

Two Dimensional Semiconducting Transition Metal Dichalcogenides *via* Thermally Assisted Conversion

Synthesis, Characterisation and Electronic Properties



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This dissertation is submitted for the degree of
Doctor of Philosophy

ASIN group

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To Janey, thank you.

Declaration

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work. Due acknowledgement and references are given to the work of others, where appropriate.

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Riley Gatensby

February 2018

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Abstract

Two Dimensional Semiconducting Transition Metal Dichalcogenides *via* Thermally Assisted Conversion

Riley Gatensby

2D transitional metal dichalcogenides (TMDs) are of major interest to the research and electrical engineering community. A number of TMDs are semi-conducting and have a wide range of bandgaps, they can exhibit *n*- or *p*-type behaviour, and the electronic structure changes with the number of layers. These interesting properties hold much promise for a host of electrical applications including low or high power field effect transistors, sensors and diodes. Moreover the unique optical properties and direct bandgap of monolayer TMDs make them attractive for optoelectronic applications such as Light Emitting Diodes (LEDs), photodiodes, couplers and photovoltaic cells.

Many reports of 2D TMDs electrical properties involve devices created by micromechanical exfoliation. While providing pristine material, this method is laborious and is not suitable for anything larger than lab-scale demonstrations. In order to fulfil the potential of these materials, a synthesis route which is well controlled, scalable, and reproducible is required. A further prerequisite is the ability of the materials to be integrated with semiconductor industry process flows. Thermally assisted conversion (TAC), a variant of chemical vapour deposition (CVD), shows much promise for meeting these requirements. This thesis provides a detailed treatise on the development and subsequent characterisation of 2D TMDs produced from TAC.

The TAC process produces thin films of polycrystalline TMDs. In order to synthesise and investigate these materials, a Low Pressure Chemical Vapour Deposition (LPCVD) system was designed and built in house. Firstly sulfide based TMDs are considered, particularly MoS₂ and WS₂. Due to well regulated metal deposition conditions, TAC was shown to be suitable for producing continuous MoS₂ thin films from bulk like thicknesses (≥ 20 nm) down to films with monolayer character. This is notable because monolayer MoS₂, is a direct bandgap material, and thus optoelectronic applications come within the remit of this scalable synthesis method. Films were characterised by a suite of methods in-

cluding scanning Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and electron microscopy.

Electronic devices fabricated from MoS₂ include Hall bars, Thin Film Transistors (TFTs) and chemiresistor gas sensors; these probed the electrical quality of the TAC materials. Unencapsulated devices exhibited room temperature Hall mobilities of 0.5-1 cm²V⁻¹s⁻¹. These values are too low for logic applications, however they compare well to literature values for MoS₂ films synthesised in an industrially relevant manner. Electrical Double Layer (EDL)-TFTs showed mobilities of 1.4 cm²V⁻¹s⁻¹ and this was increased to 10 cm²V⁻¹s⁻¹ when the synthesis temperature was increased to 1000 °C. Chemiresistor gas sensors are a very suitable application for 2D TMDs due to their high surface area to volume ratio. Sensors were created featuring low power room temperature operation, fast response times and ultra-high sensitivity. MoS₂ sensors demonstrated an empirical limit of detection (LOD) of 300 ppb, and a theoretical LOD of 51 ppb for NH₃.

TAC growth was then extended to include the corresponding selenides. Another LPCVD system was designed and built, affording the opportunity to include automation and data-logging capabilities. Selenide thin film synthesis recipes for MoSe₂ and WSe₂ were developed and optimised. Temperature was shown to be a critical parameter in film growth. The films were characterised using the same techniques as were used for the sulfides. Electrical characterisation of the selenide family of TMDs showed generally better performance than the sulfides. EDL-TFTs made from MoSe₂ synthesised at 800 °C showed a mobility of 4.3 cm²V⁻¹s⁻¹, this increased to 20.6 cm²V⁻¹s⁻¹ for samples grown at 1000 °C. Chemiresistor sensors from selenides were also very sensitive. Devices utilising MoSe₂ exhibited a LOD of 0.8 ppm for NO₂ and 2 ppm for NH₃. WSe₂ sensors displayed a LOD of 0.8 ppm to NH₃.

The TAC process is a viable method to produce 2D TMDs in an industrially relevant manner. It produces high quality thin films and it is potentially applicable for synthesising many different TMDs. The electronic quality of the material produced is such that logic applications are limited. However, there are a host of areas where TAC holds much promise, including sensing, catalysis and optoelectronics.

List of Publications

The following list illustrates the work which has been featured in peer-reviewed publications during this course of study.

1. "High Performance Sensors Based on Molybdenum Disulfide Thin Films", *Advanced Materials*, 2013, **25** (46), 6699-6702

Kangho Lee, **Riley Gatensby**, Niall McEvoy, Toby Hallam, Georg S. Duesberg

2. "Controlled Synthesis of Transition Metal Dichalcogenide Thin Films for Electronic Applications", *Applied Surface Science*, 2014 **297**, 139-146

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3. "Investigation of 2D Transition Metal Dichalcogenide Films for Electronic Devices", *Proceedings of Ultimate Integration on Silicon (EUROSOI-ULIS)*, 2015, 73-76,

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4. "Nanopatterning and Electrical Tuning of MoS₂ Layers with a Sub-Nanometre Helium Ion Beam", *Nano Letters*, 2015, **15** (8), 5307-5313

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5. "Low Wavenumber Raman Spectroscopy of Highly Crystalline MoSe₂ Grown by Chemical Vapor Deposition", *PSS(b)*, 2015, **252** (11), 2385-2389

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6. "Investigations of Vapor Phase Deposited Transition Metal Dichalcogenide Films for Future Electronic Applications", *IEEE Conference Publications, 45th European Solid State Device Research Conference (ESSDERC)*, 2015, 26-30

Toby Hallam, Hye-Young Kim, Maria O'Brien, **Riley Gatensby**, Niall McEvoy and Georg S. Duesberg

7. "Spin-Dependent Transport Properties of Fe₃O₄/MoS₂/Fe₃O₄ Junctions", *Scientific Reports*, 2015, **5**, 15984

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10. "A New 2H-2H'/1T Cophase in Polycrystalline MoS₂ and MoSe₂ Thin Films", *ACS Applied Materials Interfaces*, 2016, **8** (45), 31442–31448

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Nomenclature

Acronyms / Abbreviations

μ_{FE}	Field Effect Mobility
$2D$	Two Dimensional
AC	Alternating Current
AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
BSD	BackScattered electron Detector
CBM	Conduction Band Minimum
$CMOS$	Complementary Metal–Oxide–Semiconductor
CVD	Chemical Vapour Deposition
CVT	Chemical Vapour Transport
EDL	Electrical Double Layer
FET	Field Effect Transistor
FFT	Fast Fourier Transform

FWHM Full Width Half Maximum

h – BN hexagonal Boron Nitride

HER Hydrogen Evolution Reaction

HIM Helium Ion Microscopy

IDE InterDigitated Electrode

IoT Internet of Things

ITRS International Technology Roadmap for Semiconductors

KF Klein Flange

LED Light Emitting Diode

LPCVD Low Pressure Chemical Vapour Deposition

LPE Liquid Phase Exfoliation

MFC Mass Flow Controller

MIT Metal Insulator Transition

MOSFET Metal-Oxide-Semiconductor Field Effect Transistor

NA Numerical Aperture

PL Photoluminescence

PMMA Poly(methyl methacrylate)

ppb parts per billion

ppm parts per million

<i>PPMS</i>	Physical Property Measurement System
<i>QCM</i>	Quartz Crystal Microbalance
<i>RSF</i>	Relative Sensitivity Factor
<i>RT</i>	Room Temperature
<i>sccm</i>	standard cubic centimetres per minute
<i>SE</i>	Secondary Electron
<i>SE</i>	Spectroscopic Ellipsometry
<i>SEM</i>	Scanning Electron Microscopy
<i>SMU</i>	Source Meter Unit
<i>TAC</i>	Thermally Assisted Conversion
<i>TEM</i>	Transmission Electron Microscopy
<i>TFT</i>	Thin Film Transistor
<i>TMD</i>	Transition Metal Dichalcogenide
<i>UHV</i>	Ultra High Vacuum
<i>UV</i>	Ultraviolet
<i>VBM</i>	Valance Band Maximum
<i>XPS</i>	X-ray Photoelectron Spectroscopy
<i>X – TEM</i>	Cross Sectional Transmission Electron Microscopy

Chapter 1

Introduction

1.1 2D Semiconductors

Two dimensional (2D) materials have received an explosion of interest since Novoselov *et al.* isolated graphene from graphite via micromechanical exfoliation a little more than a decade ago.¹ Graphene has exceptional electronic, physical and optical properties arising from its 2D nature² and approximately 10,000 research papers are published on graphene each year.³ One significant limitation to using pristine graphene in electronic applications is the lack of a bandgap. This is important because channel materials in logic applications require a bandgap in order to be modulated by an electrical field. Much effort has gone into opening a bandgap, success has come in the form of applying uniaxial strain,⁴ formation of nanoribbons⁵ and doping.⁶ However these approaches all degrade the electronic properties of graphene. Other 2D materials are now being explored, some of which are promising semiconducting materials, such as transition metal dichalcogenides (TMDs).^{7–10} These materials can have intrinsic bandgaps comparable to silicon,

do not require as much processing as graphene does, and exhibit extraordinary properties arising from their two-dimensionality.

TMDs are a large class of inorganic layered materials composed of a row of transition metal (molybdenum, tungsten, niobium *etc.*) atoms sandwiched between two layers of chalcogen (sulfur, selenium or tellurium) atoms. A large number of transition metals are able to form layered TMD compounds, leading to a rich and varied source of 2D semiconducting materials. These elements are highlighted in fig. 1.1(a). The layered structure is shown in Figure 1.1(b). A number of different TMDs have been studied since the 1960s, with much of the early research focused on tribology, for example MoS₂ is now used as a high performance lubricant in car engines and in aviation and aerospace applications.¹¹ MoS₂ was used in one of the first ever semiconductor devices, the cat's-whisker detector.¹² Strong covalent in-plane bonding, and the fact that adjacent planes are only weakly held together by van der Waals interactions allows for 2D crystals to be either synthesised (bottom-up) or isolated (top-down).

MX₂ can exist in a variety of polymorphs. The two most commonly studied are the 1T and the 2H forms, which are schematically visualised in Figure 1.1(c). The nomenclature used refers to both the number of layers in the unit cell, and its stacking symmetry, *i.e.* 2H refers to a hexagonal lattice, with 2 trigonal prismatic layers (each rotated by 180° with respect to the other) in the unit cell. The 1T and 2H forms are identical except for the rotation of the chalcogen sub-lattices. They are rotated 0° with respect to each other in the 2H polytype, while the 1T form has the sub-lattices rotated by 180°. For MoS₂ the 2H trigonal prismatic form is semiconducting, while the 1T octahedral phase is metallic. There can also exist a metastable 3R (rhombohedral) form, which is not commonly found in nature. The 3R form is a different polytype of the 2H form, with the 3 lattices orientated

in the same direction and ABA stacking. It is possible to convert from the 1T or the 3R form to the thermodynamically favoured 2H simply by annealing, which also has been exploited for contact engineering.¹³

1A																		2A																												3A										4A										5A										6A										7A										8A													
1		H		1.00794																																																2		He		4.002602																																																					
3		Li		0.941		4		Be		9.012182																																										5		B		10.811		6		C		12.0107		7		N		14.0067		8		O		15.9994		9		F		18.9984032		10		Ne		20.1797																							
11		Na		22.989769		12		Mg		24.3050		13		Al		26.9815386		14		Si		28.0855		15		P		30.973762		16		S		32.065		17		Cl		35.453		18		Ar		39.948																																																															
19		K		39.0983		20		Ca		40.078		21		Sc		44.955912		22		Ti		47.867		23		V		50.9415		24		Cr		51.9961		25		Mn		54.938045		26		Fe		55.845		27		Co		58.933195		28		Ni		58.6934		29		Cu		63.546		30		Zn		65.38		31		Ga		69.723		32		Ge		72.64		33		As		74.9216		34		Se		78.96		35		Br		79.904		36		Kr		83.798			
37		Rb		85.4678		38		Sr		87.62		39		Y		88.90585		40		Zr		91.224		41		Nb		92.90638		42		Mo		95.96		[86]		43		Tc		[86]		44		Ru		101.07		45		Rh		102.90550		46		Pd		106.42		47		Ag		107.8682		48		Cd		112.411		49		In		114.818		50		Sn		118.710		51		Sb		121.760		52		Te		127.60		53		I		126.90447		54		Xe		131.29	
55		Cs		132.9054519		56		Ba		137.327		57-71		Lanthanides		178.49		72		Hf		178.49		73		Ta		180.94788		74		W		183.84		75		Re		186.207		76		Os		190.23		77		Ir		192.217		78		Pt		195.084		79		Au		196.966569		80		Hg		200.59		81		Tl		204.3833		82		Pb		207.2		83		Bi		208.98040		84		Po		[209]		85		At		[210]		86		Rn		[222]			
87		Fr		[223]		88		Ra		[226]		89-103		Actinides		104		Rf		[267]		[268]		[271]		106		Db		[271]		107		Sg		[272]		108		Bh		[276]		109		Mt		[281]		110		Ds		[286]		111		Rg		[285]		112		Cn		[289]		113		Uut		[290]		114		Fl		[291]		115		Uup		[293]		116		Lv		[294]		117		Uus		[294]		118		Uuo		[294]							

(a)

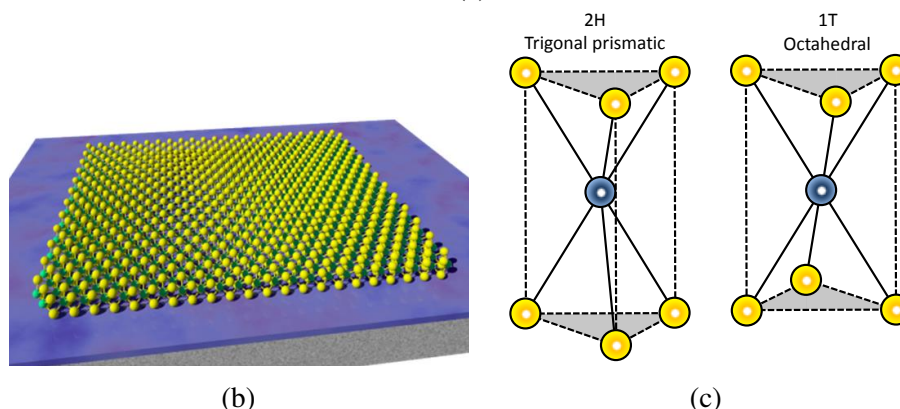


Fig. 1.1 (a) Periodic table, elements which can form layered TMDs are highlighted. Schematic representation of 2D TMD (b) layer on SiO₂ and (c) polymorphs.

For many TMDs in the semiconducting 2H form, such as MoS₂ and WS₂, the electronic structure changes with the number of layers.¹⁴ A transition is observed from an indirect bandgap (bulk) to a direct bandgap at the monolayer limit, as the form changes to 1H.¹⁵ For example, for bulk MoS₂, as can be seen in fig. 1.2(a) the valence band maximum (VBM) is at the Γ point, while the conduction band minimum (CBM) is located between the Γ and K points in the

Brillouin zone, the bandgap is 1.3 eV.¹⁶ In the monolayer case, visualised in fig. 1.2(b), both the VBM and the CBM shift to the K point and the material becomes a direct bandgap semiconductor, with a bandgap of 1.9 eV.¹⁶ These shifts are caused by the orbitals of the electronic states. At the K point, the states are comprised of strongly localised d orbitals of the Mo atoms, which are little affected by interlayer coupling, since the Mo is sandwiched by S atoms. As layer number is decreased toward the monolayer, the direct gap at the K point is relatively unaffected. However, at the Γ point there is a larger contribution from the antibonding p_z orbitals of the S atoms. This p_z contribution to the electronic states in both the valence and conduction bands is sensitive to a strong interlayer coupling effect. The absence of p_z orbital interaction between adjacent MoS₂ layers in the monolayer case causes the indirect gap at the Γ point to become much larger, due to quantum confinement effects - at which point the direct bandgap at the K point is smaller. This remarkable transition leads to much potential for TMDs in a wide range of (opto)electronic applications such as photodetectors, Light Emitting Diodes (LEDs) and solar cells.¹⁷

The indirect bandgap at the gamma point gets bigger in the ML form - at which point the direct bandgap at the K point is then smaller

Many of the TMD materials currently under investigation are intrinsically n -type (electrons are the majority carriers). They can be converted to p -type semiconductors by selective doping with phosphorus¹⁹ or niobium.²⁰ One notable exception is in the case of WSe₂, which is intrinsically p -type. A further advantage of this class of materials is that different TMDs have different bandgaps, ranging from 0.15 eV (TiSe₂) to 2.5 eV (GaS).

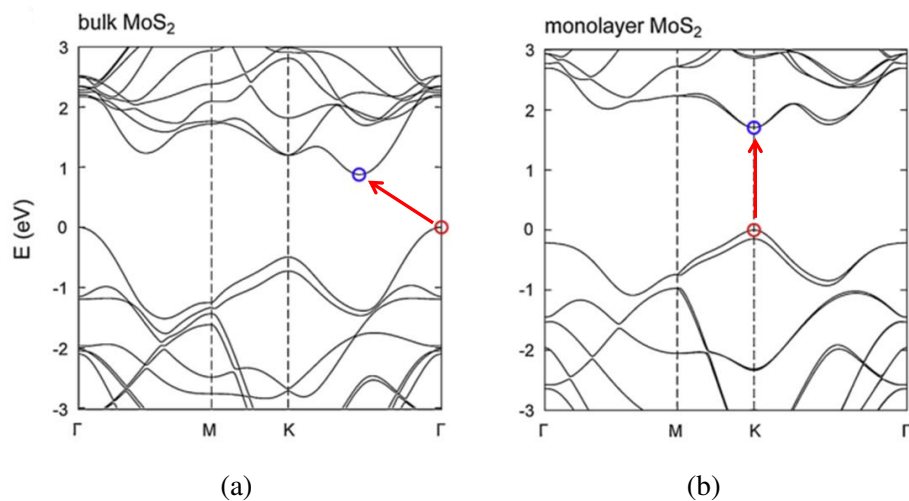


Fig. 1.2 Band diagrams of (a) bulk and (b) monolayer MoS_2 , adapted from Yazyev *et al.*¹⁸

1.2 Applications

Liquid phase exfoliation (LPE) is a scalable top down production method, supplying dispersions of nanoscale flakes which can then be used in composites and coatings. Films are generally formed via filtration, spraying or inkjet printing.²¹ However, due to interfaces and defects between the flakes, such films typically display relatively poor electronic properties.²² LPE TMDs may potentially be suitable for applications as electrodes in batteries, catalysts, supercapacitors or printable electronics.²³

Due to their two dimensionality, TMDs display a very high surface area to volume ratio, and when formed into composites, these materials are useful for a range of applications. MoS_2 composites have been used for energy conversion and storage,^{24,25} and for catalysing the hydrogen evolution reaction (HER) reaction.²⁶

Semiconducting materials that can exploit the benefits of two dimensionality hold much promise over a wide range of electronic applications. TMDs can be superior materials to silicon, when considering the ultimate scaling limit short

channel effects are not as prevalent. This is due to the uniform monolayer thicknesses, higher dielectric constants, larger band gaps and higher effective mass of the carriers, consequently reducing source drain tunnelling. Dual gated monolayer MoS₂ Field Effect Transistors (FET)s can potentially fulfil the International Technology Roadmap for Semiconductors (ITRS) requirements for high performance logic devices of 2023.²⁷

There have been several reports of high performance electrical devices produced from micromechanically exfoliated TMDs. Early reports included Radisavljevic *et al.* producing a single-layer MoS₂ dual-gated TFT encapsulated in hafnium oxide as the gate dielectric material, which featured μ up to 200 cm²V⁻¹s⁻¹ at room temperature and the current on/off ratio of 1×10^8 .²⁸ There has been some debate about the validity of this estimated mobility value, with Fuhrer and Hone claiming that the true value is lower when capacitive coupling between the top and back gates is taken into account.²⁹ Wang *et al.* produced 12 transistors side by side on a single MoS₂ bilayer flake,³⁰ demonstrating complex digital logic circuits. Recently, Javey *et al.* have demonstrated MoS₂ FETs with effective gate lengths of 1 nm.³¹

The focus of much recent research has been in combining different 2D TMDs for electronic applications, where complementary inverters,³² and monolithic (stacked) 3D Complementary Metal–Oxide–Semiconductor (CMOS) logic circuits³³ have recently been demonstrated. Further applications in high- & low-power circuits relying on the variable bandgaps have been discussed in a number of reviews recently,^{18,21,34–40} for example MoS₂ is considered to be one of the leading candidates for future low power electronic devices.

The transition to a direct bandgap material at the monolayer for some TMDs makes these materials suitable for optoelectronic applications such as photodetectors, LEDs, and photovoltaic cells.⁴¹

Other applications exploit the high surface area to volume ratio of TMDs – importantly, in the case of chemical sensors where there is an ever increasing demand for robust, low-cost low-power stand-alone devices to drive the Internet of Things (IoT). Individual sensing elements are the basic building blocks of sensor nodes, which can be incorporated into distributed sensor networks,⁴² and form an essential element for the IoT.^{43,44} The IoT is defined as a global infrastructure for the information society, enabling advanced services by interconnecting (physical and virtual) things based on existing and evolving interoperable information and communication technologies. The number of sensors in mobile devices grew from 10 million in 2007 to 3.5 billion in 2012. It is estimated that there will be 1 trillion sensors by (2020).⁴⁵ 2D TMDs are an ideal candidate for gas sensors and other sensing applications because they have a suitable bandgap, and because of their very high surface area to volume ratio.⁴⁶ Furthermore, the thin body of the 2D materials allows for flexible devices which are particularly useful for the IoT, wearable electronics and mechanical switches.⁴⁷

1.3 Thesis Scope

Many of the electronic results reported to date involve devices fabricated from micromechanically exfoliated flakes, requiring multiple complex, time intensive, electron beam lithographic steps. They represent interesting breakthroughs and offer a glimpse of the potential that these materials may hold, however they are not at all suited to large scale production of next generation electronic devices.

The body of work undertaken, from which this thesis is produced, is primarily concerned with developing the scalable synthesis and reliable characterisation of 2D TMDs. The synthesis procedure developed is termed Thermally Assisted Conversion (TAC). Rigorous physical, morphological, chemical and electrical characterisation has allowed for optimised synthesis procedures. Chapter 4 is a comprehensive study of sulfur containing TMDs, specifically MoS₂ and WS₂. Chapter 5 shows a comparable study of the corresponding selenide materials. Throughout this work, extensive characterisation has underpinned the efforts towards optimising such synthesis parameters as necessary to realise the exciting potential that TAC has in producing 2D TMD materials in a relevant, scalable manner.

TMDs produced *via* TAC in our custom-built systems have been used for a variety of novel applications, which lie outside the scope of this thesis, which is focused on determining the electronic properties of TAC synthesised TMDs and gas sensing applications. TAC produced MoS₂ films have been partnered with pyrolytic carbon to form scalable hybrid electrodes which catalyse the hydrogen evolution reaction, crucial for the clean production of hydrogen gas.⁴⁸ Z-scan measurements have probed the optical non-linearity of TAC produced materials. Giant two-photon absorption has been observed in MoS₂, WS₂ and WSe₂ with WS₂ exhibiting a nonlinear absorption coefficient of $\approx 1 \times 10^4 \text{ cm GW}^{-1}$.^{9,49} This is potentially useful in applications such as integrated optics, optical switching devices, and optical signal processing. Polymer assisted transfer of TAC produced *n*-type MoS₂ films onto *p*-doped Si substrates has been used to create novel large-area vertical-stack *p-n* hetero-junction diodes.⁵⁰ These devices are well suited as photodetectors because of the excellent optical access. They achieved a spectral

responsivity of 1.4-8.6 mA W⁻¹ in a wide spectral range, from visible to near infrared.

Chapter 2

Theory and Background

2.1 Synthesis of 2D TMDs

In order for the potential of 2D TMDs to be realised, they must be synthesised in a scalable, cost-effective, industrially-relevant manner. Due to strong covalent in-plane bonding, and weak interlayer van der Waals interactions, 2D crystals can be either synthesised or isolated. Top-down methods of isolating TMDs into 2D form involves exfoliation or shearing of bulk material. Bottom-up methods achieve synthesis of the TMD from the component elements using vapour-phase deposition methods. For electronic applications, where efforts have been focused on synthesising high-quality TMDs, thickness control and reproducible wafer-scale homogeneity are important technological challenges.^{17,51} There are several promising bottom-up synthesis methods that have been shown to be viable methods of producing 2D TMD materials, these include Chemical Vapour Deposition (CVD),^{52–54} Atomic Layer Deposition (ALD)^{55–58} and thermolysis⁵⁹.

2.1.1 Micromechanical Exfoliation

Micromechanical exfoliation (the scotch tape method) is very useful for fundamental research because it produces high-quality flakes.¹⁴ It entails using adhesive tape to detach layers of material from a parent crystal, sourced from either naturally occurring minerals or synthetic bulk crystals.^{60,61} Repeated peeling cleaves this material into few layer or monolayer flakes, which are then transferred to a substrate, as is depicted schematically in fig. 2.1(a). Micromechanical cleavage is suitable for laboratory scale investigations, however it is a serendipitous method which requires high-quality crystals and offers little prospect for scalability.⁶²

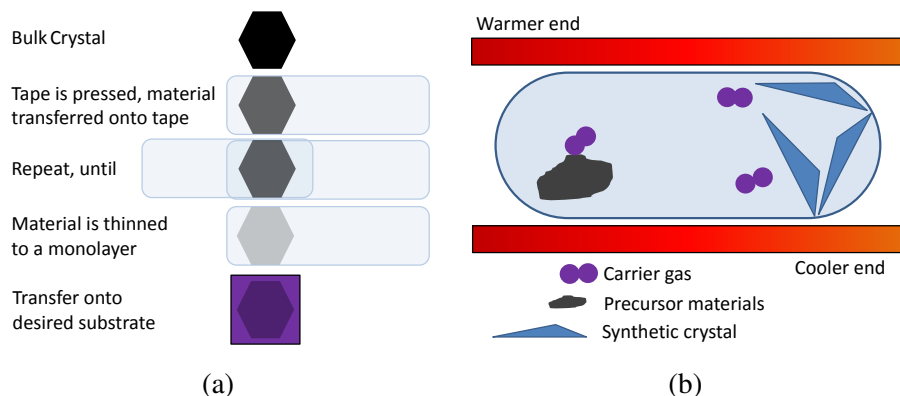


Fig. 2.1 Schematic illustration of (a) micromechanical exfoliation and (b) a CVT process.

Chemical Vapour Transport (CVT) creates synthetic crystals, suitable for exfoliation, which occurs at elevated temperatures and pressures. This method involves sealing stoichiometric quantities of the transition metal and chalcogen inside a quartz ampoule with a carrier gas.⁶³ The ampoule is heated slowly to $\approx 1000^\circ\text{C}$, with one end kept a few tens of degrees warmer, and held there for several days. Upon cooling a small fraction of the material condenses in the cooler end of the ampoule, forming bulk synthetic crystals with diameters in the millimetre range and tens to hundreds of microns thicknesses.⁶⁴ This process is

illustrated in fig. 2.1(b). The carrier gas has a profound impact on the electrical properties of the material produced, as its inclusion into the crystal lattice is unavoidable. For example, MoS₂, which is intrinsically *n*-type, can be converted to *p*-type by using iodine as the transport agent,⁶¹ or by doping with 0.05% Nb.^{65,66}

2.1.2 Liquid-Phase Exfoliation

The other top-down method commonly employed in producing 2D TMDs is LPE. This is scalable and produces gram quantities of monolayer to few-layer flakes of nanometre to micrometre dimensions. In LPE a powdered form of the mineral is sonicated or shear mixed in either an organic solvent or an aqueous surfactant.^{23,67} Post LPE, centrifugation is commonly used to separate the dispersions by size.

Alternatively, LPE can be achieved by intercalation of ions, often lithium, into the van der Waals gap, between the TMD layers followed by exposure to water.⁶⁸ The lithium reacts with the water – evolving H₂ gas, which separates the TMD sheets,⁶⁹ this is illustrated in fig. 2.2(a) Recently the use of a galvanic cell with a lithium anode and a TMD containing cathode has decreased the time required for intercalation and improved process control^{70,71} (fig. 2.2(b)).

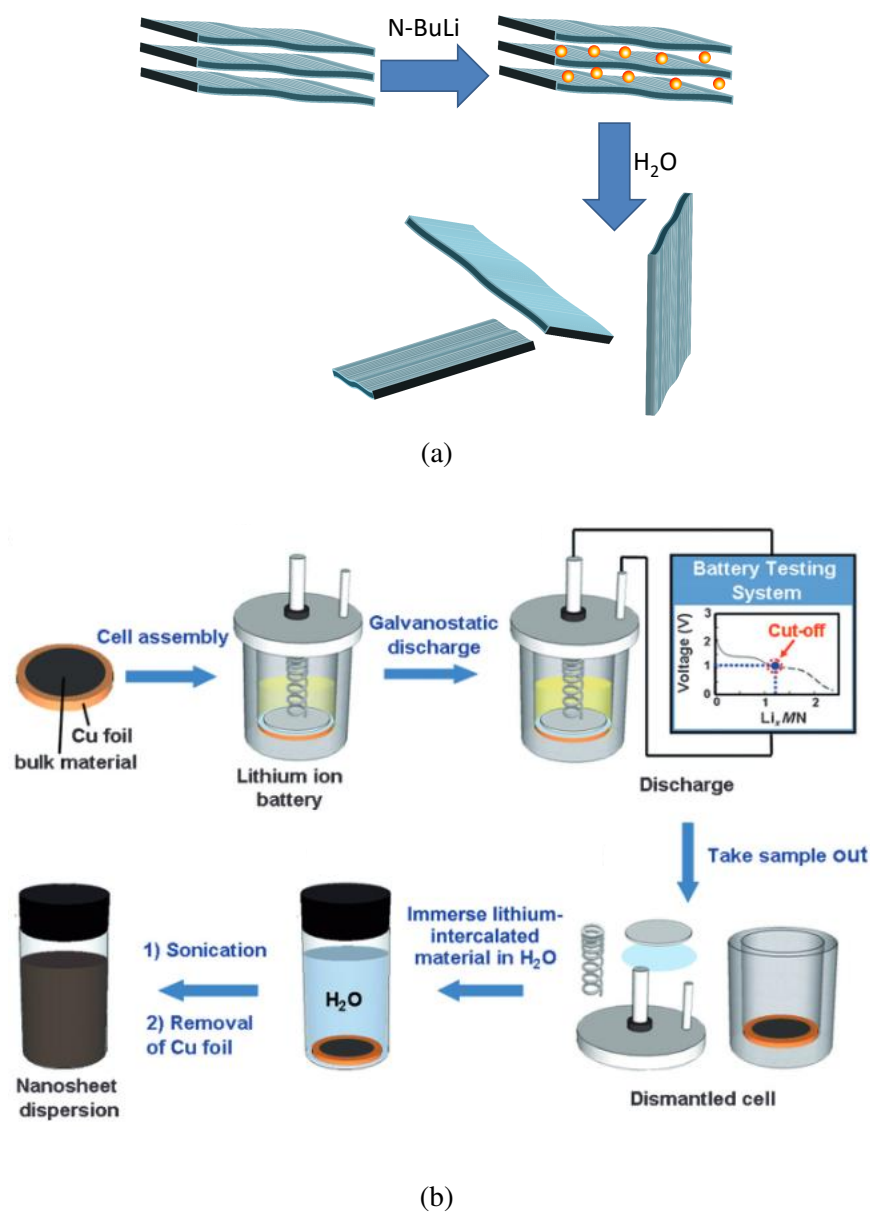


Fig. 2.2 Li^+ intercalation (a) using n-Butyllithium (b) galvanic cell assisted reaction. (b) adapted from Zeng *et al.*⁷⁰

2.1.3 Chemical Vapour Deposition

CVD is a very widely used technique for depositing uniform thin films. The films produced are usually conformal, and can be of a very high purity, due to the fact

that precursors are gaseous, and removal of impurities from gaseous species by distillation is well established.

Fig. 2.3 schematically illustrates several processes that can occur during CVD growth. Precursor gas(es) are introduced into a reaction chamber containing a heated substrate. The gaseous species will undergo chemical reactions or thermal decomposition forming reactive intermediary species. Some of which will adsorb onto the surface, forming mobile adsorbates which can react with features (such as steps) or defects on the surface, forming nucleation clusters which grow as other mobile adsorbates react with them, coating the surface.

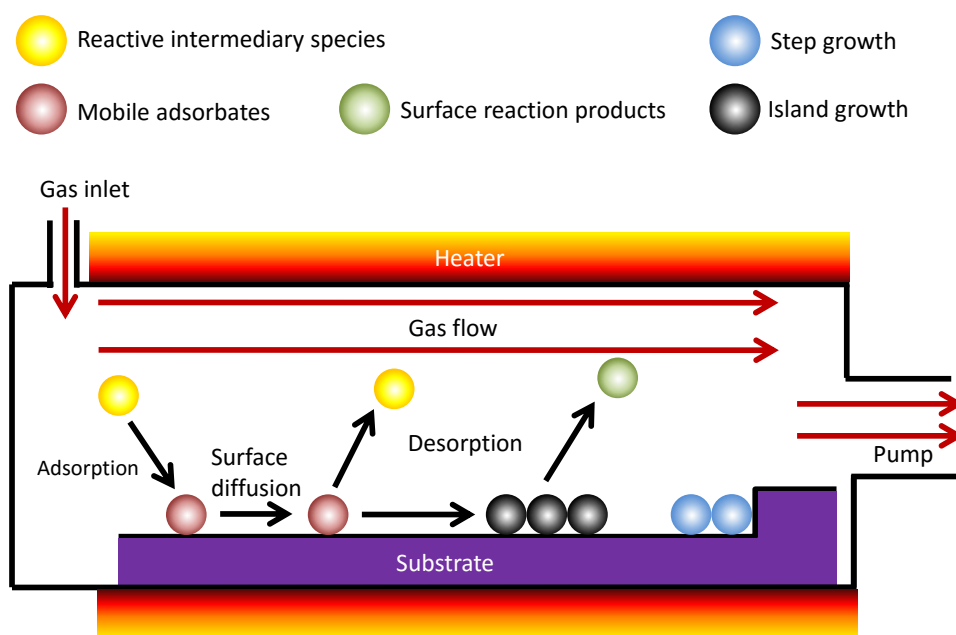


Fig. 2.3 Schematic diagram of some of the various process that can occur during CVD growths.

Since there is such a wide range of applications and materials deposited by CVD, there are many variants of the technique which have been developed.

Pressures range from Ultra High Vacuum (UHV) (10^{-3} mTorr) to 0.3 MTorr,^{72,73} temperatures range from 100 °C to 2300 °C.^{74,75} CVD processes have also been enhanced by a variety of energy sources in order to lower temperatures and/or increase deposition rates, these include the use of plasmas,⁷⁶ hot filaments,⁷⁷ lasers⁷⁸ and combustion.⁷⁹

A number of TMDs have been successfully grown by CVD including MoS₂, WS₂, MoSe₂, WSe₂, ReS₂.^{53,80–85} TMD growth processes typically entail the decomposition of a transition metal containing oxide *e.g.* MoO₃ in a chalcogen rich environment with subsequent nucleation of the TMD on a target substrate. CVD produces large, monolayer, high-quality 2D TMD atomic crystals, on the order of 10-100 μ m. Pre-treating the substrate with seeding layers of graphene-like perylene molecules helps to promote controlled growth,^{52,80} as does the use of some chlorides, *i.e.* MoCl₅ as the metal precursor.⁸⁶ However, growing the individual crystallites into a continuous film continues to be a challenge.^{54,87,88}

CVD growth of TMDs is generally not self-limiting; it leads to poorly controlled morphology and limited spatial homogeneity. Recently, Kang *et al.* have addressed many of these issues and showed that wafer-scale homogeneous films can be synthesised through a metal-organic CVD process.⁸⁹ In addition to improved scalability and film quality, CVD offers the possibility of tuning the electronic structure through monolayer alloying and doping, as discussed in a recent review by Xie *et al.*⁹⁰ and the possibility of creating atomic scale lateral heterojunctions,^{91–94} afforded by the high level of control over the gas-phase precursors.

2.1.4 Atomic Layer Deposition

ALD is a specialised type of CVD. It differs in that only one precursor is present in the reaction chamber at any given time. Growth proceeds through repeated cycles of exposure to different chemicals, each reacting with the surface groups remaining from the previous cycle. Introduction of each precursor is followed by an N_2 purge and complete evacuation of the chamber, before a different precursor is added. This process is slow, however it gives very good control over growth thickness, and can produce conformal thin films. A schematic of the ALD growth of MoS_2 is shown by fig. 2.4, in which the precursors used are $MoCl_5$ and H_2S , and the growth proceeds in a step-wise fashion, one precursor at a time.

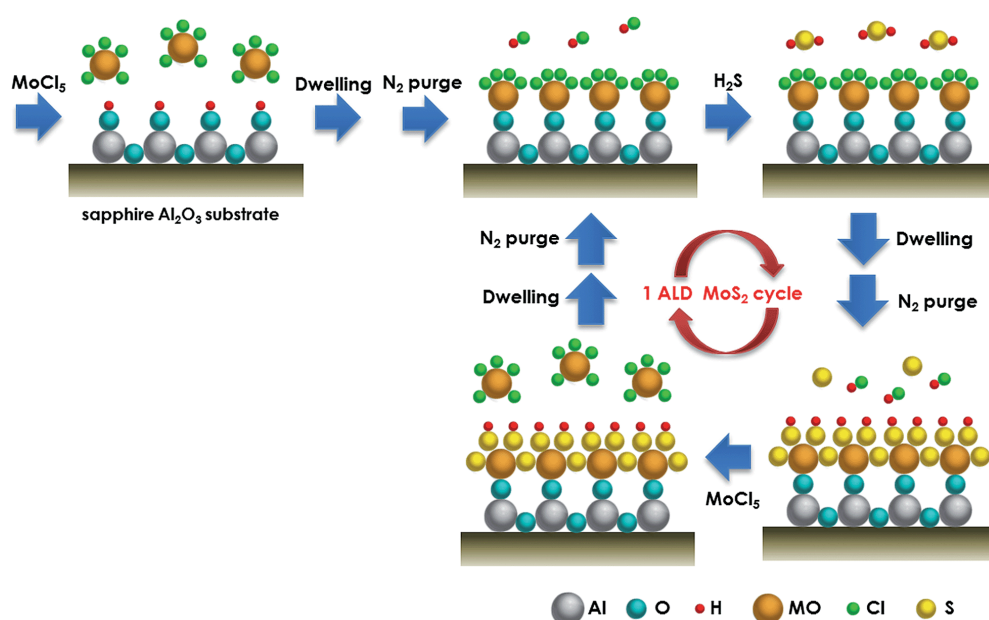


Fig. 2.4 Schematic diagram of an ALD growth cycle of MoS_2 . Adapted from Tan *et al.*⁵⁷

ALD has been used to produce high-quality layers of WS_2 on a variety of substrates with good thickness control.^{55,58,95} ALD produced monolayer MoS_2 has also recently been demonstrated although it does not form a continuous film;⁵⁷ while thicker MoS_2 films are amorphous, a high temperature anneal does improve crystallinity.⁵⁶ This method has also been used to deposit metal oxides prior to TAC,⁵⁵ and dielectric materials onto TMDs after growth.⁹⁶ ALD holds the promise for a low temperature route to synthesise TMDs on the wafer-scale, with films of quality comparable to TAC. However, this requires precursors which are typically expensive and not widely available, and this growth process only works on certain substrates; chemically inert or hydrophobic surfaces tend to inhibit growth.

