidized component of W just

increases by a negligible amount. Following the annealing the XPS spectrum of the Se 3d can be seen in Figure 9.13b. The spectrum can be fitted with one doublet associated with 2H WSe_2 only. This indicates that any residues of unreacted Se can be removed by annealing as expected as the evaporation temperature of elemental Se is ~ 270 °C.

9.3 Conclusions

In this chapter we have presented and discussed the electronic band structure and the physical characterization of CVD grown 2H WSe_2 . The CVD synthesis of WSe_2 is quite challenging and not much work has been reported so far in the literature due to the low reactivity of Se. We have concluded that the grown material is pure, and possibly have high crystallinity as demonstrated from the relatively small FWHM of the PL peak. Additionally, thanks to micrometric lateral size resolution of the XPS analysis we could distinguish and parameterise the difference in binding energy of W 4f orbitals as a function of the thickness of the flakes for the first time. Furthermore, we could prove that a small amount of WO_3 is spread all over the substrate and it is not chemically bound to WSe_2 . Similarly, it was interesting to observe the presence of elemental Se on the bare substrates. In contrast with the belief that the sticking coefficient of chalcogen elements is very low as compared to metals such as W and Mo, this evidence can shed light into the growth mechanism via CVD of atomically thin materials.

Additionally we have shown how the 1T' WSe_2 has been grown for the first time using this colloidal synthesis route. The material has then been characterised using Raman spectroscopy, XPS, TEM, and KPFM to ascertain to be in the 1T' crystal phase and to demonstrate to be metallic. Following an annealing at 400 °C the 1T' phase has been almost entirely converted to 2H. We have ascertain the presence of the 2H phase by preforming Raman spectroscopy, XPS, TEM, and characterization. This growth method therefore allows for direct deposition of metastable phase on a functional substrate. Our Raman and XPS characterization of the 1T' phase represent a reference in the literature for future synthesis of 1T' phases of TMDCs.

Chapter 10

CVD few-layered MoS_2/WS_2 heterobilayers

10.1 Introduction

One of the potential applications of the TMDC heterobilayers is as photocatalyst for water-splitting reaction. The dimensionally confined materials, such as TMDCs offer many advantages in comparison to more commonly used materials. The large surface to volume ratio allows many catalytically active sites, generally higher carrier mobility and tunable bandgap of many of the TMDCs makes them suitable for efficient absorption of sunlight. Most commonly studied TMDCs, MoS_2 and WS_2 exhibit valence band edge more positive than the oxidation potential of water (1.23 eV) and can therefore act as a photoanode.

While a single material like MoS_2 or WS_2 can be used alone as a photocatalyst by forming a type II heterojunction additional benefits can be exploited [184][185]. The presence of the heterobilayers allows for holes to migrate to WS_2 valence band while electrons move to MoS_2 conduction band. As a result the physical charge separation delays the exciton recombination and allows for efficient water splitting.

Commonly a liquid phase exfoliation (LPE) has been used to deposit TMDC layers on conductive substrates like gold. However this method results in highly defective material with small flakes and solvent residue adsorbed to the basal plane [186][187][188]. In contrast the other commonly used technique of CVD has been utilised primarily to grow TMDC layers on top of resistive substrates like SiO_2/Si [147]. It has also been shown that CVD can produce an epitaxial interface in heterostructure and as a result reduce

trap states [189]. In order to increase the size of the flakes as well as reduce the number of defects the heterobilayers were grown by CVD onto gold substrate to allow for direct application as a photocatalyst.

Such grown material can potentially result in both vertical as well as lateral heterobilayers as well as alloys. In order to effectively resolve those Raman, PL spectroscopy and XPS were employed to assess the quality of the as grown heterobilayers.

The CVD growth setup can be seen in Figure 10.1. The CVD growth was performed using recipes developed in previous work on CVD of monolayers of WS_2 and MoS_2 [147]. Since the high mobility is of upmost importance for the photoelectrocatalytic performance [190] this growth method is particularly useful. As seen in Figure 10.2 the CVD growth on Au substrate may result additionally in formation of vertical flakes [191].

