

Towards Improved Characterisation and Synthesis of Two-Dimensional Transition Metal Dichalcogenides



A thesis submitted to the School of Chemistry, The University of Dublin, Trinity College, for the degree of Doctor of Philosophy

by

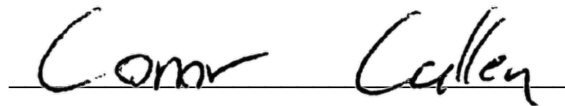
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Based on research carried out under the supervision of Prof. Georg Duesberg
and Prof. Wolfgang Schmitt

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Declaration

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Abstract

Two-dimensional (2D) transition metal dichalcogenides (TMDs) are a fast growing and highly researched area in modern materials science. The numerous potential advances, made possible by their oft-quoted, varied, and layer-dependent properties, has led to a proportionate “gold rush” across the periodic table for suitable materials to be synthesised on the nanoscale. A consequence of the “gold rush” haste is that occasionally the due diligence in terms of accurate and refined characterisation of the TMD material itself is overlooked in order to focus on more forward-looking aspects such as fabrication of electrical or electrochemical applications. This has resulted in a lack of coherency within literature, particularly between fundamental property studies which may utilise completely pristine material with few defects and no contamination or oxides present. As well as studies which are application oriented such as device fabrication or electrochemical applications. For both of these examples the TMD material is likely to be partially degraded or contaminated by some processing steps or by chemical reactions. XPS and Raman spectroscopy can both be utilised to great effect to characterise the state of a TMD material or to measure any changes or products during an experiment. This is widely known and both techniques are prevalent in 2D TMD literature, unfortunately however, the resultant data are not always appropriately analysed or well-presented from these techniques. XPS in particular is considered to be frequently incorrectly analysed in this field.

Accordingly, to improve such problematic elements of the literature, this thesis entitled “*Towards Improved Synthesis, Characterisation, and Analysis of Two-Dimensional Transition Metal Dichalcogenides*” considered a characterisation prioritised examination of the synthesis, chemical reactivity, and stability of several 2D TMD materials in order to broaden the knowledge of their analysis. Particular focus was paid to XPS, with the intention of constructing a transparent understanding of the analysis of TMD XPS spectra. This was achieved by thorough examination of the TMDs in multiple chemical environments.

The first study entailed the synthesis of the prototypical TMD, MoS₂. High-quality, largely monolayer crystals of MoS₂ were successfully synthesised on SiO₂ using a chemical vapour deposition (CVD) method. These MoS₂ crystals with sides up to ~100µm in length, displayed the prominent photoluminescence (PL) and Raman spectra characteristic of monolayer MoS₂. Metrics were established to monitor the crystalline quality of the MoS₂ using these spectra.

The effects of NH₃ plasma on this CVD MoS₂ were studied to examine the chemical reactivity of MoS₂. XPS analysis established that NH₃ plasma treatment resulted in the controllable substitutional doping of nitrogen atoms into the MoS₂ lattice with removal of sulfur atoms. The analysis of this served to clarify the XPS features attributed to nitrogen doping of MoS₂, these components have been frequently confused in the literature. Beyond this, the effects of NH₃ plasma treatment were found to have a

pronounced impact on the MoS₂. The monolayer MoS₂ PL shifted to higher energy in a tuneable and stable manner. With maximum shifts to over 2 eV (620 nm). The structural impact of this process was also examined, Raman analysis determined that NH₃ plasma was a highly surface sensitive process with plasma-treated monolayers of MoS₂ losing the characteristic Raman modes while bilayers of MoS₂ were found to transition to monolayer-like Raman signal after plasma treatment, indicating that the top-most layer was predominantly affected. Low-frequency Raman spectroscopy was used to confirm this decoupling of the bilayer stack of MoS₂. By increasing the duration of the plasma exposure it was discovered that the increasing strain in the crystal resulted in nanoscroll formation as the individual crystals rolled up.

A detailed XPS analysis of ten transition metal chalcogenides was performed. Including sulfides, selenides, and tellurides of Mo, W, and Pt, these encompass the bulk of materials studied in modern TMD literature. The materials were synthesised as large-area uniform thin-films using a direct chalcogenisation of pre-deposited metal films method called thermally assisted conversion (TAC). The XPS spectra of these materials were analysed with curve-fitting to identify the individual components of each core-level spectrum. Each fitted spectrum was discussed in detail and considered alongside the corresponding Raman spectra for each material, these complementary characterisation methods provide providing a considerably more accurate understanding of the state of the material.

To establish a wide library of consistent characterisation data, each of these ten materials were also annealed in ambient at several temperatures up to 400 °C. This forced degradation of the materials allowed their relative stabilities to be indicated as well as generating their most common oxides and other degradation products. Comprehensive analysis of these annealed materials expands the assembled library of data here substantially and increases its utility particularly for comparison to applications focused research where TMD degradation is common.

Finally, the utility of these developed synthesis and characterisation methods are exemplified with the study of the two closely linked platinum sulfide materials. Aspects of PtS₂ and PtS are frequently confused in literature due to their uncommon coexistence and limited literature data. XPS and Raman analysis were utilised here to unambiguously distinguished the two materials. This enabled optimisation of efficient methods to synthesise high-purity polycrystalline thin films of both the non-layered PtS and the layered PtS₂ using TAC methods.

In summary, this thesis prioritises the reliable characterisation of the materials, synthesis methods to produce a variety of 2D TMD materials were demonstrated including for high-quality monolayer MoS₂. Comprehensive XPS and Raman characterisations were carried out on 10 TMD materials to assemble an array of complementary characterisation data for the TMD materials across multiple chemical environments.

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List of Acronyms

2D	Two-dimensional
AFM	Atomic force microscopy
BE	Binding energy
BZ	Brillouin zone
BSE	Backscattered electrons
CB	Conduction band
CVD	Chemical vapour deposition
CHA	Concentric hemispherical analyser
CVT	Chemical vapour transport
FET	Field-effect transistor
FWHM	full width at half maximum
KPFM	Kelvin probe force microscopy
LPE	liquid-phase exfoliation
PyC	Pyrolytic carbon
PL	Photoluminescence
SE	Secondary electrons
SEM	scanning electron microscopy
SPM	scanning probe microscopy
SXI	scanning X-ray imaging
TAC	thermally assisted conversion
TMD	transition metal dichalcogenide
UHV	Ultra high vacuum
VB	valence band
XPS	X-ray photoelectron spectroscopy

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1 -Theory and Background

1.1 Introduction

Two-dimensional (2D) materials are an ever-growing assortment of materials which exist with orders of magnitude greater lateral lengths than thickness. The thickness of these materials is generally required to be less than 100 nm to fit in this category, though most here are many times thinner than this, down to the single atomic layer limit. The few atom thick nature of these materials leads to very high surface to volume ratios and causes quantum confinement within the layer, introducing new properties not present in the bulk materials.¹⁻³

The first and most well-known of these materials is graphene which was isolated by Novoselov and Geim in 2004.⁴ Graphene is a single layer of graphitic carbon, which was found to be stable in a monolayer form in ambient conditions despite its extreme anisotropy. It was also discovered that as the thickness of graphite was reduced towards a single layer, remarkable mechanical, thermal, and electronic properties emerged. These extreme properties led to a huge drive of funding and research into this new material with associated high expectations for its use in composites, barriers, and most of all in future electronic devices. The stability of graphene, combined with its high charge-carrier mobility,⁵ created expectations that it might be the key to getting towards the minimum thickness for electrical devices.

Graphene has zero bandgap; it has a Dirac point, a feature which makes graphene attractive in a range of areas, including fundamental physics. However, this property also means that it is difficult to turn off, providing poor on/off ratios when integrated as the active component in a transistor. Accordingly, the integration of graphene into the important sector of semiconductor-based logic electronics is challenging.

Due to the remarkable property change that occurs for graphite as it is reduced to graphene it was expected that this may also be the case for other layered materials. It was well known for decades that there existed layered materials which had weak interlayer bonding and could be easily reduced in thickness, the isolation of graphene drew further attention to these other materials. Many reports emerged shortly after trying to isolate single or few layers of other

known layered materials from their bulk form, such as the semiconductor molybdenum disulfide (MoS_2).

The area of 2D materials study has grown enormously over the last 15 years, and so have the number and complexity of methods to synthesise them. The family of 2D materials is quite broad now and includes a diverse range of properties, structures, and elemental compositions. They can vary from insulators, to semiconductors, to metallic, and even superconductors, while having various physical and thermal properties. The number of 2D materials also appears to be ever-growing. For example, beyond solely isolating single layers from naturally occurring bulk materials, purely artificial materials such as black phosphorous (BP), can now be synthesised following “bottom-up” methods.⁶

This array of materials, many with extraordinary properties and potentially ground-breaking applications has led to an unprecedented focusing of research and funding on this topic of 2D materials and their applications. This flurry of research in a quickly advancing field and the constant emergence of new materials has opened up the possibility for gaps and errors in the literature.

While initially the focus of 2D materials research was on the isolation of as many 2D materials as possible to study their fundamental properties, the gradual advancement into a more developed field has increased the importance of understanding and characterising the materials accurately, in order to enable their reliable progression onto the next steps of integration into real-world applications.

The rapid pace with which this field has advanced has frequently resulted in a diminished focus on characterising the material being used, and instead applications-oriented experiments and technological aspects are prioritised. The expansion of 2D materials across fields and scientific disciplines into less experienced cohorts has also contributed to an uneven and sometimes unreliable literature with limited core material characterisation.

1.2 Thesis Overview

To develop these unbalanced elements of the literature, this thesis examines the synthesis, fundamental chemistry, and extensive characterisation, primarily through X-ray photoelectron spectroscopy (XPS) of several 2D transition metal dichalcogenides (TMDs). A chemical vapour deposition (CVD) style process was used to synthesise mostly single- and few-layer samples of

high-quality MoS₂ directly on SiO₂, these were characterised using Raman, photoluminescence (PL) and XPS spectroscopies. The reactivity of monolayer MoS₂ with NH₃ plasma was explored, resulting in stark changes to the structure and optical properties of MoS₂. Moreover, 9 TMDs were synthesised and their ambient stability tested, this facilitated robust characterisation in order to construct a reliable, consistent library of reference data. Finally, two different sulfides of platinum were synthesised as thin films in a dependable and high-purity process, this gave the means to characterise and differentiate between their respective spectra which are frequently mistaken.

1.3 Transition Metal Dichalcogenides

After graphene, TMDs are the most widely studied sub-group of 2D materials. While TMDs have recently risen to a place of prominence as a result of the 2D material revolution, these materials have been long studied and have been a subject of interest due to their properties for many decades.⁷

TMDs have the general formula MX₂, where M is a transition metal (TM) and X is a chalcogen. Traditionally oxygen is not included when discussing chalcogens due to its divergent properties compared to the other elements, likewise Po and Lv are radioactive elements and are commonly excluded. This leaves the term chalcogens to be generally used in the literature and throughout this thesis to refer to S, Se, and Te only.

Many TMDs show a layered structure; where a single layer, called a monolayer, of the material consists of a sheet of metal atoms sandwiched between two layers of chalcogen atoms, together less than 1 nm thick. Within this 3-atom thick monolayer the atoms are covalently bound to one another. The layered nature of the TMDs comes from the bulk TMD having these layers stacked with interlayer bonding comprising of van der Waals forces which are significantly weaker than the intralayer bonds. This anisotropy in bonding enables the layers of TMDs to slide across each other, this similarity to the bonding in graphite/graphene and other layered materials is the origin of their similar properties. These weak interlayer interactions have made materials such as MoS₂ popular as solid-phase lubricants and was the main point of interest for their study for most of the 1900s.⁷

Despite the layered TMDs having relatively similar structures throughout the family/class, they display a diversity of electrical, optical, and chemical properties.^{1, 8}

The known layered TMDs are shown in Fig.1.1, below, with the TM in blue and the chalcogens in orange. TMDs consisting of the elements marked with a green triangle in the corner are the ones studied here. That is 9 TMDs, the sulfides, selenides, and tellurides of Mo, W, and Pt.

1

1A

H

Hydrogen

1.008

2

2A

He

Helium

4.003

3

Li

Lithium

6.941

4

Be

Beryllium

9.012

11

Na

Sodium

22.990

12

Mg

Magnesium

24.305

19

K

Potassium

39.098

20

Ca

Calcium

40.078

37

Rb

Rubidium

85.468

55

Cs

Cesium

132.905

87

Fr

Francium

223.020

2

IIA

2A

3

IIIB

3B

4

IVB

4B

5

VB

5B

6

VIB

6B

7

VII B

7B

8

VIII

8

9

VIII

8

10

VIII

8

11

IB

1B

12

IIB

2B

13

Al

Aluminum

26.982

14

Si

Silicon

28.086

15

P

Phosphorus

30.974

16

S

Sulfur

32.065

17

Cl

Chlorine

35.453

18

Ar

Argon

39.948

31

Ga

Gallium

69.723

32

Ge

Germanium

72.631

33

As

Arsenic

74.922

34

Se

Selenium

78.971

35

Br

Bromine

79.904

36

Kr

Krypton

83.798

49

In

Indium

114.818

50

Sn

Tin

118.711

51

Sb

Antimony

121.760

52

Te

Tellurium

127.6

53

I

Iodine

126.904

54

Xe

Xenon

131.294

81

Tl

Thallium

204.383

82

Pb

Lead

207.2

83

Bi

Bismuth

208.980

84

Po

Polonium

[209]

85

At

Astatine

[210]

86

Rn

Radon

[222]

113

Nh

Nihonium

[286]

114

Fl

Flerovium

[289]

115

Mc

Moscovium

[289]

116

Lv

Livermorium

[293]

117

Ts

Tennessine

[294]

118

Og

Oganesson

[294]

57

La

Lanthanum

138.905

58

Ce

Cerium

140.116

59

Pr

Praseodymium

140.908

60

Nd

Neodymium

144.243

61

Pm

Promethium

144.913

62

Sm

Samarium

150.36

63

Eu

Europium

151.964

64

Gd

Gadolinium

157.25

65

Tb

Terbium

158.925

66

Dy

Dysprosium

162.500

67

Ho

Holmium

164.930

68

Er

Erbium

167.259

69

Tm

Thulium

168.934

70

Yb

Ytterbium

173.055

71

Lu

Lutetium

174.967

89

Ac

Actinium

[227]

90

Th

Thorium

232.038

91

Pa

Protactinium

231.036

92

U

Uranium

238.029

93

Np

Neptunium

237.048

94

Pu

Plutonium

244.064

95

Am

Americium

243.061

96

Cm

Curium

247.070

97

Bk

Berkelium

247.070

98

Cf

Californium

251.080

99

Es

Einsteinium

[254]

100

Fm

Fermium

257.095

101

Md

Mendelevium

258.1

102

No

Nobelium

259.101

103

Lr

Lawrencium

[262]

Periodic Table of the Elements

Fig. 1.1 Periodic table of the elements. With the transition metals (blue) and the chalcogens (orange) for the layered TMDs highlighted. (modified and reproduced with permission from sciencenotes.org)

Group 6 TMDs are accepted by a wide margin as being the most commonly reported in the literature, with their sulfides being the most studied of these. The relative popularity of the materials studied here can be seen in their prevalence in the literature, as shown in Fig. 1.2 by graphing the number of publications for each material per year over the last decade. The common acceptance of MoS₂ as the prototypical TMD is justified in this figure, with more than 4x the number of publications for the next highest TMD over the last few years. There is also a clear order to the popularity across the three TMs focused on, with molybdenum, then tungsten, far ahead of platinum based TMDs. A similar trend is observed in terms of the chalcogen employed, wherein there is a descending popularity for the sulfides, selenides, and then the

tellurides. The relative toxicity of the chalcogens in combination with their abundance as naturally occurring minerals are expected to contribute to this trend. To gain further insights into changing priorities across the literature the relative number of publications for each material over the last 20 years was accumulated, as presented in Fig. 1.2(c), wherein the less studied materials have been rising rapidly in popularity. For example, 55% of all the papers on the topic of PtSe₂ over the last 20 years were published in the last 2 years, this is compared to 34% for MoS₂, 30% for graphene, and 14% for carbon nanotubes.