2.1.5 Thermolysis

Another route to the production of high-quality thin films of MoS_2 is through the thermolysis of precursor containing thiosalts. Liu *et al.* have developed a two-step process of annealing thermally decomposed ammonium thiomolybdate,⁵⁹ as depicted in fig. 2.5. Firstly, the substrate is dip coated in ammonium thiomolybdate, then annealed under forming gas at 500 °C to remove residual organic solvents, followed by a second anneal at 1000 °C in the presence of sulfur. This method is therefore similar to TAC (particularly the second anneal) and produces films with good electrical properties; however it is difficult to scale up because of the difficulties associated with uniform large-area ammonium thiomolybdate film deposition.

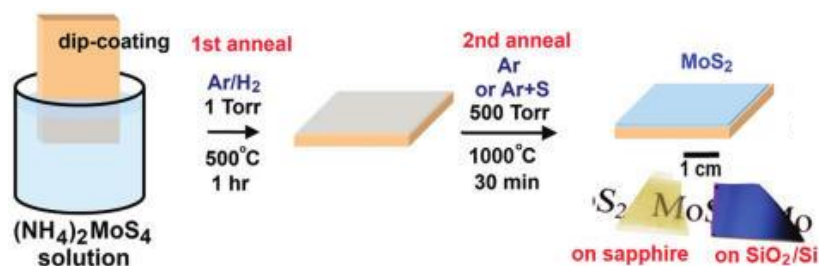


Fig. 2.5 The thermolysis process as demonstrated by Liu *et al.*, adapted from⁵⁹

2.1.6 Thermally Assisted Conversion

All of the synthesis methods so far discussed suffer from a drawback - either in scalability, quality or control of growth. This is the focus of much current research. In order to address some of these issues, a variant of CVD known as TAC was explored. The development of TAC synthesis methodologies, and characterising the resultant materials constitutes the major body of work in this thesis.

The TAC process involves depositing metal^{97–99} on a suitable substrate, followed by exposure of the metal layer to chalcogen vapour at an elevated temperature. The chalcogen diffuses into the metal layer forming an alloy, and thus the transition metal is converted into a TMD. This method produces polycrystalline films with good morphological control, due to well-regulated metal deposition techniques. Initial investigations into the TAC synthesis route focused on MoS₂. The first example of this method was by Zhan *et al.*,¹⁰⁰ who sulfurised Mo films in a hot-wall furnace, forming polycrystalline MoS₂. TMDs can be reliably synthesised at around 700 °C,^{101,102} however with plasma enhancement the temperature can be lower than 500 °C.⁵³ Any MX₃ formed during the growth decomposes to the thermodynamically more stable MX₂, at temperatures well below those used for typical growths. For example, MoS₃ decomposes to MoS₂ + S at 310 °C.¹⁰³

With TAC, selective large-area growth is easily realised; because the metal doesn't enter the vapour phase, standard lithographic techniques can be used to

define metal patterns which are then converted into TMD patterns.¹⁰¹ This enables simple fabrication schemes for a wide range of devices, as has been demonstrated for gas sensors, TFTs and Hall bars.^{102,104} Another advantage is that the thickness can be controlled in the metallisation step, and therefore produce TMDs with good thickness control, down toward the monolayer.¹⁰¹

A number of groups have demonstrated that the alignment of the TMD layers formed during TAC depends on the conversion conditions used. Cross-sectional transmission electron microscopy (XTEM) studies from several groups have shown the 2D layers to be well aligned with the substrate for thin films grown at low partial pressure, and high temperatures.^{105–108} Laskar *et al.*¹⁰⁵ have demonstrated well ordered, well aligned MoS₂ on sapphire, by TAC of 5 nm Mo, this is shown in fig. 2.6(a). Tarasov *et al.* described the synthesis of large-scale, high-quality MoS₂ tri-layer films by TAC (at temperatures above 1000 °C) of 1 nm of Mo metal.¹⁰⁸ In these cases, the material produced is continuous, and TMD layers are parallel to the substrate.

This type of behaviour is not always seen for TAC films with a thicker initial metal layer, (≥ 10 nm). Liu *et al.* have shown that under normal growth conditions (*i.e.* high temperature, low pressure) thick films grown on SiO₂ prefer to form with protruding bell-type morphology. This is imaged in fig. 2.6(b) and schematically visualised in fig. 2.6(c).^{109,110} This quality is due to the random alloying nature for the TAC process and the reduced surface energy causing the Mo to form clusters prior to sulfurisation. The clusters then convert from the outside inwards, resulting in the growth of bell-shaped TMD features.

It has also been reported that the TAC process at elevated pressure and/or lower temperature leads to the 2D layers forming perpendicular to the substrate which has allowed for novel electrical and electrochemical device structures. This

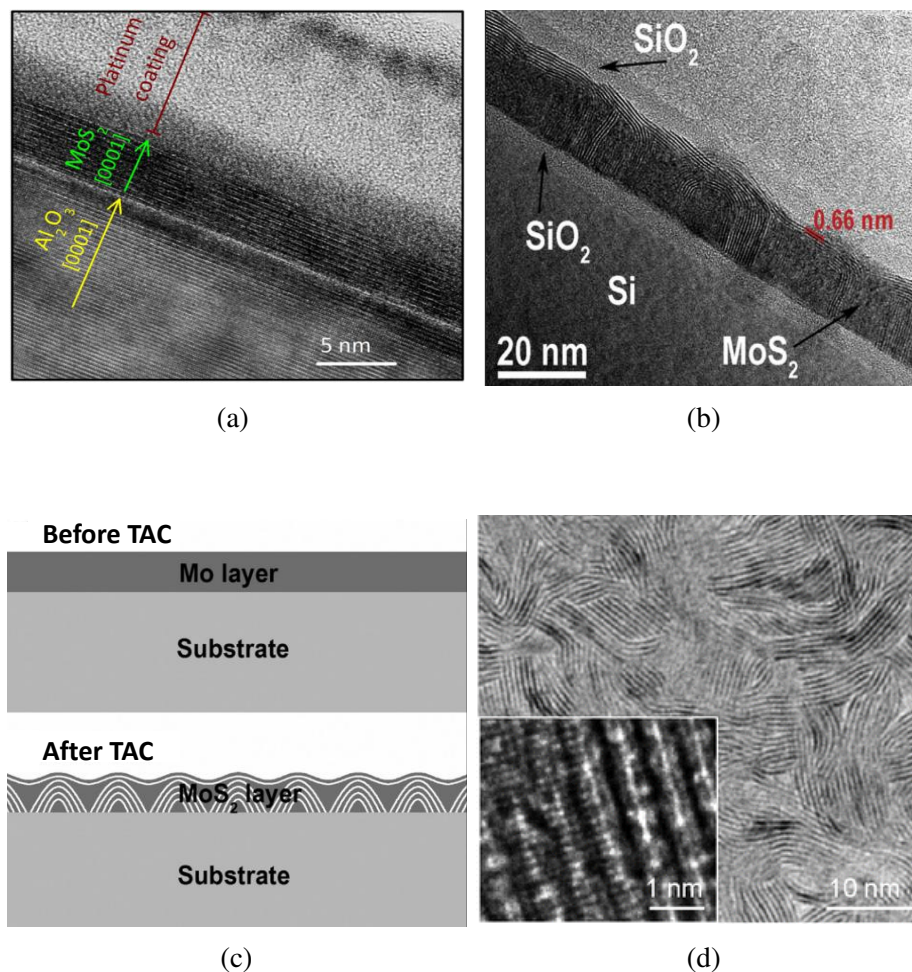


Fig. 2.6 XTEM of TAC MoS_2 (a) aligned 5 nm Mo on sapphire, (b) bell-like thicker films on SiO_2 , (c) schematic of bell-like growth, (d) vertical growth. Figures adapted from: (a) Laskar *et al.*,¹⁰⁵ (b) Liu *et al.*,¹¹⁰ (c) Liu *et al.*,¹¹¹ (d) Kong *et al.*¹¹²

was first investigated by Ganut *et al.* for WS_2 .¹¹³ They determined that low temperature (650-850 °C) and excess chalcogen availability led to vertical growth. Higher temperature (1000 °C) produced horizontal films, and the crystallinity improved with longer growth times. Recently, Kong *et al.*¹¹² have demonstrated vertical TAC growth of MoS_2 and MoSe_2 at 550 °C, (>100 mTorr) with a large excess of chalcogen, as can be seen in fig. 2.6(d). They attribute the perpendicular growth to a kinetically-driven process, with the chalcogen preferentially diffusing

into the film through the van der Waals gaps. Thickness dependence of the metal layers on vertical growth was also investigated by Jung *et al.*,¹¹⁴ who showed that preferential vertical growth of MoS₂ and WS₂ resulted only when the initial metal layer was thicker than 10 nm.

A recent study by Fei *et al.*¹¹⁵ has allowed for direct TEM imaging of MoS₂ growth mechanisms. While they do not investigate TAC growth, (their work involves the thermolysis of a single source precursor, (NH₄)₂MoS₄) their system is very similar. They show that growth around 400 °C leads to layer by layer vertical growth, while increasing the temperature to 780 °C leads to the MoS₂ structures adopting a horizontal configuration. At 820 °C precipitation of horizontal MoS₂ particles on the surface occurs, which become enlarged (with increasing temperature up to 850 °C) a variety of ways including an orientated attachment mechanism and conventional Ostwald ripening. Since TAC involves gaseous sulfur source, it is likely that growth also proceeds through a conventional crystal growth mechanism, whereby high energy facets grow faster by sulfur adsorption.

TAC is a method of synthesising 2D TMDs in a potentially industrially relevant manner. Advantages include scalable, large area growth that is well suited to lithographic processes and good thickness control. Further, the material produced is dependent on synthesis conditions and growth parameters can be easily adjusted to produce different configurations tailored to specific applications. Drawbacks include polycrystalline films and the difficulty of controlling the introduction of dopants.

2.2 Thin Film Characterisation Methods

2.2.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive spectroscopic technique which makes use of the photoelectric effect to provide quantitative data about the chemical environment and the atomic ratios of a sample. When photons of an energy higher than a material's work function interact with an atom, the photoelectric effect is observed in the emissions of photoelectrons.

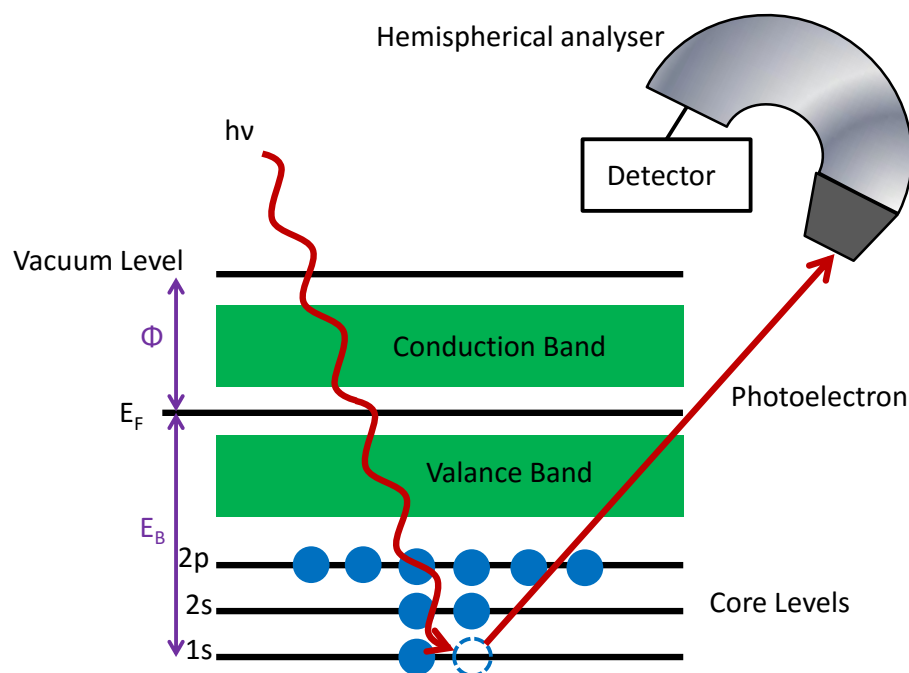


Fig. 2.7 Schematic of an XPS instrument and interaction

Elastically scattered electrons gain kinetic energy from the x-rays as given by:

$$E_k = h\nu - (\phi + E_B) \quad (2.1)$$

Where E_k is the kinetic energy of the emitted photoelectron, $h\nu$ is the energy of the incoming photons, ϕ is the material's work function and E_b is the binding energy of the affected electron.

In a typical XPS setup, as illustrated by fig. 2.7, x-rays are incident on a sample, and the emitted electrons are detected. The kinetic energy is analysed as a function of the incident energy and from this the binding energy can be determined. Binding energies are sensitive to each element as well as the chemical environment that the atom is in. Electrons with an kinetic energy of 200-1500 eV have a mean free path of 10-20 Å, this essentially is the sampling depth of the technique; emitted electrons which kinetic energies greater or less than this will not reach the surface to escape the material and hence won't be detected. The use of higher energy x-ray rather than UltraViolet (UV) photons results in core electrons being ejected rather than valence ones. As a result of these features XPS is a surface sensitive technique which probes the core electronic structure allowing for highly accurate elemental and chemical analysis of surfaces.

Emitted electrons may lose their energy through a range of interactions which must be considered so as to correctly interpret the emission spectrum. These include, in order of increasing energy loss; phonon interactions, electron-electron or plasmon interactions, and single or double particle excitations and generation of Auger electrons. The use of non-monochromatic x-rays also leads to satellite peaks. Another feature of XPS spectra is the "chemical shift" where a core peak is shifted up or down in energy in correspondence to the addition of chemical bonds. As electrons are added or removed from the atom the core potential is decreased or increased respectively. This in turn will affect the binding energy of emitted electrons and hence, the emission peak energy on the spectrum will change.

2.2.2 Raman Spectroscopy

Raman spectroscopy is a widely used characterisation technique, and it is well suited to the study of 2D TMD materials. This method is usually non destructive, it doesn't require elaborate sample preparation, and it provides much information on the crystal structure, thickness and composition of materials.

When a laser is incident on a sample, it is scattered either elastically or inelastically. These scattering mechanisms are visualised in figure 2.8. Scattering involves an interaction between electrons and photons, whereby an electron is excited from its ground state to a virtual level. Most of the time, the electron relaxes back to its ground state via the emission of a photon of the same energy as the incident light (Rayleigh scattering). However a small fraction of photons (≈ 1 in 10^7) interact with the molecular vibrational levels of a sample and are inelastically scattered before relaxation. Stokes scattering involves electrons excited from the ground state, with the emitted photons having less energy (longer wavelength) than the absorbed ones, due to the energy transfer needed to excite the molecular vibrations. Anti-Stokes scattering is the opposite, whereby electrons from an excited state interact, and they relax to the ground state, thus the emitted photons have more energy (shorter wavelength) than the incident photons. The difference in frequency between the absorbed and emitted photons is called the Raman shift, and it is used to produce a Raman spectrum, which is simply a plot of the intensity of the shifted light *versus* frequency.

Each band in a Raman spectrum corresponds to a particular molecular vibration induced by the light. In order for a mode to be Raman active, a change in the molecular polarisation potential, with respect to the vibrational coordinate, is required. If a transition is to be allowed, the symmetry of the wave function in the virtual energy state must be the same as the symmetry of the transition

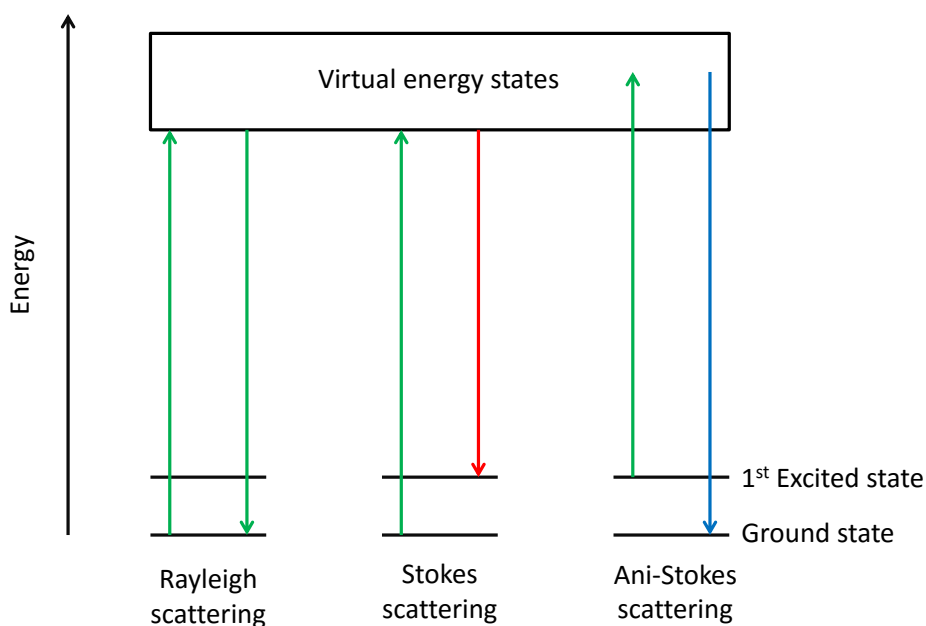


Fig. 2.8 Schematic of different light scattering mechanisms.

moment operator, otherwise the transition moment integral will be zero. In Raman spectroscopy, the operator transforms as a second order term, which can be found in the far right column in a character table.

$$I_R = \nu^4 I_0 N \left(\frac{\partial \alpha}{\partial Q} \right) \quad (2.2)$$

Equation 2.2 is an expression for the intensity of a Raman mode, where ν and I_0 are the frequency and intensity of the incident laser radiation respectively, N is the amount of molecules being scattered, Q is the vibrational amplitude and α is the molecular polarisation potential. Due to the quartic relationship between the intensity of a Raman mode, and the frequency of the excitation source, if there is a close match between the excitation energy and an electronic transition, the intensity of the given Raman mode is considered “resonant”, and it can be greatly increased.

Confocal Raman imaging is a technique whereby a confocal Raman microscope rasters along a sample, and acquires a complete Raman spectra at each pixel. A schematic of a confocal Raman microscope is given in fig. 2.9. The spatial resolution of such a system is limited by the spot size of the laser, which is approximately $0.61\lambda / \text{NA}$ (where λ is the laser wavelength). For a 532 nm laser and a 100x objective with a NA of 0.95 the spatial resolution is around 300 nm. This technique lends itself to the creation of Raman maps of a sample, which greatly enhances the power of Raman microscopy.

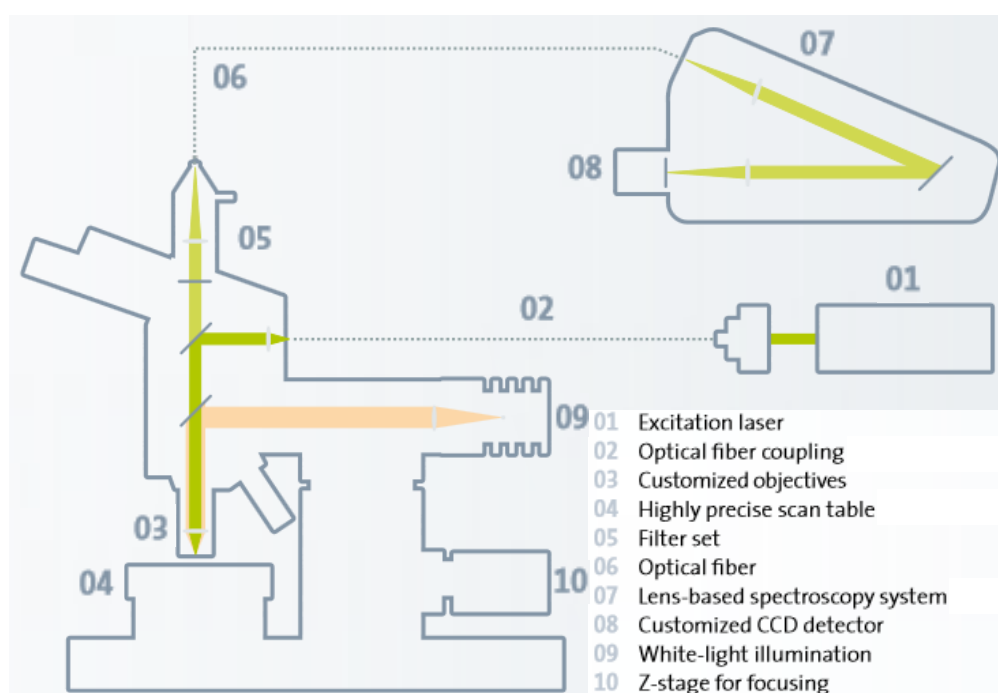


Fig. 2.9 Schematic diagram of a confocal Raman microscope apparatus, with major components labelled. Figure adapted from WITec GmbH¹¹⁶

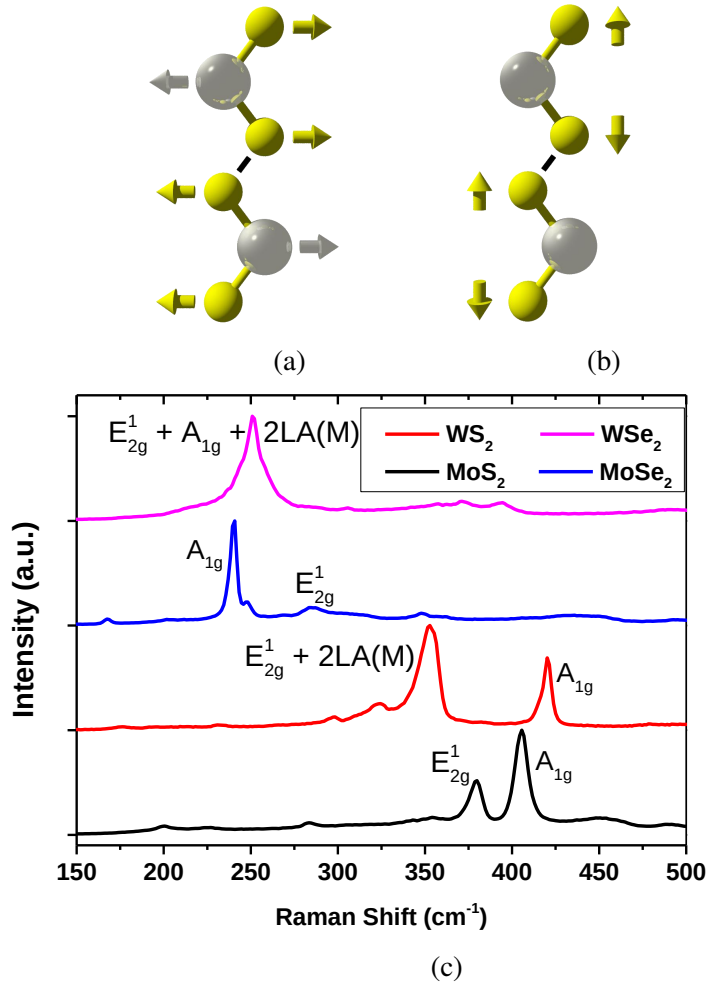


Fig. 2.10 Schematic drawings of (a) the E_{2g}^1 mode and (b) the A_{1g} mode. (c) Raman spectra of some TMDs, with modes labelled

Raman spectra of TMDs

Each covalently bonded M-X-M structure in a 2D TMD consists of two planar hexagonal chalcogenide layers, sandwiching a plane of metal atoms. For the 2H polytype, the point group of the chalcogenide atoms is C_{3v} , and that of the metal atoms is D_{3h} , the irreducible representation of C_{3v} and D_{3h} is D_{6h} .¹¹⁷ Therefore bulk samples have D_{6h} point group symmetry. Due to the lack of translational symmetry along the z-axis, few layer samples have reduced symmetry. Those

containing even numbers of layers are D_{3d} ,¹¹⁸ while odd number layers (and monolayers) lack inversion symmetry and the point group is D_{3h} .¹¹⁹ There are two main Raman bands with TMDs, the E_{2g}^1 and A_{1g} peaks. These are present in all layered TMD materials with a trigonal prismatic 2H crystal structure, *i.e.* both MoS_2 and WS_2 , and the corresponding selenides. The positions of the bands are unique to each material, because of the different bond strengths and atomic masses. The E_{2g}^1 (E_g^1 for few layer samples) peak is an in-plane vibration corresponding to the chalcogen atoms vibrating in one direction, with the metal atoms moving in the other. The A_{1g} (A_{1g}^2 for few layer samples) peak is an out of plane mode, with just the chalcogen atoms vibrating. These modes are depicted in figure 2.10(a) and (b) respectively. Another prominent feature when excitation is with a 532 nm laser, is a second order zone-edge mode which is resonant with the B exciton of WS_2 and the A' exciton of WSe_2 .¹²⁰ This 2LA(M) mode is longitudinal acoustic, and it occurs at the M point in the Brillouin zone. LA(M) phonons are in-plane periodic compressions and expansions of the lattice that occur along the direction of propagation. Fig. 2.10(c) is a plot showing the Raman spectra of MoS_2 , WS_2 , $MoSe_2$ and WSe_2 , with the major Raman features labelled. It clearly illustrates that different TMDs can be easily identified by their Raman spectra.

Transition to monolayer

The Raman signature of layered materials shows variation with layer number. From bulk to monolayer, the dimensional restriction can be seen in several ways. Li *et al.* described the evolution of the Raman signal of mechanically exfoliated MoS_2 flakes upon reducing the number of layers. They observed an upward shift of 1.7 cm^{-1} and a downward shift of 5.1 cm^{-1} in the E_{2g}^1 and A_{1g} peaks

respectively, upon going from bulk crystals to monolayers.⁴⁶ The blue shift of the E_{2g}^1 band is due to stacking induced structure changes and the decreased dielectric screening of long range Coulombic interactions between the effective charges.^{46,119} The red shift observed in the A_{1g} band is due to decreasing restoring forces as fewer layers are present.^{46,80} It is generally accepted that more work is necessary to completely clarify these trends.¹²¹

An added advantage is that the Raman apparatus can measure photoluminescence (PL) which is a signature of the direct bandgap associated with monolayer samples.¹²² Splendiani *et al.* measured PL spectra for MoS₂ flakes of different thickness.¹²³ In bulk MoS₂, with its indirect bandgap, they observed no PL emission. However, in few- and monolayer crystals they noted PL emissions at the A1 and B1 direct excitonic transitions, these emissions were particularly strong in the monolayer case due to the direct bandgap.

2.2.3 Charged Particle Microscopy

The minimum feature size that can be resolved by a given microscope is related to the wavelength of the illumination source by the the Abbe diffraction limit, given in equation 2.3. $n \sin \theta$ is the numerical aperture (NA), and it is typically around 1-1.5.

$$d = \frac{\lambda}{2n \sin \theta} \quad (2.3)$$

Optical microscopy is diffraction limited by the wavelengths associated with visible light. The minimum feature size that can be resolved is around 200 nm, however most optical microscopes can only achieve a resolution of around 1 μm . Electron microscopy circumvents this limit by imaging with high energy electrons,

which have much shorter de Broglie wavelengths. Thus it is possible to achieve resolution of features at the nanometre scale; resolution of 1 Å is possible. Two types of electron microscopy are commonly used, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Both of these methods are similar, although the sample preparation is different.

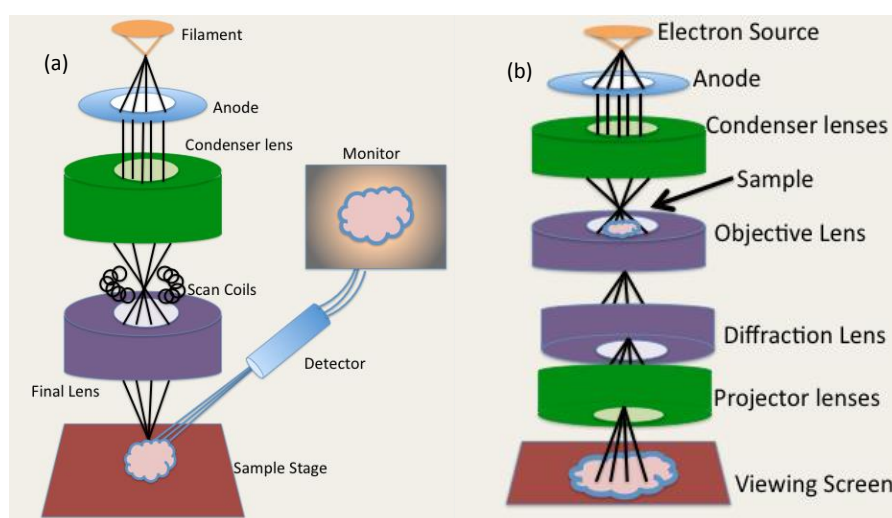


Fig. 2.11 Schematic of (a) SEM (b) TEM apparatus. Adapted from DSimaging LLC¹²⁴

Scanning Electron Microscopy

A scanning electron microscope consists of an electron-optical column which is operated under vacuum, electronic detectors, and software. These components are schematically visualised in fig. 2.11 (a). Within the column, a beam of electrons is generated, accelerated *via* high voltages, and focused by a system of electro-magnetic lenses to a spot as small as 1 nm. The lenses are also able to correct aberrations inherent in the beam. The spot is then rastered along the sample through the use of scan coils. Once incident, the electrons in the beam interact with and are scattered by the atoms in the sample. SEM utilises backscattered and

secondary electron (SE) signals, the intensities of which are detected and stored electronically as the beam is rastered along the surface. The stored intensity values are then displayed as variations in brightness, thus creating a SEM micrograph.

The low energy SE signal is generated by electrons ejected from atoms near the surface of the sample (typically 5 nm and less), through inelastic scattering interactions between the beam and k-shell electrons. The signal is detected both through the use of an Everhart-Thornley detector and an in-lens detector. An Everhart-Thornley detector consists of a scintillator near the sample (which converts the detected SE into photons), and a lightguide leading to a photomultiplier located outside of the chamber. SE generation is sensitive to interaction volume, which increases as the beam encounters edges or steps or protrusions, due to an increase in the angle of incidence. This detector provides predominantly topological information, with protrusions bright and recesses dark. An in-lens detector is also commonly used. It is located inside the electron column, rotationally symmetric around the beam. In-lens detectors detect SEs with high efficiency, mapping differences in work function as well as morphological and topographical information. Backscattered electron Detectors (BSDs) detect higher energy electrons that are reflected through elastic scattering interactions with the sample. Since the scattering cross section is sensitive to atomic number, heavier elements appear brighter than light elements, since they scatter more strongly.

An advantage of SEM is that the sample doesn't need to be electron transparent, and thus can be used to image the surface of thick samples, without the need to transfer from growth substrates. Samples need to be conductive, since the imaging electrons charge the sample. Substantially less sample preparation is needed as compared to TEM imaging methods.

Helium Ion Microscopy

Helium ion microscopy (HIM) is similar to SEM, except that helium ions are used to image the sample, instead of electrons. The use of He^+ has several advantages over electrons for imaging. Since the de Broglie wavelength is inversely proportional to momentum, and He^+ are much heavier than electrons, greater resolution can be achieved.

The field-ionisation source is unique. The tip is a three-sided pyramidal shape sharpened until it is composed of just 3 atoms at the apex, a so-called "trimer". This is held at a high positive voltage (30 kV) and cryogenic temperature, in the presence of helium gas. The very high field achieved at the trimer is intense enough to efficiently ionise the helium gas. As such, the ion emission originates preferentially from those three trimer atoms, only one of which is selected for imaging. Those atoms impinging on the tip are stripped of an electron and emitted as a very bright ion-beam due to the single atom ion source. The low temperature increases the density of available helium atoms. The beam of He ions is then accelerated down the column where it is rastered along the sample similarly to the SEM technique. Because the brightness of the beam, a very small aperture can be used, and this renders spherical and chromatic aberrations of the ion optical column insignificant. HIM therefore has a much smaller excitation volume and provides sharper images with a larger depth of field and higher resolution than traditional SEM.

When the ion beam interacts with the sample, low-energy secondary electron signals are produced which provide the information used to produce an image. Surface sensitivity is a by-product of the low-energy of the SE's that are created. These have an escape depth of just a few nanometres and do not create undesirable type-II SE's. In order to image topology with higher sensitivity, the beam energy

need not be reduced. Material contrast is also enhanced because of the high SE yield, which varies with the target material.

Transmission Electron Microscopy

TEM is a similar technique to SEM, however it forms an image from those electrons which are transmitted through the sample. A schematic a TEM system can be seen in fig. 2.11 (b). TEM requires the samples to be electron transparent, which means atomically thin. Sample preparation requires placing thin films of the material to be imaged on TEM grids. If the films are too thick, no image will resolve, due to an insufficient amount of transmitted electrons. After interacting with the sample, electrons are magnified and projected onto a charge-coupled device where they are converted into electronic images. Information on the crystallinity of surfaces is achieved by taking a Fast Fourier Transform (FFT) of the TEM diffraction pattern. If the FFT contains sharp spots, this indicates a highly crystalline sample, The location and relative brightness of the spots is related to the symmetry of the sample being investigated.

Cross sectional TEM (XTEM) is prepared by using a gallium focused ion beam (FIB) to etch a lamella, which is then mounted on a TEM grid, thinned, and subsequently polished until it is thin enough to be electron transparent. Parameters used in this work can be found in section 3.2.3.

2.2.4 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is a fast, non-destructive optical technique which is used extensively in the semiconductor industry to determine thicknesses and optical bandgap of thin films.¹²⁵ By analysing the polarisation changes caused as light reflects from a material, SE develops an optical dispersion model, from

which the film thickness, refractive index (n) and extinction coefficient (k) are determined. By relating the k values to the absorption coefficient, a Tauc plot is used to calculate the optical bandgap of the material.

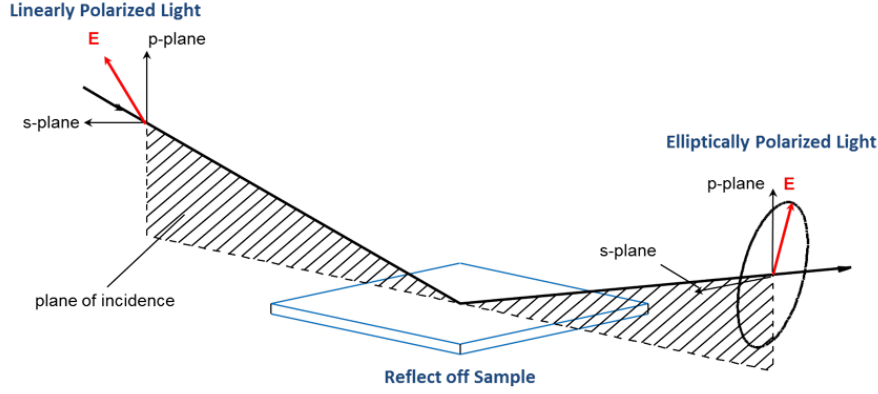


Fig. 2.12 Interaction between sample and linearly polarised light results in elliptical polarisation. Adapted from J.A. Wollam Co.¹²⁶

When linearly polarised light, containing both s and p components, is incident on a sample, elliptically polarised light is detected because of the interaction between light and the sample. This optical response (shown in fig. 2.12) is dependent on the thickness and optical properties of the material. The change in polarisation is characterised by the phase difference (Δ) and the amplitude ratio (Ψ) between both components of the reflected light, and is given by relation 2.4. Both quantities are plotted vs. wavelength, to produce a spectrum, which comprises the raw data collected by a spectroscopic ellipsometer.

$$\delta = r_p/r_s = \tan(\Psi)e^{i\Delta} \quad (2.4)$$

Where r_p and r_s are the amplitude reflection coefficients of the polarised light.

Optical dispersion models were created by Dr. Chanyoung Yim. TMDs of varying thicknesses grown by TAC on Si substrates with 300 nm SiO₂ dielectric

layer were measured. A four layer optical model was built to analyse the spectra for each material, consisting of a semi infinite Si substrate layer, an interface layer between Si and SiO₂, a SiO₂ layer, and finally a TMD layer. The optical response of the bottom three layers was defined by measuring and fitting a reference substrate using a three layer model, without the TMD. This allowed for the thickness of the interface and SiO₂ to be determined. Finally the TMD layer was added. It was fitted with a Tauc-Lorentz oscillation model, in the presence of well defined underlying layers. The thickness of the TMD layer was adjusted until the best fit between measured and modelled data was achieved, this best fit corresponded to the thickness as determined by SE.

2.2.5 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a scanning probe microscopy technique which provides information about the surface topography of a sample. A very sharp tip on the end of a cantilever is rastered across the surface by means of piezoelectric motors, this setup is illustrated in fig. 2.13. The forces, (which include Van der Waals, electrostatic, mechanical and chemical bonding) between the tip and the sample cause the cantilever to deflect. These forces can be either attractive or repulsive. The deflection of the tip is measured by reflecting a laser off the back of the cantilever, onto a photo-diode array. As the tip is rastered along the surface, the position of the laser on the photo-diode is used to produce a topographical map of the sample.

A common method of AFM imaging is the tapping mode. This involves using a piezoelectric driver to induce an oscillation in the cantilever, just below its resonant frequency. Maintaining this frequency is strongly dependent on the tip-surface interactions, and thus the distance of the tip from the surface.

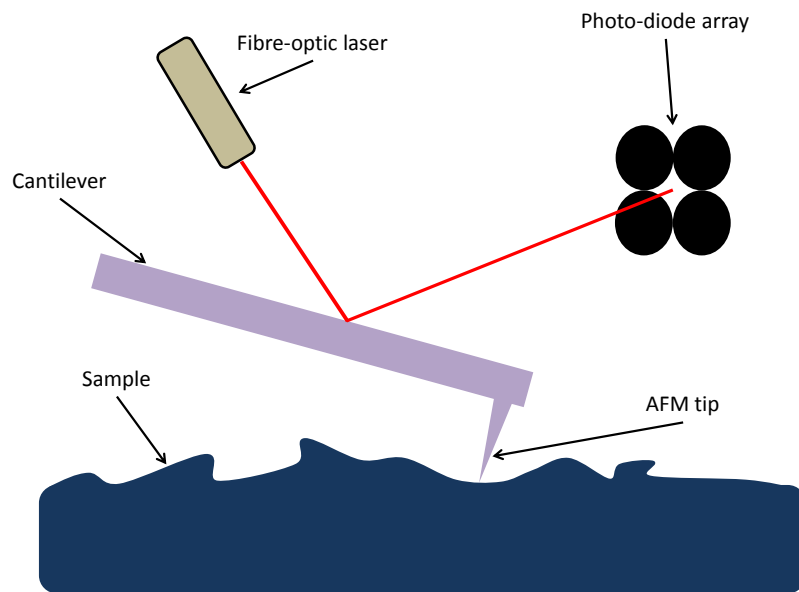


Fig. 2.13 Schematic of an AFM apparatus.

A piezoelectric motor moves the tip up or down (z-axis), through the use of a feedback loop to maintain the driving frequency, as the tip is rastered along the surface (x-y plane). The constant adjustment of the tip height allows for topographical maps to be created. This method helps to reduce damage to both the surface and the tip. Monitoring the phase lag between the signal that drives the oscillation and the cantilever oscillation output signal produces phase imaging. This is sensitive to the material being imaged, as phase lag is caused by friction, elasticity and adhesion properties of the surface.

AFM has been extensively used to image TMD topography and it is very useful for determining layer number in TMD flakes and films.^{127,128}

2.3 Electrical Properties

2.3.1 Carrier Mobility

A very important characteristic of a semiconducting material is its carrier mobility (μ). Carriers refer to electrons, or holes (the absence of an electron). Mobility can be viewed as the ease with which a carrier can traverse the material, when under an applied field. When a electric field (E) is applied across a material, electrons are accelerated to an average velocity, called the drift velocity (v_d). In a vacuum, an applied field will accelerate the electron in the ballistic transport regime. However, in a material, scattering (from ionised impurities, crystal defects or phonons) slows the carrier down to v_d . μ is a material constant which directly relates the movement of carriers to the applied field, as given by equation 2.5.

$$v_d = \mu E \quad (2.5)$$

For ambipolar materials with both electrons and holes contributing, the total conductivity is given by equation 2.6.

$$\sigma = e(n\mu_e + p\mu_h) \quad (2.6)$$

Where e is the elementary charge, n is the number density of electrons, μ_e is the electron mobility, p is the number density of holes and μ_h is the hole mobility.