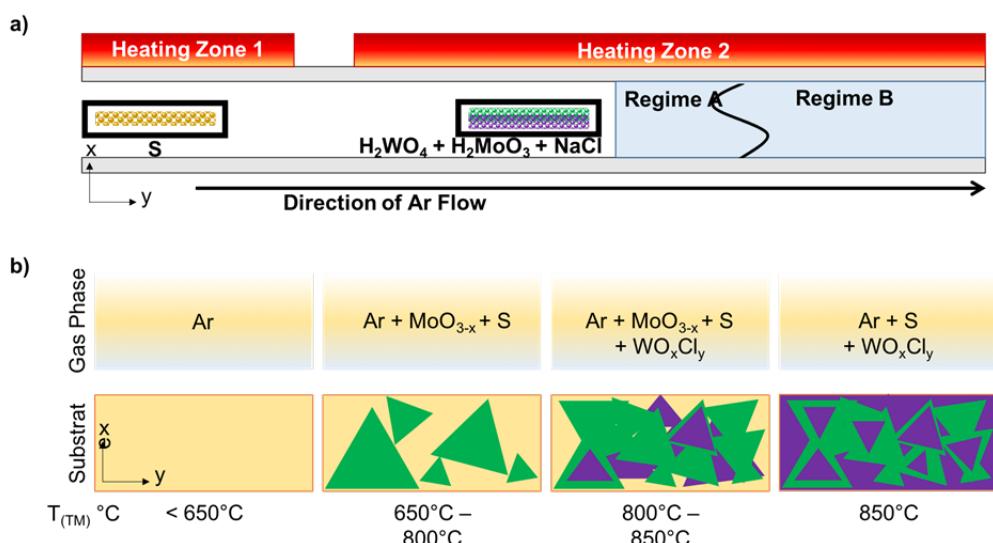


Figure 10.1: CVD furnace setup a) spatial distribution of precursors b) simplified representation of the growth result (green = Mo region; purple = W region).

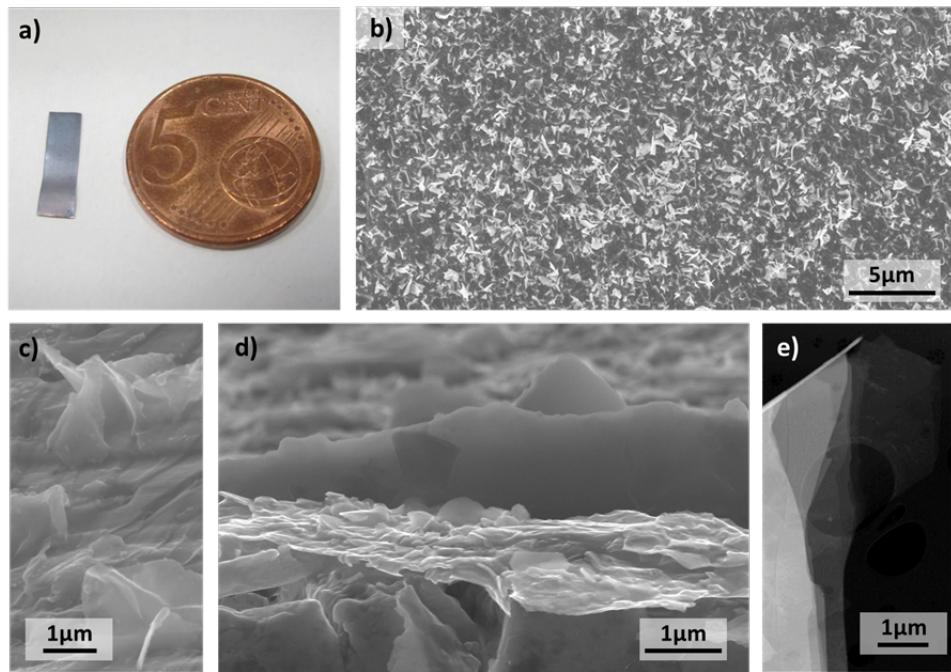


Figure 10.2: a) MoS_2/WS_2 heterobilayer on Au substrate b) SEM image of MoS_2/WS_2 heterobilayer on Au substrate c) side; d) cross-sectional SEM image e) STEM image of the flake edge. Adopted from [192].

It is especially easy to achieve vertical growth on Au substrate due to high capture rate of sulphur at the nucleation stage [137]. This results in good adhesion of the flakes parallel to the surface and high surface area caused by the vertical growths. Relatively big flakes can still be grown using this procedure (Figure 10.2).

10.2 Results

A WS_2/MoS_2 heterobilayer has been prepared by one step growth CVD as seen in Figure 10.1. The heterobilayer has been grown on SiO_2/Si using parameters developed for monolayer growth. The S precursor was placed in one crucible and placed about 20 cm upstream from the growth substrate. The W and Mo precursors, H_2WO_4 and MoO_3 respectively, were placed in a separate crucible which was located in direct contact with the substrate. The S precursor was then heated up to 150 °C while the W and Mo are heated up to 850 °C. The growth is performed in small vacuum with Ar flow. An optical micrograph of a select area of the sample can be seen in Figure 10.3. The sample contains large areas of monolayer and bilayer TMDCs with some very small flake of bulk material. Overall the material coverage is quite high.

The sample was then characterised using Raman and PL spectroscopy. A measurement of Raman spectrum was taken from heterobilayer and as seen in Figure 10.4 a distinct spectrum of WS_2 and MoS_2 can be distinguished. The Raman peak positions are 350.1 cm^{-1} , 382 cm^{-1} , 408.3 cm^{-1} and 417.7 cm^{-1} which can be ascribed to $WS_2 E_{2g}^1$, $MoS_2 E_{2g}^1$, $MoS_2 A_{1g}$ and $WS_2 A_{1g}$ respectively. Those peak positions correspond to multi layers of the individual materials which indicates a certain level of interaction between the layers.