MoS₂ is both the most studied TMD by a wide margin, and the most prominently featured throughout this thesis. In order to reflect this trend, fuller examples will be given for MoS₂ when discussing the specifics of the study of TMDs.

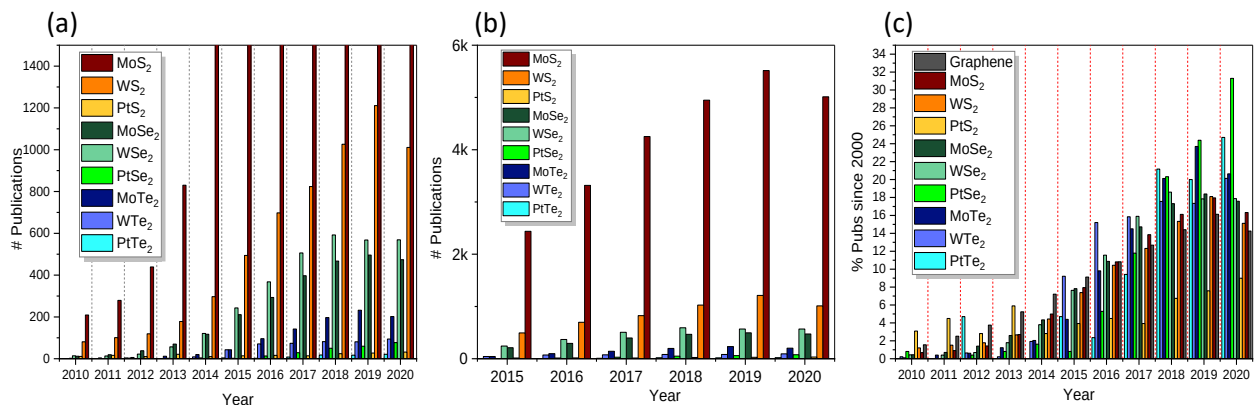


Fig. 1.2 Number of publications per year for each 2D material. (Searched as “Topic” on Web of Science correct as of 12/12/2020)

The layered nature of these materials can be understood by examining their chemical bonding structure. In TMDs each metal atom is bound to 6 chalcogen atoms (six-fold coordinated) and each chalcogen is bound to 3 metal atoms (three-fold coordinated), the formal charge of the metals is +4 and the chalcogens –2. While each chalcogen atom has three bonds to the metal atoms, they are, in fact, sp^3 hybridised, leaving each chalcogen atom with a lone pair of electrons in an orbital out-of-plane/perpendicular from the TMD layer surface. This lone pair of electrons create a fully saturated surface above and below each TMD layer, which causes both their layered structure, and their remarkable stability.⁹ This stability is lower at the edges of TMD crystals, at defect sites, or along grain boundaries, where consequently there are far more chemically reactive atoms with unsaturated bonds.^{10, 11}

While all TMDs have the above-mentioned chemical bonding configuration for every chalcogen. Layered TMDs can be synthesised with TMs from several groups of the periodic

table. The wider crystal structure is heavily influenced by the number of valence d-electrons of the TM. The 6-fold coordination of the TM atoms gives them either a trigonal prismatic or octahedral geometry, both structures are illustrated in Fig. 1.3(a, b). Of the 9 TMDs examined in this study, 4 are trigonal prismatic, 3 are octahedral, and 2 are a distorted octahedral geometry. Several of these TMDs are also able to adopt other polymorphs dependent on the conditions.

The d-orbital splitting for TMDs can show the relation between the electronic and molecular geometry of the structures. For trigonal prismatic TMDs the d-orbitals are split into 3 groups, in order of increasing energy of d_{z^2} (called a1), $d_{x^2-y^2} + d_{xy}$ (e), and $d_{yz} + d_{xz}$ (e'). For octahedral TMDs the non-bonding d-orbitals are split into 2 groups, a lower energy $d_{xy} + d_{yz} + d_{xz}$ (t_{2g}) and a higher energy $d_{z^2} + d_{x^2-y^2}$ (e_g).¹² The ligand field splitting and representative density of states in three scenarios is illustrated in Fig. 1.3(c). Firstly, the standard trigonal prismatic MoS₂ configuration where the lowest level is fully occupied, comparing this to MoS₂ in an octahedral configuration where 2 of the degenerate orbitals are only singly occupied and are at a higher energy level than the trigonal prismatic. This makes the octahedral structure less energetically favourable than trigonal prismatic for MoS₂, the partially filled level also makes octahedral MoS₂ metallic instead of semiconducting. MoS₂ can be shifted into this octahedral configuration by electron transfer e.g. from Li intercalation, wherein the triply degenerate energy levels can now be singly occupied, raising the stability of this configuration over trigonal prismatic.¹³

A group 10 TMD, such as PtS₂, adopts an octahedral structure but the lowest levels are fully filled making it semiconducting.

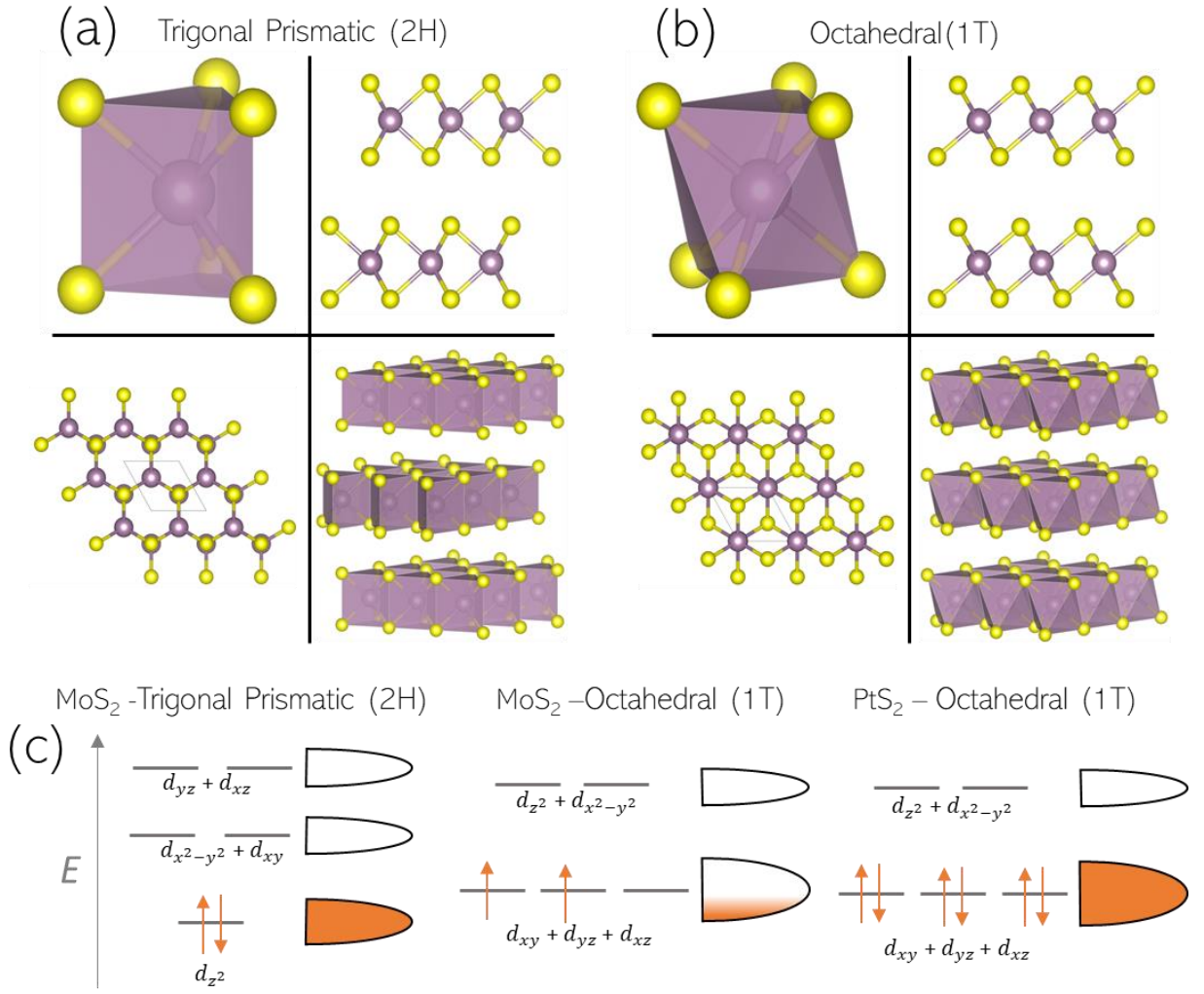


Fig. 1.3 Crystal structure diagrams for trigonal prismatic (a) and octahedral (b) TMDs. (c) Schematic of the ligand field splitting and corresponding density of states for different configurations of TMDs.

The layered nature of TMDs mean that these trigonal prismatic or octahedral monolayers have an additional aspect to their symmetry and structure, which is the stacking of the layers.

The common polymorphs for the TMDs are referred to as 2H (trigonal prismatic), 1T (octahedral), and 3R (trigonal prismatic). These letter codes are the traditional terminology for polytype description and are used ubiquitously in the literature when discussing 2D materials.¹⁴ Wherein the number refers to the number of layers in the unit cell, and the letter refers to the symmetry, with H, T, and R being hexagonal, trigonal, and rhombohedral, respectively.

Layers of trigonal prismatic TMDs can be stacked in different symmetries either 2H or 3R, 2H being the most common. 1T TMDs only have one stacking configuration, while distorted octahedral 1T' has two stacking orders, 1T' or T_d. Materials with each of these configurations, excluding 3R, can be seen in appendix Fig. A1-3.

The layer-dependent electronic and optical properties of MoS₂ are largely a result of its changing band structure, as shown in Fig 1.4. For MoS₂ the bulk material is an indirect semiconductor with a 1.3 eV bandgap. The top of the valence band is at the Γ -point here. The states near the Γ -point are due to combinations of antibonding p_z-orbitals from the sulfur and d-orbitals on the Mo atoms, while the K point states are localized d orbitals existing in the middle of the layer. As such the K point states are relatively insensitive to the layer number. While the Γ -point changes markedly with layer number, to the extent of monolayer going to a lower energy than the top of the K-point.¹⁵

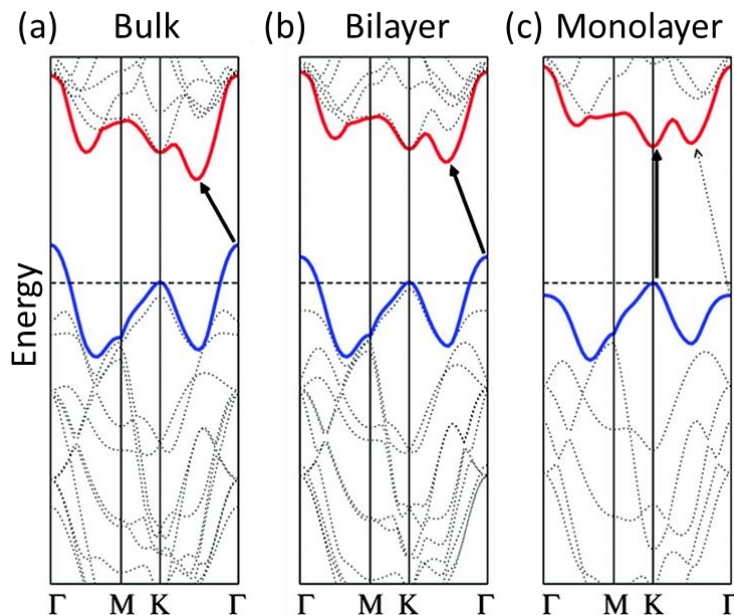


Fig. 1.4 Calculated band structures for different thicknesses of MoS₂ (a) Bulk. (b) Bilayer. (c) Monolayer. Adapted from reference.¹⁵

This change in band structure shifts MoS₂ from an indirect bandgap semiconductor with a bandgap of 1.3 eV in bulk, to a direct bandgap semiconductor with a ~1.9 eV bandgap. The large change in properties when approaching the monolayer limit for MoS₂ enables a tuneable bandgap for 2D MoS₂. The direct bandgap enables prominent photoluminescence to appear for monolayer MoS₂ as the efficiency of excitonic emission greatly increases, with ~100 times higher quantum yield when compared to few-layer MoS₂, and 10⁴ time greater compared to bulk.¹⁶

The properties of the TMDs have generated much enthusiasm towards their potential applications. The stability from their bond saturated surface, their layer-dependent electronic properties and relatively large monolayer bandgaps etc. have driven these motivations. Since the isolation of graphene with its extremely high carrier mobility, integration of 2D materials into future electronics has been a consistently popular research focus for potential applications.