Since μ is directly related to v_d , which is heavily dependant on scattering events, controlling the different types of scattering events is a way of investigating μ in a material. Many measurements use a cryostat in order to measure μ as a function of temperature.

The Hall effect is commonly used to measure carrier μ within a material. In 1879, Edwin H. Hall discovered that a small transverse voltage appeared across a current carrying thin metal strip when in an applied magnetic field. The polarity of this voltage proved that electrons were physically moving in an electric current. This was the first direct measurement of carrier density.

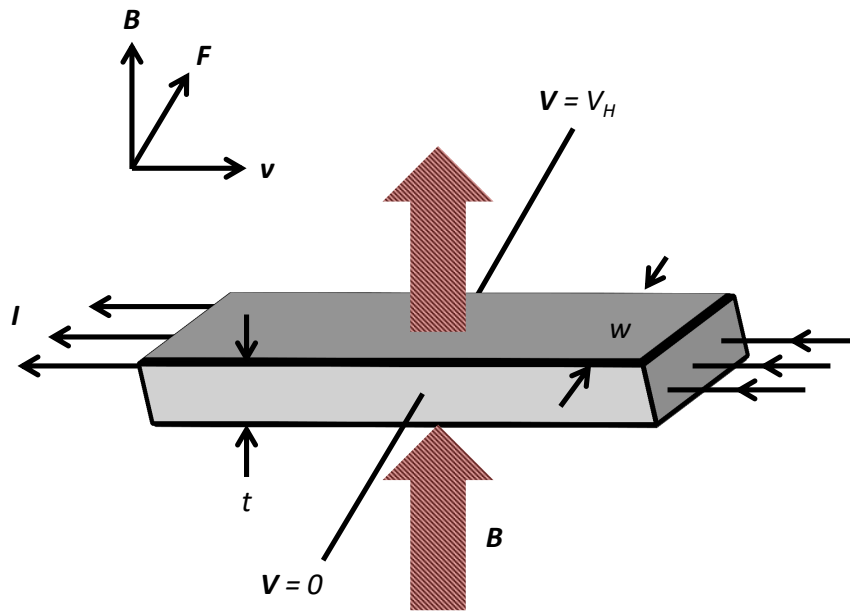


Fig. 2.14 Schematic of the Lorentz force in a semiconductor

The Lorentz force is the physical principle responsible for the Hall effect. It is a combination of both the electrical and magnetic forces. Fig 2.14 is a simplified diagram of the Hall effect in a material. When a carrier moves along an electric field direction (x-axis), and a perpendicular magnetic field is applied (z-axis), it feels a Lorentz force normal to the direction of both fields (y-axis). This is expressed in equation 2.7, where $\mathbf{F}$ is the Lorentz force, q is the elementary charge, $\mathbf{v}$ is the velocity due to the electric field ($\mathbf{E}$) and $\mathbf{B}$ is the magnetic field. All quantities in bold are vector quantities, and $\times$ is the vector cross product.

The Lorentz force deflects the carriers, causing a potential drop between the two sides, this is the Hall voltage (V_H). The magnitude of V_H is given by equation 2.8, where t is the thickness of the sample, and R_H is the Hall coefficient, defined in equation 2.9.

$$\mathbf{F} = q[\mathbf{E} + (\mathbf{v} \times \mathbf{B})] \quad (2.7)$$

$$V_H = \frac{R_H \mathbf{I} \mathbf{B}}{t} \quad (2.8)$$

$$R_H = \frac{r}{q(p - n)} \quad (2.9)$$

The Hall coefficient is a useful quantity for calculating μ_H . r is a correction factor, called the Hall scattering factor. It is dependent on the scattering mechanisms present, and it is usually between 1 and 2. q is the elementary charge, p and n are the density of positive and negative carriers respectively. Rearrangement of equation 2.8 shows that the Hall coefficient can be calculated from V_H , since $\mathbf{I}$, $\mathbf{B}$, and t are known quantities.

μ_H is related to the Hall coefficient and resistivity (ρ) by equation 2.10.

$$\mu_H = \frac{|R_H|}{\rho} \quad (2.10)$$

Therefore, a Hall measurement allows calculation of the Hall coefficient, and in conjunction with the resistivity, the Hall mobility is calculated. Fortunately, the resistivity can be measured in the same experimental setup as used for the Hall voltage. There are two commonly used experimental geometries for determination of μ_H in thin films, the Hall bar and the van der Pauw geometry.

Van der Pauw Method

The convenient van der Pauw technique is widely used in the semiconductor industry to determine both μ_H and the sheet resistivity. It is applicable for thin films that are of a uniform thickness, flat, homogeneous, simply connected (no holes or isolated voids) and isotropic. In 1958, L. J. van der Pauw solved the general problem of the potential in a thin conducting layer.¹²⁹ This method works for arbitrarily shaped samples, however measurement is simplified if approximately square samples are used. Four very small Ohmic contacts (diameter D) are placed on the perimeter, usually in the 4 corners. The contacts must be as small as possible, and at least an order of magnitude smaller than the lateral dimensions (L), as relative errors introduced by non zero contacts are on the order of D/L .

As demonstrated in fig. 2.15 the van der Pauw measurement configuration numbers the contacts in ascending order in the anti-clockwise direction, when viewed from above, with the B field pointing toward the observer. Firstly, the sheet resistance (R_S) is determined. This requires two characteristic resistances, for square samples, they can be considered horizontal and vertical, R_h and R_v respectively. Measuring each resistance is accomplished by flowing a current along one edge, and measuring the voltage across the opposite edge. Using fig. 2.15(a) as an example of measuring R_v : current flows into contact 1 from 2 (I_{12}), and voltage is measured between contacts 4 and 3 (V_{43}). Fig. 2.15(b) shows the setup for measuring R_h . These two resistances are used to calculate R_S , they are related by the van der Pauw formula (2.11).

$$\exp\left(-\pi\frac{R_v}{R_S}\right) + \exp\left(-\pi\frac{R_h}{R_S}\right) = 1 \quad (2.11)$$

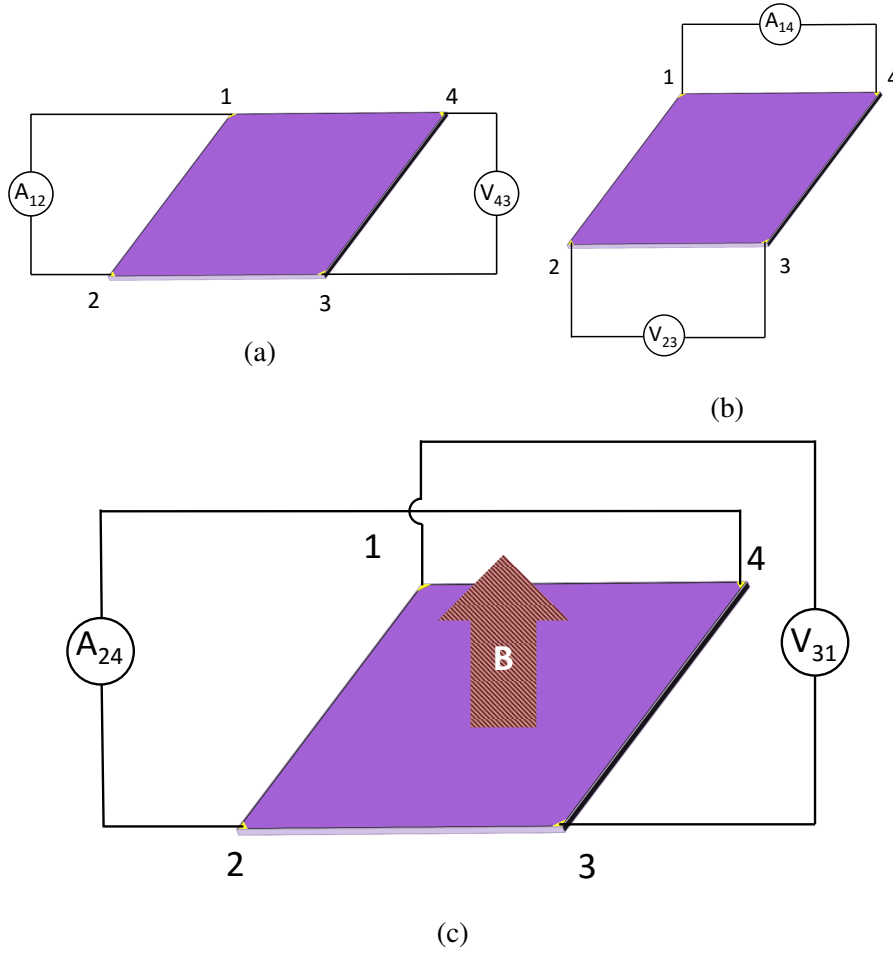


Fig. 2.15 Van der Pauw setup for determining (a) R_v , (b) R_h and (c) V_{Hall} .

Measuring all four edges and averaging both of the horizontal and vertical components through the reciprocity theorem improves measurement accuracy. Furthermore, reversing the polarity of each measurement cancels out any offset voltages due to thermoelectric effects. This is mathematically expressed by equations 2.12 and 2.13.

$$R_v = \frac{R_{12,43} + R_{43,12} + R_{21,34} + R_{34,21}}{4} \quad (2.12)$$

$$R_h = \frac{R_{14,23} + R_{23,14} + R_{41,32} + R_{32,41}}{4} \quad (2.13)$$

In general, the van der Pauw formula cannot be rearranged to give R_S in terms of known functions. Solving it numerically is typically done by an iterative process which falls outside the scope of this dissertation. However, an exception occurs when $R_v = R_h = R$, in this special case R_S is given by equation 2.14, and it holds for a perfectly square sample with small Ohmic contacts. Sheet resistance is converted into resistivity by multiplying by the thickness of the film (equation 2.15).

$$R_S = \frac{\pi R}{\ln 2} \quad (2.14)$$

$$\rho = R_S t \quad (2.15)$$

Once the resistivity of the sample is determined, the Hall voltage is measured. As illustrated in fig. 2.15(c), a constant $\mathbf{B}$ field is applied, perpendicular to the sample, and a constant current is applied to two diagonal corners (I_{24}). The Hall voltage is measured across the remaining diagonal (V_{31}). Both sets of diagonals are measured, with reversal of the polarity of the driving current and the $\mathbf{B}$ field, giving 8 total V_{Hall} measurements. These measurements are redundant in that the Hall voltage in both sets of diagonals should be the same. Any difference between them is a measure of error introduced, typically geometrical errors, error from non-zero contact size, non Ohmic contact, or thin film inhomogeneity. The

Hall voltages are averaged to remove offset voltages, and used to calculate the sheet carrier density (n_S), given by equation 2.16.

$$n_S = \frac{\mathbf{IB}}{q|V_H|} \quad (2.16)$$

Once n_S and R_S are known, they are used to calculate the μ_H , from equation 2.17.

$$\mu_H = \frac{1}{qn_S R_S} \quad (2.17)$$

Hall bar geometry

Long and narrow hall bars can be created in a range of geometries. The following illustration is of an 8-contact Hall bar. This geometry is more complex, however it allows for sample homogeneity to be confirmed, and it limits some geometrical errors by measuring V_H in the centre of the sample. Fig 2.16 is a schematic of a Hall bar, with contacts numbered. Contacts 1-4 are used for voltage measurement, while 7 and 8 are simply to maintain geometrical symmetry. The magnetic field is normal to the plane of the sample, and a current is passed along the main axis between contacts 5 and 6.

Firstly, the resistivity is measured. This is done in two regions, a and b , to ensure that the sample is homogeneous. The voltage difference between contacts 1 and 4 is measured, while current is passed through contacts 5 and 6. ρ_a is then calculated using equation 2.18. The same measurement is then performed between contacts 2 and 3, giving ρ_b (equation 2.19).

$$\rho_a = \frac{V_{14}}{I_{56}} \frac{w(cm)t(cm)}{b(cm)} \quad (2.18)$$

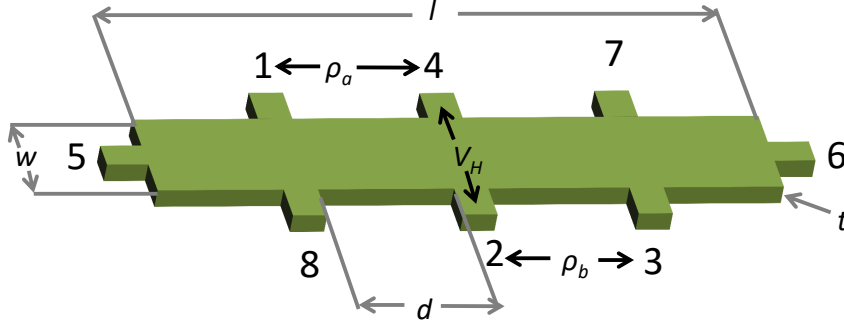


Fig. 2.16 Schematic of a 8 channel Hall bar.

$$\rho_b = \frac{V_{23}}{I_{56}} \frac{w(cm)t(cm)}{b(cm)} \quad (2.19)$$

Provided ρ_a and ρ_b differ by no more than $\pm 10\%$, the two are averaged.

In the presence of an applied magnetic field, the Lorentz force causes a Hall voltage between contacts 2 and 4, i.e $V_H = V_{24}$. The Hall coefficient is calculated by equation 2.20 .

$$R_H = \frac{V_{24}}{I_{56}} \frac{t}{B} \quad (2.20)$$

Finally, the resistivity and Hall coefficient are used to calculate the Hall mobility using the relation outlined by equation 2.10. In practice, the $\mathbf{B}$ field is reversed, as is the direction of current for each measurement, as this reduces the error introduced by offset and thermoelectric voltages, respectively. Hall bar geometries are more complex than van der Pauw geometries, they require a minimum of 6 contacts, and the accuracy of the resistivity measurements is sensitive to the geometry of the device.

Field effect measurement

A FET is a device which modulates current flow *via* an applied electric field. Traditionally, metal-oxide-semiconductor FETs (MOSFETs) have been the core of CMOS technology. A schematic diagram of an unbiased n-MOSFET in its off state is shown in fig 2.17(a). Source and drain are composed of highly doped regions within the doped Si substrate. In the off state, a depletion region exists between the source and drain, effectively limiting current flow between source and drain. Switching the device on is achieved by applying a gate voltage, the applied field causes the formation of an inversion layer, and thus a conducting channel is formed (fig. 2.17(b)).

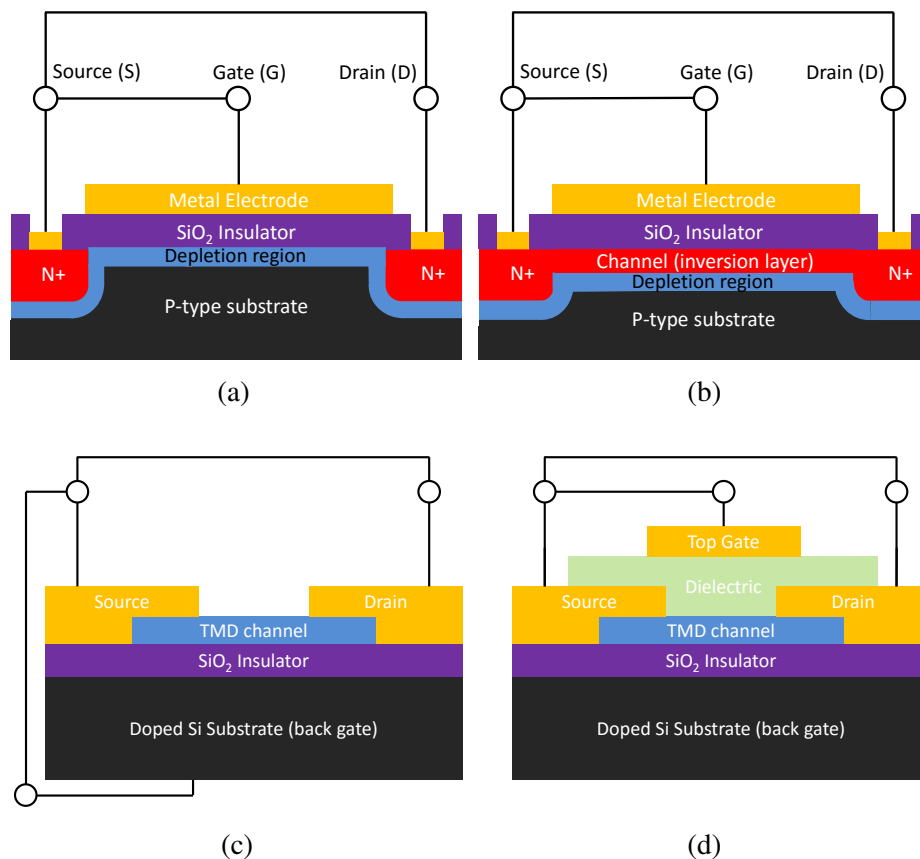


Fig. 2.17 Schematic diagrams of a n-MOSFET in the (a) off state and (b) on state. Schematics of a 2D TMD TFT (c) back gated and (d) encapsulated and top gated.

Thin Film Transistors (TFTs) utilising 2D TMDs as the channel material have the same operating principle, however the architecture is different. There are three active components, a semiconducting TMD channel, metal contacts, and a dielectric layer separating the channel from the gate electrode. The substrates typically used are heavily doped Si, capped with an oxide layer (typically 300 nm) as a dielectric. The TMD is added, forming the channel, and the source and drain electrode are deposited directly on top. The gate is either from the heavily doped silicon substrate when back gating (2.17(c)) or is deposited on top of a dielectric layer if encapsulation and dielectric engineering are used (2.17(d)). Applying a gate voltage injects charge carriers into the TMD, shifting the Fermi level into the conduction band, and switching the device on.

The output characteristics of FET devices are commonly analysed by the use of transfer plots. A transfer curve is a plot of the current between source and drain, as a function of gate voltage applied, at a set drive voltage between source and drain. A representative transfer curve is presented in fig. 2.18. The important information is the slope of the linear region.

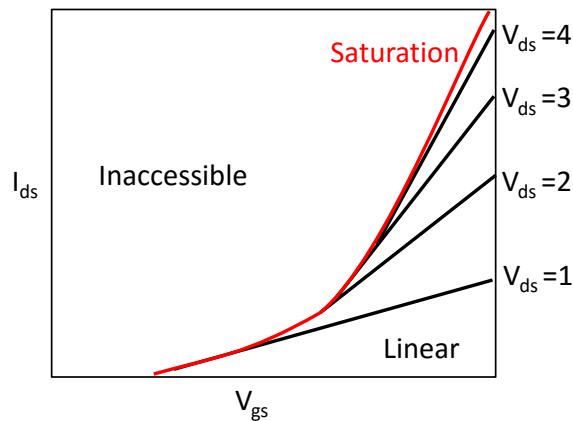


Fig. 2.18 Schematic transfer plot.

An alternative determination of mobility is through the use of a FET. There are two methods of determining μ_{FE} , saturation mode or linear region measurements. This work has used measurements in the linear region, using the gradual channel approximation. Under these conditions, for a back gated MOSFET, μ_{FE} can be estimated by equation 2.21,

$$\mu_{FE} = \frac{dI_{ds}}{dV_{gs}} \frac{1}{C_{ox}} \frac{L}{W} \frac{1}{V_{ds}} \quad (2.21)$$

Where dI_{ds}/dV_{dg} is the slope of the linear region of the transfer curve, C_{ox} is the capacitance of the gate oxide, W and L is the width and length of the channel respectively, and V_{ds} is the source-drain voltage.

An alternative route toward gating the TMD devices is through the formation of an electrical double layer (EDL) suspended in a block co-polymer gel. These EDLs are able to apply very large electric fields, and therefore induce charge carriers much more effectively than solid dielectrics.¹³⁰ The block co-polymer gel is spun on, and encapsulates the device in the same manner as a dielectric top gated device. in this case, the equation for μ_{FE} changes to:

$$\mu_{FE} = \frac{dI_{ds}}{dV_{gs}} \frac{1}{C_{IL}} \frac{L}{W} \frac{1}{V_{ds}} \quad (2.22)$$

The difference is simply that the capacitance of the SiO_2 is replaced by that of the ionic liquid.

2.3.2 TMD Electronic Properties-Sulfides

There is a sizeable difference between the theoretically-predicted electrical properties of TMDs and the electrical results reported to date, and another difference between those idealised devices fabricated by micromechanical exfoliation, and

those produced in a scalable, industrially-relevant manner. Using 2D MoS₂ as an example, the room temperature (RT) mobility is limited by phonon scattering and is predicted to be $410 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.¹³¹ The highest reported RT (μ_{FE}) from a device fabricated using a micromechanically-exfoliated flake is $200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.²⁸ For devices with MoS₂ films fabricated in a scalable manner μ_{FE} ranges from $<0.04 - 20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.^{100,104,108,132,133} The sizeable difference between the theoretical limits and the experimentally-realised values is largely due to extrinsic effects such as metal contacts, surface adsorption, dielectric interfaces and surface defects.^{38,134} Due to the 2D nature of these materials, electrons are very susceptible to scattering at impurities, both within in the TMD channels, and at the dielectric interface. When designing devices utilising 2D semiconductors as the channel material, there are a host of issues to be addressed; however, two main considerations with regard to optimising performance are the quality of the semiconductor, and the quality of the electrical contact between the semiconductor and the metal contacts.¹³⁵ In order to realise the potential of TMDs in electronic devices, it is necessary that the role of surfaces and interfaces becomes better understood, so that modifying them can lead to a route to achieve desired performance.

It is possible that the transport characteristics of 2D TMDs are more affected by interface effects, rather than the intrinsic properties of the material.^{38,51} 2D semiconductors can be contacted in one of two ways - through the top or through the edge of the TMD. Top contacts on pristine TMDs are limited by the existence of a van der Waals gap between the TMD and the bulk metal contact, due to the lack of dangling bonds.¹³⁶ This gap effectively acts as an additional tunnel barrier, reducing the charge injection from the metal contacts, and increasing the contact resistivity. On the other hand, edge contacts involve a greater degree of orbital

overlap (hybridisation) and can significantly lower the contact resistivity.¹³⁷ Gong *et al.*¹³⁸ have determined that at any metal – MoS₂ interface the Fermi level is partially pinned unavoidably by two separate interface behaviours. Firstly, because charge redistribution causes an interface dipole to form and this modifies the metal work function. Secondly, gap states (mainly of Mo *d*-orbital character) are produced as the intra-layer Mo – S bonding is weakened due to the interface metal – S interaction. Through the use of high work function MoO₂ contacts, Chuang *et al.* have demonstrated *p*-type MoS₂ transistors.¹³⁹ Conversely, Das *et al.* have produced devices displaying excellent μ_{FE} values of 184 cm²V⁻¹s⁻¹ by utilising low work function scandium contacts, and an enhancement up to 700 cm²V⁻¹s⁻¹ with dielectric engineering.¹⁴⁰

The carrier density (or Fermi energy) modulates which conduction mechanism is dominant. For unbiased MoS₂, the off state is insulating, with the Fermi level (E_F) within the bandgap. Doping, or positive gate bias, shifts E_F into the conduction band edge where thermionic emission contributes to current flow. Conduction is strongly affected by tail states and localised charge trapping due to impurities and defects.¹⁴¹ Increasing the gate bias leads to a metal insulator transition (MIT) where band transport becomes dominant.¹⁴² The doping level required for the MIT for single layer MoS₂ had been identified as 3.6×10^{13} cm⁻².¹⁴³ At sufficiently large carrier concentration and low temperature, MoS₂ becomes superconducting.¹⁴⁴

The quality of the 2D semiconductor channel is another very important factor in the device performance. Defects and grain boundaries in the TMD can lead to trap states and Fermi-level pinning in the channel, which significantly degrades the electrical properties. Interface traps are electrically active defects and act as generation/recombination centres and contribute to leakage current, low-frequency

noise, reduced mobility, drain current and transconductance.¹⁴⁵ Qui *et al.* have shown that sulfur vacancies, which are one example of interface traps, cause localised donor states inside the bandgap of MoS₂.¹⁴⁶ Yu *et al.* have shown that repairing these defects with (3-mercaptopropyl)trimethoxysilane leads to an enhanced μ_{FE} of 81 cm²V⁻¹s⁻¹.¹³⁴ McDonnell *et al.* have shown that intrinsic defects dominate at the TMD/metal interface, and a low Schottky barrier is present - independent of metal contact work function.¹⁴⁷ Gate stack engineering by inclusion of Poly(methyl methacrylate (PMMA),¹⁴⁸ and of high-*k* materials (HfO₂,^{143,149} Al₂O₃^{140,150} and hexagonal Boron Nitride (h-BN)¹⁵¹) has been shown to dramatically improve the performance of TMD devices, this is because scattering from Coulombic impurities is strongly dampened.¹⁵²

Using TFT devices fabricated from micromechanically exfoliated MoS₂ flakes, Lin *et al.* have demonstrated that the inclusion of a polymer electrolyte increases μ_{FE} of mechanically exfoliated MoS₂ from 0.1 cm²V⁻¹s⁻¹ to 150 cm²V⁻¹s⁻¹.¹⁵³ Pu *et al.* fabricated EDL-TFT devices from CVD grown MoS₂, and reported a μ_{FE} of 12.5 cm²V⁻¹s⁻¹ and an on/off current ratio of 10⁵. These devices, once transferred to flexible substrates, showed excellent bendability before electrical degradation.¹³³ Zhang *et al.* demonstrated ambipolar transport with an EDL-TFT using micromechanically exfoliated MoS₂.¹⁵⁴

2.3.3 TMD Electronic Properties-Selenides

Recently, micromechanically exfoliated MoSe₂ layers were used to produce TFT devices which show 2D excitonic control,¹⁵⁵ RT mobility of 150 cm² V⁻¹ s⁻¹,¹⁵⁶ and ambipolar behaviour.¹⁵⁷ Chamlagain *et al.* fabricated MoSe₂ TFTs on SiO₂ which exhibited a RT mobility of 50 cm² V⁻¹ s⁻¹, this increased to 150 cm² V⁻¹ s⁻¹ when parylene-C substrates were incorporated. They attributed the

difference to the surface polar optical phonon scattering originating from the SiO₂ substrate. Dual gated TFT devices from micromechanically exfoliated WSe₂ flakes encapsulated in h-BN have displayed *p*-type behaviour, a RT μ_{FE} of 140 cm² V⁻¹ s⁻¹ and an on/off ratio of 10⁷.¹⁵⁸ Unencapsulated WSe₂ flakes have exhibited a RT μ_{FE} value of 350 cm² V⁻¹ s⁻¹.¹⁵⁹ However, while producing very high-quality 2D crystals, this production method is not scalable, as discussed in section 2.1.1. Roy *et al.* have used MBE to produce thin films of MoSe₂ on sapphire, producing material which exhibits insulating behaviour, well fitted by a 2D variable range hopping model.¹⁶⁰

There are a limited number of methods that have successfully been employed in the scalable production of 2D selenides. Some recent reports have focused on the CVD synthesis of MoSe₂. Such growth has produced monolayer crystals¹⁶¹ with a bandgap of 1.5 eV⁸⁴ mobilities of 121 cm² V⁻¹ s⁻¹¹⁶² and promising photoresponse.¹⁶³ Liu *et al.* have investigated TFT devices produced from CVD grown WSe₂.¹⁶⁴ Such devices typically display mobilities of ≈ 0.2 cm² V⁻¹ s⁻¹, which were drastically improved to $\approx 30\text{-}40$ cm² V⁻¹ s⁻¹ by heating in ambient. This improved mobility was attributed to the formation of in-plane heterojunctions of WSe₂ and WO_{x-3}.

2.3.4 Sensors

Sensors based on chemical resistor (Chemiresistor) or chemical field-effect transistor (ChemFET) architectures display a difference in their conductivities when analytes are adsorbed on the surface of the active channel. The magnitude of the modulation is dependant on the electron withdrawing or donating ability of the analyte. Not all materials are suitable, difficulties include lack of selectivity and low sensitivity to analytes (due to low affinity or binding energy). Functionalisa-

tion has been shown to enhance selectivity and increase sensitivity.¹⁶⁵ 2D TMDs have varying affinities for different analytes, for example, MoS₂ is very sensitive to NO₂ and NH₃.^{46,166} It is possible that sensors built from an array of different TMDs could exhibit enhanced selectivity.

A major reason why 2D TMDs are suitable as electronic sensors is because it is the change in resistance that is being measured, the initial reading is used as a baseline. Good contact between the channel and electrodes is desired, however charge injection concerns are not crucial to device performance. Sensor measurements are performed at room temperature by biasing the device at a constant voltage, and measuring the current change upon exposure to different concentrations of gaseous analytes. The sensor performance can be evaluated in terms of sensor response (S) and response time. Sensor responses for gas injections define the sensor sensitivity. S is defined by percentile resistance change, given by equation 2.23.

$$S = \frac{\Delta R}{R_0} = \frac{R_s - R_0}{R_0} * 100\% \quad (2.23)$$

where R_0 is the initial resistance of the sensor and R_s is the resistance at gas introduction.

Chapter 3

Experimental Methods

3.1 Metal Deposition

TAC involves converting a transition metal into a semiconductor. Thin metal films have been deposited by Ar ion sputtering,¹⁰¹ electron beam deposition,^{100,105,112,167} thermal deposition (of oxides),^{97,98} magnetron sputtering deposition,^{106,109} and pulsed laser deposition.¹⁶⁸ The results presented in this work utilise two different methods to deposit the metal prior to TAC, Ar ion sputtering and electron beam evaporation. These deposition techniques were also used to deposit electrodes after TAC.

Sputtering

Sputtering is a process of depositing thin films. It occurs under high vacuum conditions, at pressures around 6×10^{-5} Torr. As can be seen in fig. 3.1, ion guns cause Ar^+ ions to bombard a target, ejecting material. The ejected material deposits onto a substrate. A quartz crystal microbalance (QCM) is used to monitor the thickness of the deposited film, as well as the deposition rate. The stage upon

which the substrate is mounted rotates and rocks, this movement improves the homogeneity of the sputtered films.

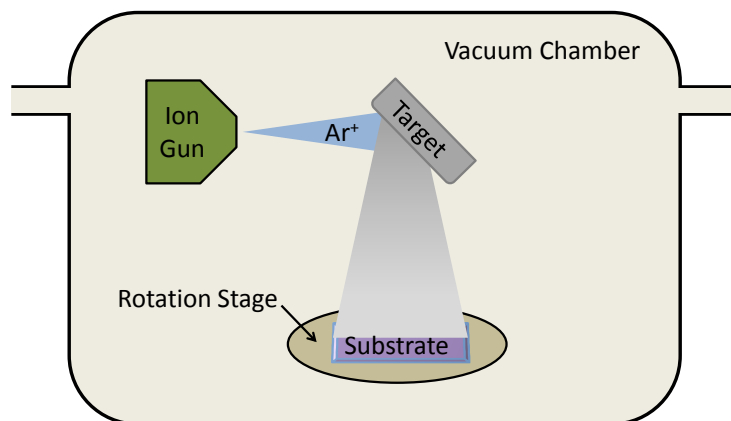


Fig. 3.1 Schematic of Ar ion sputtering metal deposition process.

The sputter coater used in this work was a Gatan Precision Etching Coating System (PECS). Metal targets were from MaTecK GmbH, 99.9% purity.

Electron Beam Evaporation

Electron beam evaporation is a physical vapour deposition (PVD) technique which utilises an intense electron beam to vaporise the source metal, under high vacuum conditions (typically 10^{-6} Torr), allowing it to coat the substrate. As depicted in fig. 3.2, the electron source generates an intense electron beam and precisely directs it onto the evaporant material. Since the heating is directly from the kinetic energy of the electrons, evaporation of high melting-point materials is accessible. The samples are loaded onto a rotating stage above the crucible, within the mean free path of the ejected material, ensuring line of sight arrival to the substrate, which is advantageous for masking. Several crucibles can be used in the vacuum chamber, allowing for multi-layer depositions.

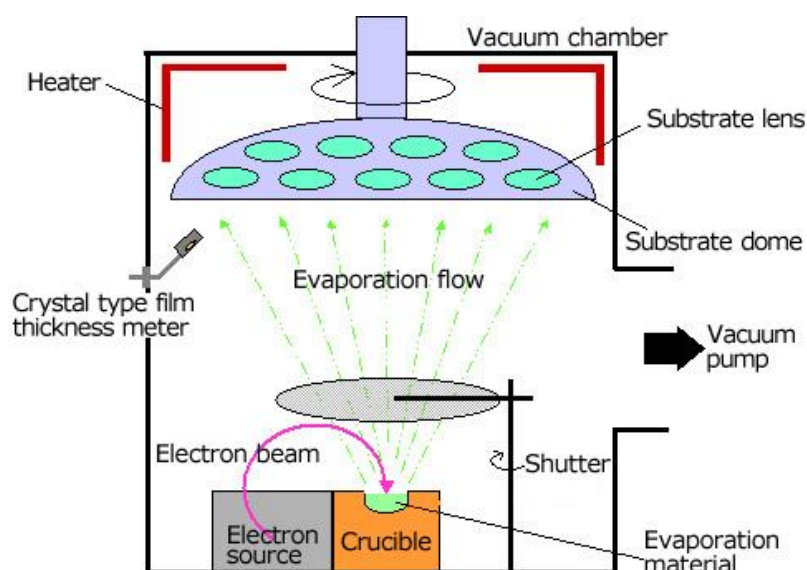


Fig. 3.2 Schematic of e-beam evaporation. Adapted from Jeol Ltd.¹⁶⁹

Electron beam deposition was performed in a Temescal FC-2000 evaporation system. Vacuum of 10^{-6} Torr is achieved via a CT-400 cryopump. The working distance from source to substrate is ≈ 80 cm. A six pocket evaporation source was used. Deposition thickness was measured using a QCM, and the deposition rate was $\approx 1 \text{ \AA s}^{-1}$

3.2 Thin Film Characterisation

Intensive characterisation of the thin films was very important because it allowed for subsequent optimisation of the growth processes. Raman, XPS, SE, AFM, TEM and SEM were all employed to characterise the films. Electrical devices were fabricated, which were characterised with needle probe stations, source meter units (SMUs), a physical property measurement system (PPMS), an alternating current (AC) Hall measurement system and a custom-built gas sensing chamber.

3.2.1 X-ray Photoelectron Spectroscopy

XPS measurements were performed under ultra-high vacuum conditions (base pressure of 2×10^{-10} mbar) with a VG Scientific ESCA^{lab} MKII system. A CLAM2 analyser and PSP twin anode, unmonochromatised Al K α x-ray source (1486.6 eV, operated at 12 kV and 12 mA) were used with 2 mm slits. For survey scans a pass energy of 50 eV was used, while higher resolution core levels were scanned with 20 eV. The spectral resolution under these conditions was 1.25 eV (FWHM on Ag 3d $_{5/2}$).

Peak fitting of high resolution core level spectra was performed using CasaXPS software. Spectra were charge compensated to the adventitious carbon peak at 284.6 eV. A Shirley background subtraction was performed, followed by the fitting of transition metal and chalcogen doublet peaks with mixed Gaussian and Lorentzian character.

3.2.2 Raman Spectroscopy

Raman measurements were performed using a Witec Alpha 300R confocal Raman spectroscopy microscope, utilising a frequency doubled Nd:YAG 532nm laser. The spectrometer utilised a 1800 lines/mm diffraction grating for Raman acquisitions, allowing for high spectral resolution. A laser power of less than 0.5 mW was used for measurements, in order to avoid sample damage. Raman spectra shown in the text were averaged from 10-20 spots in a line, each spot is typically 20 μ m apart, in order to demonstrate the homogeneous nature of the material produced from TAC. The acquisition time was chosen to show a clear signal, it was typically 10-15 ms. Scanning Raman maps were obtained by the use of piezoelectric motors stepping the sample stage. Four separate spectra were

recorded per μm in the x and y direction, allowing for a lateral resolution of 250 nm, which is close to the spot size of the laser when using a 100X objective (numerical aperture 0.95). A $20\ \mu\text{m}^2$ scanning Raman map contains 6400 discrete spectra. PL measurements were taken using the same system with a 600 lines/mm grating in the 570-710 nm (2.18-1.75 eV) range.

3.2.3 Charged Particle Microscopy

Scanning Electron Microscopy

A Zeiss Ultra field emission SEM was used to image samples. Low accelerating voltages (1-5kV) were applied. A variety of detectors were employed, including secondary electron, energy selective backscattered and in-lens. Imaging specifics are noted alongside the relevant SEM images.

Helium Ion Microscopy

A Zeiss Orion Plus HIM was used. Imaging parameters included a working distance of 8.6 mm, line averaging of 36, 30 kV accelerating voltage, 1 μs dwell time and a Blanker current of 0.6 pA.

Transmission Electron Microscopy

HRTEM bright field images were obtained using a FEI Titan 80-300 kV TEM. Top down TEM images were prepared by etching PMMA supported thin films with 15 M KOH followed by dredging onto lacey carbon grids.

XTEM was performed at Tyndall National Institute, by the group of Paul Hurley. Cross-section samples were obtained by using FEI's Dual Beam Quanta 3D 200i. On top of the MoS_2 three layers of protective material were used, namely electron

beam tetraethyl orthosilicate, electron beam W, and ion beam Pt. Lamellas were thinned and polished at 30 kV 100 pA and 5 kV 48 pA respectively on FEI Dual Beam Helios Nanolab 600i system using a Ga ion beam. Transmission Electron Microscopy (XTEM) imaging was carried out using a JEOL 2100 HRTEM operated at 200 kV in Bright Field mode using a Gatan Double Tilt holder.

3.2.4 Spectroscopic Elipsometry

The SE characterisation of the TMD thin films was conducted using an Alpha SE tool (J. A. Woollam Co., Inc.) operating in the wavelength range of 380–900 nm (1.38–3.26 eV) at an angle of incidence of 70 ° with a beam spot size of 40 mm² and a rotating compensator. SE data were analysed using CompleteEASE 4.72 (J. A. Woollam Co.).

3.2.5 Atomic Force Microscopy

AFM presented in this work was carried out either with an Asylum MFP-3D or a Veeco Dimension 3100 AFM in tapping mode. Unless otherwise noted, Si tips with a tip radius of 50 nm and a resonant frequency of 300 Hz were used.

3.3 Electrical Characterisation

3.3.1 Device Fabrication

Once thin films were synthesised and characterised, it became necessary to create electronic devices in order to elucidate the electrical properties of these 2D semi-conducting materials. One major advantage of TAC over other CVD approaches, is that the metal is deposited via traditional, well established deposition methods,

i.e. sputtering, evaporation, *etc.* and the metal doesn't enter the vapour phase. This means that lithographic techniques can be utilised to pattern the metal on a substrate, and these metal patterns convert to TMD patterns. With a further lithographic step to define metal electrodes, devices could be made, without relying on the random growth processes that distinguish true CVD growth.

Shadow Masks

Selective area deposition of the metal prior to TAC was achieved by using stainless steel shadow masks to impart the desired pattern. A shadow mask is a hardmask, it physically shields the substrate from the incoming metal flux, except where there are exposed areas. Fig. 3.3(a) is a photograph of two shadow masks, the leftmost one defines the channel (circled), and the right one defines the contacts. The corners of the shadow masks contain alignment markers to make aligning the second shadow mask easier.