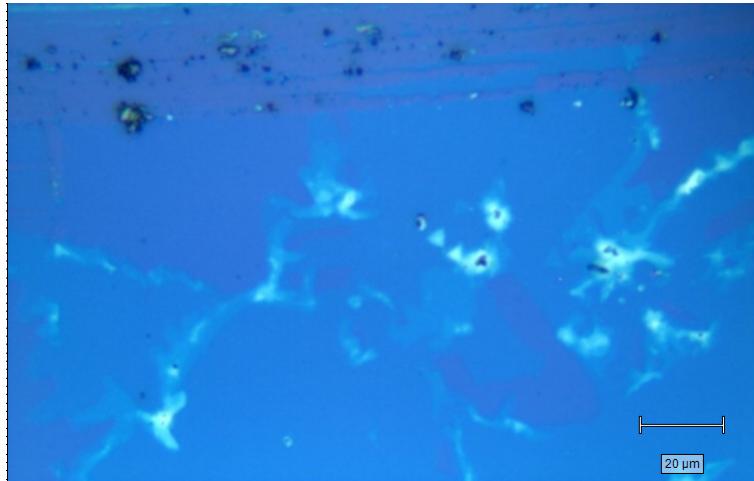


Figure 10.3: Optical micrograph of WS_2/MoS_2 heterobilayer on SiO_2/Si

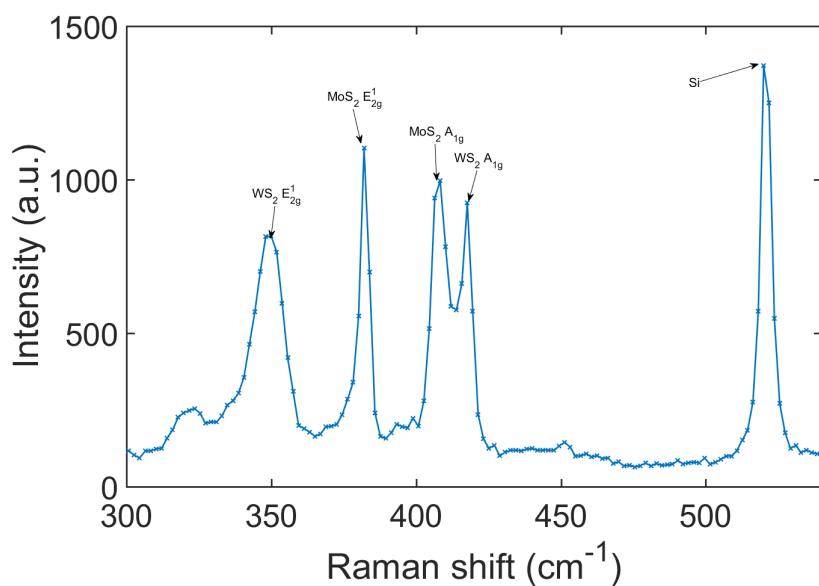


Figure 10.4: Raman spectrum of WS_2/MoS_2 heterobilayer

There is a monolayer and bilayer MoS_2 found around the heterobilayer area with no WS_2 grown indicating that the WS_2 flake has grown on top of the MoS_2 layer. The area surrounding the heterobilayer shows a spectrum as seen in Figure 10.5.

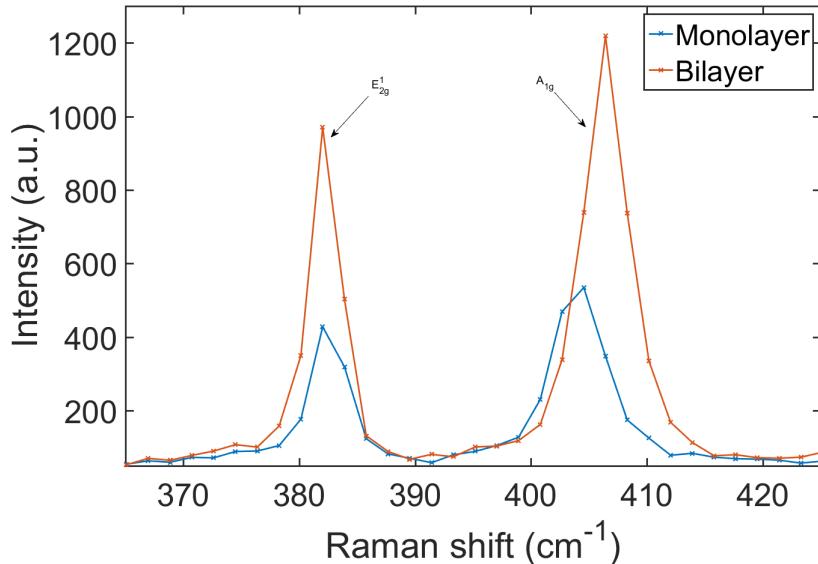


Figure 10.5: Raman spectra of mono and bilayer MoS_2

The positions of the peaks are $382.7\text{ }cm^{-1}$ and $404\text{ }cm^{-1}$ for the monolayer and $382.4\text{ }cm^{-1}$ and $406.4\text{ }cm^{-1}$ for the bilayer.