The use of semiconducting TMDs, like MoS₂, as the channel for field-effect transistors (FETs) is a common proposed application of MoS₂ in the literature. A monolayer semiconductor has enormous potential for this use case as, gating the device should be much more power efficient than current FETs. Si-based FETs are limited with further scaling by tunnelling effects. The integration of monolayer TMDs into high performance devices has not been trivial and is a complex topic worthy of further study.¹⁷

Interest in this has grown since one of the first functional monolayer MoS₂ FETs showed a high on/off ratio of 10⁸,¹⁸ considerable efforts have gone on to further optimise these structures with use of high dielectric constant (k) gates like HfO₂ and hBN substrates yielding devices with similar on/off ratio and mobilities on the order of 10³ cm² V⁻¹ s⁻¹.¹⁹ MoS₂ has also been shown to have potential applications in more complex devices such as memristors.²⁰ The mechanical properties of thin film TMDs, as well as the ability to transfer them between substrates, make them well suited for applications in flexible electronics.¹⁷

2D MoS₂ has further been studied for applications as a catalyst²¹, electrodes for supercapacitors²², for high lithium storage anodes.²³ MoS₂ has promising biocompatibility and can be used as an area selective drug delivery material due to its optical properties.²⁴ These are just a few examples of the diverse applications being sought after from just one of the many TMD materials.

1.4 Synthesis of TMDs

Many of the TMDs are naturally occurring and can be found in rock formations (e.g. *Molybdenite*) and these raw materials can be made into 2D materials through top-down processes such as mechanical or liquid-phase exfoliation. They can also be synthetically produced in high quality large bulk crystals through Chemical Vapor Transport (CVT) style

processes. There also exists a number of bottom-up methods to synthesise 2D TMDs from their base elements.

There are several commonly used methods for fabricating and synthesising TMDs. As is the case for all 2D materials, each method has its benefits and deficiencies, and with all of these materials it is very important to match the fabrication method to the desired use case. For example, for the initial discovery of graphene the main goal was to isolate any amount of it reproducibly, therefore scalability and applications were not of concern, so mechanical exfoliation was suitable.

Synthesis is not fully trivialised as of yet, where it is not simply a matter of copying a method from literature and implementing it as described. There is still significant nuance in bespoke synthesis and manufacturing of TMD materials, due to this it is still essential that adequate characterisation is consistently and frequently performed and reported. Minor changes in the material can cause significant changes in properties and stability.

The three most popular methods to synthesise TMDs are mechanical exfoliation, liquid-phase exfoliation, and vapour-phase growth. An overview of the main benefits and issues with each method is provided in Fig. 1.5.

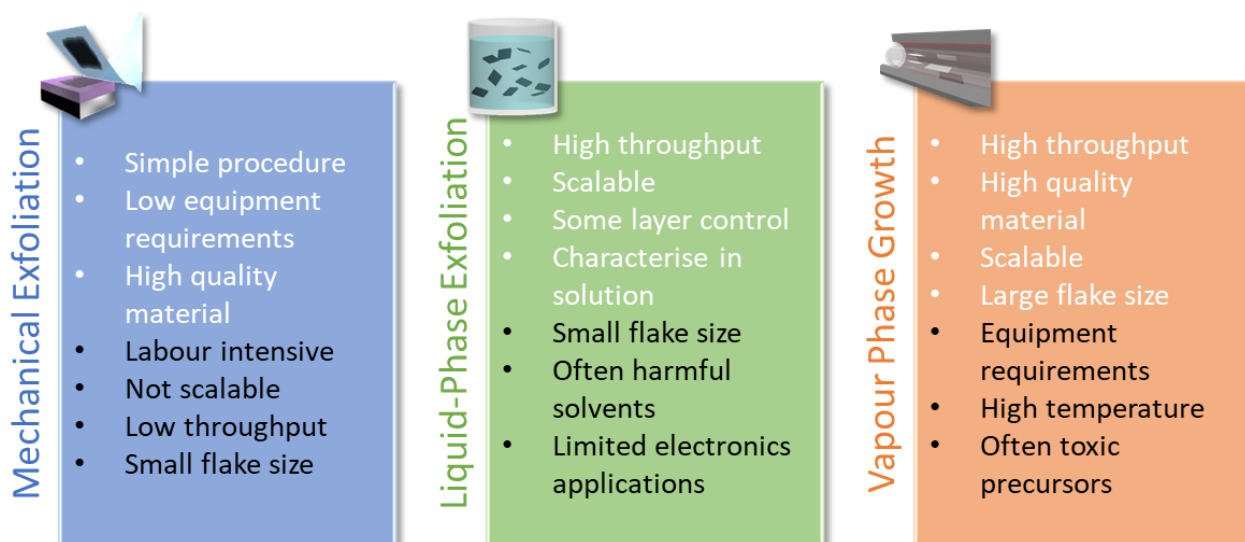


Fig. 1.5 Summary of common positives and negatives attributed to the three main methods of 2D TMD synthesis.

The two top-down methods are briefly introduced as they are important aspects of the field. While vapour-phase growth style methods were used throughout this study and will be discussed in more detail.

Mechanical exfoliation

The isolation of graphene using Scotch tape in 2004 is famous for a multitude of reasons, but one of the most notable is the simplicity of the process.⁴ This general process is known as (micro)mechanical exfoliation and remains one of the most popular methods to isolate mono–few layers of all 2D materials. Generically, the process entails using adhesive tape to remove a portion of a bulk layered material crystal. The tape is then repeatedly pressed onto other adhesives or a target substrate, this is to gradually reduce the layer thickness of the crystals and to spread the material over an area. After sufficient thinning, if not already on a target substrate, the adhesive tape is firmly pressed onto one and very carefully removed at a shallow angle to maximise deposition of material onto the substrate.

This method will yield coverage of the material across the substrate, the flake size and thickness of the flakes are uncontrolled and manual inspection is required to find regions of suspected monolayer, which must be verified through characterisation. There is also no guarantee of monolayer isolation and it is common for monolayers to appear as edges of thicker flakes. Exemplifying both the labour intensive and very unscalable aspect of this process. However, there are significant advantages of its simplicity, low equipment requirements, and substrate independence.

Another important reason for the prevalence of mechanical exfoliation as a method of 2D TMD manufacture is the very high quality of the material isolated.¹⁶ Bulk crystals of high purity TMDs are readily available and this quality is carried through to the exfoliated material. The majority of fundamental studies of the properties of 2D materials utilise mechanical exfoliation for synthesis.^{15, 16, 18}

Liquid-phase exfoliation

In contrast to mechanical exfoliation, the other most popular method of top-down synthesis is liquid-phase exfoliation (LPE). LPE is a substantially more complicated method of synthesis and is a topic with substantial depth and a large area of study in its own right.²⁵ For simplicity, LPE involves using either sonication or shear mixing to pull apart the layers of a thicker TMD

flake into many thinner flakes suspended in a solvent or surfactant. One of the clearest benefits of LPE is the enormous scalability it provides when compared to mechanical exfoliation.

Essentially, commercial layered material powders can be dispersed into a solvent. There are a number of important factors when considering liquid exfoliation, with the solvent chief amongst them. Solvents are chosen to minimise the interfacial tension between the suspended material and the solvent to minimise clumping and reaggregation.^{3, 12} The solution is then sonicated, or shear mixed to provide the energy to exfoliate the layers from one another. It is often required to introduce certain surfactants to prevent the exfoliated material from restacking after dispersion. There is limited control of the layer number of the suspended material after exfoliation, as distributions of thicknesses are generated.³ A series of cascade centrifugations can provide much greater thickness control, with mostly monolayer dispersions possible.²⁶ An inverse relationship between flake thickness and flake dimensions is one of the limiting factors of LPE.²⁶

When the optimal choice of solvent/surfactant is employed these dispersions can be very stable and possess a number of benefits over other methods. The ability to generate large volumes in dispersion facilitates in-solution characterisation of the material. LPE material can also be processed in solution, enabling its use in composites and inks.

As an example, a fully printed transistor on flexible substrates using layered materials has been demonstrated, with the contacts, encapsulation, and channel materials each comprising different 2D materials. Although the low performance of this device also illustrates how the many junctions between the small LPE flakes is a dominating factor in any electrical devices using LPE material.²⁷

1.5 Vapour-Phase Syntheses

Bottom-up manufacturing methods for 2D materials and TMDs particularly are dominated largely by vapour-phase methods such as chemical vapour deposition (CVD). Vapour-phase syntheses are an extremely popular synthetic choice for high-end applications such as electronics or optoelectronics.

The four most common methods to generate TMDs through vapour-phase methods are expressed in a simplified manner in Fig. 1.6.²⁸ There are a number of commonalities across these depicted methods. Each method involves using a controlled-pressure environment under constant carrier gas flow. The synthesis/growth substrate is brought to an elevated temperature to facilitate the chemical reaction. The methods vary in regard to the choice of chalcogen, and transition metal precursors as well as the experimental configuration. The common choice of chalcogen precursor are chalcogen solids e.g. sulfur powder, which are heated near or above melting point and so the vapours are carried towards the substrate by the carrier gas flow. This is the case for examples as shown in Fig. 1.6 (a) and (b), below. Another common method of chalcogen precursor supply is injecting a gaseous chalcogen containing compound e.g. H_2S , as illustrated in Fig. 1.6(c) and (d).

The transition metal precursor is generally in one of three forms. Similar to the chalcogen precursors, a transition metal containing powder is heated to decompose the precursor and generate a vapour containing metal atoms e.g. MoO_3 , as shown in Fig. 1.6 (a), or a gaseous metal containing precursor is injected into the system during synthesis, e.g. MoCl_5 , as shown in Fig. 1.6 (c). As transition metals typically have very high melting points, far beyond the synthesis temperatures of the TMDs, they can be pre-deposited onto the growth substrate in various forms e.g. Mo, MoO_3 , Na_2MoO_4 ,²⁹ as presented in Fig. 1.6 (b) and (d).

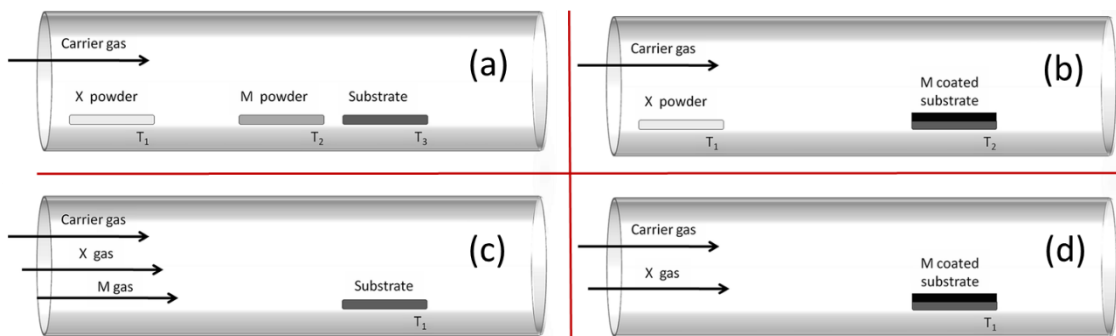


Fig. 1.6 Schematics of four common methods of vapour phase synthesis of TMDs. (a) Chalcogen (X) and transition metal (M) powders. (b) Deposited M film on substrate and X powder. (c) M and X gaseous precursors (d) Deposited M film and gaseous X precursor. Adapted from reference.²⁸

As previously mentioned, mechanically-exfoliated MoS₂ is generally considered the best method to produce a small number of the highest quality single crystals of TMDs including monolayers, these can be used for fabricating individual high-performance devices. Contrasting this vapour-phase methods can also allow synthesis of large uniform areas of thickness-controlled TMDs, in potentially patterned structures on industry compatible substrates such as SiO₂/Si.³⁰ These methods can be used to generate large amounts of large monolayer crystals, with individual crystals up to hundreds of μm in length.³¹

Vapour-phase methods also introduce features and complications not commonly seen with the previously discussed top-down methods.⁸ Defects are common features in the overwhelming majority of TMDs, including monolayers, the most commonly considered are chalcogen vacancies. For example, MoS₂ crystals generated through all methods are often observed to have a substantial amount of sulfur vacancies giving them a S: Mo of <2 .^{10, 32} The vacancy defects have several effects on the properties of the crystal itself including scattering centres, lowering the stability of the crystal, and charge traps. Vapour-phase methods of TMD production inevitably also result in grain boundaries between crystals, this is the interface and stitching together of different crystal grains into one larger material. Careful control of all parameters can reduce the presence of these defects by either aligning growth of the majority of crystallites on a substrate,³³ or by suppressing widespread nucleation ensuring fewer individual crystallites.³⁴ The grain boundaries can similarly have a pronounced impact on the properties of the synthesised material.¹¹

Thermally Assisted Conversion

The synthesis of TMD thin films by direct chalcogenisation of metal films is one the technically simplest methods and is referred to in this thesis as thermally assisted conversion (TAC).

The TAC process entails depositing a thin film of the chosen TM on a desired substrate, the substrate is then brought up to elevated temperatures, $\sim 400\text{-}800\text{ }^{\circ}\text{C}$, in an evacuated tube. A vaporised chalcogen precursor is then introduced to cause a direct chemical reaction with the metal film and convert it to the TMD. This and similar processes have been used to synthesise thin films of TMDs since at least 1996.^{35, 36}

Metal film deposition is a well-established process for methods such as sputtering and electron-beam evaporation. These deposition methods can be directly employed for high levels of control of placement, thickness, and uniformity of the initial metal film. Naturally the thickness of the converted film is directly related to this initial thickness, giving the TAC method a high level of thickness controllability over large areas. Allowing for the full range of thicknesses from bulk-like to few-layer TMDs to be synthesised.

Once temperature and chemical reactivity are considered, the method allows TMDs to be synthesised on a wide selection of substrates, including flexible substrates.³⁷ The high controllability of the various aspects of this process makes TAC a highly reproducible and scalable process, generally limited only by substrate or reaction chamber dimensions.

The relative simplicity, and limited parameter space, of this method when compared to many other bottom-up approaches enables materials which can be difficult to synthesise by other vapour phase methods to be readily made via TAC like PtSe₂.³⁸

A potential drawback of this methodology is the polycrystalline nature of the films, with small flake sizes on the order of 10s or 100s of nanometres only.³⁰ The polycrystalline nature can limit the utility as these flake-to-flake junctions and boundaries can cause scattering effects to be very prominent, similar to deposited LPE films. While there have been promising examples of well aligned crystal growth for some TAC style films,³⁹ these small crystals are generally randomly oriented. These can contribute to the comparably poor charge carrier mobilities from TAC TMDs.³⁰

These aspects of TAC growth can also be considered opportunities for further applications. The small and randomly oriented crystals in the film cause a large number of crystal edges to be exposed, as the edges of TMD crystals are well known to be more reactive than the basal plane this can increase the reactivity of the films for applications like gas sensing and catalysis.^{38, 40} TAC films are robust and can be transferred from growth substrates to arbitrary substrates, such as electrodes, using polymer transferred methods.