After TAC of the channel-patterned metal, a second shadow mask is used to pattern metal electrodes on the semiconducting films. A schematic of the entire process is shown in fig. 3.3(b). The bottom right panel in the fig. 3.3(b) is a photograph of such a device. Contacts were formed by sputtering Ti/Au (10/80 nm). The thinner initial titanium layer serves two purposes, it acts as an adhesion layer for the gold, which adheres poorly to SiO₂, and is easily scraped off by electrical probes. Furthermore, the work function (4.3 eV) of titanium closely matches the electron affinity of the MoS₂ film (4.0 eV),¹⁴⁰ thereby limiting the height of the Schottky barrier and lowering contact resistance at the interface. Because of its broad applicability, shadow masking was used for a wide range of devices including FETs, Hall bars, and transfer line measurement (TLM) structures. This facile method requires no solvent processing, or development

steps. It has a very short turn around time, and is a very robust technique. However the minimum feature size is $20\ \mu\text{m}$.

Shadow masks used were designed in house and purchased from Youngjin Astech

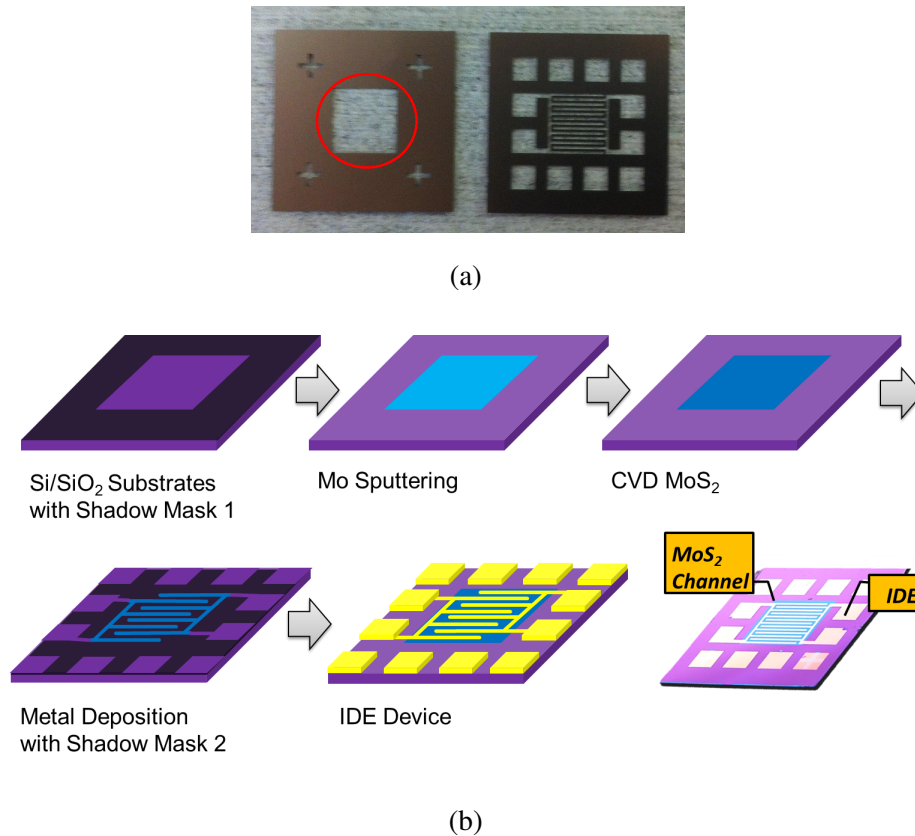


Fig. 3.3 (a) Photographs of shadow masks used in producing gas sensors. (b) Schematic representation of the process steps involved in using shadow masks to produce a TMD device.

Optical Lithography

Optical lithography is a well-established process in the semiconductor industry.

Fig. 3.4 shows a schematic of a positive tone photolithography process. To begin, (a) the substrate (usually silicon) is covered in layer of photosensitive polymer. In

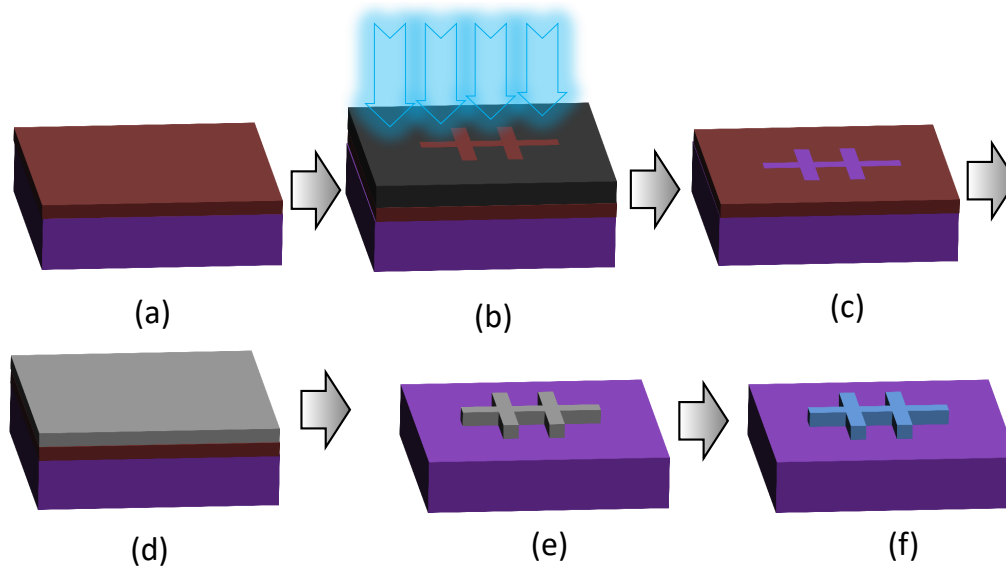


Fig. 3.4 Schematic representation of a positive tone photolithography processing used to pattern TMD materials

(b), selected areas of the photoresist are exposed to UV light through the use of a photomask, which is a metallised piece of glass, with selected regions transparent. The exposed areas are rendered soluble and thus are removed by a tetramethyl ammonium hydroxide (TMAH) based developer (c). In (d) metal is deposited over the entire sample. In (e) acetone is used to remove the photoresist and extraneous metal, revealing the pattern imparted by the UV exposure. Finally, the remaining metal pattern is converted into TMD through the TAC process in (f). The advantage of this method is the small length scales accessible, (resolution of the mask aligner tool is $0.6 \mu\text{m}$) and the corresponding ability to pack many devices onto a single chip. This procedure is well suited to be scaled up to the wafer-scale.

Optical lithography was carried out in the class 100 cleanroom in CRANN. The resist used was S1813 for positive tone lithography, The developer used was

MF 319. An OAI Model 800MBA mask aligner was used for alignment and exposure.

3.3.2 Hall Measurements

A PPMS from Quantum Design Inc. was used to measure Hall bar devices. A **B** field of 10 T was applied and liquid helium was used to cool the sample down to 4 K.

AC Hall measurements were performed using the van der Pauw geometry in Tyndall National Institute. The system used was a Lake Shore HMS 4404 Hall Measurement System. an AC **B** field of ± 1.2 T was applied at a frequency of 100 mHz, measurements were performed at room temperature.

3.3.3 TFT Measurements

EDL-TFT devices were created using shadow masks, they had a channel length of 120 μm and a width of 10 μm . Ti/Au (10/80 nm) contacts were deposited by sputtering.

The devices were gated using Poly(vinylidene fluoride- co -hexafluoropropylene), P(VDF-HFP) as the block copolymer gel and 1-Ethyl- 3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [EMIM][TFSA] as the ionic liquid. The ionic liquid was dried in a vacuum oven for 24 hours at a temperature of 70 °C. A ratio of polymer: ionic liquid: acetone of 1: 5: 15 was used and the gel was applied by spin coating at 2000 RPM for 1 minute.

Electrical measurements were performed in a JANIS probe station at room temperature under vacuum. Characterisation was carried out with Keithley SMUs, a model 2602 and a model 2400 were used. Immediately prior to measurement,

the films were annealed in high vacuum (5×10^{-5} mbar) at 130 °C for 140 minutes in order to remove adsorbates.

Gate sweeps were carried out at a rate of 85 mV/min to minimise transient charging effects due to limited ionic mobility within the gel.

3.3.4 Gas Sensor Measurements

Gas sensor measurements on TAC TMD devices were performed by Dr. Kangho Lee. For gas sensing tests, the TMD thin-film devices were placed on a custom-made chip-carrier and Au wires were electrically connected between binding pads by wire-bonding. All samples were loaded in a custom-built gas sensing chamber with a volume of $\approx 100 \text{ cm}^3$. The chip carrier was contacted to the SMU by gold coated spring-loaded probes. The analyte sources were 200 parts per million (ppm) NH_3 or NO_2 gases, which was balanced with dry N_2 carrying gas. MFCs were used to introduce the diluted analyte at a constant flow rate of 100 sccm, at a pressure of 10 Torr. An integrated heater allowed for annealing prior to measurement. The current change of TMD sensors upon interval gas exposure (2 min) was measured at a constant bias voltage at room temperature using a Keithley 2612A SMU.

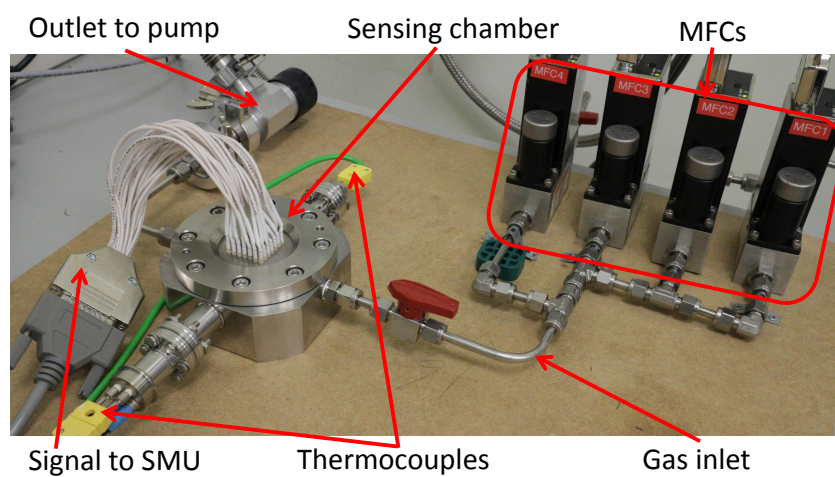


Fig. 3.5 Picture of gas sensing apparatus, with major components labelled.

Chapter 4

Transition Metal Sulfides

The need for 2D semiconductors has been described in Chapter 1, as has the suitability of TMDs for a myriad of applications in future electronics. TAC produces polycrystalline films in a scalable, potentially industrially relevant manner. Firstly, this chapter describes the LPCVD system which was designed and built specifically for TMD synthesis. Secondly the results of extensive characterisation techniques on MoS₂ and WS₂ films and devices are summarised. The work undertaken and presented here explores the question - Is TAC a suitable process for creating TMDs of a quality that is industrially relevant? Can TAC produce material with domains large enough for integration into future electronic applications?

4.1 Sulfurisation Growth System

Producing thin films of semiconducting TMD materials has been achieved by a variety of methods, as discussed in chapter 2. The focus of this research is on the development of TAC as such a method. In order to investigate TAC

methodologies, it was first necessary to design and build a system capable of reliable TMD synthesis. TAC occurs in a hot wall horizontal quartz tube furnace. This was used in the assembly of a LPCVD system. With much assistance from Dr. Toby Hallam, the apparatus was designed and built.

Item MB building kit series 8 modular system was selected to create a purpose built anodised aluminium sliding track and protective frame. Both flat cross sections and construction profiles were utilised, the design was such that it allowed for ease of sliding the furnace along the tube (plastic slide strips were used to facilitate this), but prevented the furnace from moving off axis, which could put undue stress on the tube. At both ends, a rectangular frame was constructed, in order to protect the furnace system from any knocks, add rigidity, and act as a platform from which further upgrades could be attached.

Once the frame was constructed, a split hinge Lindberg Blue tube furnace was installed inside. The reason for designing a sliding track for the furnace was to allow for rapid cooling. The system was designed to have the quartz tube stationary, clamped to laboratory jacks, to allow for precise control of height adjustment, and two independent hot zones freely movable along the length of the tube. This design allows for much more adaptability than a fixed location furnace setup.

A schematic of the vacuum system is depicted in fig. 4.1. The system was designed to address both flexibility and safety concerns. Vacuum is provided by an Edwards rotary vane (RV) 8 vacuum pump, fitted with an oil mist filter at the exhaust. The system was built with Klein flange (KF) 25 vacuum fittings, they are sealed with reusable centred elastomer o-rings, and hand tightened clamps. KF was chosen because disassembly for cleaning or modification is quick and easy. The vacuum is controlled using a right angle throttle valve (Kurt J. Lesker).

A liquid nitrogen cold trap separates the system from the pump, it both cleans the exhaust gases, and prevents oil back-diffusion into the system. Any gaseous vapours condense in the trap, and fall to the bottom. Rough vacuum was measured with a Bourdon vacuum gauge (Leybold 160 40). A baratron pressure transducer (MKS Type 728A) was used to monitor the vacuum level below 10 Torr.

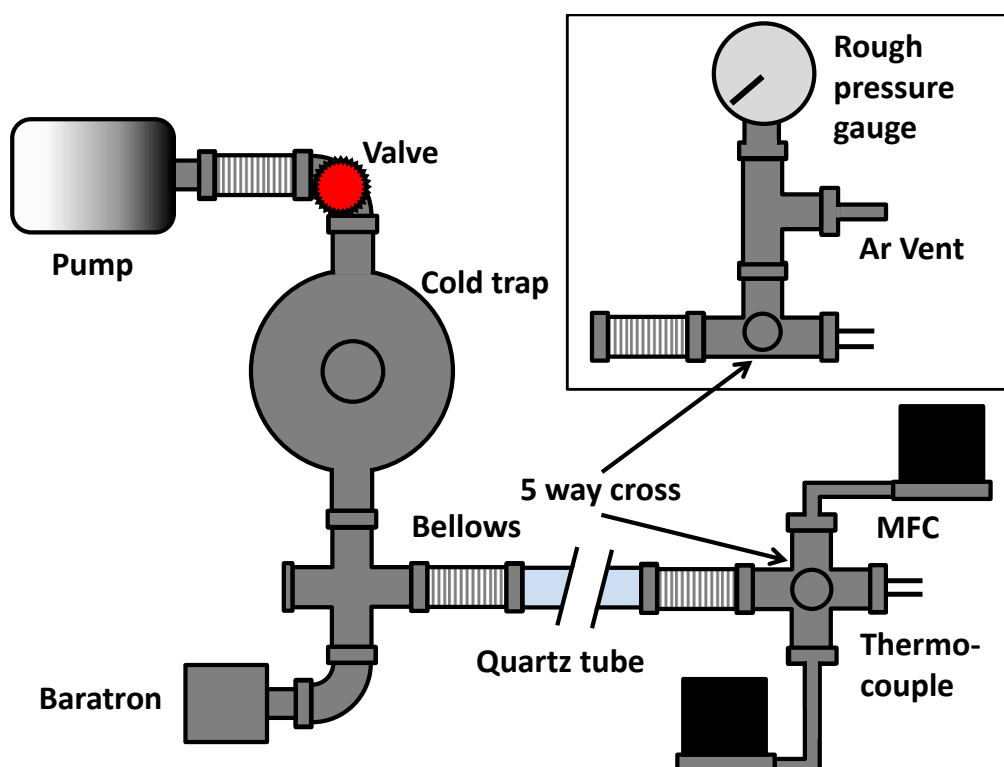


Fig. 4.1 Schematic of vacuum system for sulfurisation furnace.

Process gas delivery was controlled by MFCs and associated controller, (MKS). It was decided to use Ar as an inert gas, and also to include forming gas (10% H₂, 90% Ar) in order to provide a reducing environment. Forming gas has been shown to be beneficial for CVD growth of MoS₂¹¹¹ and WS₂⁸² from oxide precursors, and it was included to increase the type of processes that the system would be capable of. For each gas supply, Swagelok compression fittings were employed. 1/4 inch rigid stainless steel gas lines were ran from the supply

into the MFCs, and from there flexible stainless steel braided hoses went into the vacuum system. Ar supply was from a bottle, plumbed in house, the line for the furnace was teed off after a regulator. Forming gas was housed in a gas cabinet in the laboratory, the line was ran directly from a regulator on the bottle to the furnace. Once all of the necessary components had been incorporated into the tool, commissioning established that the system could reach vacuum at a base pressure of 30 mTorr, with a leak rate of around 2 mTorr per minute.

Other TMD growth furnace setups simply located a sulfur source at the edge of the furnace, at an intermediate temperature lower than at the centre, but high enough to melt sulfur. This crude method doesn't lend itself to a controllable sulfur supply. This was addressed by designing and custom-building a second hot zone utilising radiant heating from halogen bulbs to melt an upstream crucible containing sulfur.

A power supply box - consisting of a Eurotherm 2416 temperature controller, a Eurotherm TE105 thyristor solid state relay, associated circuit breakers, ground wires and fuses was built. Fig. 4.2(a) shows a wiring schematic for the power supply box. Local temperature measurement is achieved with the use of a k-type thermocouple located inside the quartz tube, contacting the sulfur crucible. Halogen lights were mounted radially around the quartz tube on a purpose-built mount. This is depicted in fig. 4.2(b) The assembly was fixed to a laboratory jack for precise height control, and it could be easily moved along the length of the tube. The halogen lights were encased in a sheet metal heat shield, which both protected the user, and stabilised temperature fluctuations. This heating system provided much better temperature control, and one could maintain a local temperature just a couple of degrees above the melting point of sulfur, and thus provide a "gentle" flow of sulfur for the TAC growth, avoiding an uncontrolled

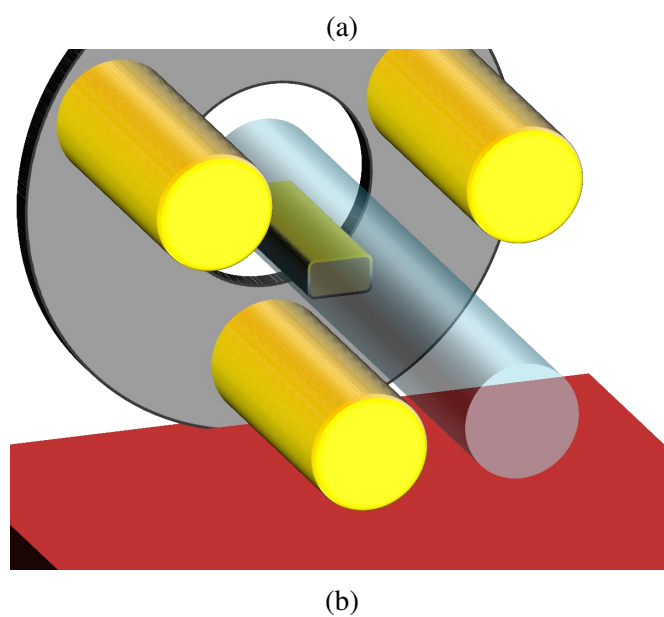
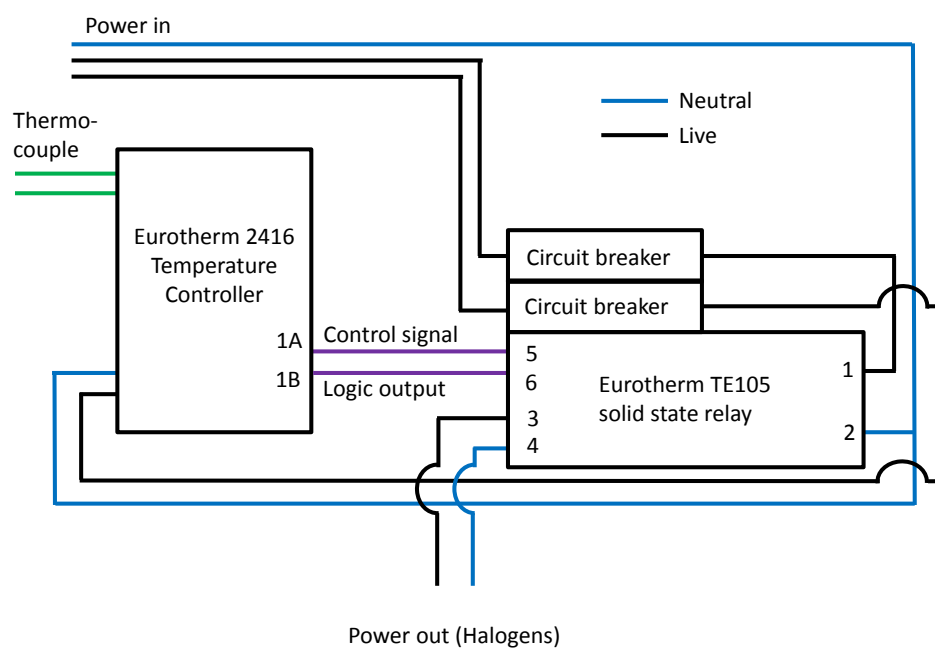


Fig. 4.2 Schematic (a) wiring diagram for halogen power control box and (b) drawing of halogen hot zone assembly.

massive overabundance. It also allowed for control over whether the sulfur was being supplied or not during the various stages of growth, as cooling by a few

degrees solidifies the molten source something not possible when the sulfur supply depends on distance from a single zone synthesis furnace.

Once the system was commissioned, it was possible to react gaseous sulfur with thin films of transition metals, and optimise the TAC processes. Temperature of both the film and the sulfur source, pressure, flow rates, gas selection and process times could all be independently controlled in order to optimise the TAC processes. Figure 4.3 shows the furnace system, with several major components labelled.

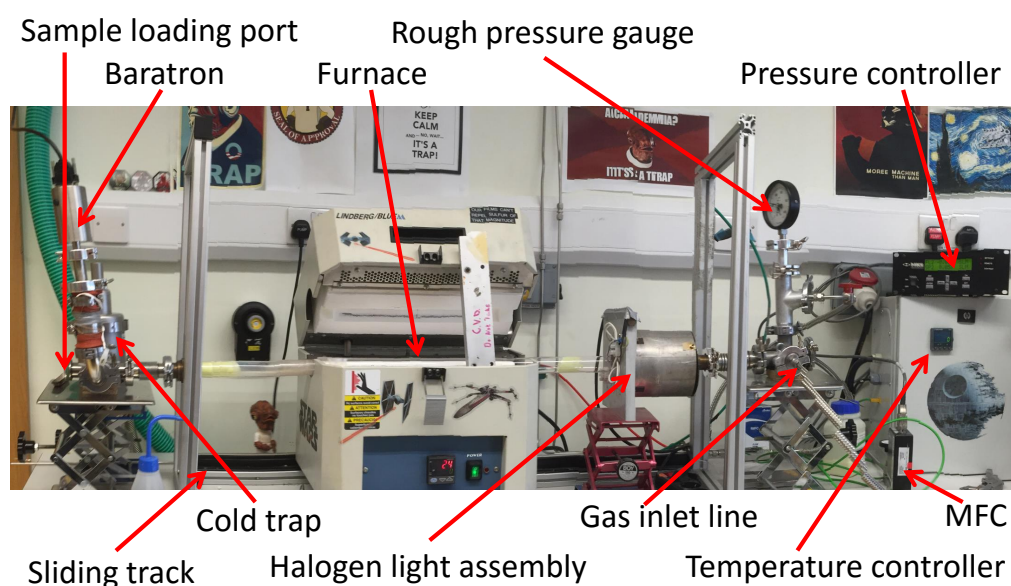


Fig. 4.3 Photograph of sulfurisation LPCVD furnace system, with major components labelled.

A persistent issue had been the failure of the baratron pressure transducer. It is likely that the sulfur rich corrosive environment was causing this failure. The solution was to purchase a heated unit that works at 100 °C, (close to the melting

point of sulfur). The reasoning is that if the working membrane is exposed to any sulfur vapours, then they would preferentially condense on the colder metal walls of the KF fittings.

The system was designed for flexibility, and has proven to be suitable for different processes. As well as TAC of metallised substrates, it is also heavily used for CVD synthesis of TMDs. For this process, a supply of the metal oxide is utilised along with the sulfur, and both reactants enter the vapour phase before condensing onto the growth substrate, forming triangular domains of the desired material.

4.2 Sulfide TAC Film Growth Parameters

The following is a general description of a typical TAC recipe that was developed for MoS₂ and WS₂. One advantage of TAC over CVD is that the thickness of the material can be controlled by the thickness of the deposited metal. Utilising either a Gatan PECS sputter coater or a Temescal FC-2000 e-beam evaporator, thin films of molybdenum or tungsten, of nominal thicknesses between 0.5 and 20 nm, were deposited on target substrates. The typical substrate size is around 1 cm², and the maximum width of substrate that can physically fit in the furnace is 1.9 cm. The metallised substrates are placed in the furnace, heated (~50 °C/min) to the growth temperature under Ar flow (150 sccm, Pressure ~0.7 Torr) and annealed for 5 min. The Ar was replaced with forming gas as a carrier, keeping the pressure constant, and the upstream halogen assembly was used to melt sulfur powder (MaTecK, 99 %) to 113 ± 2 °C for 30 minutes. Sulfur creates a reducing environment, however forming gas was used to ensure that any MoO₃ was reduced to suboxides. Following sulfurisation, the samples were kept at growth temperature for a further

15 minutes, before the forming gas was changed back to Ar and the furnace was cooled to room temperature. A schematic of this process is shown in Fig. 4.4. MoS₂ and WS₂ have proven to be robust materials. Both could be synthesised over a wide variety of temperatures, from 550-1000 °C. Changing other variables such as sulfurisation times from 15-45 minutes, the use of forming gas or only argon as the carrier, adjusting the cooling rate and ensuring that the quartz tube is as clean as possible before growth have only had a minimal effect on the resultant films. The TAC synthesis has repeatedly been successful under all conditions investigated.

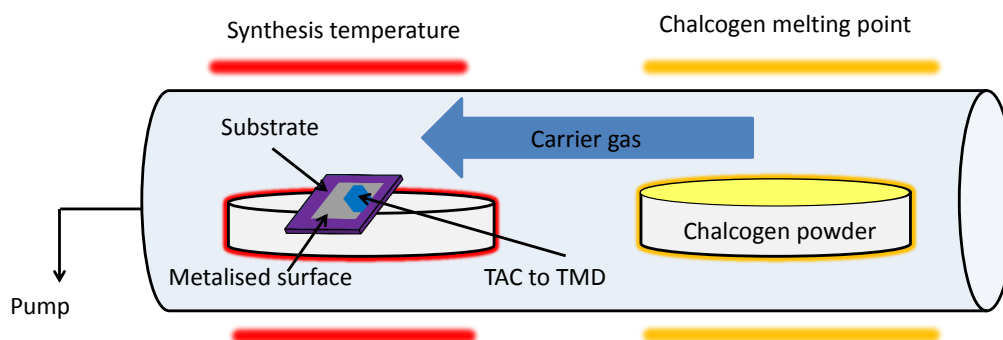


Fig. 4.4 Schematic of a TAC process and furnace setup

Films were grown primarily on SiO₂/Si, however other substrates were also successfully used, *e.g.* fused quartz and sapphire. Photographs of MoS₂ films, on both SiO₂/Si and fused quartz, are shown in Fig. 4.5, the thickness of the pre-deposited metal film is labelled. Films are easily distinguished from one another, even those with deposited metal thicknesses of 0.5 nm and 1 nm, indicating good control over film thickness. The contrast between the TMD and the SiO₂ substrate is due to the phase shift of the interference colour and the materials opacity.¹⁷⁰ This leads to drastic colour changes for nanometer scale thickness variation. Importantly, by visual inspection, and with optical microscopy, the films appear to be homogeneous over the entire substrate area.

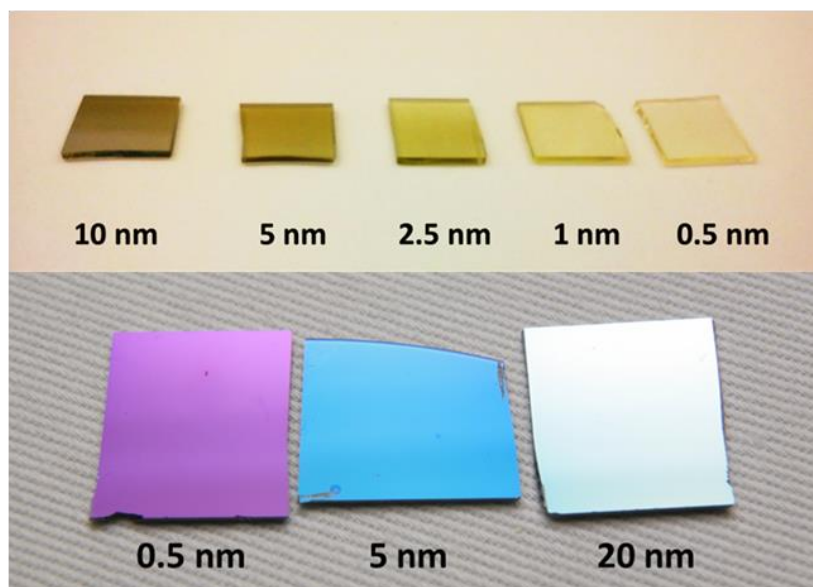


Fig. 4.5 Photographs of films of various thicknesses of MoS₂ on fused quartz (top) and SiO₂/Si (bottom) Substrates are approximately 1 cm²

WS₂ films were synthesised under the same growth conditions as described for MoS₂. In practice, it was common to place thin films of both Mo and W into the furnace at the same time, in order to minimise experimental variation, and compare like with like.

4.3 Optical Characterisation

4.3.1 Raman

Raman spectroscopy has been used to reveal information on composition, thickness, uniformity and polytype for TMD materials. For a discussion of Raman scattering in TMDs, there are extensive reviews such as those of Zhang *et al.*¹¹⁸ and Saito *et al.*¹⁷¹ As discussed in detail in section 2.2.2 The bulk Raman spectrum of MoS₂ has two characteristic modes when probed with a 532 nm excitation

laser. These are an in-plane E_{2g}^1 , and an out-of-plane A_{1g} vibration and are located at Raman shifts of $\approx 383 \text{ cm}^{-1}$ and $\approx 408 \text{ cm}^{-1}$ respectively,^{117,172} and are schematically visualised in fig. 2.10, which also displays the Raman spectrum for several TAC produced TMDs.

The positions of the Raman modes are material dependant, since the masses of the vibrating atoms are unique. For WS_2 the E_{2g}^1 and A_{1g} vibrations are located at Raman shifts of $\approx 355 \text{ cm}^{-1}$ and $\approx 420 \text{ cm}^{-1}$ respectively. A resonant 2^{nd} order LA(M) mode is observed when exciting with a 532 nm laser. This 2LA(M) occurs at $\approx 351 \text{ cm}^{-1}$.¹⁷³

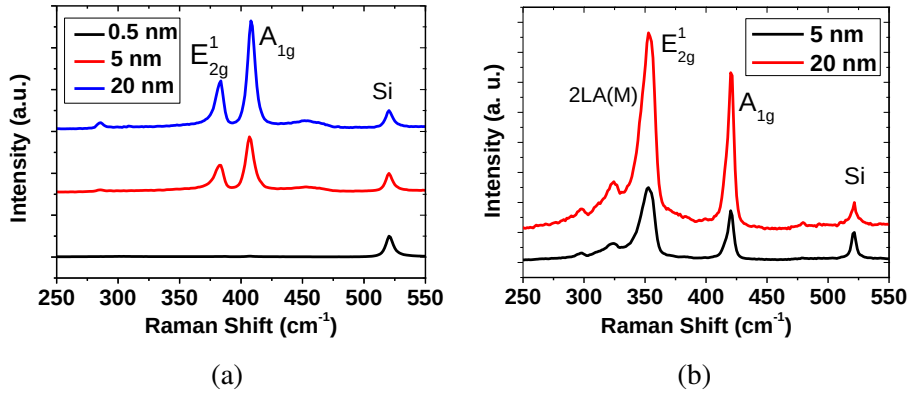


Fig. 4.6 Raman spectra, normalised to the Si mode, for TAC produced (a) MoS_2 and (b) WS_2 of different initial metal thicknesses. The characteristic E_{2g}^1 and A_{1g} modes are labelled.

Fig. 4.6 shows Raman spectra from TAC synthesised MoS_2 and WS_2 of different thicknesses on Si substrates with 300 nm SiO_2 dielectric. Crystalline Si has one feature of note, a strong peak at $\approx 520 \text{ cm}^{-1}$, caused by a triply degenerate transverse optical phonon.¹⁷⁴ Normalising the spectra to the Si peak intensity of the substrate makes it clear that the intensity of both the MoS_2 and WS_2 signals relative to the Si peak of the substrate scales with increasing film thickness. In fact, the substrate intensity completely obscures the MoS_2 signal for the 0.5 nm sample in fig. 4.6(a). For WS_2 (fig. 4.6(b)) the intensity of the TMD peaks are

much less for the 5 nm film as compared to the 20 nm sample. This shows that the thickness of the MoS₂ and WS₂ produced is directly related to the starting metal thickness, as could be expected.

Normalising the spectra to the A_{1g} peak intensity allows for the Raman features of the TMDs to be compared directly as a function of thickness. Normalised spectra of three MoS₂ films of different thicknesses are shown in Fig. 4.7(a). The peak positions both deviate from their bulk values as thickness is decreased toward the monolayer, in good agreement with the evolution of MoS₂ Raman spectra as observed by Li *et al.*¹⁷² In the case of the 5 nm sample the E_{2g}¹ and A_{1g} peaks are seen at 383.6 cm⁻¹ and 408.6 cm⁻¹, a separation of 25 cm⁻¹, which is consistent with bulk values.¹⁷⁵ However, for the 0.5 nm sample the E_{2g}¹ and A_{1g} peaks shift closer to one another, they are manifest at 385.9 cm⁻¹ and 406.3 cm⁻¹, a separation of 20.4 cm⁻¹. As monolayer is approached and fewer layers are present, there is a decrease in the interlayer van der Waals restoring force, causing a red-shift of both the A_{1g} and E_{2g}¹ bands. The observed effect of a blue-shift of the E_{2g}¹ band is due to stacking induced structure changes and long range Coulombic interactions dominating over the decrease in the interlayer van der Waals force.^{46,80} These shifts of the Raman modes indicate that the 0.5 nm sample consists of very few (1-3) layers, whereas the 5 nm sample behaves like bulk MoS₂. The laser, with a spot size of ≈ 300 nm, probes a number of different crystal sites. Different domains with different orientations, and semi-amorphous domain boundaries in between are all contributing to the Raman signal. Even though Raman can determine layer number in exfoliated and CVD produced TMD flakes, it is unsuitable for unambiguous determination of layer number of TAC films, likely because polycrystalline TAC films do not really have an associated precise layer number.

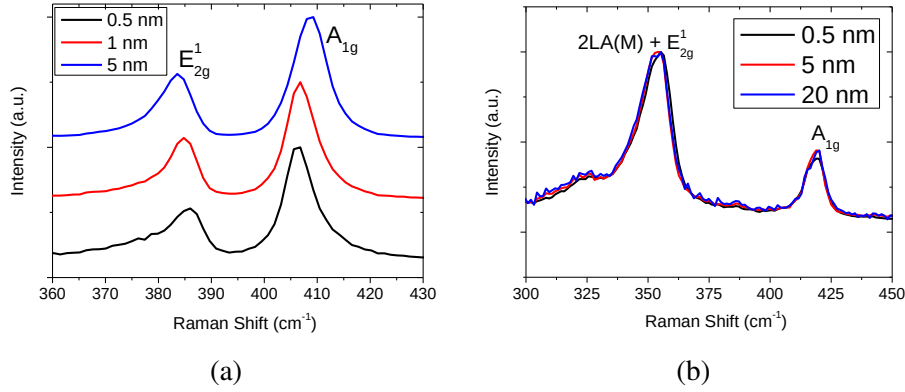


Fig. 4.7 Raman spectra, normalised to the A_{1g} peak intensity for different thicknesses of TAC produced (a) MoS_2 and (b) WS_2 .

A comparison of WS_2 spectra of different thicknesses, normalised to the A_{1g} peak is shown in fig. 4.7(b). Neither the A_{1g} nor the E_{2g}^1 mode are observed to shift any appreciable amount when thickness is varied from 0.5 nm to 20 nm starting metal thickness. Using micromechanically exfoliated flakes, Berkdemir *et al.* have observed no shift from bulk to monolayer for both the E_{2g}^1 and the 2LA(M) modes, however they did observe a shift of $\approx 3 \text{ cm}^{-1}$ for the A_{1g} mode, from 420.1 cm^{-1} (bulk) to 417.2 cm^{-1} (monolayer). Further, they identified a greatly enhanced 2LA(M) signal in monolayer WS_2 . All measured WS_2 samples exhibit bulk like Raman signatures, it is possible that the thinnest WS_2 films are thicker than expected, due to the difficulties associated with depositing a uniform film of tungsten, only 1-2 atomic layers thick. Both the density (19.25 g/cm^3) and melting point ($3422 \text{ }^\circ\text{C}$) of tungsten are considerably higher than that of molybdenum (10.28 g/cm^3 and $2623 \text{ }^\circ\text{C}$). These properties result in more difficult deposition conditions, and a possible underestimation of the metal film thickness.

The intensity ratio between the modes can be used as a qualitative measure of the film crystallinity for MoS_2 ,¹⁰⁰ because one mode corresponds to an in plane vibration, and the other - out-of-plane. Micromechanically exfoliated and bulk

geological MoS₂ flakes have a E_{2g}^1/A_{1g} ratio of 1.3,¹⁷⁵ while TMDs produced through TAC show a ratio of 0.6-0.8. This difference likely occurs because TAC films are composed of randomly orientated nanoscale domains, resulting in a lower relative in-plane E_{2g}^1 contribution. This analysis is not possible for WS₂ because the peak at 355 cm⁻¹ in the WS₂ spectra (4.7(b)) has contributions from both the E_{2g}^1 and the resonant 2LA(M) vibrations.

Recipe optimisation involved identifying key growth parameters and determining their effect on the synthesis. As mentioned previously, the sulfurisation recipes were very robust, and they consistently produced the required material, for both MoS₂ and WS₂. The effect of changing the growth parameters was investigated by Raman spectroscopy, and is shown by fig. 4.8

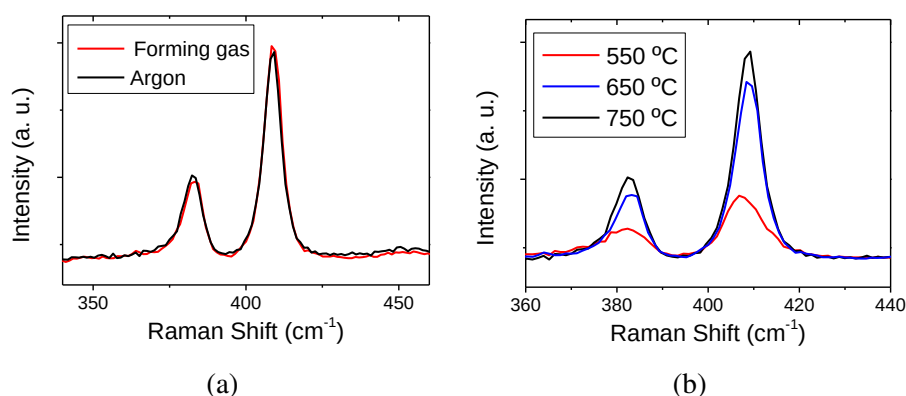


Fig. 4.8 Raman spectra of MoS₂ films showing the effect of (a) forming gas, and (b) growth temperature

Fig. 4.8(a) displays the Raman spectra of MoS₂ synthesised at 750 °C with and without the use of forming gas. The spectra are normalised to the A_{1g} peak. It is clear that the use of forming gas has no appreciable effect on the MoS₂. The sulfur provides a reducing environment, and it is not necessary to add hydrogen to enhance this, when using TAC on metal films. Forming gas is potentially

needed when MoO_3 is used as the chalcogen source. Forming gas had a similarly negligible effect when synthesising WS_2 , (not shown).