It has been shown that in $WMoSe_2$ alloy as more of the alloying metal is added the characteristic Raman peaks (E_{2g}^1 and A_{1g}) of the primary structure become less intense and shifted [14]. Due to presence of both WS_2 and MoS_2 characteristic peaks at relatively high intensity as well as lack of significant shift in the observed peak position it can be concluded that the sample is not a complete alloy. Similarly the PL in TMDC alloy, like $MoWSe_2$, shows the main A peak shifting from position of the PL peak in monolayer of one of the TMDC to the other [193]. As seen in Figure 10.8 both of the peaks from WS_2 as well as Mo_2 . It further indicates that the material is not mostly an alloy and includes pure monolayers of WS_2 and MoS_2 . It is possible that each of the monolayer in the heterobilayer is alloyed to a small degree but further studies are necessary to properly quantify these results.

The sample was then mapped using Raman spectroscopy. As seen in Figure 10.6 the intensity of E_{2g}^1 peak varies across the mapped area for both WS_2 and MoS_2 . The more intense areas indicate more layers of WS_2 which is placed on top of MoS_2 . Where the intensity of WS_2 E_{2g}^1 peak is higher and therefore there is more layers of WS_2 the intensity of MoS_2 E_{2g}^1 is reduced.

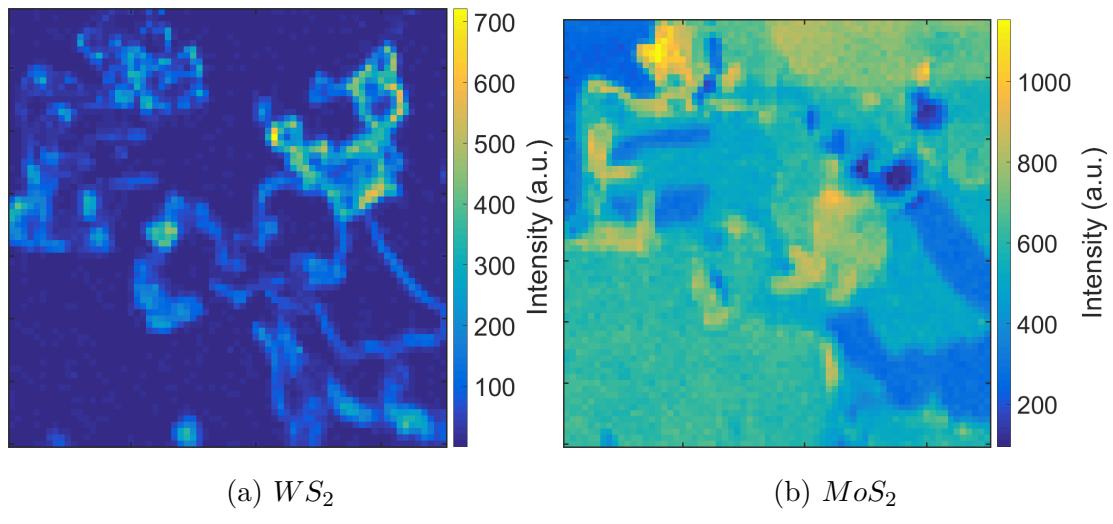


Figure 10.6: Map of Raman E_{2g}^1 peak intensity

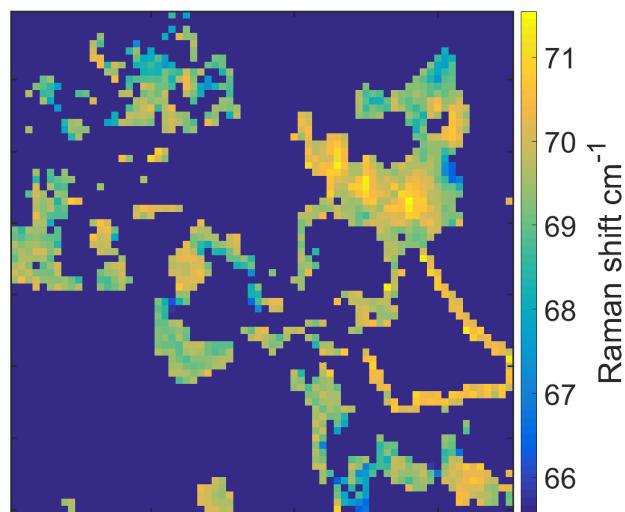


Figure 10.7: Difference between WS_2 A_{1g} and E_{2g}^1 peak position

To better estimate the number of layers the difference between A_{1g} and E_{2g}^1 peak positions has been also calculated as seen in Figure 10.7. By excluding the bulk flakes and leaving the flakes with less or equal to 3 layers of WS_2 it can be estimated that about 25% of the area is covered with WS_2/MoS_2 heterobilayer.