The high controllability of TM deposition allows simple techniques such as shadow masking to be used to create complex geometries of TMDs. Similarly, by depositing different TMs, simple heterostructures or alloyed TMDs can be manufactured using this method.

CVD

While mechanical exfoliation generally produces very small amounts of the highest quality material, and methods like TAC can produce large areas of polycrystalline, thickness controlled TMDs, CVD strikes a balance between the two.

CVD has the capability to generate large areas of high-quality monocrystalline, monolayers of TMDs on industry-compatible substrates like SiO_2 , although this is not trivial to achieve and is an area of ongoing study. This offers the most compelling route for the scalable synthesis of high-quality monolayers of TMDs, which is an essential feature for the growth of this field beyond purely scientific research applications.

Traditionally, CVD requires that the reactants interact in the vapour phase and deposit as a solid on a substrate, that is the case for many of the methods used in the literature today for TMD synthesis, but not all methods commonly referred to CVD fully conform to this. In general, the most common CVD method for 2D TMDs involves using a TM oxide such as MoO_3 and a solid chalcogen precursor such as sulfur powder, schematic of this style of process is shown in Fig.1.6(a)

CVD is one of the most industrial compatible methods of 2D TMD synthesis as thin film coatings in several industries utilise CVD methods currently. The most consequential disadvantages of CVD compared to other methods are the high temperatures ($\sim 400\text{-}1000\text{ }^\circ\text{C}$), potentially volatile or harmful precursors, and the often-toxic by-products of the reactions. These conditions increase the equipment requirements to operate CVD methods.

CVD is a far more sensitive process than TAC with many factors contributing to the process including, growth substrate, temperature, pressure, time, choice of sulfur and molybdenum precursors, precursor phases, carrier gas, flow rates, partial pressure of precursors, distance between precursors and substrate.⁴¹

While it is now possible to synthesise full coverage uniform films of TMDs by CVD,³³ it is more common for TMDs to grow on substrates in a variety of morphologies, orientations, and with several different thicknesses frequently as tiered multilayer stacked crystals. For MoS_2 , progress in CVD methodology over the last number of years has seemingly increased the size of individual MoS_2 crystals from several μm in length,⁴² up to the order of 100s of μm more recently.^{11, 43, 44}

One of the prominent challenges with CVD synthesis of TMDs is the inverse relation between nucleation density and crystallite size. Nucleation density is affected by many factors including substrate, temperature, local precursor concentration.¹¹ Seeding promoters, gaseous precursor supply, and alternate system configurations³⁹ can be used to attempt to maximise and control the individual crystal size.⁴¹

Some of the more advanced CVD-style processes in development can resemble atomic layer deposition processes more than traditional CVD with volatile gaseous precursors, different equipment layouts, and bursts of exposure.^{39, 45} This has been shown to enhance thickness control and uniformity of the TMD films.

As mentioned previously, defects and grain boundaries are highly important aspects to vapour-phase synthesis. Even with recent improvements in individual crystallite sizes, uniform CVD films of TMDs over large areas $>500\text{ }\mu\text{m}^2$ are polycrystalline, they consist of many single crystals coalesced into a larger material at grain boundaries. Grain boundaries in these materials are the most likely sites for defects and can be detrimental to long-range properties such as carrier mobility.⁴⁶ Grain boundaries in monolayer CVD MoS_2 show a dependence on the difference in orientation between the intersecting crystals, with lower angles forming more traditional bonding between the crystals via dislocations and also nanopores being formed, while higher misorientation angles lead to crystal overlap forming bilayers with no bonding.^{11, 46, 47} Control of the growth orientation of TMD monolayers can be strongly influenced by substrate interactions, with the crystal orientation of sapphire substrates shown to strongly influence the alignment of crystal growth.⁴⁸

The wide parameter space with CVD synthesis can enable targeted synthesis depending on the desired applications, whether they require extended uniform thickness films over a sample, or very high quality isolated single crystals for fundamental investigations.

CVD methods have also been used to synthesise heterostructures of TMD materials. CVD can be used in one or two step processes to synthesise heterostructures with different TMDs, these can be controlled to have vertical or lateral heterojunctions between monolayer crystals.⁸ Less controlled mixed heterostructures can also be synthesised which have shown promise as electrocatalysts.⁴⁹

1.6 Functionalisation and Plasma Treatments of TMDs

While considerable progress has been made on the synthesis of 2D TMD materials, less research has been concerned with methods to control and tailor the properties of these materials after synthesis, this is seen as one of the important next steps towards practical application of 2D TMDs.⁵⁰ The extreme surface to body ratio for 2D materials makes them very sensitive to their environment and any defects, changes, or functionalities in or near the crystal can have pronounced effects that would be usually quenched in a bulk material. This ratio is a key factor which makes the functionalisation and post-synthesis treatment of these materials a rising point of interest in the literature. Functionalisation is a broad umbrella term which is frequently used when discussing 2D TMDs, referring to the many different processes which are used to modify the properties of TMDs to tailor their properties for a function or to add new capabilities. As MoS₂ is the prototypical TMD it has been subject to the most experiments in this area also.

As mentioned previously, many of the 2D TMDs are noted for their ambient stability, strongly influenced by the lone-pair of electrons in out-of-plane orbitals on the chalcogen atoms, both above and below the TMD monolayers. This combination of a lack of dangling bonds across the basal plane, and screening/shielding of the metal atoms causes the basal planes of TMDs to be considered relatively inert.⁹ However, this is not the case at the edges of TMD crystals, at defect sites, or along grain boundaries, where naturally there are far more chemically reactive atoms with unsaturated bonds.⁵¹

MoS₂ has consistently been found to have significant amounts of point defect vacancies along the basal plane, which are most commonly in the form of chalcogen vacancies,¹⁰ these common reactive sites are often the target for functionalisation processes.

Several of the most common approaches to functionalisation of 2D TMDs will be briefly introduced herein.

Physisorption

Physisorption methods are the simplest method of functionalisation, this category generally covers all non-bond-forming (non-covalent) methods whereby the surface of the TMD is decorated with molecules which are electrostatically attracted to the TMD surface. This is most commonly achieved with LPE TMDs or with wet chemistry methods on TMD films.⁵² These

can be large self-assembled monolayer structures used for charge doping of TMDs⁵³ or thin coverage layers to enhance interfaces.⁵⁴

Chemisorption

Conversely, chemisorption is used to refer to all bond-forming interactions between TMDs and molecular functionalities. This is generally through formation of covalent bonds.⁵⁵ While the surface of MoS₂ is regarded as being relatively chemically inert, strong electrophiles can be used to bond to the surface sulfur atoms of pristine MoS₂. Aryl diazonium chemistry has been used to generate an aryl- radical group which can form a C-S bond at the MoS₂ surface. This technique can be used to attach a large variety of molecules by using the aryl-diazonium as anchor site.⁵⁶

Phase engineering

Phase engineering methods capitalise on the ability of many TMDs to adopt more than one crystal phase. While MoS₂ is thermodynamically stable in the trigonal prismatic (2H) structure, it can be converted to the meta-stable octahedral (1T) structure. The most common method to achieve this conversion is with lithium intercalation with butyllithium. This is a well-established process which has been demonstrated since at least 1991.⁵⁷ Li ions intercalate between the MoS₂ layers, they can then transfer charge to the MoS₂ which is resolved by changing phase to the metallic 1T structure. This meta stable structure has been frequently observed to show much higher chemical reactivity than 2H MoS₂ and has been used to covalently bond functional groups on 1T MoS₂, which can then be re-stabilised by annealing to the 2H structure without losing the functional groups.¹³

Plasma

The methods discussed thus far generally require applying liquid solutions or require the TMD material to be in dispersion. However, plasma processes are both industrially compatible and versatile, with the ability to uniformly apply them to large areas. Plasma treatments are also commonly used in the semiconductor industry for cleaning of surfaces and substrate preparation which inherently increases the likelihood of plasma methods being used to facilitate the integration of 2D TMDs into applications in the near future.

To put it simply, there are two main intentions behind the many different methods of plasma treatment of 2D TMDs, either bombardment of the surface with high energy ions, or to expose the material to highly chemically reactive species. While a combination of these two main

effects is common, the influence of one or the other can be controlled through several factors including the gases used, pressure, flow rates, the reactor type and its geometry, generator power, and time of exposure. As an example, high energy plasmas of O_2 are frequently used to clean substrates by oxidising and removing organic material this is commonly referred to as “ashing”, this can also be applied to oxidise and/or etch 2D materials on substrates.

By controlling the parameters of O_2 plasma it is possible to gently partially oxidise just the surface layers of material, this has been used to create ambipolar contact junctions for MoS_2 devices.⁵⁸ Slightly more aggressive O_2 plasma can be used to fully oxidise surface layers of TMDs which can enable layer thinning, as a method of producing monolayer crystals.⁴³

The high chemical reactivity or high kinetic energy of the species generated in some plasmas can overcome the relative stability of TMD materials. H_2 plasma has been demonstrated to remove sulfur atoms from the surface of MoS_2 due to the strong reducing environment of H^+ ions⁵⁹. While Ar plasma can similarly remove sulfur atoms from the surface of MoS_2 due to their high kinetic energy etching the surface⁶⁰. The energy/ exposure times of these plasmas can be controlled to enable controllable vacancy site or defect level creation.

The removal of sulfur atoms by plasma has been applied to enable the synthesis of exotic materials. Pristine monolayers of MoS_2 synthesised by CVD were exposed to H_2 plasma to remove the sulfur atoms from the top-side surface, the subsequent material was then selenised using a Se CVD process. The resultant material is known as a Janus structure, a two-faced TMD, with a S-Mo-Se structure.⁶¹

1.7 Characterisation

1.8 X-ray Photoelectron Spectroscopy (XPS)

The use of XPS features heavily in this thesis and is also one of the most widely used and important tools in 2D materials science⁶². It has significant complexity in its *operation and*

measurement, as well as in its *data analysis*. For the purposes of completeness, those two areas will be treated separately here. This section is adapted from a combination of the book by Watts and Wolstenholme⁶³, and several recent guides on XPS.⁶⁴⁻⁶⁹

XPS has grown to be one of the most common characterisation techniques for 2D TMDs for a variety of reasons. It displays extreme surface sensitivity, with only the first few nm's of a material being probed. XPS can be used to analyse a wide variety of samples to determine their constituent elements, except for H and He. Beyond this the chemical state information of these elements can be revealed and quantitatively analysed to determine the composition of a surface or material. This is enormously valuable information and combined with the surface sensitivity allows 2D materials to be examined accurately, comprehensively, and non-destructively.

1.8.1 Theory and History

A combination of discoveries have led to the modern iterations of XPS. Starting from world-changing events with Hertz's 1887 discovery of the generation of sparks from shining light on certain charged metals, Planck's discovery of the packet-based nature of photons, to Einstein's 1905 description of the photoelectric effect.

Many experiments involving the generation and measurement of electrons from metals using photons were performed over the next 50 years, but it was not until 1954 when Kai Siegbahn and group in Uppsala University recorded high-resolution spectra of NaCl that the vast potential was explicitly demonstrated, he was awarded the Nobel prize in physics for "his contribution to the development of high-resolution electron spectroscopy." With the first commercial systems sold in 1969, XPS has been ever upwards in utility and popularity since then.

A simplistic description of how XPS operates is that by shining a beam of X-rays onto a sample material, these high-energy X-rays cause photoemission from the core-level electrons. When in ultra-high vacuum (UHV), these emitted electrons can elastically travel through the system where they are detected and measured by their kinetic energy. The kinetic energy of the detected electron is related to the binding energy (BE) of the orbital that the electron originated from.

The detailed theory behind photoemission is complex and is not the focus of this thesis, a simplified and more basic approach to the theory which is sufficient to understand the state of modern XPS and the work in this thesis is given instead.

Photoionization

The photoelectric effect tells us that a photon interacting with an atom can cause the emission of an electron when $\lambda \geq \lambda_t$ where λ_t is a threshold wavelength. As the photon transfers all of its energy to the electron, the kinetic energy (KE) of the electron is directly proportional to the energy of the photon. Einstein's equation allows us to relate this to the BE of the electron in the atom, slight modification for the specifics of XPS and the barriers to electron emission gives us

$$BE = h\nu - KE - \phi \quad (1.1)$$

$h\nu$ = photon energy

ϕ = the spectrometer work function

The BE of the electron (referenced to the Fermi level) is specific to the atom, and for XPS specifically the atomic orbital from which it originated. Using monochromatic X-rays and an electron analyser to detect the KE of the emitted electrons we can determine the BE. While KE is the measured quantity, BE is of more interest. Due to the established KE and BE relation, it is convention for XPS data to be presented with BE going from higher to lower across the x-axis.

A simplistic three-step method approximation of photoemission can be thought of, where first a high-energy photon excites an electron, this excited electron travels to the surface of the material, the electron escapes the forces of the atom after overcoming the work function and is released into the vacuum at a KE specific to its conditions, illustrated in Fig. 1.7, below.

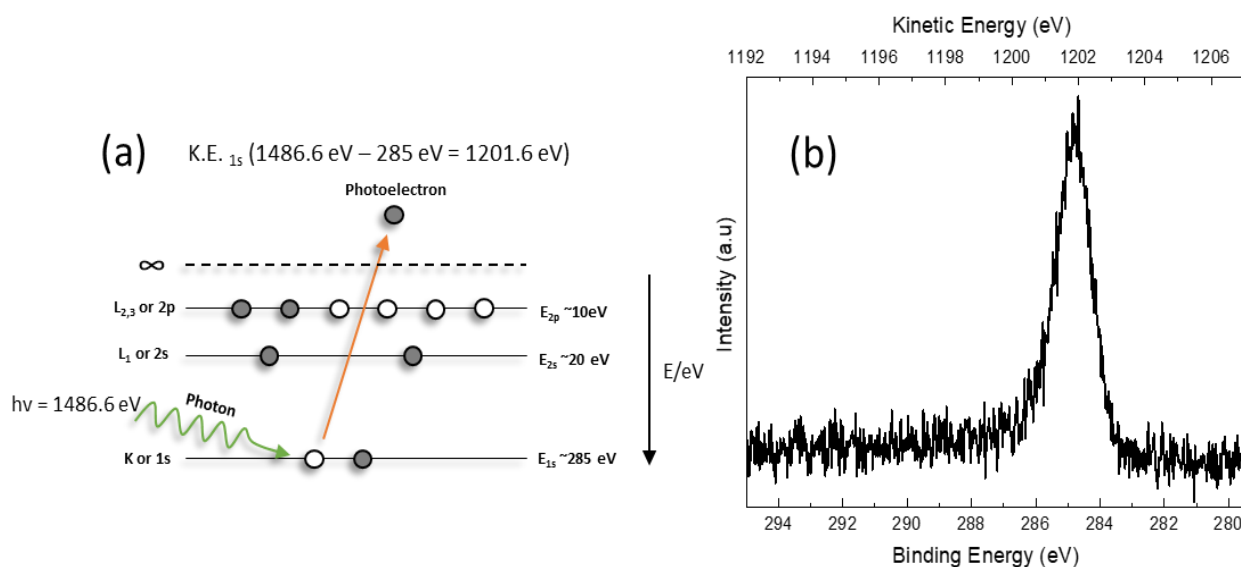


Fig.1.7 (a) Schematic representation of photoemission process for a C $1s$ electron excited by an Al $K\alpha$ X-ray. (b) An example XPS spectrum for the C $1s$ core-level, showing kinetic energy and binding energy scales.