The effect of synthesis temperature is displayed in fig. 4.8(b), which shows Raman spectra of selected MoS_2 growths normalised to the Si peak at 520 cm^{-1} . TAC synthesis of MoS_2 was successful for a wide range of temperatures, from $550\text{ }^\circ\text{C}$ to $1100\text{ }^\circ\text{C}$. The spectra for growth temperatures above 650 are very similar, and they all overlap (not shown for clarity). The growth at $550\text{ }^\circ\text{C}$ produced MoS_2 , however the characteristic peaks are lower intensity than those from synthesised at higher temperatures. This means that less MoS_2 was produced, relative to the substrate. Further the higher FWHM infers that the film is more disordered. It is likely that synthesis at $550\text{ }^\circ\text{C}$ leads to incomplete growth.

Scanning Raman spectroscopy was employed to assess the uniformity of a MoS_2 film over a large area. An optical image and Raman maps of a shadow mask patterned sample, with a starting Mo thickness of 10 nm , are shown in Fig. 4.9. These demonstrate good uniformity in the film, with no cracks or tears observed over the scan area, within optical resolution. Additionally, no MoS_2 is observed outside of the patterned region, signifying good control over feature placement when using shadow masks.

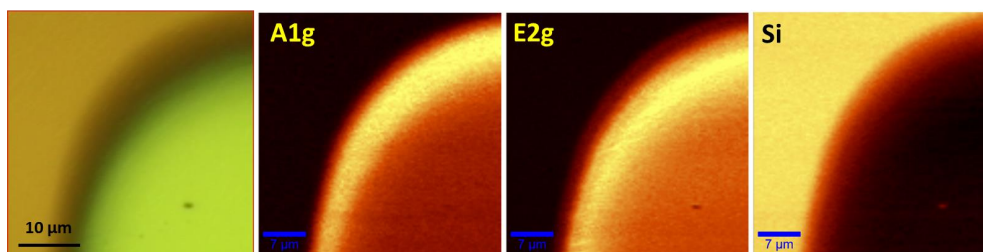


Fig. 4.9 Optical image and scanning Raman maps of the E_{2g}^1 , A_{1g} , and Si modes of a shadow mask patterned film of MoS_2

PL studies offer an alternative route to probing the thickness and electronic properties of MoS₂ films. At the monolayer limit, the spectrum for MoS₂ changes, as explained in section 2.2.2. As the bandgap becomes direct, a strong PL signal is observed at 627 and 677 nm corresponding to the B1 and A1 excitons originating from the *K* point.^{123,176} Fig. 4.10 consists of PL spectra from the same films that were used for the Raman analysis (4.7(a)). In each case, the PL intensity is normalised to the A_{1g} Raman signal. The 5 nm film shows minimal PL, further implying that it constitutes bulk material. MoS₂ synthesised via TAC from 1 nm or less starting metal thickness exhibits a direct exciton PL signature characteristic of few layer crystals. These spectra were all acquired under identical acquisition conditions and so the high spectral intensity and relatively high intensity of the A1 compared to the B1 emission observed for the 0.5 nm film imply that it is, at least partially, monolayer in nature.

None of the WS₂ films showed appreciable PL. Monolayer WS₂ exhibits a PL signature at ≈ 637 nm.¹²⁰ It has been shown to have much stronger PL than MoS₂ when measured with a 532 nm laser,¹⁷⁷ so this offers further evidence that the deposited W was thicker than desired.

This is a significant result, since it shows that the TAC process can be well controlled enough to produce MoS₂ films with monolayer characteristics. The creation of direct bandgap materials utilising TAC has the potential to greatly expand the applicability of this scalable process methodology. TAC could prove to be a viable route of producing materials, with properties suitable for a wide range of optoelectronics applications.

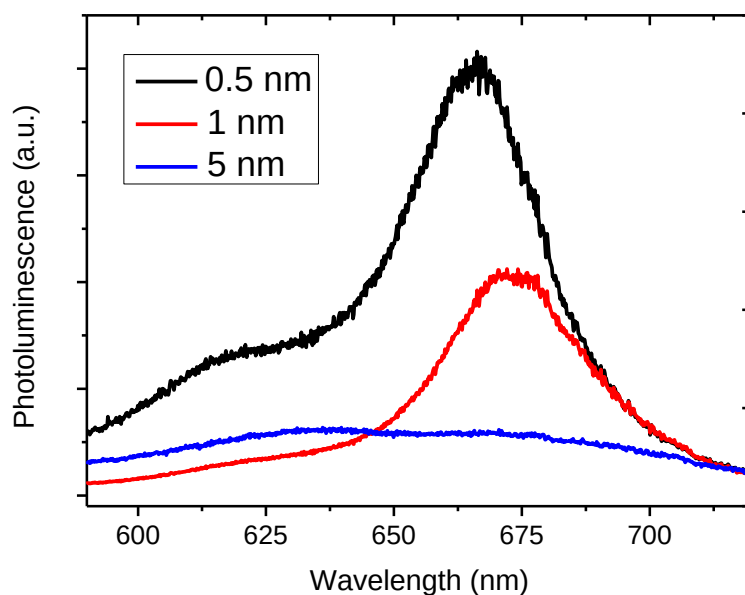


Fig. 4.10 PL spectra of TAC MoS₂, labels refer to different thicknesses of deposited metal.

4.3.2 Spectroscopic Ellipsometry

Spectroscopic Ellipsometry (SE) was used to measure the thickness of the metal film before and the TMD film after the TAC process. The models for each material were developed by Dr. Chanyoung Yim, and they were used to determine the film thickness, refractive index (n) and extinction coefficient (k). The models were confirmed by x-ray diffraction data.¹²⁵ The ellipsometer used had a large spot size, and took an average over an area of 2-3 mm². This was necessary to accurately determine the thicknesses of TMD films over large areas. SE improved metal deposition, allowing for optimisation of the TAC processes.

The thickness results of molybdenum thin films are displayed in table 4.1a. Before TAC, the molybdenum film thicknesses as measured by SE and the tools QCM agree to within 2 nm, for the thicker samples, this is acceptable. However, for those samples with a thickness on the order of 2 nm it is difficult to unambigu-

ously measure the sample thickness. This highlights a limitation in the deposition tool's measurement capabilities. It was necessary to optimise the metal deposition before TAC processes could be well understood. In order to limit error, and to improve homogeneity between samples, the sputter tool was calibrated with a thicker sample, and thinnest depositions were timed, rather than relying solely on the thickness monitor.

SE was then used to determine the thicknesses of the TMD films. After TAC, the MoS₂ films expanded by a factor of around 2. A similar expansion has also been observed by others.^{20,114} This expansion is expected, due to the addition of sulfur and the formation of van der Waals layered TMD structures. In a Mo BCC crystal, the lattice constant is 3.15 Å, while d-spacing in MoS₂ is 6.14 Å. This difference is the reason that twofold expansion is observed.

The SE results for WS₂ show a much larger variation between the metal thickness as measured by SE and the thickness as measured by the QCM. It appears that the QCM drastically underestimated the thickness of the tungsten films. This explains why monolayer WS₂ was not observed via Raman or PL spectroscopies. One reason for this could be the challenging deposition conditions that were needed to deposit tungsten. The expansion of W was also around a factor of 2, similar considerations as discussed for MoS₂ are relevant for WS₂ as well.

4.4 Morphological Characterisation

In order to progress toward producing materials suitable for electronic device applications, it is essential to understand the morphology of the TMDs and determine the effect of the physical structure on the electrical properties. TEM^{178,179}

Table 4.1 SE thickness results for sulfides

(a) SE thickness results MoS ₂			(b) SE thickness results WS ₂		
QCM Mo (nm)	SE (nm)		QCM W (nm)	SE (nm)	
	Mo	MoS ₂		W	WS ₂
0.5	1.92	3.45	0.5	4.06	5.07
2	3.61	5.33	2	4.97	10.03
5	6.19	13.69	5	9.17	16.33
20	17.89	47.19	20	34.31	45.04

and AFM¹⁸⁰ have been used to investigate the morphology, roughness and grain sizes of TMDs. The microstructure of TAC films has been investigated in several microscopic studies which have shown that the morphology and quality of TAC films can be strongly influenced by growth conditions.^{59,97,100,181}

4.4.1 Scanning Electron Microscopy

TAC films are known to grow as a disordered polycrystalline film. In order to image the crystalline domains, films of MoS₂ and WS₂ synthesised at 750 °C were investigated by SEM. However, as can be seen in fig. 4.11, features such as grain boundaries could not be clearly resolved. The MoS₂ samples appeared homogeneous at a magnification of 11,000 X (scale bar 500 nm). Different thicknesses were investigated, and all samples from a starting metal thickness > 1 nm appeared to form a continuous layer, *e.g.* fig. 4.11(a). In the case of the thinnest (0.5 nm metal) samples, the MoS₂ layer does not appear complete (fig. 4.11(b)). A scratch has been introduced, (highlighted by the red line) showing the SiO₂ substrate, and it appears that the substrate is also visible in other regions. Fig 4.11(c) is a higher magnification image of MoS₂, it reveals either a decoration or domains on the order of 10s of nm, it is unclear which is

the case. It is possible that excess sulfur could have condensed onto the sample after TAC, forming this decoration. WS_2 was also investigated, and is shown in fig. 4.11(d), It appears to form a continuous film, somewhat rougher than MoS_2 , with different regions having different thicknesses.

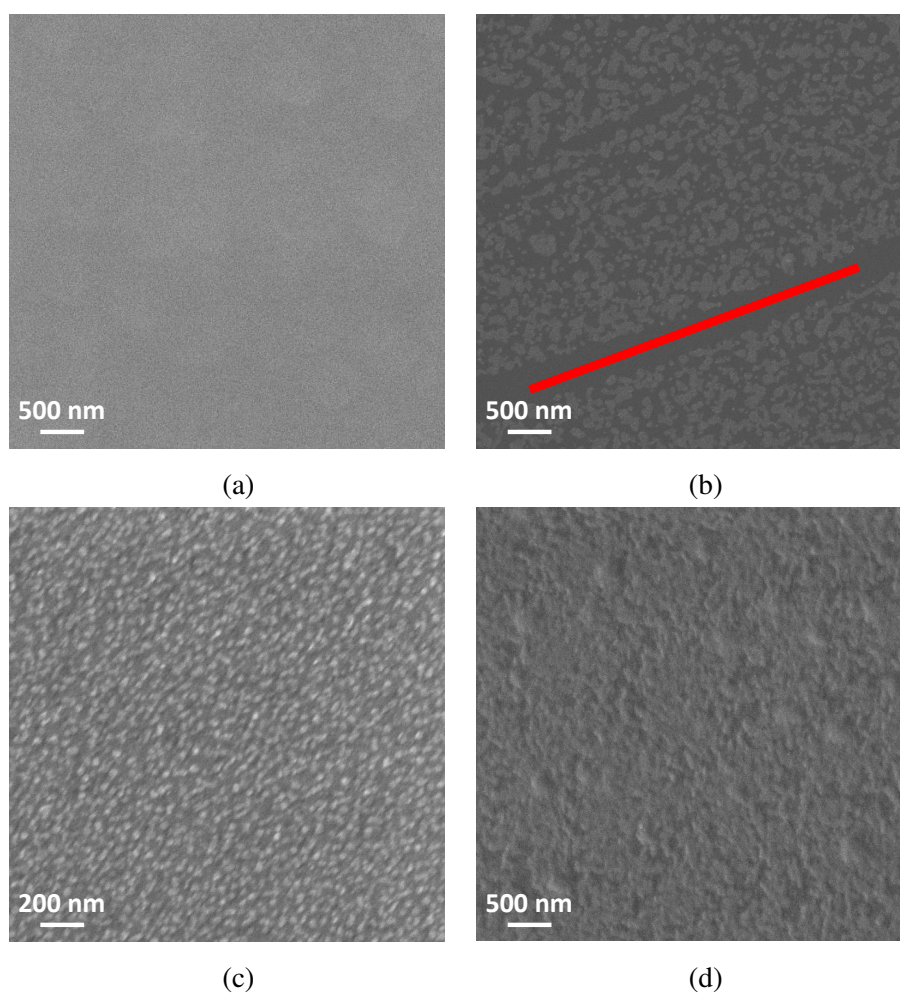


Fig. 4.11 SEM of TAC films of (a), (b) and (c) MoS_2 and (d) WS_2 . All films were synthesised at 750 °C from 5 nm metal thickness, except for (b) which is from 0.5 nm the red line highlights a scratch which had been introduced to show the substrate.

4.4.2 Helium Ion Microscopy

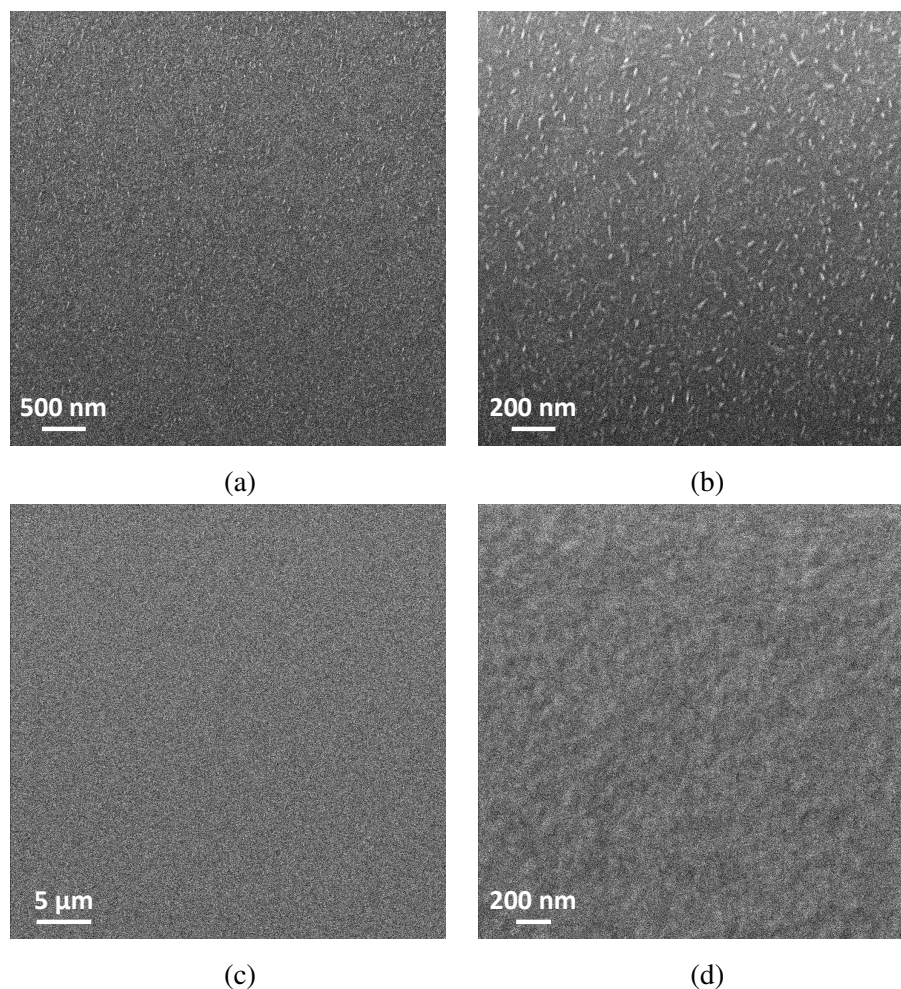


Fig. 4.12 Scanning helium ion micrographs of (a),(b) MoS_2 and (c),(d) WS_2 TAC films synthesised at 800 °C, with 5 nm metal thickness, on sapphire substrates.

Scanning HIM was used in an attempt to image the TAC films. It was hoped that the smaller excitation volume and consequent larger depth of field would produce sharper images than those imaged with SEM. Fig. 4.12 shows HIM images of both MoS_2 and WS_2 films at different magnifications. The films were grown on sapphire, at 800 °C with 5 nm deposited metal. The sapphire lattice is commensurate with MoS_2 , and it has been shown to produce more crystalline

MoS₂ growth.¹⁰⁵ It is clear that the MoS₂ is homogeneous, however no domains could be resolved (4.12(a)). At higher magnification, (4.12(b)) some decoration is visible, it is in the few tens of nanometres range. As discussed in section 4.4.1, the decoration is possibly sulfur which had condensed post TAC. WS₂ films were homogeneous at both low (4.12(c)) and high (4.12(d)) magnification, with no features of note resolved. This shows that the TAC grown MoS₂ and WS₂ films are homogeneous and continuous. Unfortunately, these methods have proven to be largely unsuccessful in imaging domains. SEM and HIM are more suited to confirm the quality of TAC films, and locate any micro-fractures, tears, cracks, voids, or inhomogeneities present. However, these techniques are not able to clearly resolve the polycrystalline structure likely because the adjacent domains are very similar in appearance to one another, differing only slightly in orientation. Microscopy with atomic resolution is required in order to differentiate grains, or another technique which could better highlight grain boundaries.

4.4.3 Transmission Electron Microscopy

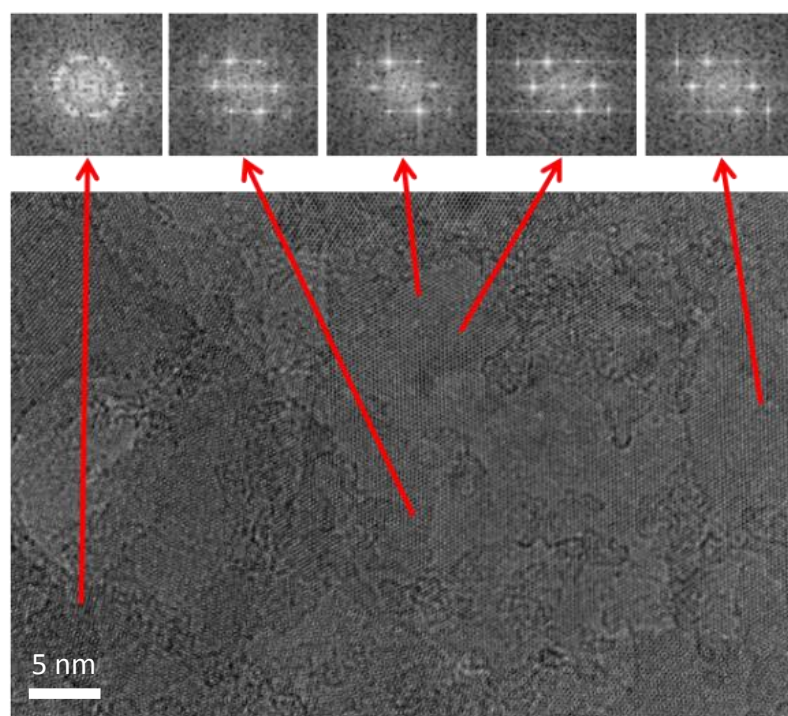


Fig. 4.13 TEM image of a polycrystalline TAC MoS₂ film, grown at 750 °C. Red arrows point to different diffraction patterns from various regions.

In order to better understand the structure of TAC grown films, samples were prepared for TEM. TEM only works for samples thin enough to be electron transparent, therefore 2D nature of TMD films makes them very suitable. Furthermore, inorganic TMDs (with strong covalent intralayer bonding) are more resistant to electron dosage than organic or biological samples. The ultra-high vacuum environment of a TEM instrument requires elaborate sample preparation for water-based biological samples. Further, organic molecules are primarily composed of lighter elements, which do not interact strongly with the electron beam and therefore do not provide as much contrast as the heavier transition metals. The TEM presented here was imaged by Maria O'Brien. Fig. 4.13 shows a TEM image of a typical 1 nm thick MoS₂ film grown by TAC on a SiO₂ substrate then transferred

onto a TEM grid. Inspection of these images shows that the domains are typically around tens of nanometres in size, and applying fast Fourier transform processing to several regions shows that the individual domains are highly crystalline, and randomly orientated with respect to the others. FFTs of highly crystalline samples exhibit sharp spots. The location and relative brightness of the spots is related to the symmetry of the sample. Other TEM studies have shown that each grain is highly ordered, with hexagonal symmetry and a mixture of stacking types.¹⁰¹ The size and orientation of the individual domains is dependent on the synthesis conditions (temperature, metal thickness, pressure and substrate). However, most reports describe TAC films with domains ranging from tens to several hundreds of nanometres.¹¹¹

XTEM was also used to investigate the structure and orientation of TAC grown films, XTEM was performed in collaboration with Dr. Paul Hurley and the Micronano Electronics group at Tyndall National Institute. Fig. 4.14(a) is a XTEM image of MoS₂ from 5 nm starting metal thickness, synthesised on sapphire, with a gold layer deposited above. It has expanded to around 10 nm, a factor of 2, which agrees well with SE and XPS measurements. The film is well aligned, with the the predominant alignment of the basal plane parallel to the substrate.

XTEM of a thicker MoS₂ film, also deposited on sapphire, is depicted in fig. 4.14(b). In this case 10 nm of metal underwent TAC, and the resultant film is not as parallel to the surface as the 5 nm case. The film expanded to around 20 nm, again expanding by a factor of two. Grain boundaries and regions where domains overlap can be seen. The lattice spacing is consistently 0.6 nm, indicating that the layered material is MoS₂.

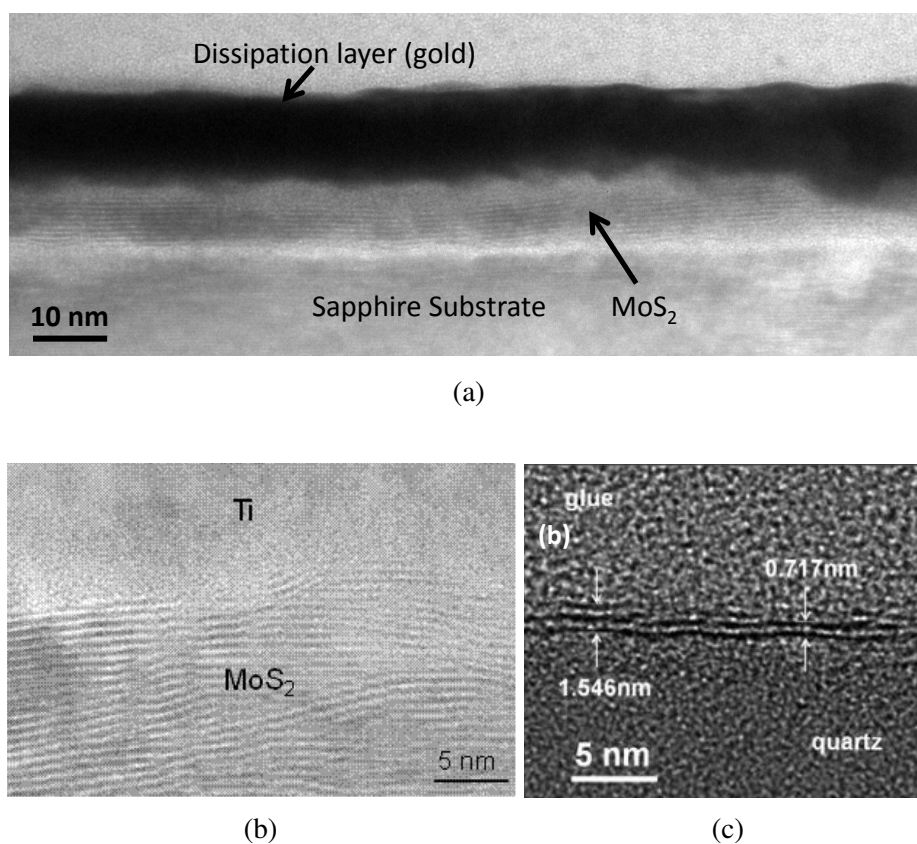


Fig. 4.14 XTEM characterisation of TAC grown MoS₂. Starting metal thickness is (a) 5 nm, (b) 10 nm and (c) 1 nm. Analysis was performed through collaboration with (a), (b) Tyndall National Institute, Cork and (c) SIOM, Shanghai

Additional XTEM studies carried out in collaboration with the group of Prof Jun Wang in SIOM, Shanghai showed that thin MoS₂ films grown from 1 nm Mo are well aligned to the quartz substrate. As is shown in fig. 4.14(c), films are predominantly monolayer, with some bilayer regions. Lattice spacing also confirmed that the film is MoS₂. Quartz is more amorphous than crystalline sapphire, so it is encouraging that MoS₂ with monolayer character could be produced by TAC, even under less ideal conditions.

4.4.4 Atomic Force Microscopy

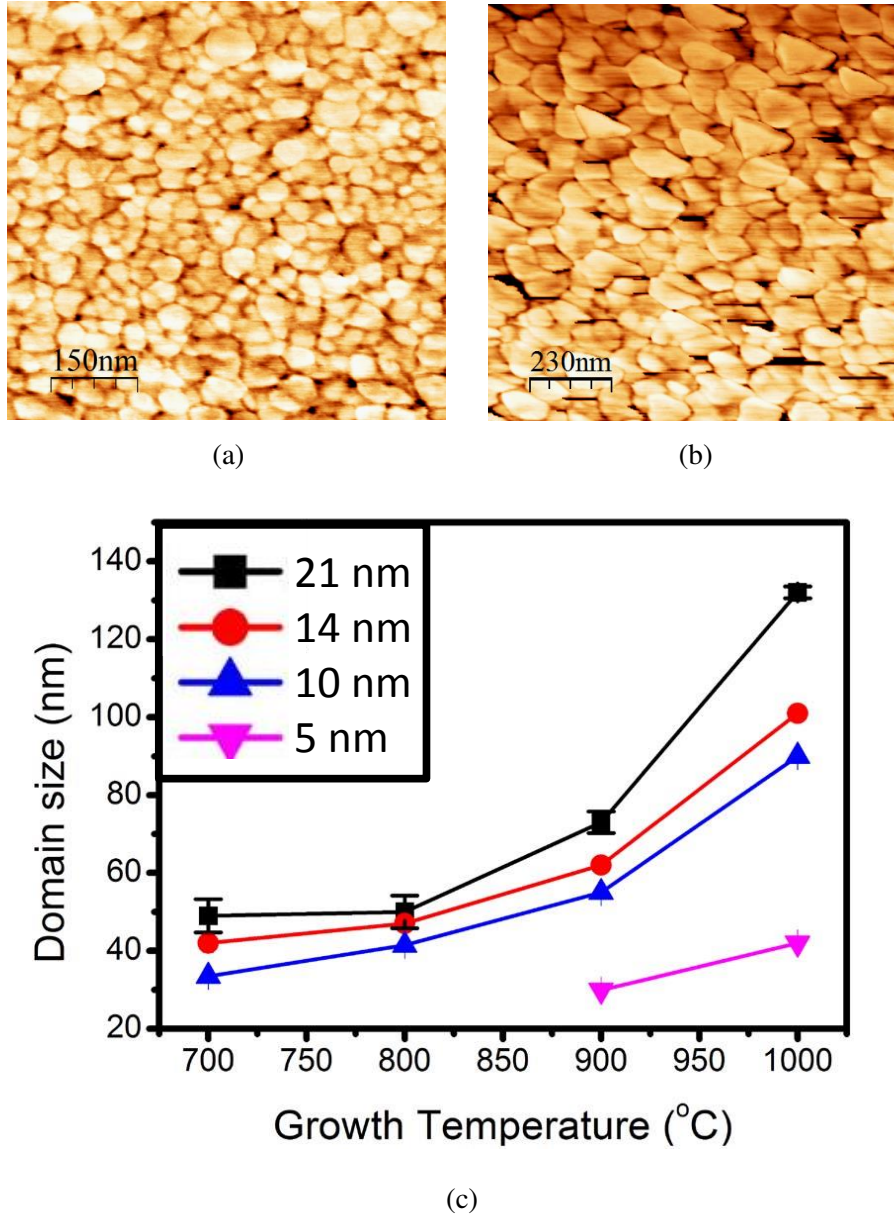


Fig. 4.15 AFM images of MoS₂ grown at (a) 700 °C and (b) 1000 °C. (c) relationship between domain size and growth temperature and initial metal film thickness.

AFM studies have identified a strong relationship between the growth temperature, thickness and the crystallinity in TAC based TMD films.^{104,105} Statis-

tical analysis of AFM phase maps, such as those presented in fig. 4.15(a) and fig. 4.15(b) shows a clear relationship between domain size and both growth temperature and thickness of the metal precursor. Fig. 4.15(a) shows a MoS₂ film from an initial Mo thickness of 10 nm synthesised at 700 °C; the average grain size was 35 nm. Fig. 4.15(b) shows a similar film synthesised at higher temperature (1000 °C). The average grain size is enlarged significantly to 90 nm. A comprehensive study on the film formation reveals that higher crystallinity i.e. larger domains are formed at higher temperatures and when thicker Mo films are converted, a plot of the relationship is shown in fig. 4.15(c). At all temperatures, grain size is smaller for thinner films. This is likely due to the restricted mass transport availability of MoS₂ on the solid surface and the limited source of material. The growth mechanisms of MoS₂ are still under investigation. Further improvements in crystallinity have also been seen through the use of more crystalline substrates such as sapphire. Laskar *et al.* reported large-area well-aligned TAC MoS₂ films grown on monocrystalline sapphire substrates.¹⁰⁵ These results clearly show that there is considerable scope for optimising the quality of thin TMD films synthesised via the TAC process, by adjusting parameters such as the growth temperature, growth pressure, choice of substrate and starting metal thickness.

4.5 Chemical Characterisation

4.5.1 X-ray Photoelectron Spectroscopy

XPS measurements provided further information about the composition, purity and thickness of TMD films through quantitative analysis of atomic ratios and

identification of contaminants. TMD films which were produced from nominal Mo and W thicknesses of 0.5, 1 and 5 nm, deposited onto Si/SiO₂ substrates were analysed, as well as a clean Si/SiO₂ surface as a reference for film thickness estimation. XPS measurements were also performed on samples synthesised at different temperatures. Temperature was found to have no significant affect on the materials properties which influence XPS measurements. From 600 - 1000 °C, there was no discernible difference in atomic ratios, purity or chemical environment for either MoS₂ or WS₂. The samples presented here were synthesised at 750 °C. XPS survey spectra of MoS₂ (fig. 4.16(a)) and WS₂ (fig. 4.16(c)) films with a starting metal thickness of 1 nm and 5nm respectively show the presence of both the metal and the chalcogen, as would be expected. Apart from a weak adventitious carbon signal, which is generally unavoidable, and is useful for charge compensation, very rarely were other contaminants observed, indicating the high purity of the samples. The measured films occasionally display a weak F 1s signal, as shown in fig. 4.16(c), originating from organic fluoride species, which are commonly observed surface contaminants, arising from exposure to ambient atmosphere.

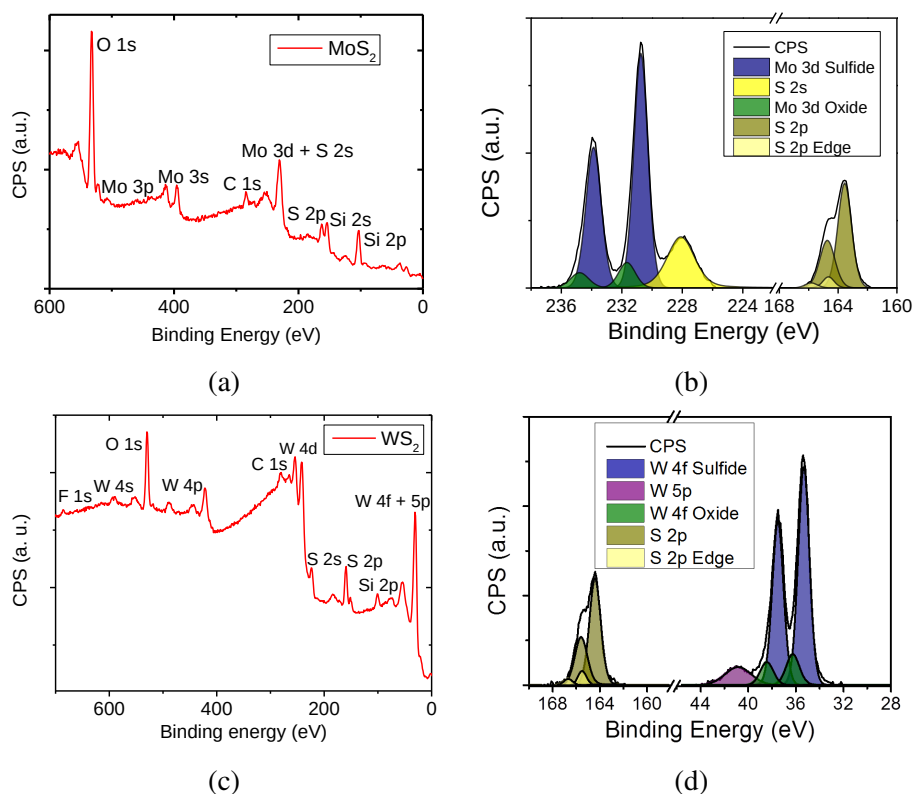


Fig. 4.16 XPS survey (a), (c) and core level (b), (d) spectra of MoS_2 and WS_2 respectively. Samples were from 5 nm starting metal thickness, grown at 750 °C on Si/SiO₂ substrates.

By comparing the areas of the silicon XPS peaks before and after growth of MoS_2 films on the Si/SiO₂ substrates, and using the exponential decay relation of photoelectrons emitted through an overlayer, the film thicknesses of different samples were estimated. The average thickness of a film with an initial nominal Mo thickness of 0.5 nm was found to be 2 nm. This corresponds to ≈ 2 -3 layers, given a typical MoS_2 interlayer thickness of 0.66 nm.¹⁰⁰ Similarly, after sulfurisation films with starting thicknesses of 1 nm and 5 nm were measured to be 4 nm (6-7 layers) and 6 nm (9-10 layers) respectively. This is an expected result, as the film will expand upon the addition of S between the Mo layers, as previously discussed. These estimated values are in close agreement with the Raman and PL

observation which suggest thickness close to a monolayer for the films with a Mo thickness of 0.5 nm. This method of thickness determination is not as accurate as SE, due the fact that low resolution survey scans are used. However, they do confirm the trend of expansion, and it is likely that the the thicker layers are underestimated. Because XPS is such a surface sensitive technique, this estimation becomes less accurate as thickness increases.

High-resolution XPS core level spectra contain information about atomic ratios, chemical environment and compounds present in a sample. Fitting the spectral components gives a quantitative measure of oxide levels, and chalcogenide:metal ratios. All spectra presented were fitted with the CasaXPS software, after subtraction of a Shirley background. As the samples were not sufficiently conductive, an electron flood gun was used for charge compensation, further, all spectra were shifted to the adventitious C 1s peak at 284.8 eV. Fig. 4.16(b) displays a typical MoS₂ spectra. The spin-orbit splitting in the Mo 3d doublets is 3.25 eV and the branching ratio (Mo 3d_{3/2} to Mo 3d_{5/2}) is 2:3. All components of the Mo 3d line have been fitted using a mixed Gaussian-Lorentzian line shape with a FWHM of 1.3 ± 0.1 eV. The Mo 3d core-level is fitted with one main component at a binding energy of 230.8 eV for the Mo 3d_{5/2} peak (blue), which originates from sulfurised Mo, and two smaller components on the high binding energy side of the peak which are related to residual oxides (green). These oxides were present in all samples, and they are typically less than 5 atomic %. Since all samples were exposed to ambient after synthesis, it is likely that these are native surface oxides. Because of the surface sensitive nature of the XPS technique, the oxide contribution is likely overestimated when the whole film is considered. The feature at 228 eV (yellow) is the S 2s peak. It was fitted with a FWHM of 1.6 ± 0.1 eV. The S 2p_{3/2} core-levels could be fitted with one main component at

a binding energy of 163.5 eV, and another minor peak at 164.7 eV. This small contribution is attributed to sulfur at edge sites, which are bound to fewer molybdenum atoms.¹⁸² The well defined peaks indicate that there is no unreacted sulfur on the surface.

High resolution core level spectra were also analysed for WS₂. As can be seen in fig. 4.16(d), the W 4f_{7/2} is fitted with one main component at 34.9 eV (blue), originating from sulfurised tungsten. The spin-orbit splitting in the W 4f doublets is 2.18 eV and the branching ratio is 3:4. The W 4f line components have also been fitted with a mixed Gaussian-Lorentzian line shape (FWHM of 1.2 ± 0.1 eV). Similarly to the MoS₂ samples, residual oxides are also present at the higher energy side of the peak (green), they also are typically less than 5%. This region also contained a W 5p_{3/2} component at 40.9 eV (purple). This broad peak was fitted with a FWHM of 2.4 eV. The S 2p peak is also well fitted with a main component at 164.1 eV, with a smaller peak at 165.3 eV from edge sulfur.

In a previous XPS study on bulk MoS₂, Baker *et al.* show that the difference in binding energy between the Mo 3d_{5/2} and the S 2p_{3/2} peaks can be related to the stoichiometric composition of the MoS₂.¹⁸³ As the compound becomes sulfur deficient, the Mo 3d_{5/2} peak position shifts to lower binding energies, commensurate with the changing electrostatic environment due to the loss of sulfur atoms bound to the molybdenum. There is no such shift in the position of the S 2p_{3/2} peak, indicating that the oxidation state is independent of stoichiometry. Measured MoS₂ samples consistently showed a ΔE value of 67.1 eV, corresponding to a stoichiometric ratio of $x = 1.9 \pm 0.1$, close to the nominal value of 2 for MoS₂. Another common method of determining stoichiometry in compounds is to compare the area under the peaks from each element, and normalise to the relevant sensitivity factors (RSFs). RSFs account for the fact that different

elements (and orbitals) have different probabilities of producing a photoelectron. This is shown by formula 4.1. All RSF values used were obtained from the Casa XPS library.

$$\frac{\left(\frac{\text{Area of chalcogen peak}}{\text{Chalcogen peak RSF}} \right)}{\left(\frac{\text{Area of metal peak}}{\text{Metal peak RSF}} \right)} \quad (4.1)$$

Applying this method to both WS₂ and MoS₂ samples gives a stoichiometry of 2.0 ± 0.1 for both materials, for a wide range of synthesis temperatures, from 600 - 900 °C. XPS measurements have shown that TAC produces both MoS₂ and WS₂ with the correct stoichiometry, and low levels of contaminants. Both the metal and the sulfur core levels are well fitted with components corresponding to the respective TMD. In all cases, minor contributions related to residual oxide species are also present, and these are most likely due the exposure to atmosphere prior to measurement. Thickness estimations have shown that the films expand during TAC, and that the thinnest films produce TMDs that are on average 2-3 layers. The high-quality nature of TAC produced MoS₂ and WS₂ thin films is evident from XPS characterisation. While these results are encouraging, it is worth highlighting that XPS is a chemical characterisation technique, and it is not able to reliably detect differences in doping levels which may have a large impact on electrical properties. For example, if one out a thousand sulfur atoms is a vacancy site this heavily *p*-dopes the material but it would not be visible with XPS.

4.6 Electrical Results

4.6.1 Hall Effect Measurements

Hall bar structures were fabricated in order to determine μ_H . Shadow masks were used, as was optical lithography. For the shadow mask devices discussed, the process flow involves depositing 10 nm of Mo on Si substrate with 300 nm thermal SiO₂. TAC was performed at 750 °C, and second shadow mask was used to sputter Ti/Au contacts (10/40 nm). An overnight vacuum anneal at 80 °C (10^{-5} mbar) was included to improve the contact by removing adsorbates such as water between the contacts and the channel. Shortly after the anneal, the devices were encapsulated in PMMA in order to protect them from ambient.

Fig. 4.17(a) is an optical micrograph of such a device. The long axis is 1.4 mm, and the width is 100 μm . It is clear that the device is well aligned, and there is $>1000 \mu\text{m}^2$ overlap on all contacts. Before contacting the samples to a chip carrier, the 2-point resistance along the long axis (R_1) and between the opposing arms (R_2) was measured in ambient with a needle probe station. The results of this are shown by fig. 4.17(b). This allowed for the homogeneity of the MoS₂ to be confirmed, and the measurements were repeated after one day to see if there was any degradation. The resistance of both sets of arms was identical, showing that the sample is very homogeneous. The results of the second set of measurements (not shown) lines up precisely with the first, showing that these samples did not significantly age after one day.