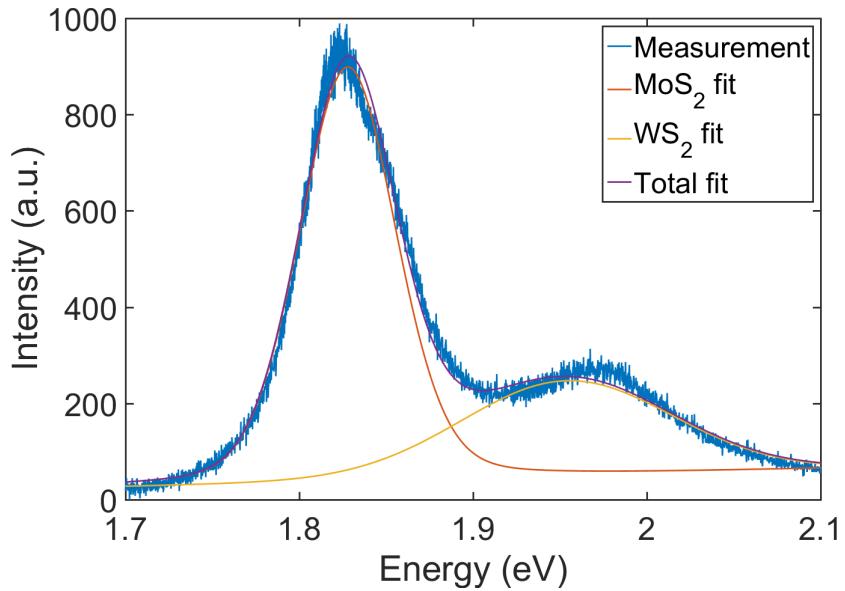


Figure 10.8: PL spectrum of MoS_2/WS_2 heterobilayer

The PL spectrum of heterobilayer can be seen in Figure 10.8. There are two distinct peaks, one at 1.824 eV and second at 1.971 eV. The position of the MoS_2 PL peak is consistent with the position of the monolayer MoS_2 as seen in Figure 10.9 which is 1.825 eV. Those PL peaks from heterobilayer therefore correspond to both MoS_2 and WS_2 monolayers indicating that the spectrum is additive. The MoS_2 peak is also much stronger than WS_2 despite the fact that isolated monolayer of WS_2 shows much stronger PL than a monolayer of MoS_2 . The MoS_2 peak has a FWHM of 65.47 meV while the WS_2 PL peak has a FWHM of 142.4 meV.

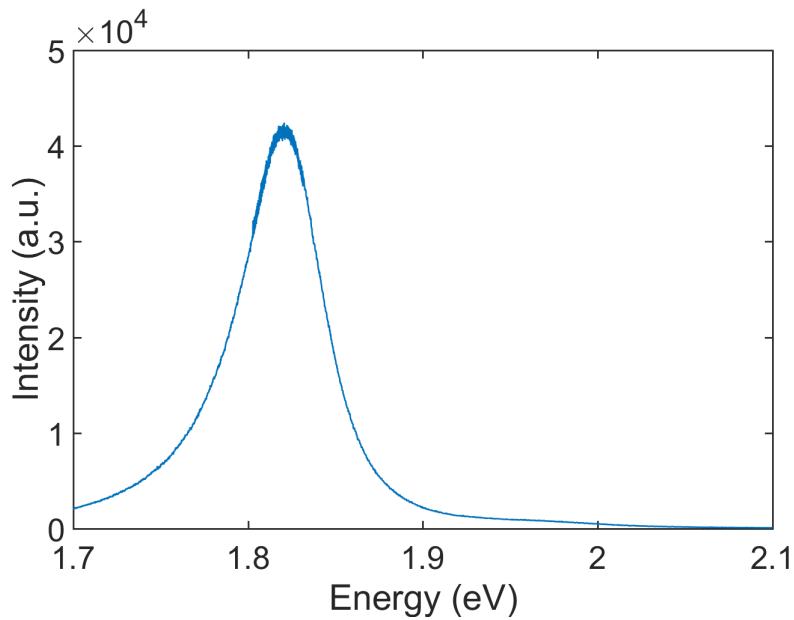


Figure 10.9: PL spectrum of MoS_2 monolayer

The sample was also mapped using PL spectroscopy as seen in Figure 10.10. The most intense PL can be observed in areas of monolayer MoS_2 and much weaker everywhere else. The position map of PL peaks from both MoS_2 and WS_2 can be seen further in Figure 10.11. Most of the PL of MoS_2 is centred around 1.82 eV with smaller part ($\sim 8\%$) centred around 1.802 eV. It seems therefore that majority of the MoS_2 is a monolayer MoS_2 while the PL peaks at 1.802 eV indicate a MoS_2 bilayer. The WS_2 PL position map reveals most of the PL peaks centred around 1.965 eV and smaller part ($\sim 16\%$) centred around 1.935 eV. Similarly to MoS_2 the majority of the WS_2 is therefore monolayer with small part of it being bilayer WS_2 .