Notation

As XPS evolved and its use has broadened in interest its notation has become more standardised. There is still some legacy, non-IUPAC, influences which are noteworthy. The most prominent in literature, and the only X-ray source utilised in this thesis, is an Al anode, and the Al $K\alpha$ X-ray line. $K\alpha$ is legacy notation using the Siegbahn notation system (a different Siegbahn than the XPS pioneer) but it is the most commonly used when referring to the X-ray source, outlined in Table 1.2. Using IUPAC notation this would be the Al KL_3 X-ray. Al has two most prominent characteristic X-ray lines, the $K\alpha_1$ (KL_3) and $K\alpha_2$ (KL_2), the $K\alpha_1$ is emitted with $\sim$ twice the intensity of the $K\alpha_2$, these are very close in energy and are generally averaged to 1486.6 eV.

Table. 1.2 Quantum numbers for common orbitals and their corresponding X-ray notation. Alongside a comparison of the Siegbahn and IUPAC notations for X-ray lines.

Quantum Numbers				Atomic Notation	X-ray Notation	Siegbahn Notation	IUPAC Notation
n	l	s	j				
1	0	$\pm 1/2$	$1/2$	1s	K_1	$K\alpha_1$	K-L ₃
2	0	$\pm 1/2$	$1/2$	2s	L_1	$K\alpha_2$	K-L ₂
2	1	$-1/2$	$1/2$	2p _{1/2}	L_2	$K\beta_1$	K-M ₃
2	1	$+1/2$	$3/2$	2p _{3/2}	L_3	$K\beta_3$	K-M ₂
3	0	$\pm 1/2$	$1/2$	3s	M_1	$L\alpha_1$	L ₃ -M ₅
3	1	$-1/2$	$1/2$	3p _{1/2}	M_2	$L\alpha_2$	L ₃ -M ₄
3	1	$+1/2$	$3/2$	3p _{3/2}	M_3	$L\beta_1$	L ₂ -M ₄
3	2	$-1/2$	$3/2$	3d _{3/2}	M_4	$M\alpha_1$	M ₅ -N ₇
3	2	$+1/2$	$5/2$	3d _{5/2}	M_5		

The Spectrum

The X-ray photon energy is significantly higher than the material work function, as such, electrons will be excited from many orbitals all the way down to the core levels. This effect results in a many-component spectrum which has several important features discussed herein. Elastically scattered electrons are the only ones of interest in XPS but there is a significant proportion of inelastic interactions possible during the emission and journey to the XPS

detector, these inelastically scattered electrons contribute to the background in XPS. An example of a spectrum is illustrated in Fig. 1.8.

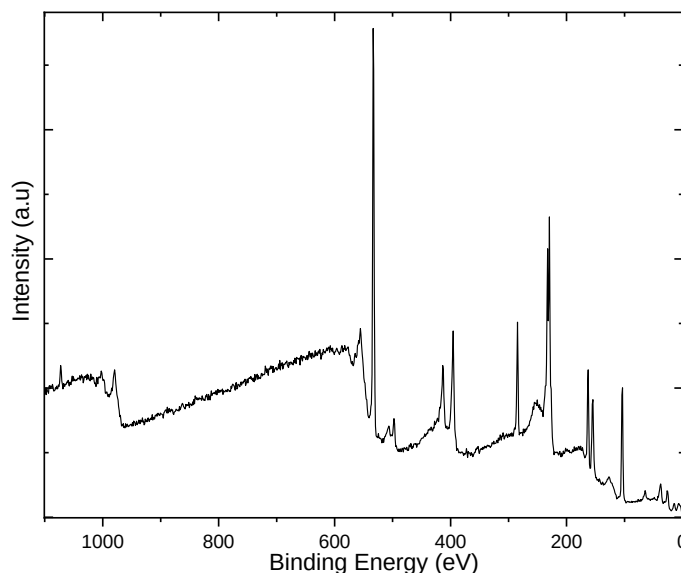


Fig. 1.8 An XPS Survey spectrum showing the many peaks and features present.

Core-levels

The primary features of interest in XPS spectra are the core-level components of the elements being investigated. These are described using their quantum number notation nl_j , outlined below:

n = Principal quantum number 1, 2, 3 etc

l = orbital angular momentum 0, 1, 2, 3 (s, p, d, f subshells)

s = spin angular momentum $+1/2$, $-1/2$

j = $|l + s|$ total angular momentum

The quantum numbers of the different orbital core-levels convey information about their features in XPS. All orbitals investigated using XPS are fully occupied, but spin-orbit splitting results in doublet peaks for non-s orbitals, with the doublets having different occupancy dependent on their quantum numbers.

For an element, the intensity of the XPS spectra increases for higher level occupied orbitals $s < p < d < f$. The relative intensity of the spin-orbit coupling induced doublets are given

by the degeneracy of the orbital $(2j+1)$. This gives the relative ratios of the doublets for the different l numbers, s orbitals - no splitting, p orbitals - 1:2, d orbitals - 2:3, f orbitals - 3:4. In XPS discussion the notation for these split pairs is given for example as Mo $3d_{5/2}$ and Mo $3d_{3/2}$, W $4f_{7/2}$ and W $4f_{5/2}$, and S $2s$ etc.

Satellites

While monochromatic X-rays are essential for optimum operation of XPS, older and simpler X-ray sources, only entail the bombardment of a metal source with electrons without any further selectivity, as represented in Fig. 1.9. This can produce weaker satellite XPS peaks from the small number of other characteristic X-rays generated. For Al X-rays, several satellite peaks can be generated including Al $\alpha_{3,4}$, $K\alpha_{5,6}$, and the $K\beta$. These have the potential to generate XPS features which can complicate the spectrum, as the BE of a feature is a property of the exciting photon, these satellites are only an issue if they coincidentally overlap with a region of interest or are misidentified.

Bremsstrahlung radiation

Bremsstrahlung radiation which are photons produced from the deceleration of high energy electrons can contribute to the background spectrum for non-monochromated X-ray sources. This occurs when for example the accelerated source electrons are scattered by a nucleus, the rapid change in momentum is released as a low energy X-ray. These low intensity varying energy X-rays can cause some unintended photoemission from a sample if they are not removed.

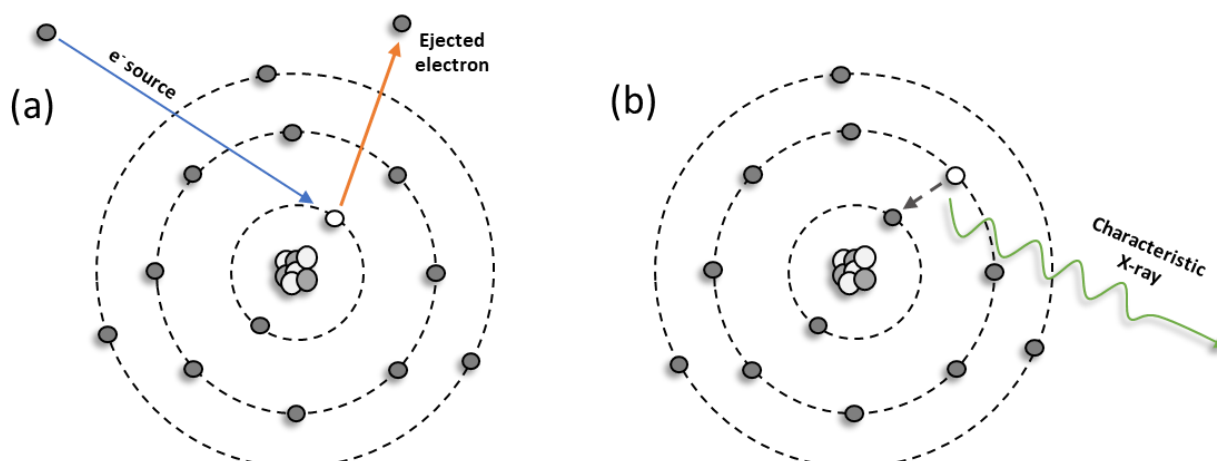


Fig.1.9 Traditional representation of the X-ray generation process (a) a high energy electron ejects a core-level electron from a material, e.g. Al (b) This core-hole is filled from a specific higher energy level which emits an X-ray characteristic of the energy gap between the energy levels.

Auger electrons

One of the important methods of relaxation of the post-photoexcitation atom is the Auger process. Auger relaxation occurs when the core-hole after photoemission, is filled from a higher-level state where there is a sufficient energy gap that another photon is emitted, illustrated in Fig. 1.10. The emitted X-ray can interact with the same atom and emit a new photoelectron. As this process involves 3 separate levels, the core-hole's, the filling electron's, and the emitted electron's it is referred to using all three levels with IUPAC notation e.g. KLL. The BE of the Auger electrons will be independent of the experimental X-ray source.

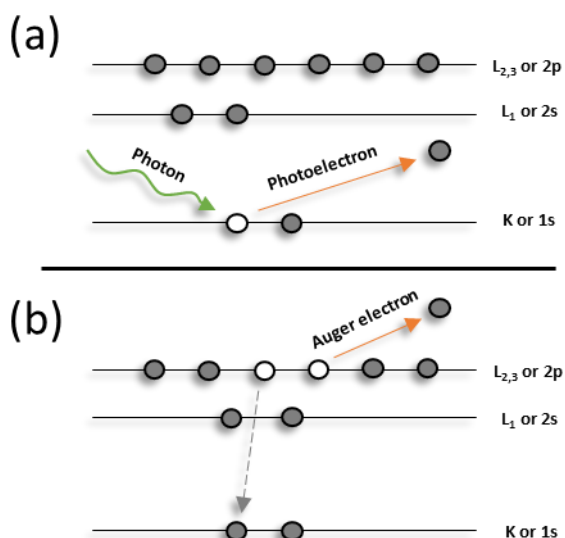


Fig. 1.10 Representation of (a) photoemission and (b) subsequent Auger electron emission.

Cross section

The probability of an X-ray exciting an electron out of an orbital varies for each orbital and is also a function of X-ray energy. As this work utilises a single, non-tuneable X-ray source, Al $K\alpha$ X-rays, there is no scope to adjust these values but the difference in photoionization cross-section for different core-levels is important, as it is a major factor in the intensity of peaks in the spectra and plays a significant role in influencing which core-levels are the most studied in literature.

Escape depth

The prominence of XPS in surface science and its rise to be one of the most common characterisations of 2D materials is largely related to its extreme surface sensitivity. While X-rays have substantial penetration through most materials, electrons do not, elastically scattered electrons have an even shorter range.

As photoelectrons can undergo some elastic scattering before emission from the surface, it is not fully correct to use the inelastic mean free path (IMFP) of an electron when estimating escape depth/sampling depth. Nevertheless, this is often used as a rough value. Traditionally it is estimated from the Beer-Lambert law that 95% of the measured electrons are emitted from within a depth of $3 \times \text{IMFP}$. This analysis depth varies for the materials being measured with a few factors being involved including, the angle of emission, the energy of the emitted electron, and the X-ray source energy. The sampling depth here is generally estimated as being the first $\sim 2\text{--}10$ nm of sample. The IMFP of electrons through various materials is presented in Fig. 1.11, below.

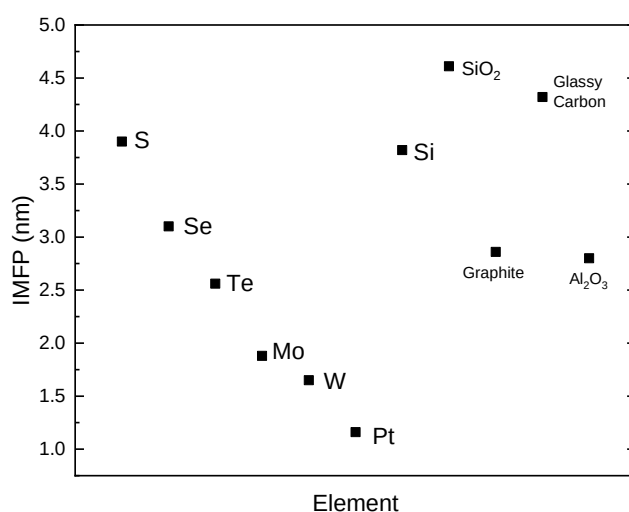


Fig. 1.11 Inelastic mean free path (IMFP) of electrons through various materials at 1486 eV. (Data provided by the NIST electron IMFP database version 1.2)

Background

The background in XPS spectra is generated by inelastically-scattered electrons, this is an inherent, prominent, and continuous feature in XPS spectra. The background has characteristic

and successive jumps in intensity as higher binding energies are measured, where a characteristic peak from a material's core-level is accompanied by an increase of the background from that energy onwards.

Initial and Final-state effects

The complex process of photoemission and the KE of the emitted electron can be affected by a number of initial and final state effects.

Initial effects

While the ability to detect what elements are present in the first few nanometres of a material is in itself clearly very useful, the ability of XPS to differentiate between the various chemical states of those elements is the most important aspect to its modern utility. While, as previously discussed, the only electrons of interest in XPS are elastically scattered electrons from the core-levels of an atom, those electrons are still subject to forces from their environment. The electrostatic fields in an atom are a combination from the nucleus and the electrons bound to it. When a photoelectron is emitted from a core-level in XPS, it travels outward through the electrostatic fields of the atom, and naturally as an electron is a charged particle its KE is affected by this. Any change to these atomic forces would be reflected in a change to the measured KE of the core-level electron. This is the basis for XPS's chemical sensitivity, as forces generated by the valence band of the atom have a small effect on the KE of the core photoelectrons. The chemical environment/charge of the atom changes with bonding, with greater or lower electron density existing on the atom depending on the bond. Less electron density on an atom will result in a lower KE for the measured photoelectrons, due to the nucleus being less screened by other electrons, this gives a corresponding increase in calculated BE. Correspondingly the reverse is true for more electron density on the atom, giving a lower calculated BE of the electron. Comparing the electronegativity of the different elements involved in a material is a simplistic method to indicate if the measured photoelectron energy will increase or decrease for a bond between elements, an electronegativity scale is provided in Fig. A4.