The samples were then contacted to a chip carrier, with silver paint and silver leads, in order to be loaded into a PPMS for Hall characterisation. Measurements were performed at a range of temperatures between 5-300K, For each measurement, the zero field resistance along the main axis was measured in a

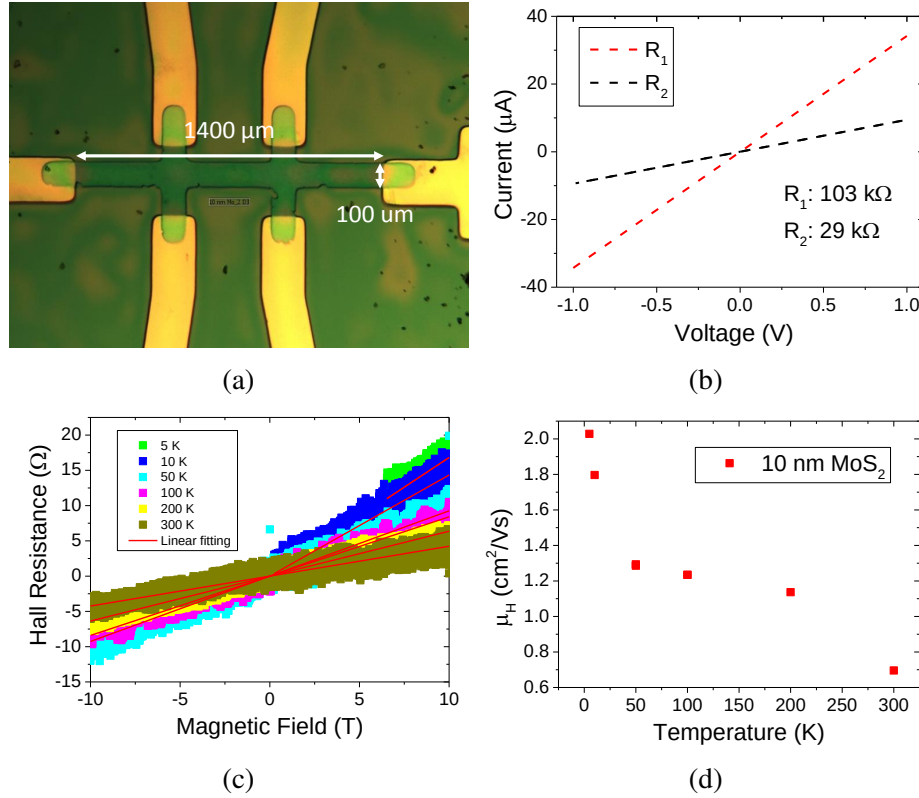


Fig. 4.17 (a) Optical image (b) 2-terminal I - V s of 10 nm thick MoS₂ Hall bar device. (c) Plot of Hall resistance vs $\mathbf{B}$ field and (d) calculated values of μ_H at different temperatures.

4-point configuration and the Hall resistance was measured as the $\mathbf{B}$ field was swept ± 10 T. When using this measurement technique, the slope of the Hall resistance vs. $\mathbf{B}$ can be used to determine μ_H , by using equation 4.2, which is a rearrangement of equations 2.10 and 2.20

$$\mu_H = \frac{V_H}{I\mathbf{B}} \cdot \frac{l}{wR} \quad (4.2)$$

where $\frac{V_H}{I\mathbf{B}}$ is the slope, R is the measured resistance, and $\frac{l}{w}$ is the length to width ratio (which is 6 for these devices) The data obtained by this technique are shown by fig. 4.17(c). As can be seen, the data is noisy, Each colour refers to a measurement performed at a different temperature. It is clear that the Hall

resistance became higher as the temperature was lowered. Linear fitting was performed in order to obtain the slope at each temperature. This fitting also verifies that there is no Hall resistance at zero field.

Fig. 4.17(d) is a plot of μ_H at each temperature. Values increase from $0.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature to $2.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 5 K. These compare well when one considers literature values of mobility extracted from MoS_2 synthesised in a similar manner. Typically μ_{FE} ranges from $0.05 - 0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for devices made from CVD MoS_2 . There are very few reports of μ_H , Zhu *et al.* have demonstrated room temperature μ_H of $4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ using CVD grown MoS_2 and a top gated device encapsulated in HfO_2 .

4-point resistance was measured as the temperature ramped down. As shown in fig. 4.18(a), which is a plot of ρ against temperature, semiconductor behaviour was observed. The resistivity increased with decreasing temperature. This information can be used to obtain the activation energy of the on state current. Equation 4.3 is the Arrhenius equation relating the resistivity to the activation energy. Rearrangement gives equation 4.4 where it is clear that plotting $\ln \rho$ against T^{-1} allows for calculation of E_a as $\text{slope}(2k_B T)$.

$$\rho = \rho_0 \exp \left[\frac{-E_a}{2k_B T} \right] \quad (4.3)$$

$$\ln \rho = \left(\frac{-E_a}{2k_B} \right) \left(\frac{1}{T} \right) + \ln \rho_0 \quad (4.4)$$

Fig. 4.18(b) is an Arrhenius plot. The linear region from 220-300 K was used to calculate E_a because the slope changes as the material became extrinsic at lower temperatures. The calculated value of E_a was 0.17 eV. This agrees well with the value of 0.18 eV obtained by Duffy *et al.*¹⁸⁴ who used a circular

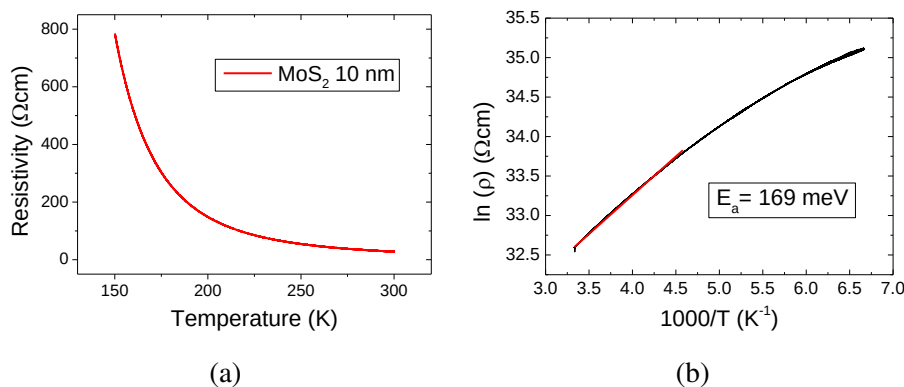


Fig. 4.18 Plot of (a) ρ vs. temperature, (b) $\ln \rho$ vs. T^{-1} for a 10 nm MoS₂ Hall bar device.

transfer length method on TAC synthesised MoS₂ films which were synthesised in the sulfurisation furnace and provided. An activation energy in this range is reflective of deep donor levels, possibly caused by unintentional doping. Carvalho *et al.* reported Density Functional Theory (DFT) calculations of impurities in MoS₂. Br and Cl substitutional impurities were found to introduce deep donor levels at 0.15 eV and 0.18 eV below the conduction band edge respectively.¹⁸⁵ Sulfur vacancies were also found to cause deep donor traps.¹⁸⁶ Another origin of the deep trap states is density of defects and grain boundaries commensurate with polycrystalline material. Increasing grain sizes through higher temperature synthesis is a route toward improving carrier mobility.

To address the high noise levels observed in the Hall bar device design a simpler van der Pauw design was also utilised. Since the V_H values were so low, and the associated noise levels so high, another, more suitable measurement method was needed. Alternate Current (AC) Hall measurements were performed by using an AC $\mathbf{B}$ field. This is advantageous because it negates two of the largest sources of error that are present in DC Hall measurements, a misalignment voltage V_O and a thermoelectric voltage (V_{th}). In a DC Hall measurement, field reversal

and current reversal are used to remove the effects of V_O and V_{th} respectively. The problem in low mobility materials is that the V_O contribution can be much larger than V_H . Subtracting two very large numbers gives a very small result, and consequently any noise in the measurement can easily dominate the calculation, giving an imprecise result. Hall measurements performed using an AC field effectively separate the Hall signal from the V_O . Applying a sinusoidal AC magnetic field causes V_H to be time dependant as well, however V_O remains a DC signal since it is independent of the magnetic field. A lock-in amplifier is used to separate the AC V_H signal from the DC V_O signal. One further complication is that applying an AC field causes another AC signal to be measured. This is proportional to the inductance of the sample and the time derivative of the applied field, and it is independent of current. This term can be removed through a combination of current reversal and phase management, and is generally carried out automatically by the lock-in amplifier.

Both DC and AC Hall measurements using the van der Pauw geometry were performed with the assistance of Dr. Scott Monaghan in Tyndall National Laboratory. The substrates used were 1 cm by 1 cm sapphire, MoS_2 was synthesised from 10 nm of deposited metal. After TAC, the corners had small (<1mm) triangular Ti/Au contacts sputtered on (10/40 nm). Early attempts used highly doped p++ Si substrates with 300 nm SiO_2 dielectric, however the corner contacts ended up short circuiting to the substrate, the use of sapphire substrates prevented this from being an issue.

When using the van der Pauw method, contact resistance is a critical issue. Error introduced by non zero sized contacts, and geometric factors also play a significant roll in these measurements. 1 cm by 1 cm samples were contacted to the measurement system by a gold probe in each corner, which were screwed

down to both electrically contact and physically hold the sample to the card. For low mobility and/or high resistance materials, such as our TMD films, the contacting is critical and extremely difficult. It has a very large effect on the Hall voltage, more so than on the resistivity measurements. Attempts at reducing contact resistance included direct gold probe contacting, the use of indium solder, contacting to the Ti/Au contact pads and using conductive silver paint.

Unfortunately very few of these samples gave reliable AC Hall measurement results. The most robust results involved a 10 nm thick MoS₂ sample on sapphire, synthesised at 800°C. Indium solder contacts placed in the corners on the film were attached to gold probes on the card. During resistivity measurements the sample showed Ohmic behaviour (correlations > 0.998), sheet resistivity was $\approx 247 \text{ M}\Omega/\square$ with a good signal to noise ratio of 900:1. The F value = 0.98 showed good geometry and configuration symmetry. AC Hall measurements were then performed, using the geometry averaged result of 10 measurements in order to increase the signal to noise ratio. The sample displayed *p*-type behaviour, and μ_H was $0.049 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The AC Hall signal to noise ratio was the highest of all measured samples at 3.55:1, however the AC phase range was -0.3° to 10.7° . Ideally the phase should be either 0° or -180° . This shows the measurement limitations for this type of TAC films. The low signal to noise and large phase range demonstrate that these results can best be considered indicative rather than quantitative. The low μ_H value is unlikely to be accurate, It is very sensitive to contact resistance. The TAC films measured were of too low a mobility and/or too high a resistivity for this system to measure accurately.

In order to address these issues, a different van der Pauw configuration was used with a 50 nm thick MoS₂ sample, synthesised at 800 °C Rather than use a 1 cm^2 piece of sapphire, entirely covered by the TMD, a central 0.5 cm by 0.5 cm

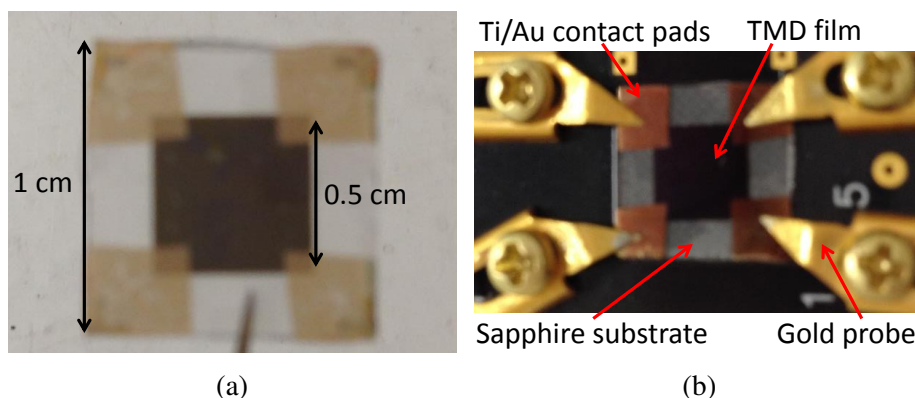


Fig. 4.19 Picture of (a) MoS₂ film on sapphire as used for van der Pauw AC Hall measurement, (b) device contacted to measurement card *via* gold probes

area was defined and converted and the edges were used for Ti/Au contacts. This refined layout, pictured in fig. 4.19(a), allowed ample electrical contact to the edge of the TMD film, rather than only on the basal plane; ideally improving adhesion and reducing contact resistance. The sample was contacted to the chip carrier by directly contacting the gold probes to the contact pads, as illustrated by fig. 4.19(b). Resistivity measurements showed excellent Ohmic correlations (> 0.999). The F value was 0.99 indicating very good geometry and configuration symmetry. Sheet resistivity was $0.79 \text{ M}\Omega/\square$, with a good resistivity signal to noise ratio of 1000:1. AC Hall measurements revealed a μ_H of $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, with a much higher signal to noise ratio of 200:1, p -type behaviour, and the AC Hall phase range was a reasonable -0.1° to 0.3° . This revised layout improved the contact resistance issues, and the corresponding twofold increase in the mobility is probably more accurate. Further, the thicker films have been shown to have larger domains, so this reduced density of defects and grain boundaries likely also contributed to increasing the mobility to a more measurable level.

Measuring μ in 2D TMD polycrystalline materials is very challenging due to structural defects such as vacancies, grain boundaries, charged inter-facial sites,

dislocations *etc.* The high density of localised states result in a small signal to noise ratio in Hall measurements. AC Hall measurements using an optimised van der Pauw layout improved this issue and allowed for measurement with reasonable signal:noise ratio. There have been very few reports of μ_H of 2D TMDs produced from scalable processes, and none from TAC produced TMDs. This is a first step, the results of these measurements indicate that the room temperature μ_H of TAC produced MoS₂ is $<1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, without the use of dielectric engineering.

4.6.2 Ionic-Liquid Gel-Gated TFTs

Field effect measurements were performed as an alternate method of determining the mobilities of TAC synthesised TMD materials. In idealised systems investigating TFT devices produced from micromechanically exfoliated MoS₂ flakes the interface between the TMD channel and the SiO₂ gate dielectric is one of the primary factors limiting carrier mobility.¹⁸⁷ Strong SiO₂-MoS₂ interfacial trapping leads to carrier localisation. For this reason traditional back gating was avoided. Hall effect measurements have indicated that defects and crystallinity are the limiting factor for TAC grown films. In order to circumvent these problems, an alternative system was investigated: top gated EDL-TFT devices. These devices utilise an ionic-liquid within in a block co-polymer gel as a top gate. Fig. 4.20(a) is a schematic, and fig. 4.20(b) is a photograph of an ionic-gel-gated EDL-TFT device. Applying a voltage to an adjacent contact pad (as seen in the corners of fig. 4.20(b)) causes the formation of an EDL which acts as a nanogap capacitor with extremely large specific capacitance.¹⁸⁸ This causes very large electric fields which can induce charge carriers much more effectively than solid dielectrics.

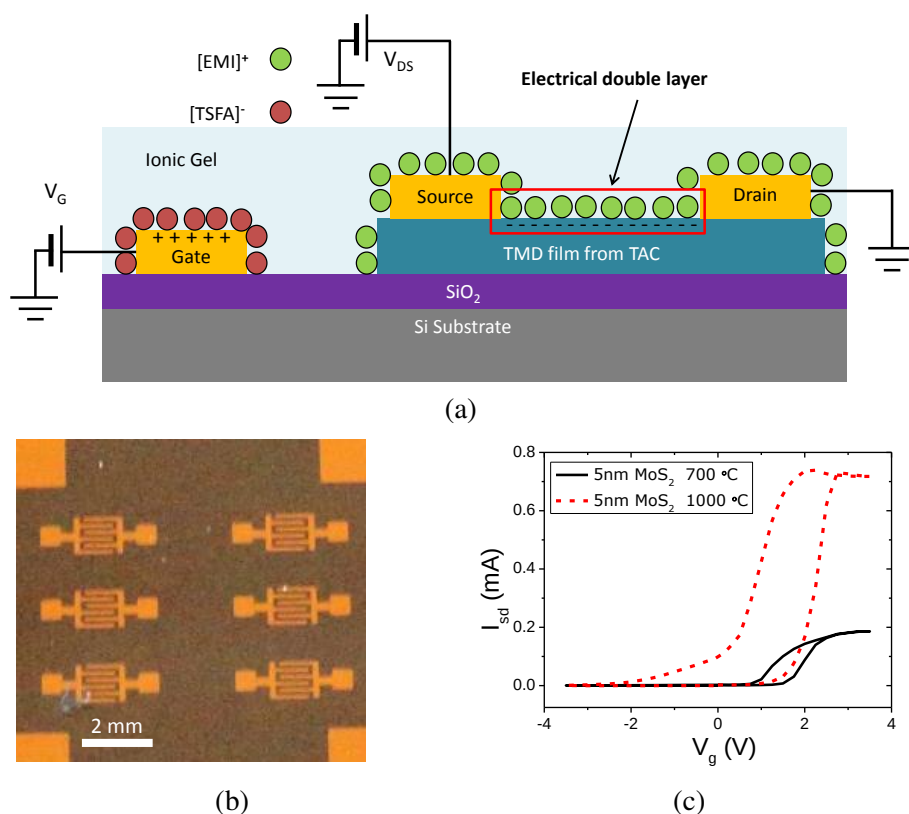


Fig. 4.20 (a) Schematic representation and (b) photograph of an EDL-TFT device. (c) Transfer curves for low and high temperature MoS₂ EDL-TFTs.

The devices were gated using Poly(vinylidene fluoride- co -hexafluoropropylene), P(VDFHFP) as the block copolymer gel and 1-Ethyl- 3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [EMIM][TFSA] as the ionic liquid. All devices were produced using shadow masks, with a channel length of 120 μm . The ionic liquid was applied by spin coating at 2000 RPM. The EDL-TFTs were vacuum annealed at 130 °C directly before measurement in order to remove dissolved water and other adsorbates from the film. All devices exhibited linear $I - V$ characteristics, which may be an artefact of Fermi-level pinning rather than true Ohmic behaviour.^{138,189}

Transfer curves were obtained by sweeping the gate voltage at a "slow" rate of 100 mV min⁻¹ in order to minimise transient charging effects which are due to

limited ionic mobility within the gel. It took this long for the EDL to form under each applied gate voltage. I_{sd} was measured in 300 mV increments with a drive voltage of 100 mV.

Transfer curves for 5 nm films synthesised at 700 °C and 1000 °C are shown in fig. 4.20(c). These films are synthesised under the same conditions as those used for AFM analysis in section 4.4.4. The drive current for the 1000 °C film is much higher before saturation is reached. The μ_{FE} values for the low and high-temperature films were calculated using equation 2.22, they are $1.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. For μ calculations, the slope of the linear region of the transfer curve was used, and $5 \text{ } \mu\text{F cm}^{-2}$ was used as the capacitance of the ionic liquid. The value of $5\text{-}10 \text{ } \mu\text{F cm}^{-2}$ was measured by Pu *et al.* as the specific capacitance of the [EMIM] [TFSA]/MoS₂ interface, through impedance measurements.¹³³

Generally, the observed values for mobility in EDL-TFTs are larger than those obtained by the Hall effect methods. The reason is because the EDL has very high specific capacitance, and is able to generate such large localised fields. It is likely that these devices display a metal-insulator transition (MIT), with a shift from defect mediated to band-like transport. The transfer curves show a very large transconductance, indicative of such a transition. No temperature dependent measurements were performed in order to verify a MIT, however gating with ionic-liquid has previously been shown to dope MoS₂ sufficiently to induce band-like transport.¹⁹⁰ It has also been shown that the use of ionic liquid top gating has the effect of reducing the Schottky barrier at the source and drain contacts.¹⁸⁸ Electrostatic screening in the ionic-liquid can reduce the width of the Schottky barrier down to the ionic-liquid screening length, tunnelling then becomes more likely than thermal activation¹⁹¹

The mobility enhancement with increasing synthesis temperature is most likely due to a higher crystallinity as shown by AFM and the corresponding reduced density of grain boundaries. Due to strong transient effects, which could not be avoided, the hysteresis for gel-gated devices is high and parameters such as threshold voltage and subthreshold slope are obscured. The on:off ratio for the few-layer films was 10^4 .

4.6.3 Gas Sensors

2D TMDs are an ideal candidate for gas sensing applications because they have a suitable bandgap, and because of their very high surface area to volume ratio.⁴⁶ Mechanically exfoliated MoS₂ flakes have been shown to exhibit a selective response to electron donors.¹⁹² When the MoS₂ film is exposed to gaseous NH₃, adsorbed molecules on the surface of MoS₂ donate electron density - thus shifting the Fermi level toward the conduction band, resulting in an observed resistance decrease. In order to produce commercially-viable 2D-TMD sensors, scalable, low-cost, high-yield production of active channel material is essential. TAC meets these requirements and is generally compatible with existing semiconductor industry process flows.¹⁰²

Chemiresistor gas sensors were fabricated using shadow masks, and tested in a custom-built gas sensing chamber. The devices utilised an interdigitated electrode (IDE) pattern with a channel length of 200 μm and a width of 5.54 cm. A large width:length ratio was chosen because TAC films typically have high resistance (van der Pauw measurements showed that MoS₂ sheet resistivity was $\approx 146 \text{ M}\Omega/\square$). Ti/Au (10/80 nm) contacts were deposited by sputtering. Titanium was chosen as the contact metal because it more closely matches the work function of the MoS₂, thereby limiting the height of the contact resistance at

the interface, and it also acts as an adhesion layer. The sensor devices were tested in the presence of NH_3 gas of various concentrations, from 200 parts per million (ppm) to 300 parts per billion (ppb). They were biased at ≈ 0.2 V, and changes in the resistance were measured at room temperature.

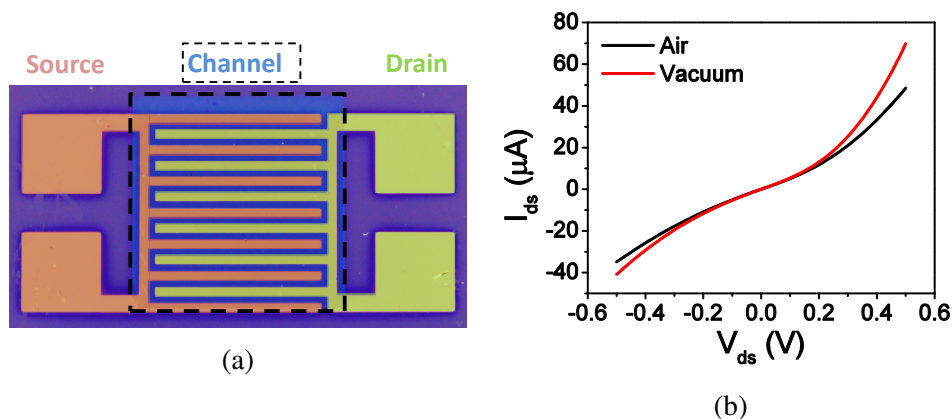


Fig. 4.21 (a) photograph of a chemiresistor gas sensor. The dashed lines indicate the channel region. False colour is used on the electrodes in order to highlight the channel. (b) Source drain I - V plot of the device.

Fig. 4.21(a) is a photograph of a chemiresistor gas sensor; the dashed line highlights the active channel area, the source and drain are colour coded to more clearly show the IDE pattern. The source-drain current versus source-drain voltage (I_{ds} - V_{ds}) characteristics are shown in Fig. 4.21(b). A typical 20 nm thick MoS_2 film exhibits non-linear behaviour at a bias sweep in the range of ± 0.5 V, implying the existence of a Schottky barrier between the metal contact and the semiconducting channel. The increased current level observed in vacuum suggests the removal of adsorbates from atmosphere, *e.g.* water vapour, from the surface of the MoS_2 . For this reason, the films were first exposed to vacuum after being loaded into the gas sensing chamber. For sensor tests, the devices were biased at 0.2 V, therefore the measured changes in resistance are determined from a range where the source-drain I - V relationship is linear, simplifying the measurements.

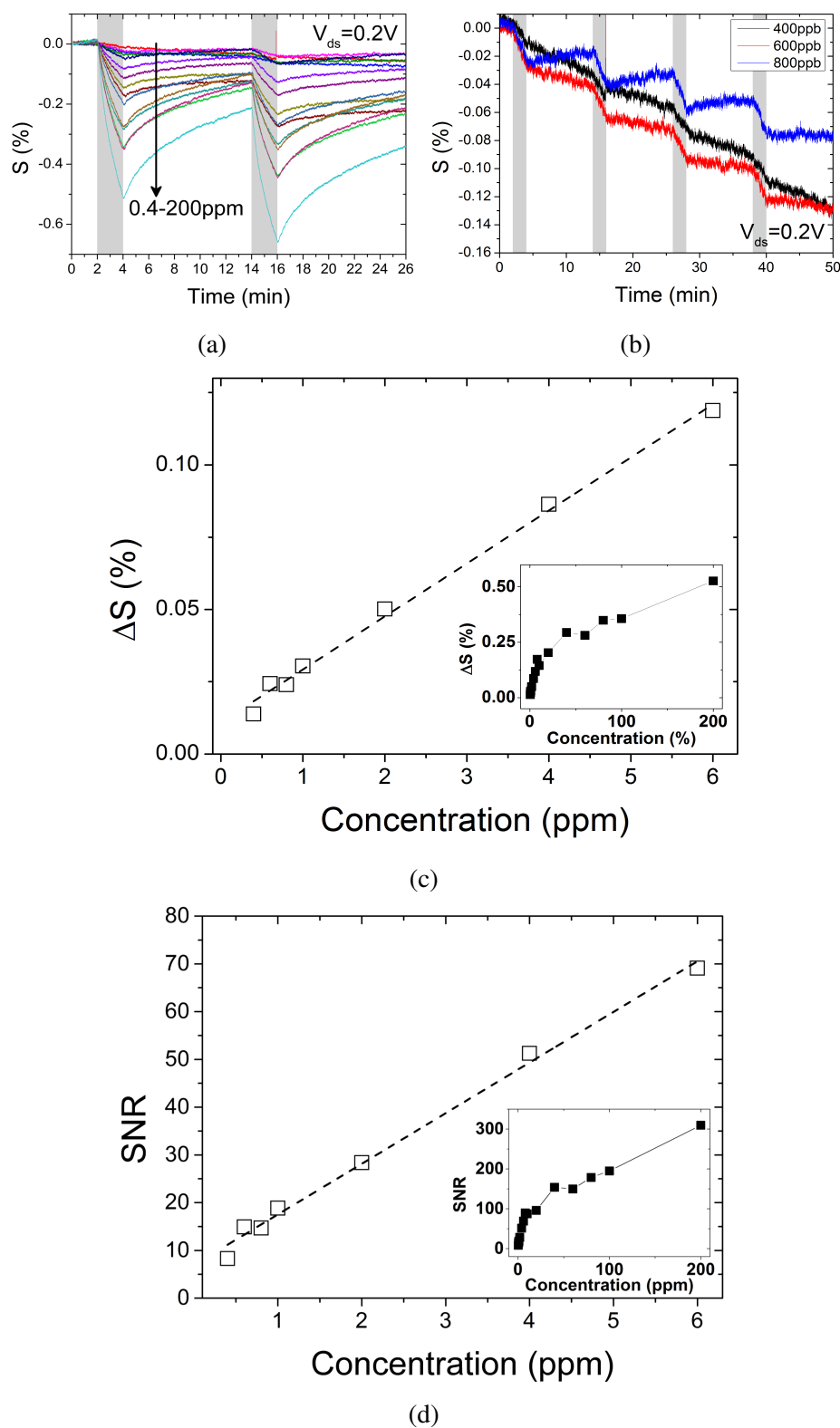


Fig. 4.22 (a), (b) Sensor response curves for a 20 nm thick MoS₂ device at various NH₃ concentrations from 400 ppb to 200 ppm. Grey vertical bars indicate NH₃ gas injections for 2 min. Plots of (c) sensitivity and (d) SNR vs. concentration. Open boxes and broken lines indicate measured data and linear fitting respectively. Insets: full-scale plots from 400 ppb to 200 ppm.

Fig. 4.22(a) shows typical gas sensor response curves of a 20 nm MoS₂ device at various concentrations of NH₃, from 400 ppb to 200 ppm. NH₃ is an electron-donating moiety and the sensor devices show *n*-type behaviour, thus adding majority carriers has the effect of increasing conductivity (in this case, the sensor response is a negative quantity). The sensor response curves immediately indicate NH₃ injections, even at sub-ppm levels as can be seen in fig. 4.22(b). It takes 2-3 secs for the MFCs to operate each proportional valve after receiving an input signal. The signal to the MFC is from multiplex switching which occurs over milliseconds. The sensor's response time is less than a second, and it is therefore limited by the MFCs rather than the chemiresistor sensor. This is faster than current state of the art sensors, for example polyaniline nanocomposite based chemiresistor sensors exhibit a response time to NH₃ of 5-200 seconds.¹⁹³ The sensors' recovery is slow in pure N₂ flow at room temperature; and baselines gradually shift downward for consecutive NH₃ injections. This indicates that the NH₃ molecules may bond tightly to the MoS₂ channel, as has commonly been observed for nanomaterial-based sensors with extremely high sensitivities. The recovery speed could potentially be accelerated by ultra-violet illumination or annealing.^{194,195}

The sensor sensitivity is indicated by the change in *S* between the initial resistance and peak value of the first gas sensing cycle, this value is linearly proportional to the concentration of NH₃ introduced in the low concentration range, as illustrated by fig. 4.22(c), and a full-scale plot shows a hyperbolic curve (inset Fig. 4.22(c)). This hyperbolic behaviour, exemplified by a linear relationship in the lower concentration range, and saturation at higher concentration is due to a high intrinsic carrier concentration.¹⁹⁶ As a result, a practical detection limit of 400 ppb was obtained, which could be confirmed by signal to noise ratios (SNR)s,

based on simple signal processing. From the first 4000 data points (about 2 min), the initial resistance and root-mean-square (RMS) noise of sensors were derived using the following equation;

$$Noise_{RMS} = \sqrt{\frac{\sum (R - R_0)^2}{N}} \quad (4.5)$$

where R is the measured resistance and N is the number of data points.

According to the IUPAC definition,¹⁹⁷ a sensor should have a signal at least three times larger than the RMS noise. As can be seen in fig. 4.22(d), TAC produced MoS_2 sensors have a SNR of 8.3 at 400 ppb, and the SNR increases with increasing NH_3 concentration. Overall, this sensor performance is superior to previous reports on MoS_2 based ammonia sensors, produced from liquid phase exfoliated flakes, which show poor recovery at higher concentrations.¹⁹⁸

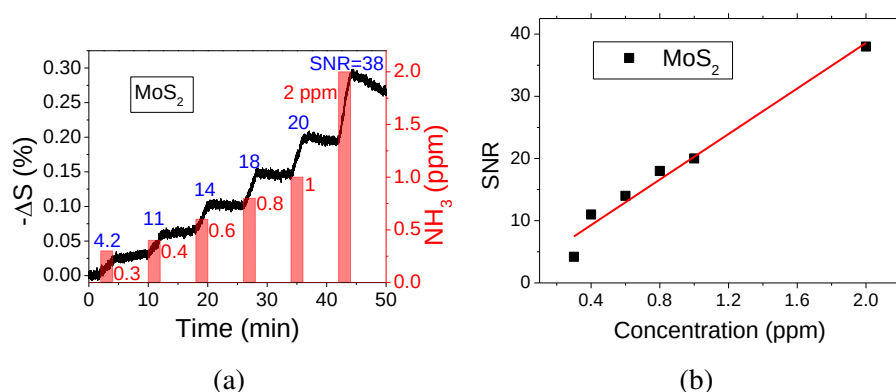


Fig. 4.23 (a) Gas response plot for MoS_2 sensor, showing SNR and sensor response at various concentrations of NH_3 (b) SNR plotted against concentration, linearly fitted.

Following on from initial sensor tests, MoS_2 sensors were created using a different TAC recipe. The synthesis temperature was 800 °C instead of 750 °C, and a 30 min high temperature dwell was included before cool down. The results are summarised in a gas-response plot, fig. 4.23(a). The sensing measurement

methodology is slightly different, in that the concentration was varied during the measurement, rather than taking several sets of measurements, one for each concentration. Also, the negative ΔS is plotted, in keeping with convention, and making the plot easier to read. The sensor displays an ultra-high sensitivity to ammonia of 300 ppb. The red shaded regions correspond to gas injections, and the SNR at each concentration is given in blue. 300 ppb is the empirical limit of the gas measuring apparatus, due the minimum accurate gas flow capabilities of the MFCs. At this low concentration the SNR was 4.2.

Plotting the SNR against concentration displays a linear relationship, as shown in fig. 4.23(b). The concentration where the SNR is 3 is considered the theoretical LOD, since it is the minimum required to be considered a true signal. Extrapolation of the linear fit to an SNR of 3 shows the theoretical LOD to be 51 ppb. When considering the effect of the growth parameters, the SNR at 400 ppb is 8.3 for the sensor synthesised 750 °C and higher at 10.9 for the device grown using the optimised recipe.

The results of TAC produced MoS₂ sensors demonstrate that TAC is very well suited to making low power room temperature operated chemiresistor gas sensors. This ultra low detection limit signifies that it is a strong candidate for future electronic gas sensing applications. Ideally, for this type of application selectivity is required, along with sensitivity. It is possible that a sensor built with different TMDs could allow for selective gas sensing, as different TMDs have different affinities for different analytes. It is envisaged that an array of different TAC produced TMDs could be placed on a chip and thus provide a route toward selectivity, however that is beyond the scope of this work.

Conclusions

This period of work began with the design and fabrication of a two-zone LPCVD furnace for the TAC synthesis of 2D TMDs. Using this apparatus, recipes were developed and optimised for thin films of several sulfide based TMDs, including MoS₂ and WS₂.

After synthesis, the thin films were thoroughly characterised using a wide range of methods including Raman spectroscopy, XPS, SEM, HIM, TEM, AFM and SE. The results of these characterisations allowed for the recipes to be optimised. TAC produces homogeneous films which are polycrystalline in nature, grain sizes are in the tens of nanometer range. It was shown that crystallinity can be enhanced by using higher synthesis temperatures, or more crystalline substrates.

Electrical properties were investigated by using Hall bars, van der Pau measurements and EDL-TFTs. These results indicate that TAC produced TMDs are most suitable for applications in sensing, optics and catalysis. The electronic quality is not suited for logic applications, due to the polycrystalline nature of the material. Sensor devices were created using a facile process flow involving shadow masks. These chemiresistor devices proved to be ultra sensitive, with MoS₂ showing a theoretical limit of detection of 51 ppb to NH₃. Further they showed good recovery, and were low power, operating at room temperature.

Chapter 5

Transition Metal Selenides

Due to the generality of the TAC process it is very easy to substitute one element from the recipe for another. Selenide TMDs are an obvious choice as they are complementary to the sulfides and they have some unique properties. While MoS₂, WS₂ and MoSe₂ are all intrinsically *n*-type, WSe₂ is intrinsically *p*-type. The ability to use TAC to synthesise WSe₂ and incorporate it into heterostacks is a potential route toward atomic scale *p-n* junctions. Room temperature μ_{FE} of 50 cm²V⁻¹s⁻¹ for MoSe₂¹⁹⁹ and 350 cm²V⁻¹s⁻¹ for WSe₂¹⁵⁹ have been reported for micromechanically exfoliated samples.

5.1 Selenisation Growth System

Motivation

A new quartz tube, thermocouple and crucible loaded with Se powder were installed in the furnace, and trial growth runs were performed. Unfortunately Raman analysis showed that sulfides, not selenides were being produced. Residual sulfur in the furnace system was preferentially reacting with the metal films and

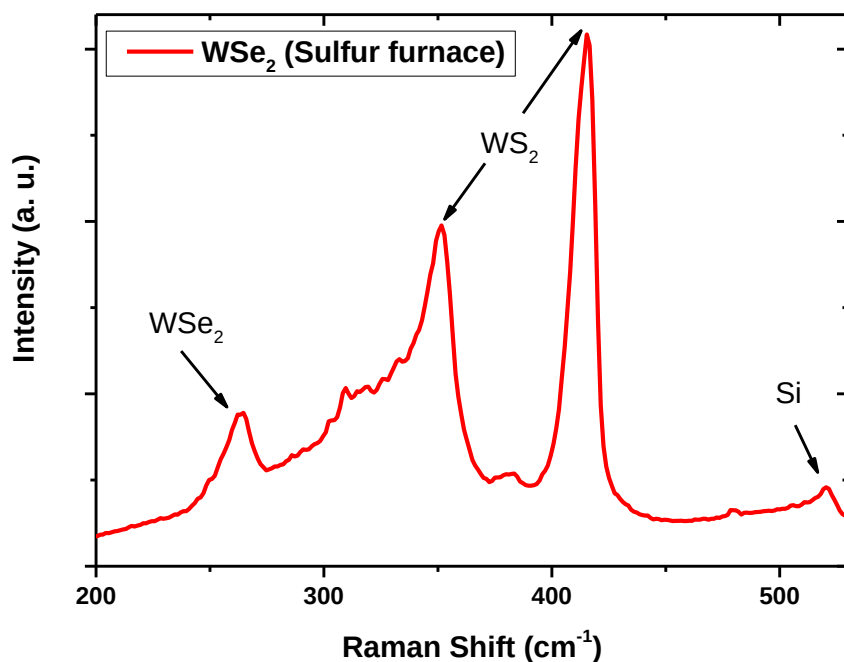


Fig. 5.1 Raman spectra of material produced after converting the sulfurisation furnace for selenisation. Due to persistent sulfur poisoning, the material produced contains a predominant WS₂ component, labelled.

affecting the resultant films. Several runs were performed, at various temperatures, with a large excess of selenium - however, sulfur poisoning was still dominant. One final effort was made to resolve the issue: KF fittings were replaced, the system was very thoroughly cleaned and conditioned, more selenium was added, and several additional synthesis runs were attempted, using both molybdenum and tungsten coated substrates. However, Raman analysis confirmed that the excess sulfur remained. Fig. 5.1 is a Raman spectra obtained from the fifth attempt, after the cleaning and reconditioning efforts. As can be clearly observed, the dominant features at $\approx 352\text{ cm}^{-1}$ and $\approx 419\text{ cm}^{-1}$ are the signature of WS₂. There is a feature at $\approx 260\text{ cm}^{-1}$, which could be from WSe₂. It is clear that excess sulfur was such an issue that it rendered the sulfurisation furnace unsuitable for

producing selenides. It was therefore decided to build a second LPCVD furnace system to be used exclusively for selenide growth.

Design

Taking into account elements learned from building and operating the sulfurisation furnace, it was possible to improve upon the design for the selenium furnace. The diameter of the tube was a limiting factor in the sulfurisation setup. The selenisation system was designed and built with larger diameter quartz tube, allowing for larger samples to be synthesised. During the design phase, it was decided that two horizontal furnaces would be best rather than another halogen setup. The hot zone where TAC occurs was designed to be stationary, however it was specified to be a split tube, allowing for rapid cooling. In order to create an independent hot zone to melt the selenium, a second furnace was utilised. This was designed to slide back and forth over a stationary crucible containing the selenium source. The ability to automate the process as much as possible was very compelling, as this would improve process reproducibility. A LabView program was developed for the LPCVD system by Dr. Kangho Lee which could automatically control and data-log the temperature of the furnaces, the gas flows, and the pressure. Further design upgrades specified that the MFCs and their controller could be used to maintain a constant pressure. In order for the automation, all major parts were specified to have either RS-485 or RS-235 functionality.