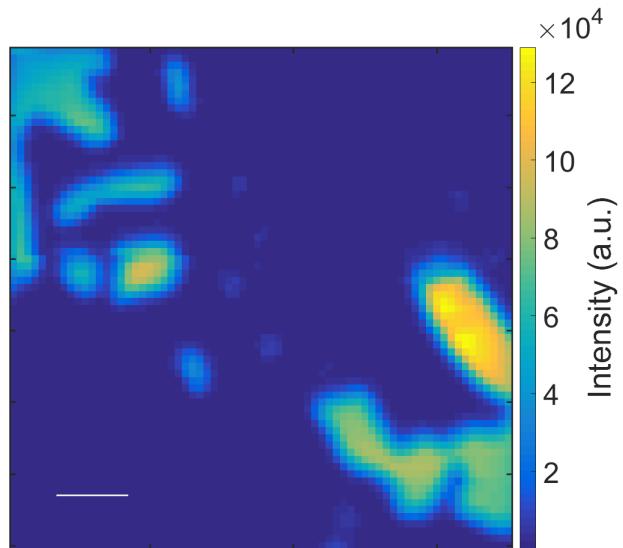


Figure 10.10: Integrated PL intensity map. Scalebar is $10\mu m$.

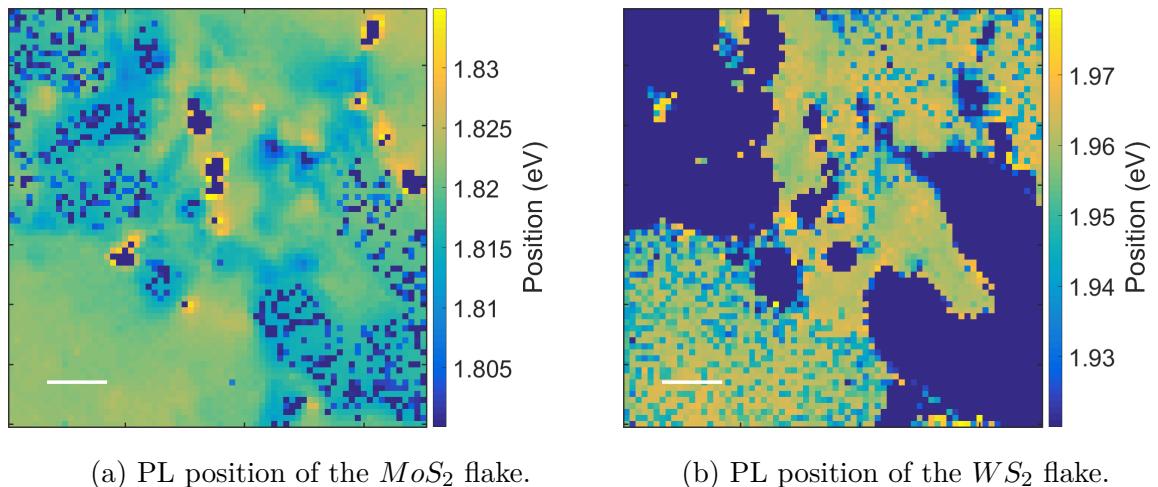


Figure 10.11: Map of PL peak positions. Scalebar is $10\mu m$.

The similar growth procedure was then used to grow WS_2/MoS_2 heterobilayer on a gold substrate. As seen in Figure 10.12 the material coverage of the substrate is complete. The material also seems to be thick with irregular, rough surface. There are no visible triangles or continuous layers like seen in a SiO_2/Si substrate. This is most likely due to vertical growth which can occur on gold substrate as opposed to SiO_2/Si substrate.

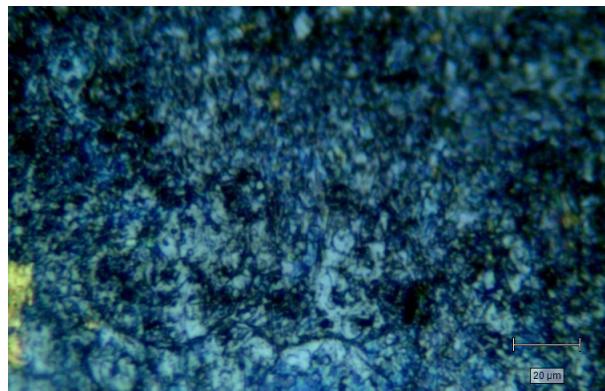


Figure 10.12: Optical micrograph of the WS_2/MoS_2 on Au substrate

The sample was then mapped using Raman spectroscopy. As seen in Figure 10.13 the WS_2 and MoS_2 Raman peaks E_{2g}^1 and A_{1g} can be identified.