The shift in XPS peak energy, if measured correctly, can therefore be used to elucidate the composition of the material being analysed.

Final-state effects

There are a number of so-called final-state effects which can contribute to the XPS spectrum. The first is what are known as shake-up peaks. The emitted photoelectron can transfer a fixed amount of energy to a valence electron, exciting it into a new state, which is reflected in the spectra as a low intensity peak shifted to higher binding energy. Similarly, if the excited valence electron is also emitted from the surface this is known as a shake-off event, this can lead to broadening of the core-level peak.

Further, it is often observed that metals have asymmetric peaks in XPS, with a ‘tail’ on the high binding energy side. This is a complex process, wherein a significant contribution comes from photoelectrons transferring energy to the valence electrons in a metal, but, unlike shake-ups, if these valence states can occupy a continuum of energy states an extended tail is observed on one side of the peak instead of a discrete second peak.

Plasmon loss

Plasmon losses are final-state effects which are attributed to metallic materials, where the photoelectron loses energy to long-range oscillations from conduction-band electrons in the metal. This can be a prominent effect which is important when examining metallic surfaces, as plasmon-loss related peaks can be easily attributed to chemical shifts or other features. The common plasmon losses for metal films are well known and can be found in the common literature databases such as the totemic *Handbook of X-ray Photoelectron Spectroscopy*.⁷⁰

Multiplet splitting

Finally, another important final-state effect is multiplet splitting, this can occur when there are unpaired valence electrons in a material. Photoemission from certain core-levels can result in different final-state electron-spin configurations of an atom, particularly transition metals. This can lead to many extra peaks for a core-level’s spectrum, with energy shifts similar to chemical states. The common multiplet peaks for TMs are well described in the literature.⁷⁰

1.8.2 Measurement

Simple configuration, source, sample, analyser, detector

XPS measurement tools have increased in complexity and capability over the last 50 years, there are now various types of equipment for all of the important components. The 3 most essential components of an XPS tool are the X-ray source, the sample and its environment, and the electron analyser.

Sources

X-ray sources generally operate by accelerating high-energy electrons into a metal target, this energy is dissipated both by generating significant amounts of heat, requiring liquid cooling, and emitting characteristic X-rays of the metal, as presented in Fig. 1. 12. As briefly outlined in previous sections, Al $K\alpha$ is the most common X-ray line used for XPS, Mg $k\alpha$ is also very commonly used. XPS tools frequently have the capability to use multiple X-ray lines for characterisation.



Fig. 1.12 Photographs of a dual X-ray source used in a non-monochromated XPS system here, alongside a representation of the various components of a standard source.⁷¹

Older and simpler XPS systems use non-monochromatic sources, non-monochromated X-rays can have a significantly higher photon flux and therefore yield significantly higher XPS intensity. This higher intensity signal comes with several drawbacks as non-monochromated X-rays result in wider peaks, satellite peaks, and a higher background intensity.

It is very common now to use monochromatic X-rays for XPS, the reduced peak width is extremely beneficial for accurate analysis and discriminating between close-in-energy peaks. For Al $K\alpha$, the intrinsic linewidth is reduced from approximately 0.9 eV to 0.25 eV when applying a monochromator.

Monochromator

XPS monochromators operate via diffraction, wherein a quartz crystal is used to diffract Al $K\alpha$ X-rays. The geometry for XPS monochromators requires the source, diffraction crystal, and sample all lie on the Rowland circle so that the diffracted X-rays are focused onto the sample. This is very effective at selecting the primary Al $K\alpha$ X-ray, removing satellite peaks and Bremsstrahlung radiation but consequently it reduces the flux of X-rays significantly.

Samples, charge compensation, Fermi level, vacuum compatibility

The physical properties of a sample and its preparation can affect its XPS measurement and the quality of data obtained. As XPS analysis occurs in a UHV environment, any volatile material cannot be measured, and samples such as compressed powders, which tend to have trapped volumes that will degas in a UHV system, can require pre-treatment or extensive pump-down time. XPS analysis at its core assumes that the sample is in good electrical contact with the spectrometer and that there is Fermi-level alignment.

Insulating samples, and those poorly in electrical contact with the spectrometer, can also be measured. In these scenarios the binding energy numbers calculated by the detector will be incorrect as there will be a difference in the work functions of the sample and the analyser. This can be further complicated by several factors. Samples can have a variety of materials on them e.g. isolated MoS₂ monolayers on SiO₂, in various states of Fermi level alignment, this will cause inconsistency in the accuracy of the measured energies. A common occurrence during XPS analysis is sample charging, this is as electrons are emitted from the surface a positive surface charge develops, this is proportional to the X-ray flux on the sample. The surface charge can affect the kinetic energy of the electrons shifting them to lower kinetic energy (higher binding energy in the spectrum).

To account for this, it is normal procedure to use a low-energy electron flood gun to compensate for these surface charges. The energy of this should be similar to the amount of charging on the surface, generally relying on charge referencing to the C 1s peak. This will be discussed further in the XPS analysis section.

Analysers

The most common form of XPS analyser, and the only type utilised in this study, is a hemispherical sector analyser (HSA), as shown in Fig. 1.13. This type of analyser is also known by several names including concentric hemispherical analysers (CHA) and spherical sector analyser (SSA). The photoemitted electrons first pass through a series of electromagnetic lenses, the first lens focuses the electrons and controls the acceptance angle and area, the second lens is used to slow down the electrons and is essential for providing electron-energy selectivity.

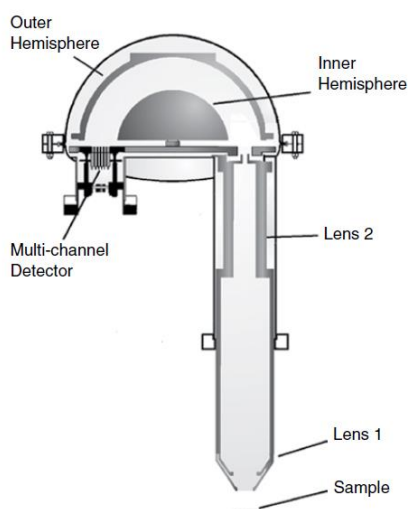


Fig. 1.13 Schematic of a hemispherical sector analyser.⁶³

The analyser functions by applying a high negative voltage to the outer hemisphere relative to the inner hemisphere this creates an electrostatic force on the electrons entering the analyser and allows only electrons with a so-called pass energy E_p to make it to the detector. The measured KE of the electrons is given by

$$E_p = k_s e \Delta V \quad (1.2)$$

Where

$k_s = k$ is a spectrometer constant based on the design of the detector.

e = the charge on the electron

ΔV = the voltage difference between the hemispheres

The analyser is generally operated in constant analyser energy (CAE) mode, in this mode the pass energy of the analyser is fixed at a user specified value. The second lens in the system is then used to slow electrons to fit this pass energy. The full range of kinetic energies of the electrons is therefore measured by scanning through retarding voltages in the second lens.

The energy resolution of the analyser is dictated by

$$\Delta E = E_p \left(\frac{W}{2R} + \frac{\alpha^2}{2} \right) \quad (1.3)$$

Where

W= Width of the slit at analyser entrance

R= the mean radius between the hemispheres

α = angle of electrons entering the analyser

Equation 1.3 outlines that lower pass energies result in better energy resolution in the spectrum. Whereas higher pass energies yield higher intensity signal. This trade-off is managed depending on the requirements of the measurement with low pass energies of ~10-50 eV used for core-level scans, and higher pass energies ~100-200 eV for survey scans for elemental identification.

Modern tools

In the modern era of XPS measurement there have been many interesting developments. One of the limiting factors in the utility of XPS for 2D materials characterisation has been its poor spatial resolution of ~mm². The development of commercial micron-level XPS tools has made the characterisation of individual CVD-grown or exfoliated TMD crystals feasible. A complementary development to the small spot size of these systems is the ability to perform mapping or scanning XPS. Achieved by using similar monochromators as introduced before, the key difference for a mapping XPS system is the electron beam used to generate X-rays at the anode. The electron beam is focused onto a micron sized spot on the anode, generating X-rays from only that small area. After these X-rays are diffracted on a curved quartz diffraction monochromator, they are focused onto the sample with a similar micron sized XPS spot size. By moving the electron beam over the anode, the X-ray spot can be moved on the sample. This enables measurement of smaller structures alongside mapping.

A side effect of the small area X-ray spot is very localised charging in micro-XPS which heavily reduces the effectiveness of the electron flood gun to compensate for the charging at one spot on a larger sample. This has been improved by using a complementary low-energy Ar⁺ ion source, and the combination of ions effectively neutralises surface charges across the sample including at the micro-XPS spot.

Modern XPS tools are often incorporated into larger cluster tools allowing a variety of materials characterisation such as Ar-ion sputtering, X-ray Diffraction (XRD), to be performed without leaving UHV.

A beneficial consequence of the rising popularity of XPS as a standard characterisation technique in materials science is the increasing development of more automated processes and tools to allow wider use of the technique without requiring time consuming expertise to be developed.

1.8.3 Analysis and Curve Fitting

XPS analysis can be considered as a process of two, almost equal, halves: measurement and data analysis.

XPS can be used for qualitative analysis with little expertise, relying on literature and database resources to identify the constituent elements in a spectrum, particularly a survey scan of the full energy range. Modern XPS use for 2D materials usually includes a survey spectrum, and several core-level scans of the elements of interest. These core-level spectra require rigorous peak-fitting analysis to deconvolute the spectra into their various components. If done correctly, these curve-fitted spectra can be used to identify the different chemical states and their relative amounts in the material. While some identification of the different chemical states present in core-level scans can be possible without curve-fitting or more in-depth analysis, this is sample specific and can have a high potential for error.

Any analysis of XPS spectra without curve-fitting has the potential to leave significant amounts of information unretrieved. As this is the case, the majority of XPS found in the literature will include curve-fitting, however problems can arise due to widespread inappropriate fitting. XPS analysis often requires a considerable degree of user decisions and compromises to be made, this can lead to significant variation in the result of analysis between users.

A recent letter from twenty-two of the world's experts in XPS data analysis declared on the subject of XPS "In some areas, the proliferation of advanced analytical instruments appears to have exceeded the world's supply of expertise necessary to collect, interpret, and review the results obtained from them".⁷²

The considerable spread in the quality of XPS data in literature can compound problems as poor-quality works can then be used as the basis of new work without any recognition or acknowledgment of the faults. XPS data in scientific journals focused on developments with next generation materials has been found to contain roughly 30% completely incorrect XPS analysis.⁷²

In an effort to counter this, several in-depth guides, overviews, and methods of best practice have recently been published.^{62, 64-69, 73-76}. The Journal of Vacuum Science & Technology A has also published a collection "Reproducibility Challenges and Solutions" entirely focused on this issue containing 26 articles. These accessible resources should be essential references for XPS containing publications in the future.

A rough summary of accepted practice for XPS analysis includes, but is not limited to:

- Sensible measurement (signal to noise ratio, appropriate energy window size, charge compensation).
- Survey scan for elemental identification.
- Charge correction of binding energy to peak of known position.
- Appropriate background choice per core-level scan.
- Components with appropriate quantum number and literature determined parameters.
- Fairly adjusting peak shapes for the data.
- Small deviation of fitted peak envelope from raw spectrum.
- Using a sensible number of spectral components.
- Reality check in terms of expected results and reference to good literature values.
- Serviceable calculated stoichiometric values.

Backgrounds

There are many types of backgrounds used for core-level XPS analysis which have a substantial impact on the quality and accuracy of the final fit, an example is presented in Fig. 1.14. There is no fully scientifically correct form of XPS fitting background as all commonly used backgrounds are approximations and can contribute to the error in the final curve fit. The theory behind each individual type of background goes beyond the scope of this thesis but an introduction to each major type of background is provided briefly herein.⁶⁶

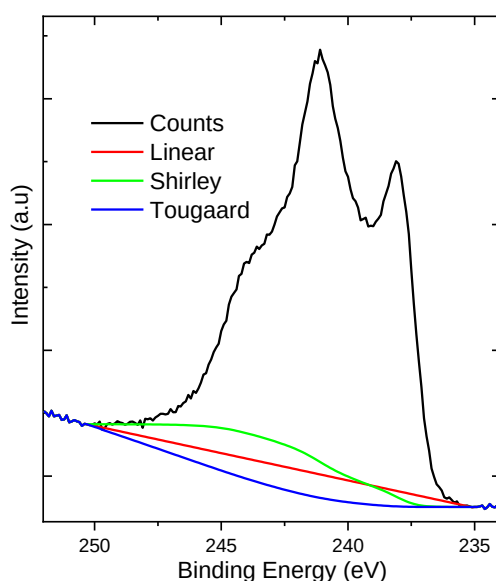


Fig. 1.14 XPS core-level spectrum showing the three most common fitted XPS backgrounds.

Linear

The simplest type of background that can be used in XPS fitting is a linear background, while it is generally inadvisable to use this as it has no physical basis, it can still be of use in specific circumstances, for example where there is no discernible change in background across a core-level.

Shirley

By far the most common XPS background used in the literature, and the method utilised for the vast majority of spectra in this thesis is the Shirley background. The Shirley background is an iterative calculated background which aims to account for the rising background from inelastic scattering of electrons when going to higher binding energy. The height of the background is a

function of the intensity of the XPS signal at that point, the choice of start and end points is important for this method.

Tougaard

The Tougaard background is also commonly used, this background can be of particular use when measuring metals, it accounts for the background caused by inelastic losses using an algorithm approximation. Tougaard backgrounds have been shown to be more accurate over longer ranges ~50 eV than Shirley type backgrounds. However, for core-level measurements, which are generally much smaller than that, iterative Shirley backgrounds are generally regarded as being the most applicable.⁶⁶

Core-level components

As mentioned previously, the most valuable information from XPS can be determined by curve-fitting the acquired core-level spectra. The identification of what core-levels to acquire for which element, what their energies are, and roughly expected peak positions for different chemical states, can all be found in a number of popular reference books or databases.⁷⁰ These data sources provide essential information which cannot be intuited, and are essential for peak identification, as the differences in relative sensitivity for elements and their various orbitals can easily lead to misidentification of peaks.