Build

A similar aluminium sliding frame (Item series 8 modular system) as was used for the sulfurisation furnace was designed and built. A major difference being that the split tube furnace was stationary, and only the furnace used for melting

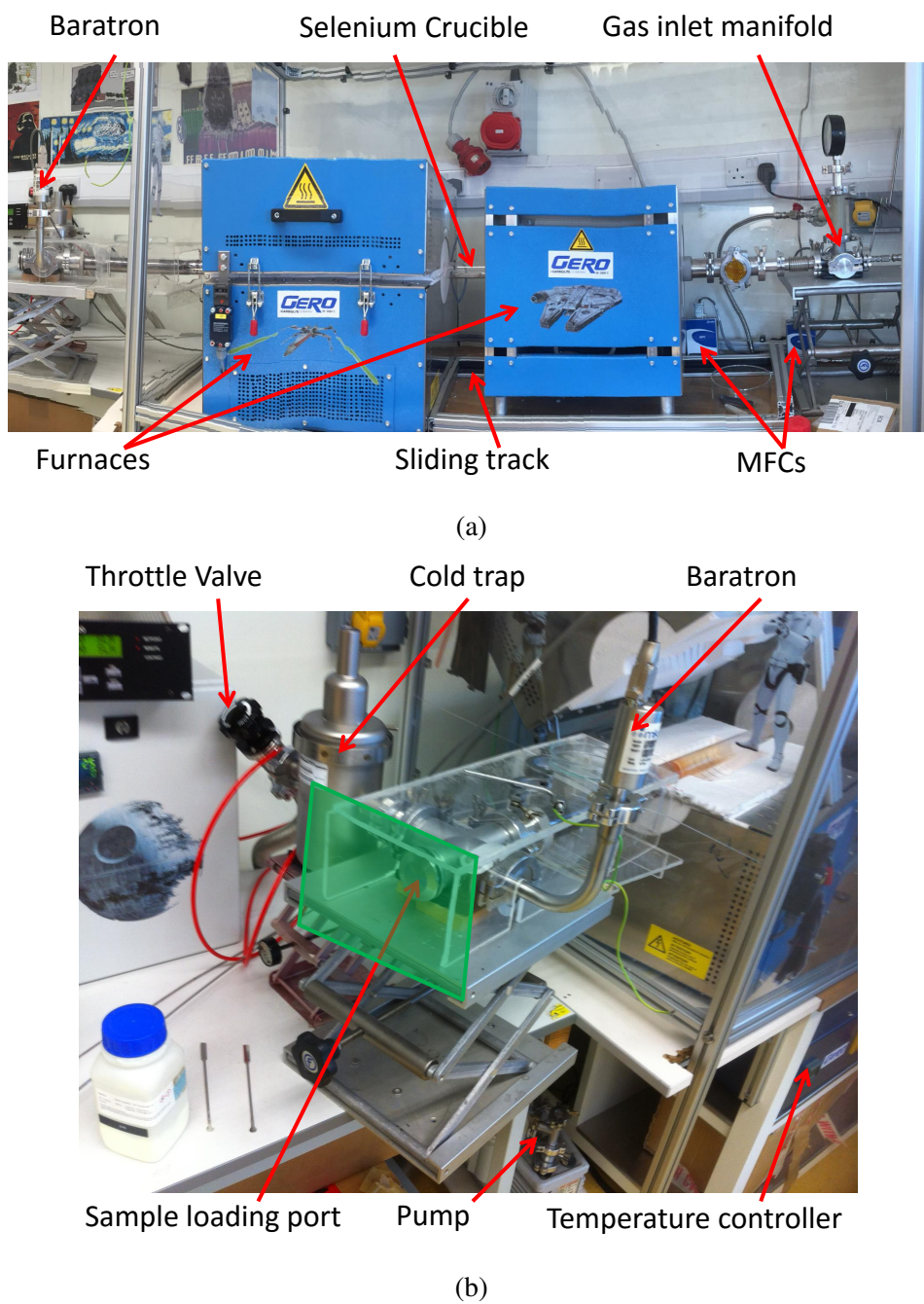


Fig. 5.2 Photographs of selenisation LPCVD furnace apparatus, with components labelled. The green shaded area in (b) indicates the extent of the negative pressure region.

selenium was made to slide along the track. The furnaces were purchased from Gero GmbH, one was a horizontal split tube type SR-A 40-250/11, the other a standard horizontal model (type SR 40-200/12). Both furnaces were powered by Gero RES-E 230/3 temperature controllers. The MFCs (GE50A 1 SLM) and the baratron (750B, 10 Torr) were connected to a four channel controller (647C), all from MKS, allowing for twice as many process gas options as in the sulfurisation setup. Only two of the four gas channels are currently used, however the system is capable of supporting two other gases, which is useful for future expansion. 1/4 inch stainless steel lines were branched off from the Ar and forming gas lines near the sulfurisation furnace, and were used to supply the respective MFCs in the selenisation system. Flexible braided stainless steel tubing ran from the MFCs to the system inlets. Fig. 5.2 shows photos of the assembled system, with several major components labelled.

The vacuum system was KF 40 instead of KF 25. This, along with a larger diameter quartz tube and allowed for larger samples to fit in the furnace (maximum substrate size is approximately 35 mm). Vacuum is provided by an Edwards RV12 pump, the layout of the vacuum system is the same as that designed for the sulfurisation furnace, diagrammed in fig. 4.1, the singular difference is that only one end of the tube contains a bellows. This change was made in order to simplify the sample loading process.

Safety

To avoid potential exposure to toxic byproducts of TAC, (Se and H_2Se), it was decided that the furnace should be encased in a protective shield. It was not feasible to move the furnace into a fume cupboard, so one was designed and built instead. An aluminium frame enclosing the system was constructed from

Item series 8. All four sides and the top were then cladded with 6 mm thick acrylic perspex panels in order to create a large transparent box around most of the system, the sample loading region extended out from the side of the enclosure. The front panel was made to slide upwards within the frame rails, in order to access the furnaces. Air entered from an adjustable gap between the enclosure and the table (≈ 2 cm), running around the entire perimeter. Exhaust ducting was through a 20 cm diameter flexible hose inserted into the top panel, and routed through the ceiling to the building's gas handling infrastructure. This ensured that the air around the system was constantly being extracted.

Through the use of hot glue and excess perspex, an extension to the enclosure was fashioned. It covered the sample loading port while still allowing adequate access to load and unload samples. Thus the area all around the system was actively exhausted. Fig. 5.2(b). is a photograph of the extension, the green shaded region highlights the extent of the negative pressure region. In order to ensure the safety of all users, a sample loading procedure was developed whereby the pump remains on and the valve is throttled, with Ar venting until the end cap can be removed. Immediately afterwards - the pump valve is re-opened during loading. This ensures that the harmful byproducts do not escape and that the furnace is not unduly exposed to oxygen.

Automation

Dr. Kangho Lee created a LabView program that automated the growth, allowed for more reproducible runs and accurately data logged the growth conditions. Parameters such as temperatures in both hot zones, process gas selection and flow rates, and time for each process step can be easily adjusted. The program displays real time pressure, temperature and furnace power output, and a temperature

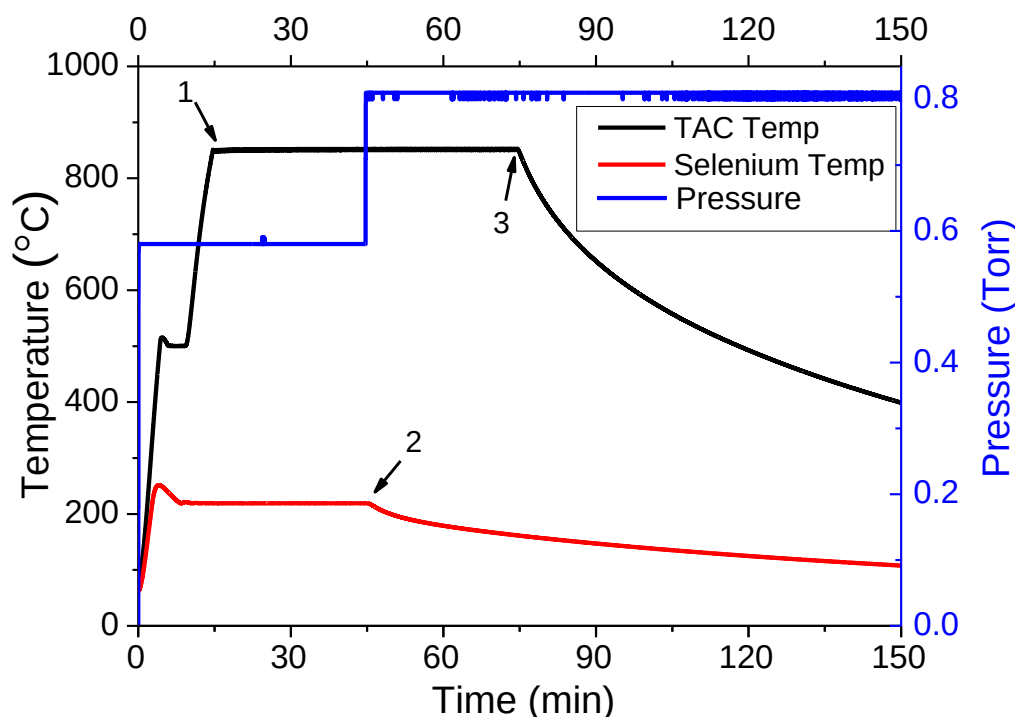


Fig. 5.3 Plot of data collected by the LabView program, growth steps are numbered, and referenced in the text

profile of each hot zone is created. Fig. 5.3 is a plot of the data that is collected from a typical run. The growth can be conveniently divided into three steps, as labelled. Prior to step 1 is an initial temperature ramp. It involves a two step ramp with a 5 minute delay for the TAC hot zone. This delay is needed in order to limit temperature overshoot and allow the selenium hot-zone to stabilise at the desired temperature before growth. At point 1, the furnace that melts the selenium is manually slid over the crucible, thus starting selenium flow. Between step 1 and 2 is the TAC phase, where growth occurs. At step 2, selenium flow is finished. The program switches from forming gas to Ar and turns off the selenium furnace. In order to stop the Se flow more abruptly, the furnace is manually slid away from the crucible. Between steps 2 and 3 is a high-temperature dwell, included in

order to improve the crystallinity of the films. Step 3 is the end of the growth, and the program shuts off the TAC furnace, thus allowing the samples to cool. The program continues recording data until the furnace lid is opened.

This apparatus was designed and built in order to be as flexible and adaptable as possible. As well as TAC synthesis, it has been successfully used to synthesise several different TMDs such as MoSe_2 , WSe_2 , ReSe_2 and PtSe_2 by CVD, where both the metal and selenium are in the vapour phase.

5.2 Selenide TAC Growth

Most of the research into 2D semiconducting TMDs has thus far focused on sulfides, particularly MoS_2 , with considerably fewer reports extending to the corresponding selenides. There have been few reports of TAC synthesised thin films of selenide TMDs.

TAC recipes were successfully developed for both MoSe_2 and WSe_2 . Growth temperature turned out to be a critical parameter in the film conversion process. Its effect was determined by synthesising films over a range of temperatures (550-800 °C) on Si/SiO_2 substrates with 5 nm starting metal thickness. Raman spectroscopy, XPS and SEM were used to characterise the material produced at each temperature. This revealed an optimal temperature range for a given material. Once this was established, the recipes were optimised further by investigating the effect of other variables such as substrate, gas composition, synthesis time and metal thickness.

5.3 Optical Characterisation

5.3.1 Raman

Raman spectroscopy was used to investigate the composition and quality of MoSe₂ films. As can be seen by fig. 5.4(a), typical MoSe₂ samples displayed four peaks characteristic of 2H-MoSe₂,²⁰⁰ namely the E_{1g} ($\approx 170 \text{ cm}^{-1}$), A_{1g} ($\approx 243 \text{ cm}^{-1}$), E_{2g}¹ ($\approx 286 \text{ cm}^{-1}$) and B_{2g}¹ ($\approx 350 \text{ cm}^{-1}$). The B_{2g}¹ mode is Raman inactive, however it becomes active in few layer TMDs due to the crystal symmetry breaking along the c-axis.¹⁷⁶ The presence of these features in the spectra confirm that selenisation was successful, and that 2H-MoSe₂ was the resultant material. Of these modes the A_{1g} and E_{2g}¹ are the most heavily investigated as they are related to out-of-plane and in-plane vibrational modes, respectively and can be used for layer number assessment.¹⁷⁶ The Raman spectra for the metastable 1T polytype is markedly different. The A_{1g} and E_{2g}¹ modes disappear, and are replaced by J₁₋₃ modes located at 106.4 cm^{-1} , 150.7 cm^{-1} and 221.4 cm^{-1} respectively.²⁰¹ In all cases the MoSe₂ produced was of the 2H polytype.

The effect of synthesis temperature was investigated. This is displayed fig. 5.4(b), in which the Raman spectra for films synthesised at different temperatures are normalised to the A_{1g} peak. The sample grown at 550 °C does not appear to be fully selenised. It displays an additional peak at $\approx 252 \text{ cm}^{-1}$ which may be due to unreacted selenium.²⁰² Further, the relative intensity of the MoSe₂ modes compared to those of the Si substrate and a noticeable blue-shift of the A_{1g} mode implies incomplete selenisation at 550 °C. Spectra of samples grown in the temperature range 600-800 °C are very similar with no significant changes in peak positions or relative intensity ratios. A small red-shift of the A_{1g} mode with

increasing temperature is observed. At each temperature above 550 °C Raman spectra indicate that MoSe₂ is produced.

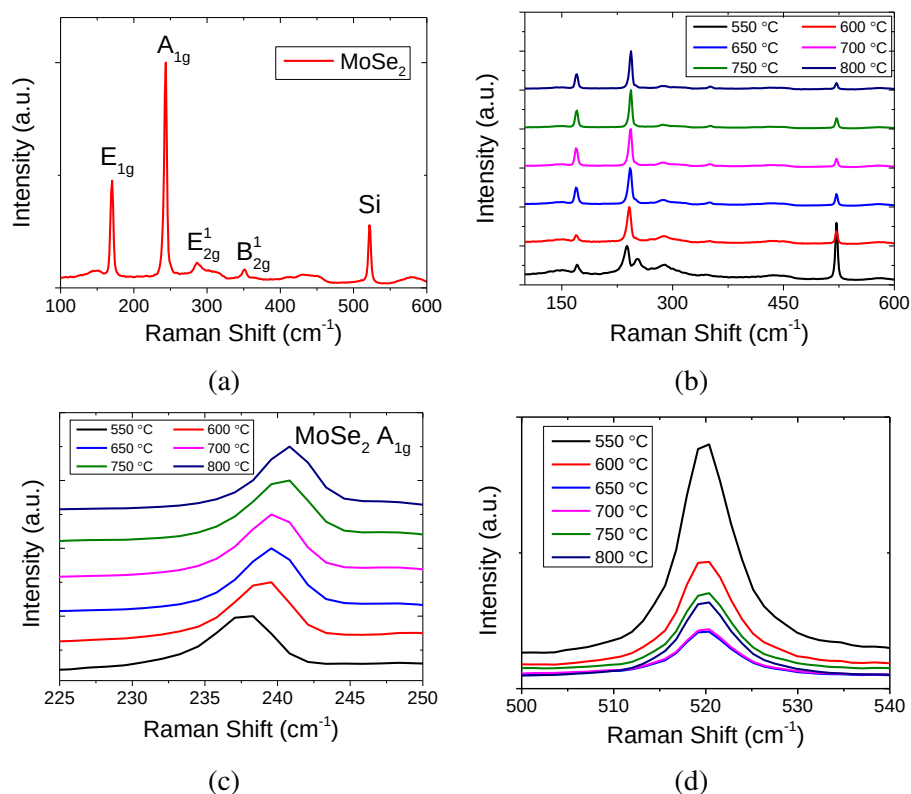


Fig. 5.4 (a) Raman spectrum of a typical MoSe₂ sample. (b) Raman spectra (c) A_{1g} region (d) Si region of 5 nm MoSe₂ on SiO₂ synthesised from 550–800 °C, normalised to A_{1g} peak.

In order to better analyse the shift of the A_{1g} mode, the region between $\approx 225 \text{ cm}^{-1}$ and $\approx 255 \text{ cm}^{-1}$ was plotted, and is displayed in fig. 5.4(c). A trend of A_{1g} peak position red-shifting with increasing temperature is clearly evident. This is most extreme in the 550 °C case, manifest at $\approx 237.5 \text{ cm}^{-1}$. The A_{1g} peak position for all other temperatures fall within the $\approx 239\text{--}241 \text{ cm}^{-1}$ range. In order to confirm that this effect was not an artefact, the Si peak was similarly plotted as a reference. As can be seen in fig. 5.4(d), the Si peak shows no appreciable shift

confirming that the A_{1g} shift is real. It is probable that the higher temperature growth creates films with higher crystallinity.

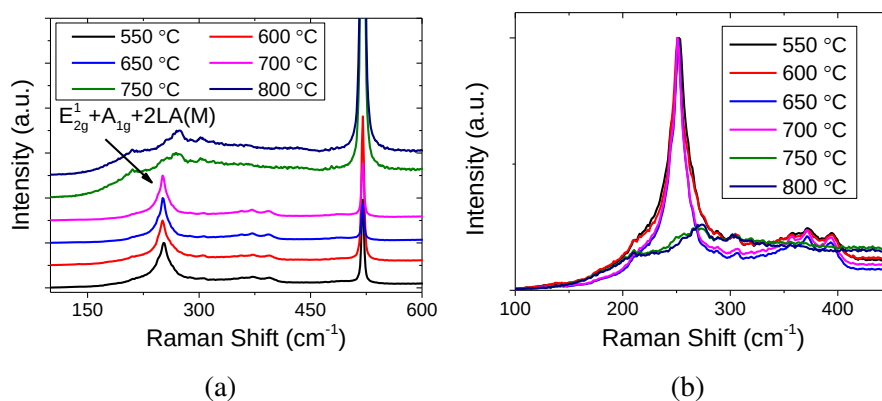


Fig. 5.5 (a) Raman spectra of 5 nm WSe₂ synthesised from 550–800 °C on SiO₂ substrates (b) E_{2g}^1 , A_{1g} and 2LA(M) region

An investigation of temperature dependant synthesis was also performed on WSe₂, results of Raman measurements are given in fig. 5.5. In this case, it was observed that the synthesis only worked at lower temperatures. The growth at 750 °C and 800 °C did not produce WSe₂. This is clearly evident by fig. 5.5(a), displaying Raman spectra normalised to the broad, yet sharp feature at $\approx 252 \text{ cm}^{-1}$. This peak is a signature of 2H-WSe₂, it consists of a combination of E_{2g}^1 , A_{1g} , and 2LA(M) modes. They are present at ≈ 248 , ≈ 250.8 and $\approx 260 \text{ cm}^{-1}$ respectively.^{173,176} To date, the vast majority of WSe₂ Raman information published in literature is obtained from either micromechanically exfoliated or CVD grown samples. These reports describe very crystalline, idealised systems. Tonndorf *et al.*¹⁷⁶ have resolved the E_{2g}^1 and A_{1g} peaks in bulk MoSe₂, in order to accomplish this, they used a very high resolution spectrometer grating with $2400 \text{ lines mm}^{-1}$. The growths at 750 °C and 800 °C do not exhibit this peak and therefore these temperatures are too high to produce WSe₂. In order to show this more clearly, the spectra are displayed (fig. 5.5(b)), with the lower temperature spectra normalised

to the WSe₂ peak at 252 cm⁻¹. The small peak at 302 cm⁻¹ is a second order transverse optical phonon band, originating from the crystalline Si substrate. It is approximately the same intensity for all of the WSe₂ samples. The samples grown at 750 °C and 800 °C were normalised to this Si peak. It is clear that the higher temperature synthesis failed to produce any WSe₂. 1T-WSe₂ exhibits features with very much reduced intensity, also peaks at ≈ 50 cm⁻¹ and ≈ 150 cm⁻¹ emerge.²⁰³ These features were not observed, therefore the TAC process produced no appreciable amount of 1T-WSe₂.

5.4 Morphological Characterisation

5.4.1 Scanning Electron Microscopy

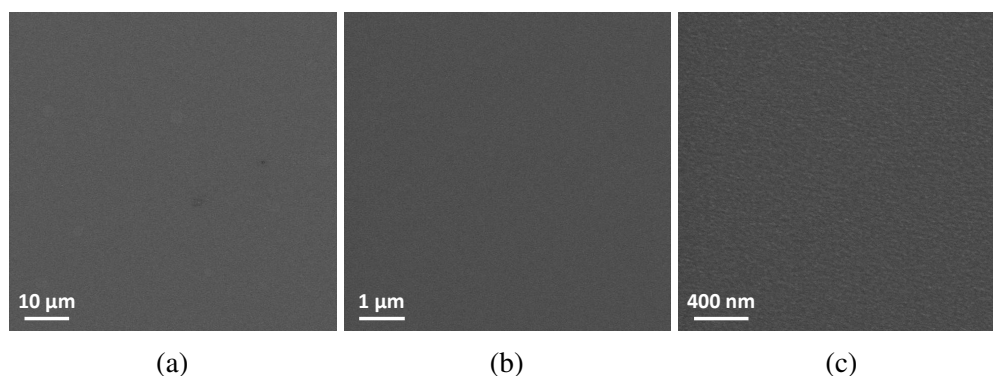


Fig. 5.6 Scanning electron micrographs of MoSe₂ with 5 nm starting metal thickness, synthesised at 700 °C. Magnification was (a) 1 kX, (b) 10 kX, (c) 30 kX.

The morphology of the MoSe₂ thin films was investigated by SEM. A secondary electron detector was used with a working distance of 1.5 mm and an accelerating voltage of 2 kV. SEM images of MoSe₂ synthesised at 700 °C taken at low magnifications are displayed in fig. 5.6. These films are homogeneous,

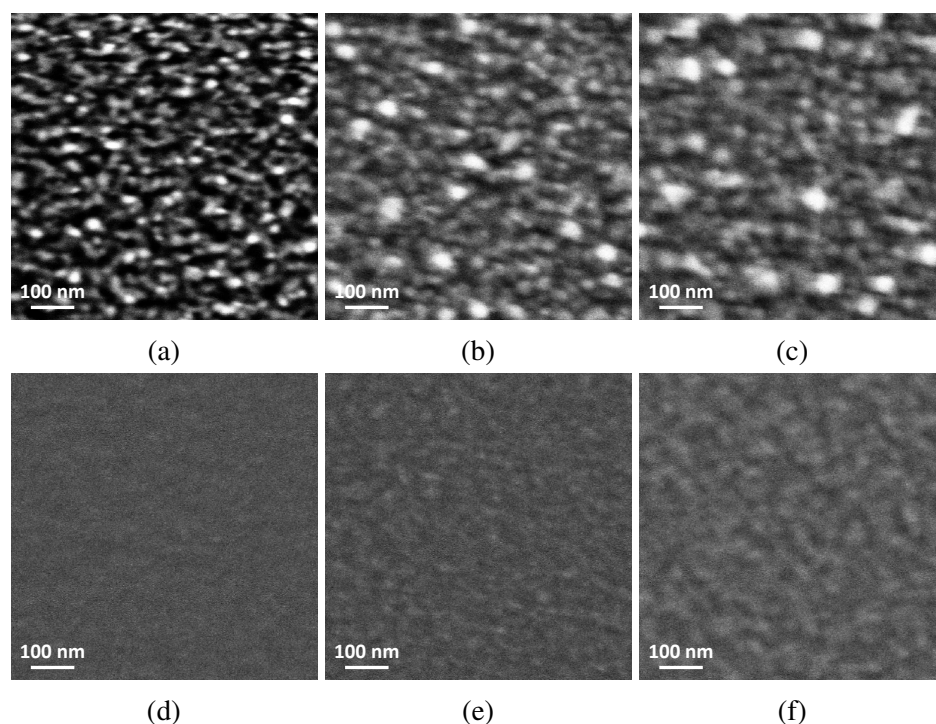


Fig. 5.7 Scanning electron micrographs of MoSe₂ with 5 nm starting metal thickness, secondary electron detector utilised, 100 kX magnification. Films were synthesised at (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, (e) 750 °C, (f) 800 °C.

with no features of note visible. The films are free of cracks, voids, tears, and delamination in good agreement with previously discussed Raman results. At these magnifications, no grain structure is discernible, for samples grown at various temperatures.

Increasing the magnification to 100 kX does show more detail, as can be seen in fig. 5.7 and allows for a comparison of films grown at different temperatures. Fig. 5.7(a) shows the morphology of the film grown at 550 °C. It shows a disordered film, with black regions, possibly due to pitting and bright protrusions. This is the only temperature where these black regions are observed, and this correlates well to Raman spectra where the growth at 550 °C showed incomplete conversion. At 600 °C (fig. 5.7(b)) The black regions are gone, and the grains appear more

homogeneous. No major difference is observed at 650 °C (fig. 5.7(c)). At 700 °C (fig. 5.7(d)) the decoration disappears, and the films appear very homogeneous. As the temperature is increased further to 750 °C, some structure begins to appear (fig. 5.7(e)), and the grains are somewhat enlarged at 800 °C (fig. 5.7(f)). SEM agrees with Raman in that the growth at 550 °C is the most disordered, with another material perhaps present at this low temperature. The other growths appear to be more homogeneous, and the grains appear to become enlarged as temperature is increased. Protrusions are featured at lower growth temperatures, and they disappear at temperatures above 700 °C.

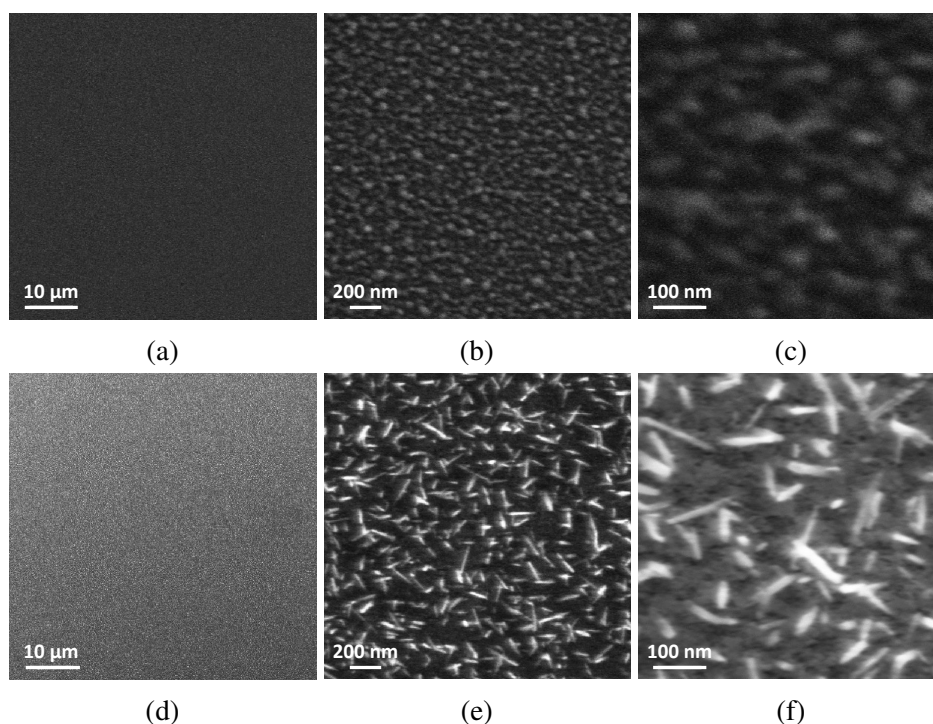


Fig. 5.8 Scanning electron micrographs of WSe₂ with 5 nm starting metal thickness. Films were synthesised at (a - c) 550 °C, (d - f) 650 °C.

WSe₂ synthesis was also investigated by SEM. Growth at 550 °C is displayed with increasing magnification along the top row of fig. 5.8, while the bottom row shows growth at 600 °C. At a magnification of 1 kX (fig. 5.8(a), (d)) both films

are observed to be homogeneous. When the magnification is increased to 30 kX, some structure becomes resolved. the growth at 550 °C (fig. 5.8(b)) shows some faint features 20-50 nm across. There is a distinct change to the sample grown at 650 °C. Wire like protrusions are observed. Further magnification to 100 kX allows for better visualisation of these features. The grains in the 550 °C sample appear to be around 50-100 nm in size. Investigation of the wire like features observed in the 650 °C growth show that they are 50-150 nm in length, and around 20 nm wide. They are easily distinguished from the underlying material. Similar features have been identified as vertical WSe₂ crystallites which are orientated perpendicular to the substrate.²⁰⁴ Preferential orientation of these platelets has been attributed to compressive stress in the metal film prior to TAC.²⁰⁵

5.4.2 Helium Ion Microscopy

HIM was also used to examine the morphology of the MoSe₂ and WSe₂ films, in an effort to overcome the limitations of SEM imaging. Samples produced from a metal thickness of 5 nm on sapphire were synthesised and imaged. Fig. 5.9 (a - c) are of MoSe₂, while (d - f) are WSe₂. Low magnification images (a, d) show that both materials are homogeneous, with no cracks, tears inhomogeneities or holes present. The WSe₂ was synthesised using the same temperature and growth parameters as the sample analysed by SEM. The only difference was the use of a sapphire substrate. Interestingly, no needle like protrusions are observed for the sample grown on sapphire. This result is not surprising. If the needle like feature were a result of vertical TMD growth arising from compressive strain during metallisation, it is probable that the more crystalline sapphire substrate, which is known to allow for larger TMD domains, could allow for synthesis with

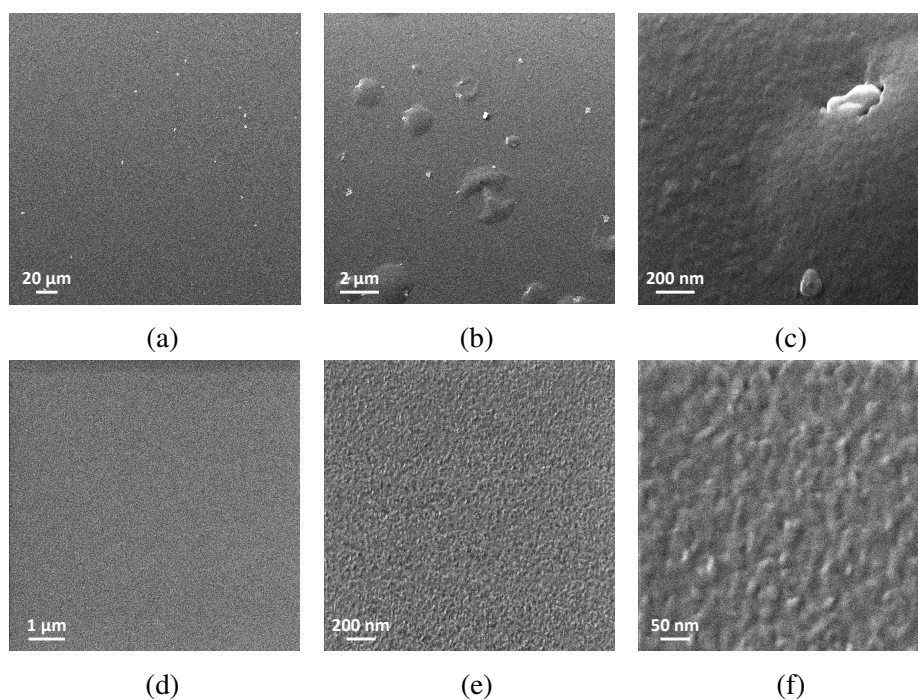


Fig. 5.9 Scanning helium ion micrographs of (a - c) MoSe₂ and (d - f) WSe₂. TAC films synthesised from 5 nm metal thickness on sapphire substrates, at 800 °C for MoSe₂, and 650 °C for WSe₂.

less strain in the film. At the highest magnification WSe₂ shows what appears to be domains, around 30-60 nm in size.

5.5 Chemical Characterisation

5.5.1 X-ray Photoelectron Spectroscopy

XPS measurements were performed on MoSe₂ and WSe₂ samples, produced from a nominal metal thickness of 5 nm, grown under varying conversion temperatures from 550-800 °C. In each case, the atomic ratio was estimated by comparing the area under the fitted Mo 3d_{5/2} and the Se 2p_{3/2} peaks, while accounting for the relative sensitivity factors (RSFs).

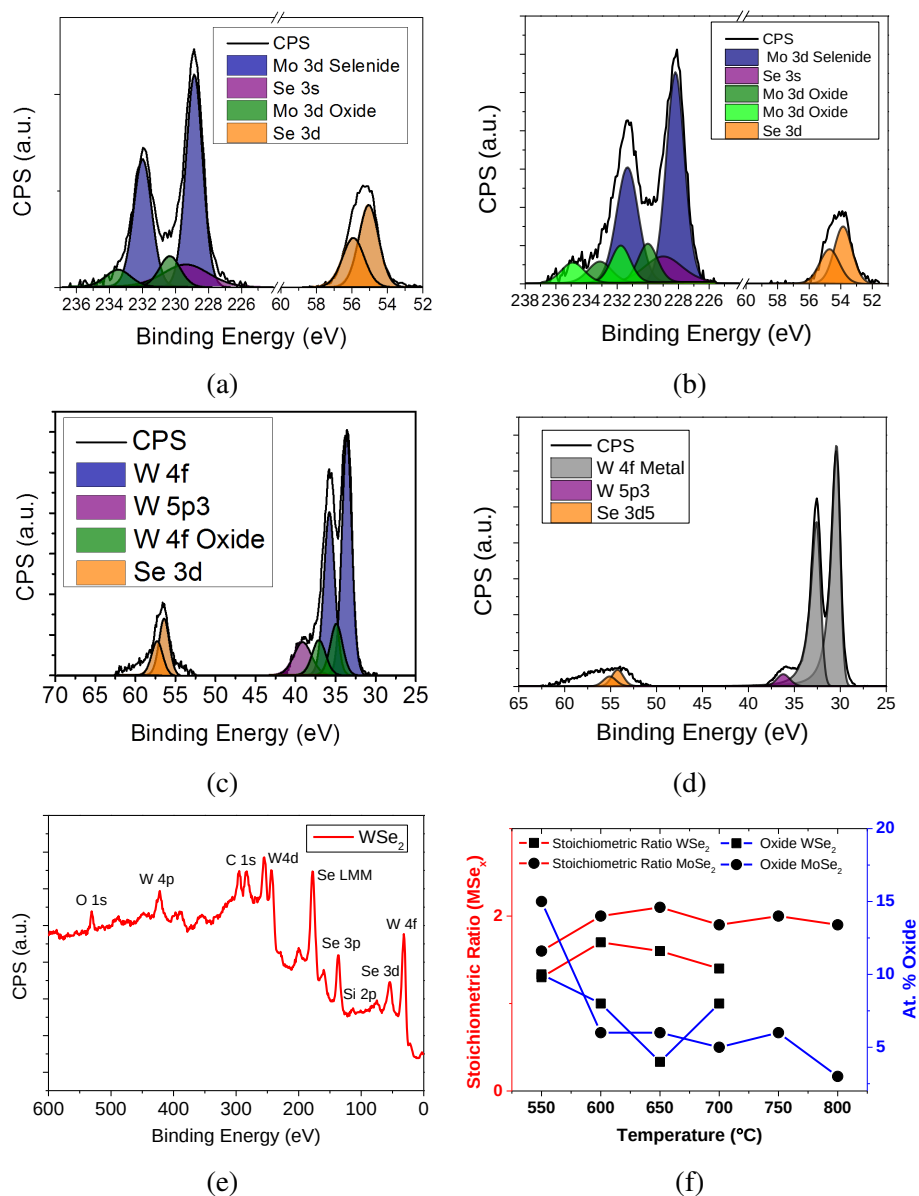


Fig. 5.10 XPS core level spectra of 5 nm (a) MoSe₂ grown at 750 °C, (b) MoSe₂ (550 °C), (c) WSe₂ (650 °C) and (d) WSe₂ (750 °C) with fitted components, after subtraction of a Shirley background. (e) Survey scan of WSe₂ synthesised at 650 °C. (f) Plot relating the stoichiometric ratio and oxide levels to growth temperature for both WSe₂ and MoSe₂.

As shown in Fig. 5.10(a), the Mo 3d core-level can be fitted with one main component at a binding energy of ≈ 228 -229 eV for the Mo 3d_{5/2} peak (blue), which originates from selenised Mo, and one smaller component on the high binding energy side of the peak (green) which is most likely related to residual oxides.²⁰⁶ The spin-orbit splitting in the Mo 3d doublets is 3.14 eV and the branching ratio (Mo 3d_{3/2} to Mo 3d_{5/2}) is 2:3. All components of the Mo 3d line have been fitted using a mixed Gaussian-Lorentzian line shape with a FWHM of 1.3 ± 0.2 eV. These spectra are complicated by the fact that they lie on top of the Se 3s level, which has been fitted with a FWHM of 3.5 eV (purple), and normalised to the Se 3d. The Se 3d core-level (orange) could be fitted with only one component at a binding energy of 55 eV, indicating that there is no unreacted selenium on the surface. Stoichiometric MoSe₂ was found for each sample in the range of 600-800 °C, *i.e.* $x = 2 \pm 0.1$. Further the oxide contributions were found to be minimal, and around 5% for these samples, which is most likely a surface oxide, occurring while the samples were exposed to ambient environment prior to XPS analysis. Similar residual oxide is observed for all samples, regardless of temperature or composition, including the sulfides. At 550 °C (fig. 5.10(b)) the material produced is not entirely MoSe₂. Higher oxide contributions (16 atomic %) are present and the stoichiometric ratio was found to be 1.6. The survey scans for all MoSe₂ samples (not shown) display a lack of any appreciable contaminants, demonstrating the high purity of the films. These XPS measurements are in excellent agreement with the Raman results and they confirm that MoSe₂ could be synthesised in a wide range of temperatures, from 600-800 °C, with incomplete conversion at 550 °C. Based on Raman analysis, it was expected that amorphous unbound selenium might be present at the sample grown at 550 °C, however no unbound elemental selenium was observed by XPS.

XPS analysis was also performed on WSe₂ samples grown at the same temperatures. As can be seen in fig. 5.10(c), for WSe₂ synthesised at 650 °C, the majority of the metal is bound to selenium, which is manifest as the large doublet (blue) at 33 eV with some residual oxides still present (green).²⁰⁷ The spin-orbit splitting in the W 4f doublets is 2.18 eV and the branching ratio (W 4f_{5/2} to W 4f_{7/2}) is 3:4. All components of the W 4f line have been fitted using a mixed Gaussian-Lorentzian line shape with a FWHM of 1.2±0.2 eV. At all temperatures, there exists some considerable background contribution around the selenium peak (orange), which could be due to an amount of excess amorphous Se on the surface. The atomic ratio was found to be around 1.3-1.7 for samples grown from 550-700 °C. It is possible that this ratio is underestimated, due to the difficulty in deconvoluting the Se peak from the background.

Synthesis temperatures above 700 °C did not produce WSe₂. As depicted in fig. 5.10(d), the higher temperature spectra were well fitted with an asymmetric doublet for tungsten metal (grey), with a FWHM of 1.0 eV. Further, there was no observable Se doublet, indicating that the films synthesised above 700 °C did not contain any selenium covalently bound to tungsten, rather any selenium on the surface was present as an amorphous layer. XPS makes it clear that WSe₂ was not produced at temperatures above 700 °C, the material appears to be predominantly W metal. These XPS results are in excellent agreement with the Raman spectra for WSe₂. They confirm that synthesis is successful at temperatures up to 700 °C. Higher temperatures do not produce WSe₂

The survey scan of WSe₂ shown in fig. 5.10(e) shows an absence of unwanted contaminants. All major peaks are due to either selenium, tungsten, silicon or oxygen indicating that within the detection limit of the XPS the material is pure. Charge compensation for all selenide spectra was achieved by shifting the

survey spectra such that the O 1s peak was centred at 531 eV. There exists a Se LMM Auger line at 287 eV, this overlaps with the adventitious carbon C 1s peak, rendering it unsuitable for charge compensation. The error associated with peak positions for this system is ± 1.0 eV.