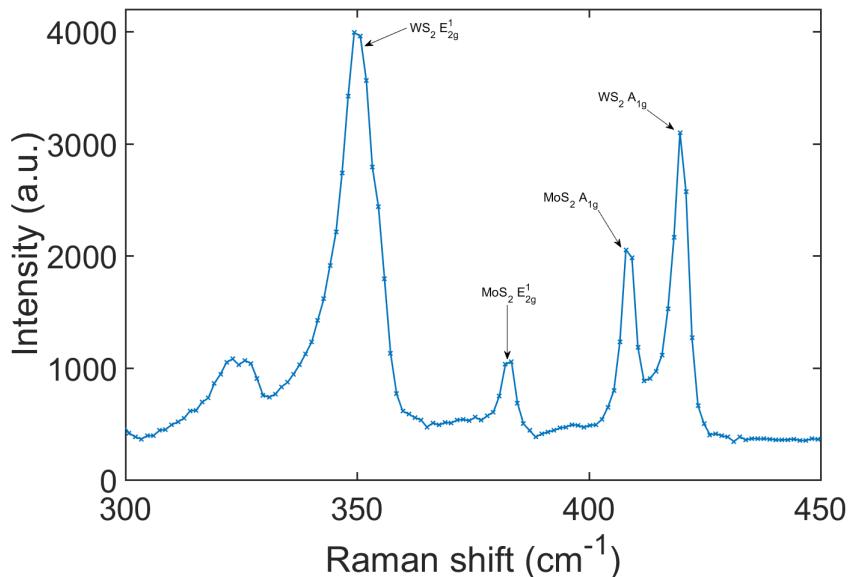


Figure 10.13: Raman spectrum of WS_2/MoS_2 on Au substrate

As seen in Figure 10.14 the $MoS_2 E_{2g}^1$ can be seen across the entire scanned area. On the other the $WS_2 E_{2g}^1$ peak can be seen less spread around. Additionally the areas with high intensity $WS_2 E_{2g}^1$ coincide with low intensity $MoS_2 E_{2g}^1$. It implies therefore that similarly to the SiO_2/Si substrate the WS_2 grows on top of the MoS_2 which results in a weaker Raman signal from MoS_2 from areas where thick WS_2 has grown on top of the underlying MoS_2 .

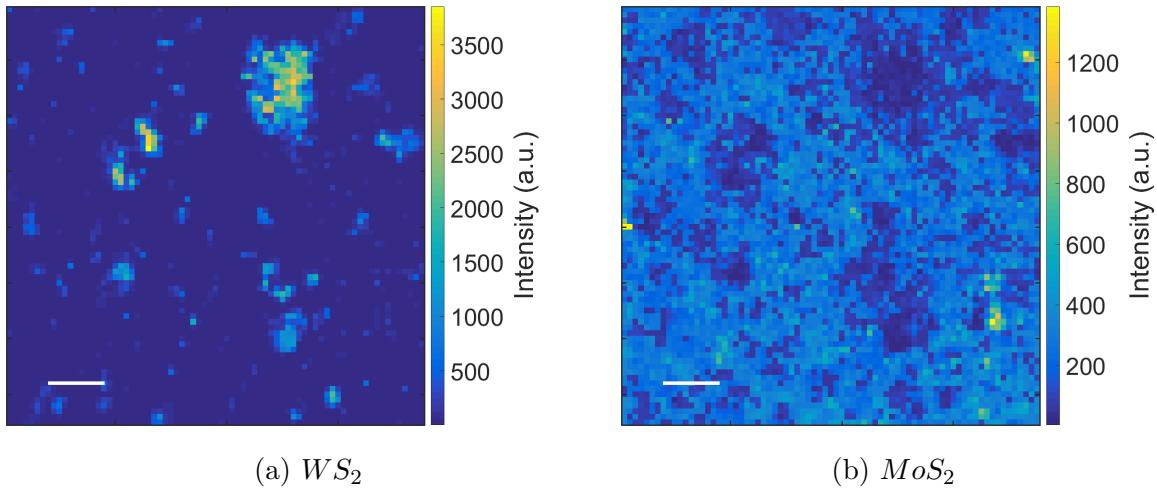


Figure 10.14: Raman E_{2g}^1 intensity maps. Scalebar is $10\mu m$.

The peaks positions for WS_2 are on average $349.1\text{ }cm^{-1}$ and $418.5\text{ }cm^{-1}$ for E_{2g}^1 and A_{1g} respectively. Similarly for MoS_2 the peaks positions are $382.5\text{ }cm^{-1}$ and $408.6\text{ }cm^{-1}$ for E_{2g}^1 and A_{1g} respectively. This indicates that both MoS_2 and WS_2 are mostly few layers thick. It can be estimated that in the measured area the WS_2 coverage and therefore the WS_2/MoS_2 heterobilayer presence is at least 8%. Due to the gold substrate the PL is partially quenched which combined with weak PL signal coming from few layer WS_2 and MoS_2 makes it difficult to make any meaningful measurement.

Compared to previously reported work on TMDCs, the performance in both hydrogen evolution ($\sim 0.1\%$ IPCE) and water oxidation ($\sim 0.1\%$ IPCE) is improved [135]. Further data and analysis of the photoelectrocatalytical performance of this heterobilayer has been reported in [192].