These reference libraries also contain information on the peak-splitting for each element's orbitals, expected peak shapes, and will often also highlight satellites, plasmons, and other features which can cause confusion. Modern XPS fitting software programs such as CasaXPS and PHI MultiPak may also have this information from these libraries built in. These fitting software programs are essential for XPS analysis but are not capable of performing accurate XPS analysis automatically. XPS fitting requires a large amount of user input, frequently by determining limits and constraints over factors such as peak position, the software will then operate inside those limits to match the fitted spectrum to the measured data as close as possible. While most elements will give a few intense XPS peaks across the XPS spectrum, there are generally only one or two core-levels per element which are thoroughly studied in the literature. As referencing to reliable literature is an essential part of XPS, these are usually the regions that should be analysed.

After applying a background to a core-level spectrum, the individual peaks and components can be fit. Peak shapes are another aspect of XPS analysis which requires user input and can be

a source of error. The most common peak shape is a Voigt function, which is a combination of a Gaussian and a Lorentzian distribution. The relative amounts of Gaussian and Lorentzian components are not fixed and can vary for several reasons, thus it must generally be input by the user and is usually constant for most components in a spectrum. The line shape of the photoemission itself is a full Lorentzian but experimental factors introduce Gaussian elements. As mentioned previously, some metal peaks display asymmetry which must also be accounted for with the peak shape.

Peak width is a separate factor and can have a major impact on the accuracy of a fitted spectrum, particularly for overlapping peaks. This is mostly user constrained, peaks from the same material are mostly of similar peak width, this can serve as one of the many “sanity checks” of the fitting model. It is important to maintain a level of qualitative and quantitative consistency when performing XPS analysis, i.e. MoO_3 should have a Mo-O, and a O-Mo component in the Mo and O core levels respectively, they should also, when accounting for relative sensitivity factors (RSF), be in a roughly 1:3 ratio.

The quantum number determined values, such as doublet peak occupation, and the fixed doublet separation from literature-measured values are advisable to be fixed by the user in the fitting software.

The above information for XPS analysis is readily accessible but is not consistently implemented through 2D materials XPS literature. XPS appears to frequently be treated as an add-on characterisation method for 2D materials and so it is not always given the same scrutiny as other characterisation techniques by authors or reviewers, this has led to a high frequency of XPS errors in the literature.

There are a number of simple errors that can be made with XPS fitting which can lead to faulty results. These errors can be very important if conclusions are made solely from XPS data.

Common errors

While the types of errors and common mistakes are numerous, a few examples are included here.

Acquiring or displaying too narrow of an energy range can be misleading as relevant components may not be measured or the background may be incorrect due to XPS peaks at the edge of the energy window.

Mislabelling is also a common issue. While reversing the labelling on a doublet pair is generally not too damaging to a result, mislabelling of peaks can contribute to confusion in the literature. A more severe error is misattributing a component to the wrong chemical state, or even core-level or element. There are many coincidentally overlapping core-levels across the XPS range, and it is important to be aware if you have overlapping elements present in your sample.

There a variety of mistakes which can lead to a “bad fitting”. Two of the most impactful are when the quantum number determined doublet occupation or the accepted doublet peak separation is not adhered to, these should be fixed parameters but often are not in literature. It is also common to see a large number of components in a spectrum which do not have a fair correlation to the physical/chemical reality of the sample, components should only be included if they can be justified, even at the loss of fitted-envelope to raw-data matching. This does not mean that unknown peaks in the spectrum should be ignored, which is another issue frequently observed. Poor background implementation and poor peak-shape parameters can often also be sources of error. A less obvious issue can be with the presentation of data, where fitted XPS spectra are frequently presented in ways which are difficult to discern all of the important features. All of these issues are exacerbated when noisy spectra are used for XPS fitting, this can lead to overconfident conclusions being draw from problematic fitted data.

Several specific examples will be provided here to demonstrate the impact and frequency of this in the literature, with particular focus on XPS of nitrogen doping of MoS₂ as an example.

In “Nitrogen-Plasma-Treated Continuous Monolayer MoS₂ for Improving Hydrogen Evolution Reaction”⁷⁷ like many papers concerned with the nitrogen doping of MoS₂, several critical mistakes are made. The authors do not report the characteristic core-level region for Mo, which is the Mo 3d. It is necessary to report both the TM and the chalcogen core levels for TMDs to confirm the data, in particular when using XPS to measure doping or chemical functionalisation. This is very important as the Mo 3p core-level is very close in energy to the N 1s, this leads to overlap of some of their components, which often results in misidentification. Fortunately, there is a large spin-orbit splitting of the Mo 3p components of ~15 eV. If both doublets are measured it is trivial to identify which components are Mo 3p doublets and which are N 1s singlet peaks. The authors do not measure the second half peak here, making this determination impossible. The most impactful XPS overlap for nitrogen doping of MoS₂, is the MoO₃ (Mo 3p_{5/2}) at ~398 eV and the N-Mo (N 1s) at ~397 eV, both peaks are separated by only ~1-3 eV. The authors here do not include this, and instead attribute the entirety of signal at this

point to N-Mo bonding confirming doping. They also include this feature in the “as-grown” MoS₂ before doping, where it is almost certainly MoO₃. This issue is very prevalent in nitrogen doping of MoS₂, in part due to the Mo 3d core-level being the focus of XPS in the literature and so the Mo 3p is often poorly described, works such as this only further add to the confusion.

Similar mistakes can be seen in much of the N-doped MoS₂ literature, with the Mo 3d core-level cut off in this example before the MoO₃ doublet can be measured, introducing doubt into the fitted N-Mo peak.⁷⁸

Another example of these issues can be seen in “Self-assembled N-doped MoS₂/carbon spheres by naturally occurring acid catalyzed reaction for improved sodium-ion batteries”⁷⁹ Here, the MoO₃ (Mo 3p) component is incorrectly fully attributed to N-Mo (N 1s). The energy window is too restricted to provide good background fitting. The S 2s component at ~226 eV is mislabelled as S 2p, even though the actual S 2p region is also included in a different figure. A peculiar error in this work is the absence of MoS₂ signal in the Mo 3p region for bulk MoS₂ even though the other MoS₂ peaks are present. This is nonsensical and is either an odd mistake or intentionally misleading. The authors also do not describe the data fairly, referring to components which do not appear to be possible to fairly include as they are extremely broad and overlap with 2 other components as being “prominent peaks”. Similarly to this mislabelling of a likely MoO₃ component as N-Mo, and also labelling the S 2s as S 2p is also presented in the work by Liu *et al.*⁸⁰

In “Plasma-assisted controllable doping of nitrogen into MoS₂ nanosheets as efficient nanozymes with enhanced peroxidase-like catalysis activity”⁸¹ there are concerning errors in almost every aspect of the XPS analysis. The sulfur region has very poor peak labelling which could lead to confusion. The previously described issue where the Mo-O peak is labelled N-Mo in the Mo 3p region is present here, but unlike the previous works, both halves of the Mo 3p doublet are included in the measurement here which should enable trivial differentiation between N 1s and Mo 3p states. Unfortunately, the authors confuse this by mislabelling most peaks, including for the second half of the Mo 3p doublet, with the Mo-O Mo 3p_{3/2} peak erroneously attributed to N 1s. The N 1s does not shift greatly for different chemical states, and it is absurd to imply it is shifted ~15 eV. Errors in the Mo 3d region here are less clear as there is good agreement between the fitted peak envelope and the raw data, the authors do not appear to constrain the doublet peak areas, which is giving a misleading fit. It is not possible to

determine the accuracy of the peak attribution in this figure, but based upon the Mo 3p error, it is more likely the sample contains a Mo^{5+} oxide than a Mo-N state.

These examples above make up a significant portion of the literature for nitrogen doped MoS_2 . This may be an example of poor quality XPS literature causing confusion or misleading others into making the same mistakes. In all of the reports outlined thus far in this section, XPS is used as the main or only method to verify and measure the nitrogen doping of MoS_2 , the majority of these works are applications oriented and therefore make conclusions on the properties of this doped MoS_2 which may not, in fact, be doped at all.

Erroneous XPS for 2D TMDs goes far beyond just the doping of MoS_2 . In “ WX_2 (X=S, Se) Single Crystals: A Highly Stable Material for Supercapacitor Applications”⁸² the authors do not appear to use a background related to the data at all, instead an arbitrary horizontal line is used, not to be confused with a linear background. This paper characterises WS_2 and WSe_2 , it is well known that the W 4f core-level region is complicated by the coincidental overlap of the W 5p_{5/2} peak ~5 eV above the W 4f_{7/2} peak. The authors instead label the three peaks in the spectrum as W 4f_{7/2}, W 4f_{5/2}, and W 4f_{3/2}. There are no triplet peaks in XPS which indicates ignorance of the basic principles of the technique, the mislabelled W 5p peak is fitted with an exceptionally broad peak which does not correlate to the data at all. This is particularly unfortunate as the raw data is of good quality and does indeed appear to show high purity WS_2 and WSe_2 upon visual inspection. In another instance the author does not use the fixed doublet peak area restrictions, leading to substantial error, there is also inconsistency with some components in the sulfur spectrum not given doublet peaks.⁸³

A further example of impactful misidentification of peaks is given in “High-performance lateral MoS_2 - MoO_3 heterojunction phototransistor enabled by in-situ chemical oxidation”⁸⁴, wherein the coincidentally overlapping S 2s singlet in the Mo 3d of MoS_2 is attributed to MoS_xO_y . The background in this work is clearly unacceptable with little similarity to the data. The clear peak indicative of MoO_3 at ~236 eV is also not included in the fit.

While a linear background is used for all spectra in this work by Zhai *et al* which examines NiTe_2 and MoS_2 heterostructure devices,⁸⁵ that is not a substantial error. A major issue is the assignment of the very prominent doublet in its Te 3d spectrum as a NiTe_2 satellite, when it is most likely showing a large amount of TeO_2 is present in the material which may have a substantial contribution to the results.

Presentation of XPS results is also frequently a significant problem in 2D TMD literature. In “Atomically thin noble metal dichalcogenide: a broadband mid-infrared semiconductor”,⁸⁶ it is extremely unclear how the fitted peaks match the data, with the Pt doublet peaks having different baselines and both appear unconnected to a background fit. While it is often seen that the second doublet of a state may have increased peak width compared to the first half, the Se doublet in this paper goes beyond a reasonable broadening, it also does not use fixed doublet peak areas, to the extent that the second half of the doublet is a much larger area than the first half- a physical impossibility, this paper also misidentifies the measured core-level as Se 4d, when it is in fact the Se 3d.

Another further example of presentation being a limiting issue can be seen in “Direct Tellurization of Pt to Synthesize 2D PtTe₂ for High-Performance Broadband Photodetectors and NIR Image Sensors”,⁸⁷ where the stoichiometry of the PtTe₂ material is verified from questionable XPS spectra which are particularly difficult to assess.

As a final example in “Layered Platinum Dichalcogenides (PtS₂, PtSe₂, and PtTe₂) Electrocatalysis: Monotonic Dependence on the Chalcogen Size”⁸⁸ the XPS spectra of several Pt TMDs are measured after electrochemical reactions. These materials little reported and there is scarcely any reliable XPS literature, while this makes mistakes more understandable, it also increases the negative effect of publishing faulty or misleading data, as it has a higher likelihood of being used by others as a reference. There are several errors in this report due to the excessive number of components used, particularly given the poor signal to noise ratio of the data, often excessive numbers of components are added to ensure better correlation between the peak envelope and the raw data. These errors result in enormous variations in peak widths, which seem highly unlikely.

The above-listed examples are a small snapshot of how pervasive XPS related issues are in this field and indicate the importance of establishing quality literature references for XPS of 2D TMDs.

1.9 Raman Spectroscopy

This section will introduce the history of Raman spectroscopy, the key principles behind it, and its utility in 2D materials study. This section draws knowledge from the book by A. Kolobov and J. Tominaga,¹² and the books edited by PH. Tan⁸⁹ and Challa S. S. R. Kumar.⁹⁰

Raman is likely the most ubiquitous characterisation technique used in the study of 2D materials today, it is widely applicable, non-destructive, and has a broad compatibility with different experimental setups. It can be used to investigate many aspects of 2D materials including identifying the number of layers and probing the mechanical, optical, and sometimes electrical properties of a material.

Raman Spectroscopy takes its name from Chandrasekhara Venkata Raman. In 1928, Raman, alongside his student Kariamanikkam Srinivasa Krishnan experimentally discovered that when light scatters off a material it can change frequency by a specific amount which corresponds to certain molecular vibrations. Raman was awarded the Nobel prize in physics for this discovery in 1930.

Raman spectroscopy rose in its practical utility after the development of lasers in the 1960s as the high intensity monochromatic light from a laser allowed much greater intensity Raman signals to be acquired rapidly. Not long after this, it was used prominently in the characterisation of carbon materials such as graphite. Pioneers in developing the field of Raman spectroscopy of graphite such as Mildred Dresselhaus naturally went on to apply this to novel carbon structures as they were discovered, from fullerenes to carbon nanotubes and to eventually graphene.⁹¹

Raman spectroscopy became one of the most common methods to characterise carbon nanotubes⁹² and graphene, this factor along with its good relative surface sensitivity, encouraged Raman spectrometers to be deployed in the vast majority of 2D materials laboratories, this allowed it to naturally become the preeminent technique for characterising all 2D materials as the area has developed.

When light interreacts with a surface the most common forms of interactions are through reflection, absorption, and scattering. The overwhelming majority of photons which scatter from matter are elastically scattered, where a photon with frequency ω_0 is absorbed temporarily by the matter entering a virtual excited state (not an electronic excited state), it then very quickly

returns to the original energy level with re-emission of a photon of the same frequency as the initial one. This elastic process is known as Rayleigh Scattering and occurs for most photons.

Approximately 1 in every 10^7 photons undergoes inelastic scattering where there is a notable frequency shift from the incident photon, this energy difference is characteristic of phonon modes from the molecular or lattice structure of the material. This inelastic scattering is known as Raman scattering.

There are two energy paths which are both forms of Raman scattering. For the more common pathway the molecule is in the ground state and is excited by a photon, but with relaxation it will emit a lower frequency (lower energy) $\omega_0 - \omega_q$ photon, this change from the initial frequency ω_0 corresponds to the molecular vibration which is now left in an excited state above the ground state. This process is known as Stokes Raman scattering, Fig. 1.15(a).