Fig. 5.10(f) is a plot of both the oxide % (blue lines) and the stoichiometric ratio (red lines) for both MoSe₂ (circles) and WSe₂ (squares). It is clear that MoSe₂ is produced at all temperatures above 550 °C, and oxide contributions are negligible. It is also clear that the stoichiometric ratio for WSe₂ is >1.5 produced at all temperature below 750 °C, as discussed, this is possibly an underestimation due to the amorphous selenium signal. Oxide levels are < 10 % for WSe₂ and ≈ 5 % for MoSe₂ samples.

5.6 Recipe Optimisation

Through extensive Raman, XPS and SEM characterisation of films grown at different temperatures, recipes were developed for both MoSe₂ and WSe₂. Optimised recipes resulted through further refinements of the growth, and are summarised in table 5.1. A synthesis time of 2 hours led to more reproducible growth, this became standard procedure early in recipe development. When synthesis time was 30 minutes or 1 hour, occasional growth runs inexplicably failed. This was no longer an issue when the synthesis time was extended to 2 hours. Forming gas had a negligible effect, it was included in the majority of the runs, however excluding it did not negatively affect the material. The temperature of the selenium furnace was calibrated so that an excess was present during growth. This was easily observed by selenium deposits on the tube downstream of the synthesis hot zone.

Table 5.1 Selenide recipe optimisation details

Parameter	MoSe ₂	WSe ₂
Forming gas pressure (mTorr)	580	580
Argon pressure (mTorr)	800	800
Growth time (mins)	120	120
Cool down time, synthesis to room temperature (mins)	210	195
Growth temperature (°C)	800	650
Selenium temperature (°C)	220	220

Increasing the selenium temperature by as little as 2 degrees drastically increased the amount of excess selenium, however it had no effect on the material produced.

Cooling time was also investigated, with the theory that slower cooling might lead to films with larger domains, and less stress or strain. There was no appreciable difference whether the split tube furnace was opened immediately after growth, reaching RT in less than an hour, or if the furnace was kept closed overnight, cooling to RT over several hours. Typically, the furnace was opened after the temp was below 500 °C, this was done in order to allow as much time as possible for high temperature processes such as grain ripening to occur. The effect of varying these parameters was investigated through Raman or XPS, and as these results are very similar to those already reported, they are not shown.

Fig. 5.11 is a photograph of MoSe₂ grown at 750 °C and WSe₂ synthesised at 650 °C, from different starting metal thicknesses (labelled), on 1 cm² pieces of fused quartz. It is clear that the opacity increases with thickness, films of starting metal thickness of 10 nm or greater appear metallic.

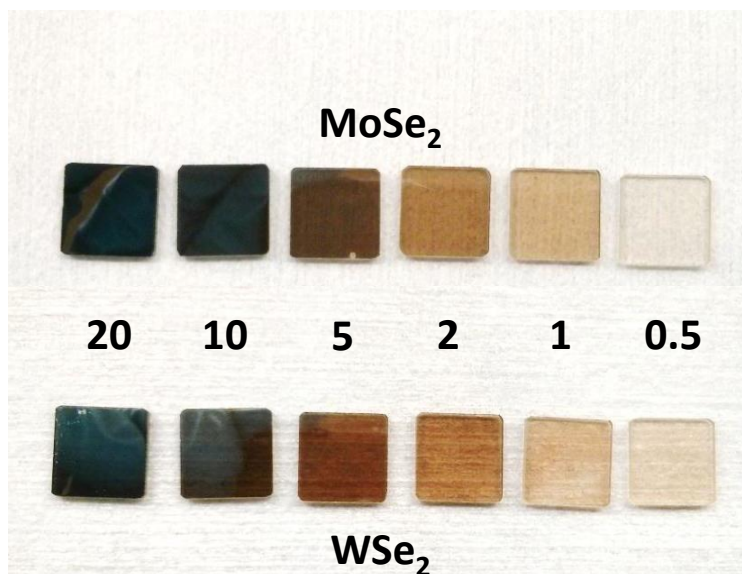


Fig. 5.11 Photograph of films of MoSe₂ (top) and WSe₂ (bottom) on fused quartz , substrates are 1 cm².

5.7 Electrical Results

5.7.1 Si/ SiO₂ Back-Gated TFTs

Heavily doped (p++) Si substrates with 300 nm SiO₂ dielectric layer were used to fabricate back gated TFTs. TAC was performed on a film with a starting W thickness of 5 nm. After conversion, EBL was used to define electrodes and create a TFT, as can be seen in fig. 5.12(a), which shows a picture of the device. Device lithography and measurement was performed by Wungyeon Kim. The channel width was 80 μm , and various channel lengths, from 1-10 μm were defined. The following discussion refers to those measurements performed on a device with a channel length of 3 μm . Source drain *IV* measurements were performed at various gate biases (V_g). from -60 to 60 V. As can be seen in fig. 5.12(b), the I-V relationships are linear, and the resistance increases with increasing V_g .

Fig. 5.12(c) is a transfer plot of the device, the drive voltage is 100 mV. The transfer plot shows *p*-type behaviour, as expected for WSe₂ type TFTs. The current on:off ratio is 2. Using equation 2.21, the hole field-effect mobility was calculated to be $0.91 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This is much lower than mobilities reported for WSe₂ thin film TFTs produced using micromechanically exfoliated flakes and dielectric encapsulation. This measurement was performed using a Si/SiO₂ substrate, TAC synthesis, and no encapsulation. Each of these factors are not ideal, and they negatively affect the electrical properties, however, the system is much more industrially relevant than idealised systems which report higher mobilities. Similarly to the sulfides, it is likely that the performance is limited by domains in the TAC films.

It is an important result that TAC can be used to produce *p*-type TFTs as well as *n*-type. This is a potential route toward applications requiring complimentary materials.

5.7.2 Ionic-Liquid Gel-Gated TFTs

The field effect mobility of MoSe₂ was measured using top-gated EDL-TFTs similar to those described in section 4.6.2. The only change was the length of the channel, a nine-finger IDE pattern with a width of 15 mm and length of 120 μm was employed in order to increase the size of the channel, and increase I_{sd} . The measurement apparatus, ionic-liquid block co-polymer gel top gate and metal contact thickness were all the same as was used for MoS₂. The gate voltage was swept at 100 mV min^{-1} , and a drive voltage of 100 mV was used in measuring I_{sd} every 300 mV.

Fig. 5.13 shows transfer curves for MoSe₂ synthesised at 800 °C and 1000 °C. Using equation 2.22, the μ_{FE} values for MoSe₂ produced at 800 °C and 1000 °C

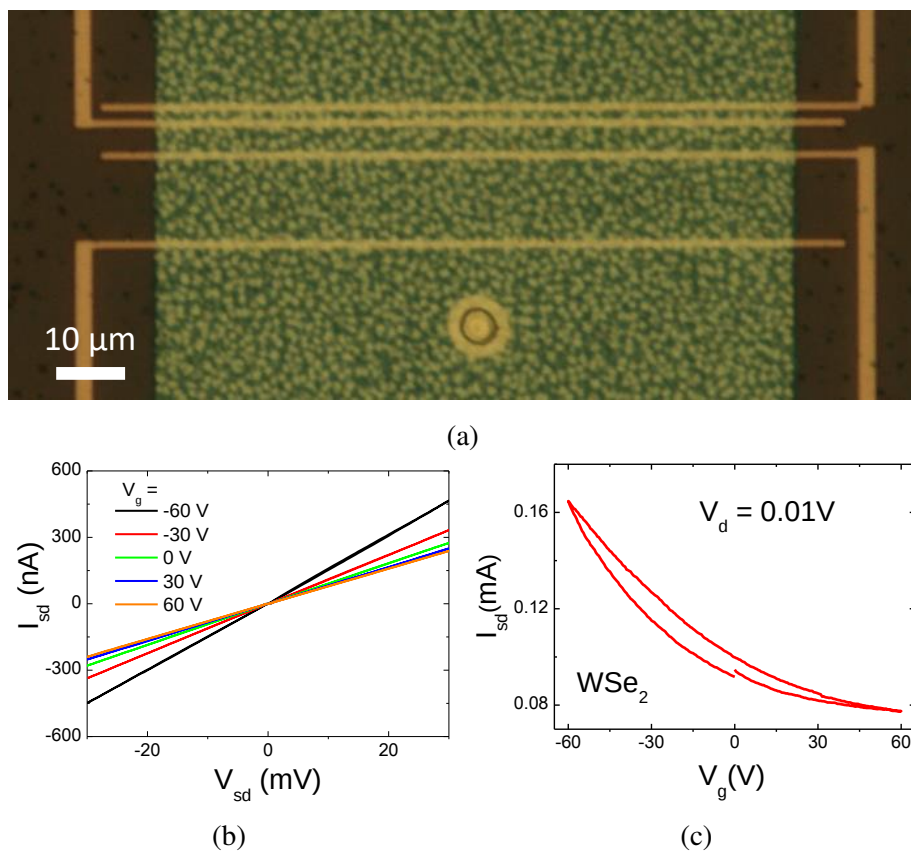


Fig. 5.12 WSe₂ TFT (a) optical image, (b) linear I - V plot, (c) transfer plot.

were calculated as $4.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $20.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively. The on/off ratios were also determined to be at least 900 and 250 for MoSe₂ grown at low and high temperatures, respectively. These ratios are most likely higher, since saturation was not reached within the available electrochemical stability window of the ionic-liquid.

These μ values were lower than those reported for CVD or micromechanically exfoliated samples. The reasons for this discrepancy arise from the polycrystalline nature of TAC grown films, limited by defects, grain boundaries *etc.* For both low and high temperature growth, MoSe₂ displays a higher μ_{FE} value than MoS₂ this

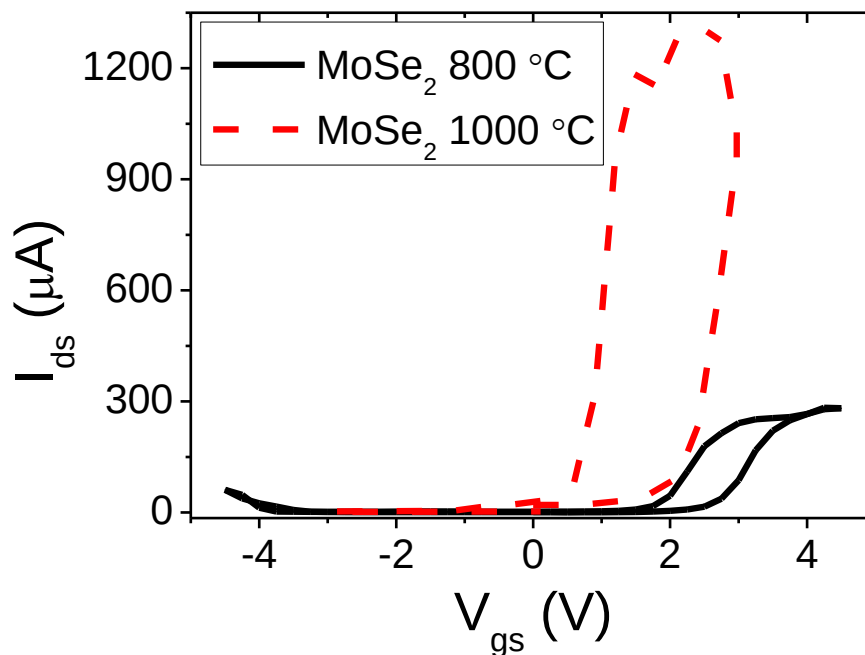


Fig. 5.13 Transfer curves for EDL-TFTs using MoSe₂ as the channel material

is in agreement with theoretical predictions and experimental measurements¹⁵⁶ it is due to a higher m_e as the atomic number of the chalcogen increases.²⁰⁸

5.7.3 Gas Sensors

MoSe₂

Gas sensors utilising MoSe₂ active layers were created in analogy with the MoS₂ sensors described in section 4.6.3. The same IDE device design was used, including titanium contacts. MoSe₂ TAC synthesis was performed at 800 °C, with a starting metal thickness of 5 nm. An IV of one such device is presented in fig. 5.14(a) showing a device resistance of 4.62 kΩ, and very linear behaviour between a bias sweep of ±100 mV.

Sensor devices were tested in the presence of both NH₃ and NO₂ gases, which decreased and increased, respectively the resistance of the MoSe₂ films.

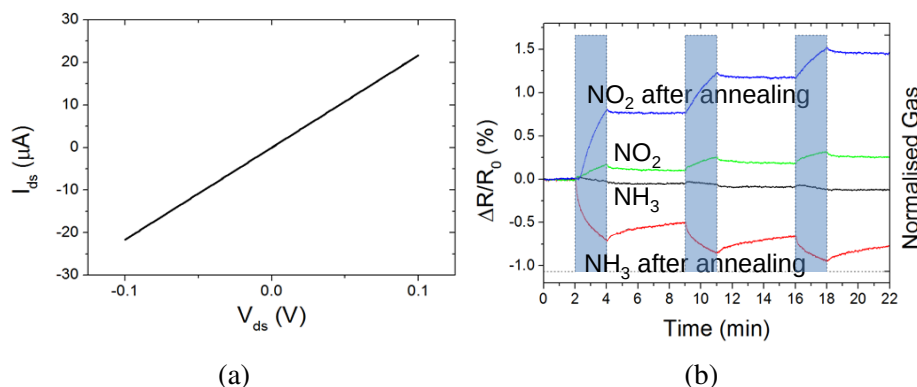


Fig. 5.14 MoSe₂ chemiresistor sensor (a) linear I - V (b) sensor response plot showing the effect of annealing and analyte

Adsorbed NH₃ molecules donate electrons and shift the Fermi level towards the conduction band, resulting in a resistance decrease as MoSe₂ sensors displayed n -type behaviour. In the case of NO₂ introduction, its electron-withdrawing ability increases the resistance by shifting the Fermi level towards the valence band. These contrasting behaviours are well depicted in fig.5.14(b), where gas injection is represented by the blue shaded regions. The sensitivity of the MoSe₂ sensor was improved by annealing at 100 °C for 1 hour. This removed adsorbates and residues on the surface (NH₃: red line, NO₂: blue line).

Sensor sensitivity was evaluated through closer inspection of the sensor response plots at low gas concentrations. As discussed in section 4.6.3, signal processing provides SNRs through equation 4.5 which allows for determination of the sensor LOD. Fig. 5.15(a) and 5.15(b) are gas response plots for a 5 nm MoSe₂ sensor tested in the presence of NH₃ and NO₂ respectively. The blue shaded regions represent 2 minute gas injections. The gas response is more pronounced for higher concentrations, as expected. It is also evident that recovery in pure N₂ flow is not complete, as the baseline shifts during consecutive gas injections. Tight-bonding between MoSe₂ and gas molecules may be responsible

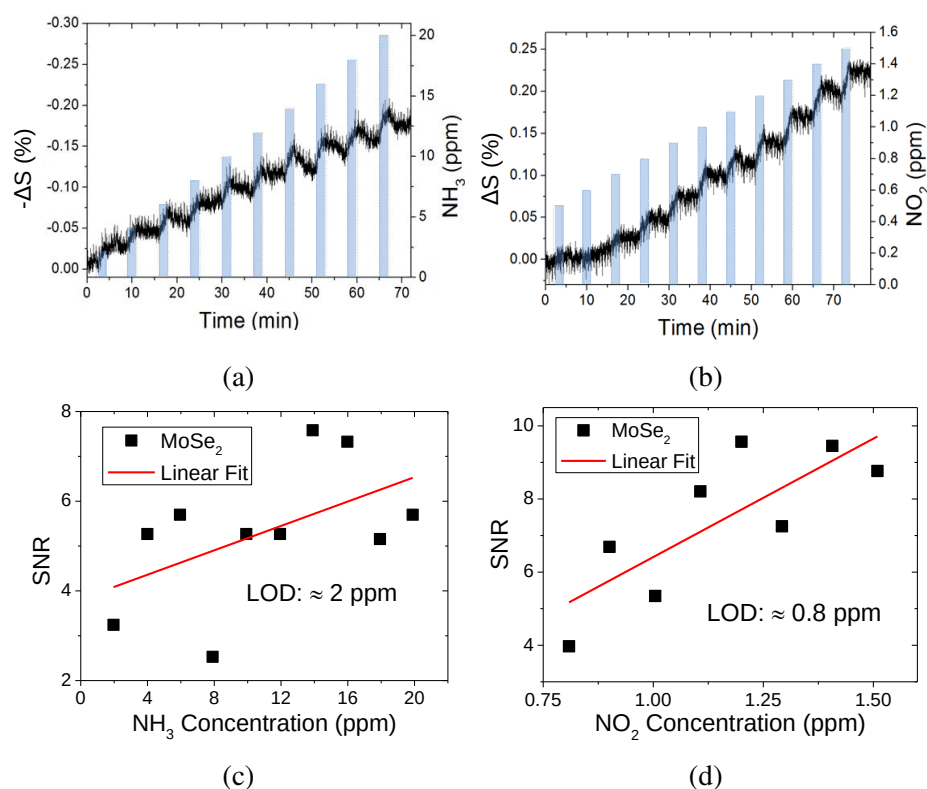


Fig. 5.15 MoSe_2 sensor response plots for (a) NH_3 and (b) NO_2 . SNR vs. concentration plots for (c) NH_3 and (d) NO_2 .

for this slow recovery, as discussed with MoS_2 sensors. Fig. 5.15(c) and 5.15(d) are plots of SNR vs. gas concentration for NH_3 and NO_2 respectively, with data linearly fitted. Extrapolating the fitted line to a SNR of 3 gives the theoretical LOD for each gas. The LOD was 800 ppb for NO_2 and 2 ppm for NH_3 .

These values are ultra-low and they show that MoSe_2 is a very promising material for future sensing applications. Importantly, these sensors operate at room temperature, they only require 2 min gas exposure times, and they are low power, stand alone devices. Other materials demonstrate similar sensing performance, however they operate at elevated temperatures, and require much longer analyte exposure times, and they often display inferior recovery.

WSe₂

WSe₂ based chemiresistor gas sensors were also investigated. The same IDE device design was used, with the same choice of contacts. WSe₂ TAC synthesis was performed at 650 °C, with a starting metal thickness of 1 nm. The devices exhibited a very linear IV (not shown) between a bias sweep of ± 0.5 V, a resistance of 10.2 k Ω was calculated.

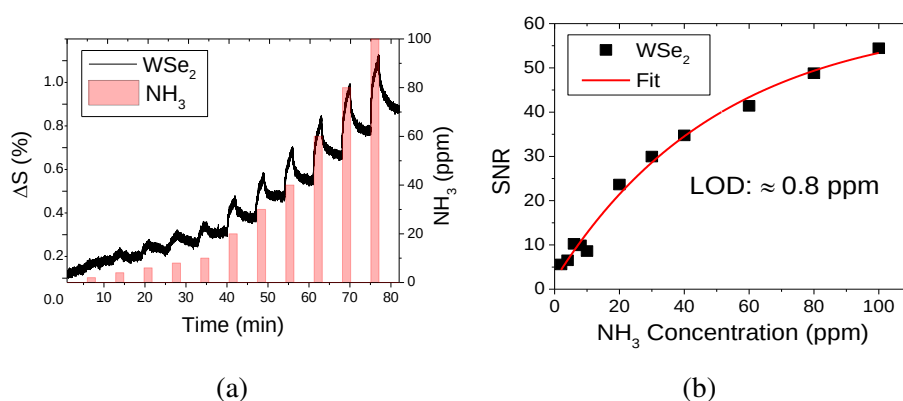


Fig. 5.16 WSe₂ sensor plots for NH₃, (a) sensor response plot (b) SNR vs. concentration.

The full-scale sensor response plot for exposure to NH₃ is shown in fig. 5.16(a), red lines indicate NH₃ injections for two minutes. The *p*-type nature of the material is evident by the increased resistance upon gas exposure. As the NH₃ injects electrons into the system, these added electrons reduce the amount of holes contributing to current, thus increasing the resistance of the device. The sensor response plot also features gradual baseline shifting, and a larger response at higher concentrations, as previously observed with other TMD sensors. Signal processing was used to determine the SNR for each injection. Because the SNR data was very noisy at the lower concentrations, the entire range was fitted with an exponential in order to determine the theoretical LOD. Fig. 5.16(b) shows

the fitted SNR data, and the sensor displays a theoretical LOD of 0.8 ppm. This compares favourably with the NH_3 LOD of MoSe_2 , which was 2 ppm.

Conclusions

Due to catastrophic sulfur poisoning, an entirely separate and upgraded LPCVD system was designed and built, solely for selenide growth. Similarly to the sulfides, thin films of Mo and W underwent TAC in a selenium environment, forming the corresponding semiconducting 2D TMDs. Temperature proved to be a crucial parameter in selenide synthesis, and optimised recipes for both MoSe_2 and WSe_2 were successfully developed. There was an overlap in the temperature ranges which led to successful growth, and it was determined that from 700–800 °C both materials could be synthesised concurrently, which is advantageous for heterostack growth applications and bandgap engineering.

After characterisation including XPS, Raman spectroscopy, HIM and SEM, various electronic devices were created. Measurement of mobility was accomplished using EDL-TFT architecture. MoSe_2 displayed values of $20.6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for films synthesised at 1000 °C. This is higher than the corresponding sulfide, and the increased mobility is attributed to the increased mass of the chalcogen atoms.

Chemiresistor gas sensors were also developed. MoSe_2 sensors exhibited a LOD of 2 ppm to NH_3 and 800 ppb to NO_2 . WSe_2 sensors displayed a LOD of 0.8 ppb to NH_3 . These ultra sensitive sensor results are very promising for future IoT related applications.

Chapter 6

Conclusions and Outlook

6.1 Conclusions

The work undertaken in this thesis has been in the development of TAC as a useful method of producing 2D semiconducting TMDs. This began with designing and building a specialist LPCVD furnace system for the sulfide family of TMDs. Using this apparatus, recipes were developed and optimised for converting thin films of transition metals, on arbitrary substrates, into the corresponding metal disulfides. Once 2D TMD films were synthesised, they were thoroughly characterised, both chemically and morphologically. This information was used to adjust the TAC process conditions, and thus optimise the resultant film recipes.

The films produced are polycrystalline, which affects their electronic properties. Mobility is limited by the density of defects, and the size of grains. So far, devices fabricated from TAC produced TMDs display inferior mobilities and on:off ratios when compared to devices utilising micromechanical exfoliation. The electronic properties of TAC produced TMDs are not suitable for many logic applications, however there is scope to enhance grain sizes, potentially improving

electronic properties. Higher conversion temperatures create larger domains, as does the use of highly crystalline sapphire substrates. Both of these approaches could lead to enhanced mobilities, however neither is favourable from an industrial standpoint. TAC produced TMDs are most suitable for applications in sensing, optics and catalysis.

A highly relevant application of TAC films presented in this thesis is gas sensors. A simple process flow using an IDE electrode pattern and shadow masks allowed for facile fabrication of low power chemiresistor gas sensors. MoS₂ sensors achieved an ultrahigh theoretical LOD of 51 ppb for NH₃. These sensors have the further advantages of room temperature operation, very fast response time and they show good recovery. Further, with suitable metal deposition techniques such as MBE, TAC can potentially be used to form vertical heterojunctions between different TMDs. This is an exciting development, as it is a route toward bandgap engineering.

The TAC growth method was then extended to the selenides. Once again, a bespoke LPCVD system was designed and constructed. Thin films of molybdenum and tungsten underwent TAC under a selenium environment, and they were characterised in the same manner as the sulfides. It became apparent that temperature played a crucial role in the selenide synthesis. Stoichiometric MoSe₂ was produced in the 600-800 °C range while WSe₂ was best synthesised at temperature below 700 °C. MoSe₂ chemiresistor gas sensors were also tested in the presence of NH₃ and NO₂, they exhibited a LOD of 2 ppm to NH₃ and 800 ppb to NO₂. WSe₂ sensors displayed a LOD of 0.8 ppm to NH₃.

TAC has proven to be a valuable procedure for creating TMD thin films. The well controlled metal deposition methods allow for films to be synthesised down toward the monolayer, as confirmed by PL measurements. This exciting devel-

opment can potentially make TAC suitable for a range of optoelectronic devices which require the direct bandgap of monolayer TMDs. Further advantages of this facile method include scalability, compatibility with semiconductor industry processes, ease of device manufacture (*i.e.* no transfer from growth substrate is required), lithographically patterned growth, and applicability to a wide range of semiconducting materials with different bandgaps.

The work undertaken here has consistently underscored the importance of using methods and materials which are industrially relevant. TAC synthesis on Si/SiO₂ substrates at 600 °C produces materials that are similar (if less crystalline) to those produced on sapphire at 1000 °C, and are often more relevant for many applications. It is only necessary to increase complexity and or cost of the TAC growth if a specific property is required. Further, the difference between chemical characterisation (XPS, Raman) and electrical performance (mobility measurements, TFT characteristics) of 2D semiconducting materials has become obvious. For example, changes in doping levels can have a very large impact on electrical performance, even changing MoS₂ from *n*-type to *p*-type, however they are not observable under chemical characterisation techniques.

6.2 Future Work

There are several areas where the work in this thesis can be extended. Firstly, in the recipe development and synthesis of thin films. Other exotic TMDs such as PtSe₂, SnSe₂, TiS₂, HfS₂ *etc.* can be further developed, and optimised. There are many layered semiconducting TMDs, and therefore there is significant scope to expand TAC synthesis.

Another area is in further determination and improvement of the electrical properties of TAC grown materials. This is largely in the process engineering domain. There are still many challenges associated with electronic measurement of 2D TMDs. This is an area that is being actively researched, and progress is being made through such avenues as dielectric engineering, encapsulation, and improving crystallinity. As progress is made, the applicability of 2D TMDs is set to increase, and TAC grown TMDs are envisioned to become suitable for more types of devices.

Determining the mobilities of TAC produced 2D TMDs has proven to be very challenging. As the problems and issues have been resolved, and improved methodologies developed, it is likely that successful and reliable AC Hall measurements can be performed on the selenides and other sulfide TMDs. This work could answer some important questions about which applications are suitable for various TMDs.

Higher temperatures produce TMDs with improved electrical properties, however high temperature synthesis is not industrially desirable. One route that could potentially lower synthesis temperature is plasma enhanced (PE) TAC growth. The selenisation furnace and enclosure described in section 5.1 has been designed to accommodate a downstream RF plasma generator. The next major upgrade to the system should allow for investigation of PE TAC synthesis.

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Appendix A

MoS₂|WS₂ Heterostack Synthesis

A very important application of 2D TMDs is enabling functionality through the formation of 2D heterostacks. The ability to create heterojunctions of different materials with variable band structures is essential to realise the full potential of 2D TMD semiconductors. It is expected to allow for the development of high-performance electronic and optoelectronic devices with precisely tuned electronic functions and desired band alignment. The ultimate limit would be in creating an atomic $p - n$ junction. Labour intensive aligning and stacking of micromechanically exfoliated samples by the dry transfer technique has been used to produce heterojunction transistors²⁰⁹ and $p-n$ diodes.²¹⁰

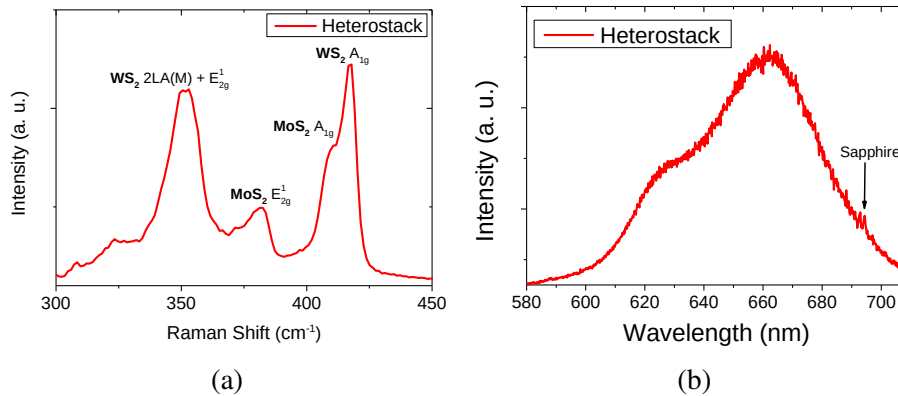
Several methodologies were attempted in order to create heterostacks of MoS₂ and WS₂. Neither deposition of different metals prior to TAC, nor depositing a thin film of a second metal onto a TMD film, followed by a second TAC growth were successful in creating a sharp interface. The major problem was that the second deposition typically damaged the existing bottom layer. Both e-beam deposition and sputtering were too destructive. A gentler deposition method would likely be more suitable for creating TMD heterostacks.

Table A.1 MBE deposition parameters

Material	Thickness (nm)	Growth temperature (°C)
WO ₃	1.0	650
MoO ₃	0.5	470
WO ₃	1.0	570

Molecular beam epitaxy, (MBE) is a UHV technique that deposits material very slowly and gently, with good thickness control. It is a technique that could be well suited to creating TMD heterostacks. In collaboration with Prof. Igor Shvets, in the TCD School of Physics, TAC of layered transition metal oxides deposited *via* MBE was investigated.

MBE was used to deposit either 2 or 3 layers of transition metal oxides, onto sapphire substrates, as outlined in table A.1. This produced heterostacks of Mo and W oxides, with well defined thicknesses, and high quality, as was verified by RHEED (not shown). The substrates were then placed in the sulfurisation furnace, where they underwent TAC at 750 °C. A 30 min dwell at growth temperature, under forming gas prior to sulfurisation was included in order to reduce the metal oxides.

Fig. A.1 (a) Raman and (b) PL spectrum of a WS₂|MoS₂|WS₂ heterostack.

Raman spectroscopy was used to examine the resultant material. As can be seen in fig. A.1(a), the Raman signals for MoS₂ and WS₂ are both clearly evident. If a Mo_{1-x}W_xS₂ compound were to be formed, localised strain and disorder in an alloy of two domains with different lattice constants would cause the MoS₂ E_{2g}¹ and A_{1g} peaks to broaden and shift down to lower wavenumbers (373 and 395 cm⁻¹, respectively).²¹¹ The clear separation of the Mo and W A_{1g} components also indicates that no significant alloying is occurring.²¹² The material is composed of both discrete TMDs, instead of a random alloying effect.

Inspection of the WS₂ 2LA(M) peak at 350.4 cm⁻¹ with a shoulder at ≈ 355 cm⁻¹ and the A_{1g} peak position at 417 cm⁻¹ indicates that mono - few layer WS₂ growth is achieved. A PL spectra (fig. A.1(b)) shows a strong signal at 660 nm, with a shoulder at 620 nm, this is the signature of monolayer MoS₂. The doublet feature at 694 nm is from the sapphire substrate. This shows that monolayer MoS₂ is sandwiched between few layer WS₂.

The heterostack is shown schematically in fig. A.2(a). Expansion due to the inclusion of sulfur was offset by the loss of oxygen, therefore the amount of expansion upon conversion is expected to be minimal. A scanning Raman map was acquired over a 20 by 20 μm area, as outlined by the optical image (fig. A.2(b)) and intensity sum maps were produced in the region of the E_{2g}¹ peak for MoS₂ (fig. A.2(c)) and the E_{2g}¹ + 2LA(M) peak for WS₂ (fig. A.2(d)). As can be seen by the Raman mapping, the signal appears to be from either the MoS₂ or the WS₂. Dark regions in one map correspond to bright regions in the other, which indicates that discrete MoS₂ and WS₂ materials are being produced, rather than an alloy. It is possible that the WS₂ top layer is not continuous, allowing for an enhanced MoS₂ signal to be detected in places.

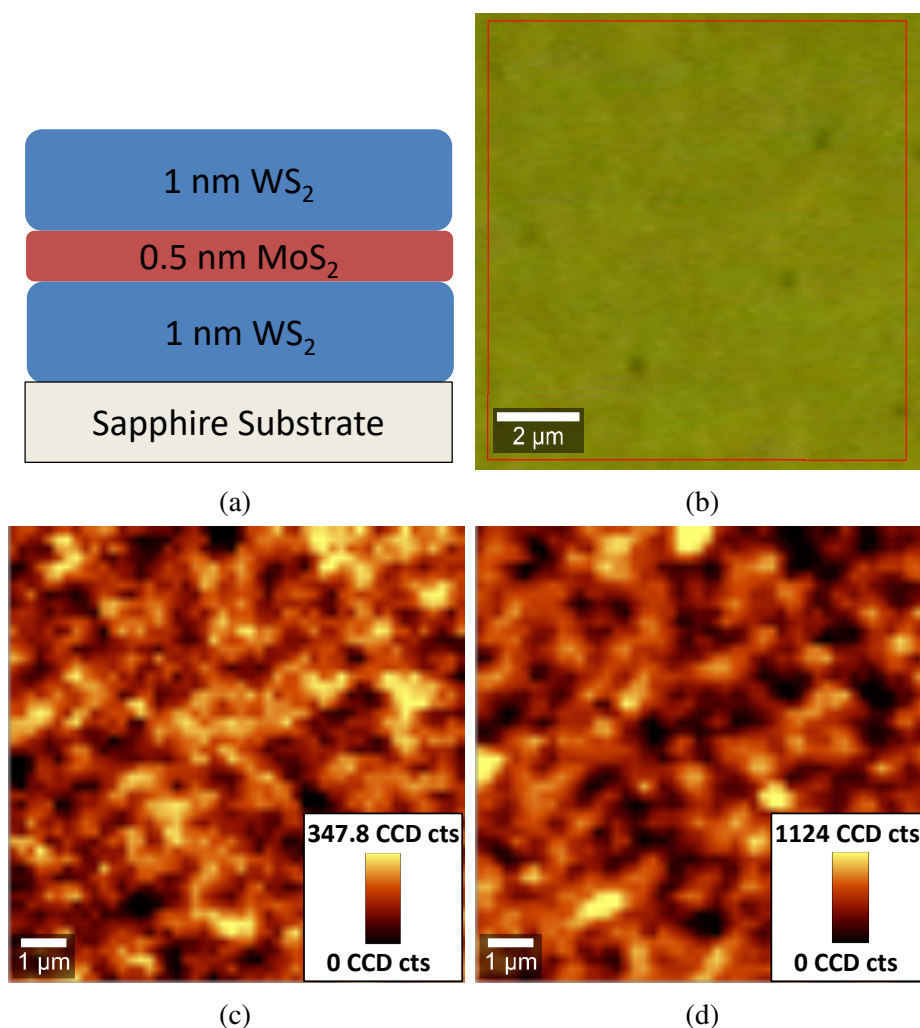


Fig. A.2 (a) Schematic of the heterostack. Raman mapping was performed in the area outlined in the optical image (b). Sum maps of (c) MoS₂ and (d) WS₂ E_{2g}¹ regions.

In order to further verify the quality of the material produced, a combined study of Electron Energy Loss Spectroscopy (EELS) with the Z-contrast high angle annular dark field (HAADF) imaging technique in a scanning transmission electron microscope (STEM) was performed by Dr. Manuel Roldan Gutierrez and Dr. Anas Mouti using a Nion UltraSTEM 200. Fig. A.3 shows the results of this technique. Figs. A.3(a) and A.3(b) show HAADF images of two and three layer samples, respectively. The layers are clearly separated from and parallel

to each other. The amorphous material between the layers and the substrate is indicative of unreacted metal. Fig. A.3(c) shows the extracted core-loss spectrum, featuring the Al, W, and Mo peaks. The Al signal is from the sapphire substrate. Fig. A.3(d) features ADF images of the EELS maps. From left to right, the maps are: Simultaneous image of the EELS map, followed by the W map, followed by the Mo map, and finally a RGB combination of Al (blue) W (green) and Mo (Red). This further verifies that parallel, well-ordered discrete-layered heterostacks are produced, with minimal alloying.

MBE deposited of layers Mo and W oxides have been converted into TMD heterostacks *via* TAC, without appreciable alloying. This is a significant result since it reveals that TAC is suitable for creating vertical heterostacks of 2D materials. This potentially expands the range of suitable applications to include photovoltaics, photodetectors, LEDs, laser diodes and complementary logic circuits.²¹³ Issues such as polycrystallinity, incomplete conversion, and lateral grain size limitations still exist, however it is likely that further investigation could improve these properties.

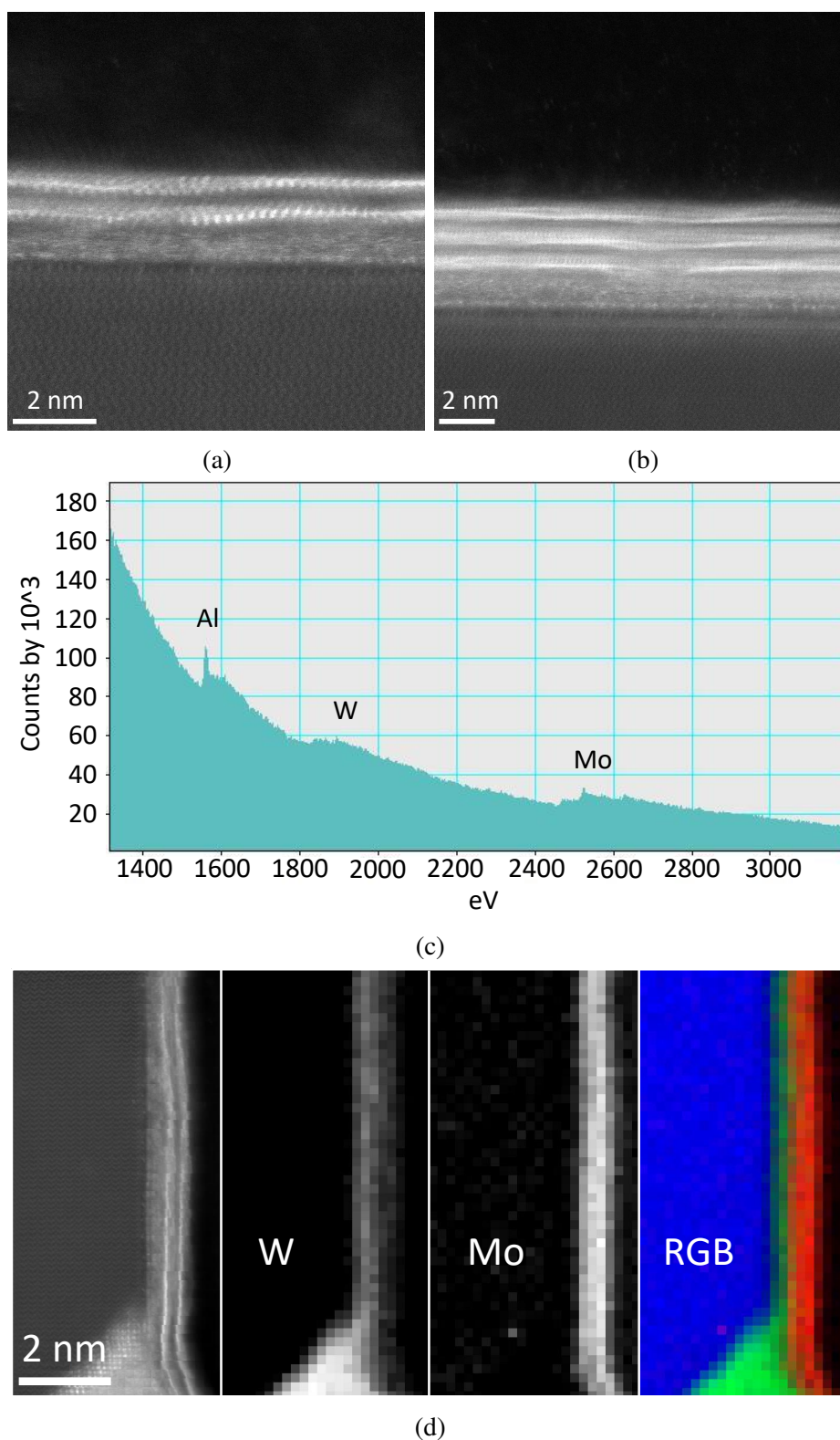


Fig. A.3 HAADF images of (a) 2-layer and (b) 3-layer heterostacks, respectively. (c) EELS spectrum showing Mo, W and Al features. (d) (left to right) Simultaneous ADF image of the EELS map, followed by the W map, followed by the Mo map, and finally a RGB combination of Al (blue) W (green) and Mo (Red).