10.3 Conclusion

The MoS_2/WS_2 heterobilayer has successfully been grown on SiO_2/Si as well Au substrates. Their structure has been then successfully assessed with the help of PL and Raman spectroscopy. Raman and PL maps revealed that at least 8% of the investigated areas has been covered in heterobilayers. Their performance as an photoelectrocatalyst for water oxydation and hydrogen evolution has been further evaluated and found to be superior to the previously reported values. Overall those promising results warrant further research and development of one step growth to achieve better heterobilayer coverage and performance.

Chapter 11

Conclusions and future work

We have shown that the CVD synthesis of WS_2 using novel precursors can result in formation of high quality atomically thin flakes at low temperatures up to hundreds of μm in size. In particular this method proves to result in better flakes in essentially every way in comparison to more common oxide precursor like WO_3 . A very narrow PL of 36 meV and record high room temperature electron mobility of $52\text{ cm}^2/V\text{s}$ proves quality that exceeds even a naturally occurring WS_2 . The used precursors also avoids the problems of commonly used oxy-carbon based precursors of W in that it does not contaminate the synthesis products and does not produce toxic by products. It has also been shown that Raman spectroscopy and PL spectroscopy can be used as a reliable tool to map the as-grown samples and easily extract properties of the material. The insights brought about through those characterisations can prove to be useful moving forward and applying them to a host of other TMDC materials and systems. Additionally the synthesis routes and the precursors developed here can prove useful for fabrication of high-quality large-scale low-cost flakes in future. Similarly the presented precursors and synthesis method can be expanded to other TMDCs such MoS_2 , WSe_2 or $MoSe_2$ to produce material of quality higher than has been otherwise reported in literature.

The synthesis method developed for WS_2 has been then applied to produce WSe_2 flakes. By utilising the tungstic acid (H_2WO_4) and Se powders a similar low temperature synthesis resulted in flakes of up to $30\text{ }\mu m$ in size. Similarly the PL and Raman spectroscopy has been utilised to characterise the samples and a strong PL with FWHM of about 66 meV in monolayer WSe_2 has been demonstrated. The XPS studies show presence of WO_3 in the as-grown sample which indicates that the synthesis method for WSe_2 needs to be further refined to produce high quality flakes, the likes of which has

been demonstrated for WS_2 . In principle it has been shown that the method developed for WS_2 is transferable and can be further utilised in production in a number of other TMDC materials.

The transfer of TMDC flakes as well as flakes of other 2D materials can prove to be a crucial element in a production route of any future device utilising these materials. We have therefore studied the effects of transferring as grown WS_2 flakes from one SiO_2/Si substrate onto another SiO_2/Si substrate to asses the quality of the transferred material and therefore the impact of the transfer. One of the most commonly used methods of wet transfer utilising PMMA has proven to alter the distribution of PL and Raman peaks across the samples. One of the most common effect cited in literature regarding the transfer is that of strain relaxation that can build up during CVD growth due to the high temperatures during the synthesis. Based on our experiments it cannot however be definitively concluded whether the transfer reduces or induces strain in the sample as a whole. There has been however demonstrated potential change in distribution of strain across the sample which manifests itself in shifts in PL peak positions as well as Raman peak positions. Any transfer attempts must therefore be considered carefully and preferably a different, more reliable transfer method be used.

In order to further study the PL behaviour in WS_2 flakes a low temperature studies were performed. It has been demonstrated that low pressure induces changes in PL behaviour due to desorption of O_2 , H_2O and N_2 molecules which otherwise result in p-doping. The exciton peak with FWHM of 32 meV has been observed which is higher than expected assuming the temperature is a main contributor to the width of the room temperature PL peak of 36 meV. A number of possible effects, such as sample heating due to poor thermal contacts or fogging of the chamber window can be attributed to the resulting width. Additionally a trion peak has been clearly resolved with binding energy to be about 45 meV.

By using same synthesis method vertical heterostructures of Mo_2/WS_2 have been grown. A single step, one pot growth has been achieved with a degree of tunability. The resulting heterostructure has been shown to be more closely packed than a material produced more commonly via a mechanical transfer. This results in a greater degree of interaction between the layers which in turn manifests itself in both PL and Raman spectroscopy. The growth has then been also performed on a conducting substrate, such as gold. This allows such prepared heterostructure to be readily available as a photoelectrocatalyst for a reaction of water-splitting. Using developed understanding of Raman

and PL spectroscopy it has been shown that at least 8% of the surface has been covered with heterostructures which leaves room for improvement and further refinement of the synthesis.

The developed synthesis methods as well as the characterisation understanding of the as grown samples can form a basis for further improvement of the performance of those materials. One of the promising approaches to enhancing the opto-electronic performance of devices is the use of plasmonic nanoparticles. These nanoparticles have been shown to enhance local electromagnetic field of incident light as well as reflect it to improve the absorption rate of light. This can therefore find application in solar cells or photoelectrocatalysis as presented in our work, the latter of which has not been presented yet.

Additionally further characterisation of the 1T'/2H systems is necessary to evaluate the stability. In particular synthesis of and systematic Raman mapping of large areas could prove useful in understanding these phases.

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