The less probable pathway is if the molecule is initially in the excited state, it can similarly interact with a photon ω_0 by transferring energy to it, this increases the frequency compared to the initial photon, with the emitted photons frequency of $\omega_0 + \omega_q$ also corresponding to the frequency of the molecular vibration. This is known as Anti-Stokes Raman scattering. Examples of these are presented schematically in Fig. 1.15(a) below.

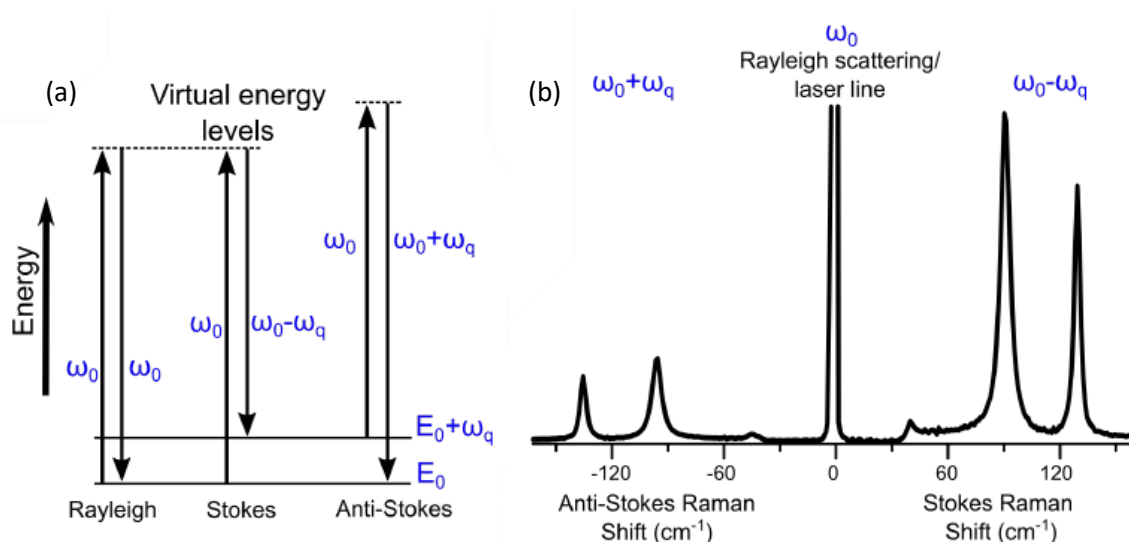


Fig. 1.15 (a) Jablonski diagram showing the changing energy levels involved with Rayleigh and Raman scattering. (b) Example Raman spectrum showing the Raman scattered peaks. (Figure courtesy of Dr John McManus)

Raman spectra are displayed in terms of Raman shift with units of wavenumbers (cm^{-1}) relative to the excitation light. Resulting in a spectrum with a large intensity at 0 cm^{-1} where all reflected and Rayleigh scattered light will be detected. The Raman signals for the molecular vibrations then appear mirrored at the same positive and negative Raman shifts, for Stokes and Anti-Stokes Raman respectively, this is presented in Fig. 1.15(b).

If the excitation light is close in energy to an electronic transition for the material being measured then a resonant Raman scattering effect can occur, this yields substantially higher intensity Raman signals. Classical Raman theory proposes that the photon interacts with the harmonically oscillating atoms in a material to induce an oscillating electromagnetic field, this generates a molecular dipole moment in the larger molecule. Described as Equation 1.4,

$$\mu = \alpha E \quad (1.4)$$

Where

μ = molecular dipole moment

α = polarizability of the molecule

E = Electric field

While a fuller understanding of Raman scattering requires a quantum mechanical explanation, from Equation 1.4 it can be deduced that a molecular vibration needs to change the polarizability of the molecule to yield Raman scattering. Vibrations which fulfil this requirement are referred to as Raman-active vibrations.

The symmetry of a material therefore plays a very important role in Raman spectroscopy. The point group of a materials unit cell structure allows us to determine which vibrational modes we can expect to be Raman active using group theory, but it cannot determine the magnitude of their Raman shift. Through a combination of the list of Raman active modes and phonon dispersion curves the estimated Raman shift of the modes can be predicted.

As an example, the Raman spectrum of MoS_2 is analysed. As previously discussed, MoS_2 generally exists as a 2H trigonal prismatic structure. The symmetry of this structure is complicated by the layered nature of MoS_2 . Bulk MoS_2 has the point group D_{6h} (space group P63/mmc), and a unit cell consisting of two layers of MoS_2 (6 atoms). The Raman-active modes for this symmetry are $A_{1g} + 2E_{2g} + E_{1g}$, the $2E_{2g}$ modes are separated as E_{2g}^1 and E_{2g}^2 . Representations of these molecular vibrations are given in Fig. 1.16.

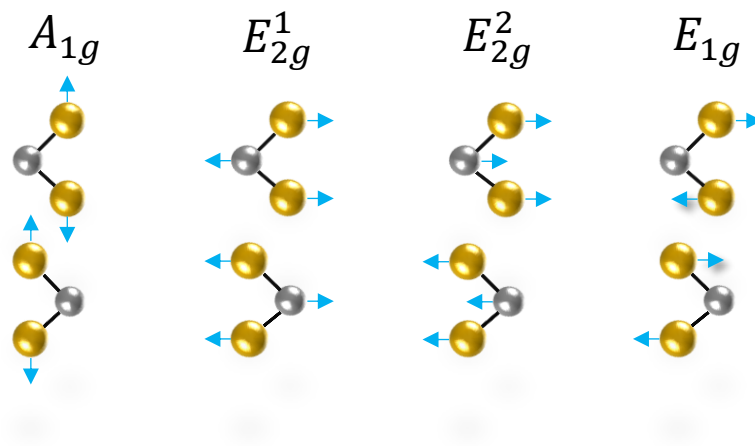


Fig. 1.16 Representations of the Raman active modes of bulk MoS₂ (D_{6h})

The symmetry of few-layer MoS₂ is more complicated due to the difference in symmetry of even and odd layer numbers. Even layer numbers of MoS₂ have a D_{3d} symmetry which yields Raman-active modes encompassing $3A_{1g} + 3E_g$, while odd layer numbers have D_{3h} symmetry. This extends to monolayer MoS₂ which also has D_{3h} symmetry, this has Raman active modes of $A'_1 + E'' + 2E'$.

This can lead to confusion when discussing Raman spectroscopy involving several different layer numbers of MoS₂, it also requires exact layer counting when discussing few-layer MoS₂ to be correct. These molecular vibrations are all related, with the only Raman modes generally used in the characterisation of MoS₂ being a Raman peak at $\sim 385 \text{ rel cm}^{-1}$ which is the E_{2g}^1 in bulk (E_{1g}^1 in bilayer, and E' in monolayer) and a peak at $\sim 405 \text{ rel cm}^{-1}$ the A_{1g} for bulk (A_{1g}^2 in bilayer, and A'_1 in monolayer) in an effort to avoid confusion it is common practice to use the bulk notation when discussing MoS₂ Raman regardless of the layer number, that convention is followed here. It is worthwhile to note, as displayed in Fig. 1.16, that the A_{1g} Raman mode entails only sulfur atoms vibrating out-of-plane, while the E_{2g}^1 involves all 3 atoms vibrating in-plane, these modes are sometimes referred to by those designations as the *in-plane* and *out-of-plane* modes.

There are several other common features in the Raman spectra of MoS₂ which will be briefly mentioned. MoS₂ possesses two noteworthy *interlayer* vibrations, the first involves shear vibrations of MoS₂ layers vibrating across one another, known as the shear mode (SM). The second interlayer vibration involves the MoS₂ layers vibrating out-of-plane, away from one

another, known as the layer breathing mode (LBM). Both of these low-energy vibrations are observed at corresponding low Raman shifts. The spectral width of the magnitudes more intense Rayleigh scattering line at 0 cm^{-1} generally obscures these low Raman shifts $\sim <50\text{ rel cm}^{-1}$ entirely. It is difficult to sufficiently block the Rayleigh scattering line and so sophisticated or newer equipment is generally required to filter out this signal, this results in the interlayer vibration modes often being absent in literature studies of MoS₂. These low-frequency interlayer modes can be a useful method to confirm the presence of monolayer MoS₂ as it does not possess any interlayer interactions. The lack of any interlayer Raman modes for monolayer, and the far greater relative intensity of the intralayer over interlayer Raman modes of thicker MoS₂ are indicative of the van der Waals nature of the interlayer interactions.

The MoS₂ Raman spectrum and the Raman spectra of several TMDs often contain peaks related to second-order interactions, often overtones of Raman modes or phonon interactions. The Raman spectrum of MoS₂ has a prominent component at $\sim 420\text{ rel cm}^{-1}$, this complex peak is attributed to a second order longitudinal acoustic mode at the M point of the Brillouin zone (BZ), referred to as the 2LA(M).

The Raman spectrum of MoS₂ is commonly used for characterisation, primarily for layer number identification as the Raman shift of the A_{1g} and E_{2g}^1 modes change with layer number. Interestingly, the two modes shift in opposite directions with decreasing layer number. If we propose that the MoS₂ layer is a harmonic oscillator then by removing layers we would expect both modes to red shift, *i.e.* to lower Raman shift, due to the lower restoring force on top. This behaviour is observed for the A_{1g} out-of-plane mode of MoS₂ with the peak shifting from $\sim 408\text{ rel cm}^{-1}$ in bulk, to $\sim 403\text{ rel cm}^{-1}$ in monolayer. The in-plane E_{2g}^1 mode shifts counterintuitively in the other direction; the mode stiffens when overlayers are removed, with the peak moving from ~ 382.5 to $\sim 384.5\text{ rel cm}^{-1}$ for a bulk-to-monolayer transition. This phenomenon has been explained multiple ways, including as being due to atomic stacking or distance changes, interlayer coulombic interactions, or changes to surface charge states.

Experimentally, these opposite shifts in the Raman peak positions have been used to track layer number with peak separation of $\sim 18\text{--}20\text{ cm}^{-1}$ being attributed to monolayer, with a gradual broadening up to $\sim 25\text{ cm}^{-1}$ for bulk. This common method of layer number identification is flawed as the Raman modes of MoS₂ are sensitive to a variety of other factors which do not always affect the Raman modes uniformly. The quality of monolayer MoS₂ crystals can generally be characterised by Raman peaks with narrow FWHM, high intensity, and similar

intensities for the A_{1g} and E_{2g}^1 Raman modes. These factors are also subject to other aspects making them nuanced and not clear-cut metrics.

The multitude of factors that can affect the Raman spectra of MoS₂ include substrate, temperature, defects, dopants, grain boundaries, dielectric environment, strain, and pressure. As examples, monolayer MoS₂ transferred onto six common substrates showed large variations in the A_{1g} Raman mode position and small variations in E_{2g}^1 mode, with SiO₂ showing the largest Raman peak separation and h-BN the least.⁹³ Suspended CVD MoS₂ shows a marked lowering of frequency for both modes, alongside substantial broadening of the Raman modes.⁹⁴

Raman of monolayer MoS₂ has been observed to shift non-linearly with temperature, both Raman modes shift to higher wavenumbers with cooling.⁹⁵

Various defects can affect the Raman of MoS₂, it has been shown that ion bombardment with He⁺ or Ne⁺ ions cause a variety of defects in monolayer MoS₂. The clearest indication of defects in these structures was found to be quenching, broadening, and separating of the MoS₂ Raman modes. At high ion doses there was emergence of a new peak at $\sim 227\text{ cm}^{-1}$ attributed to the LA(M).⁹⁶

Oxygen doping of CVD MoS₂ by injecting oxygen as a flow gas during synthesis was found to have similar effects with a broadening and widening separation of the MoS₂ Raman modes, alongside new modes attributed to Mo-O at 287, 331, and 464 cm^{-1} .⁹⁷

The Raman modes of monolayer MoS₂ are sensitive to electron doping. A simple top-gated transistor with a monolayer MoS₂ channel revealed the stark difference in sensitivity of the Raman modes. With an applied gate voltage of 2V the A_{1g} Raman mode shifts to lower frequencies (red-shifts) and shows peak broadening, with a -4 rel cm^{-1} shift in peak position and a doubling of peak width, the E_{2g}^1 showed little sensitivity with only a shift of $<1\text{ rel cm}^{-1}$ and no discernible broadening. It is proposed this is due to their disparate electron-phonon coupling related to the symmetry of MoS₂.⁹⁸

P-type doping of MoS₂ is similarly found to have an outsized effect on the A_{1g} mode. With the A_{1g} mode shifting to higher frequencies (blue shift) while the E_{2g}^1 mode is unperturbed.⁹⁹

In direct contrast to the unbalanced doping sensitivity of the A_{1g} and E_{2g}^1 modes of MoS₂, the E_{2g}^1 mode is found to be more sensitive to strain than the A_{1g} . Compressive strain is found to shift both Raman peaks to higher Raman shifts (blue shift), with the E_{2g}^1 showing a $\sim 50\%$ higher

shift.¹⁰⁰ Tensile strain contrastingly shifts the Raman modes to lower frequencies (red shifts), with a consistently larger effect on the E_{2g}^1 mode and inconsistent, but much lower sensitivity for the A_{1g} .^{101, 102} High levels of tensile strain on monolayer MoS₂ cause splitting of the E_{2g}^1 mode into two peaks $\sim 5 \text{ cm}^{-1}$ apart.¹⁰³

1.10 Photoluminescence

Photoluminescence (PL) spectroscopy is an important tool used in the characterisation of semiconducting materials and is prominently used for analysis of semiconducting 2D materials. This section adapts knowledge from the optical properties sections of the books by NS. Arul and VD. Nithya,¹⁰⁴ and A. Kolobov and J. Tominaga.¹²

Similar to Raman spectroscopy, PL is also non-destructive, non-contact, and compatible with a wide variety of experimental setups while also being capable of analysing monolayers of material.

The process of PL in semiconductors can be simplified to three steps, photoexcitation, relaxation and recombination, presented in Fig. 1.17. First, a photon with energy greater than the bandgap is absorbed by a material, it can excite an electron into a higher electronic energy level in the conduction band, this creates a corresponding hole in the valence band. This electron-hole pair can couple to form an exciton due to the coulombic attraction of their charges, TMDs have a noteworthy high excitonic binding energy. The second step in this process is non-radiative relaxation, wherein the excited state loses energy through phonons, settling near the bottom of the conduction band. The final step is the recombination of the charge-pair via the emission of a photon. This can be affected by a variety of factors, importantly mid-gap states from defects or other causes can enable other recombination pathways.

PL spectroscopy is used to study many semiconducting TMDs, as they go through pronounced band structure changes with layer number. As an example, the PL spectroscopy of MoS₂ is discussed.

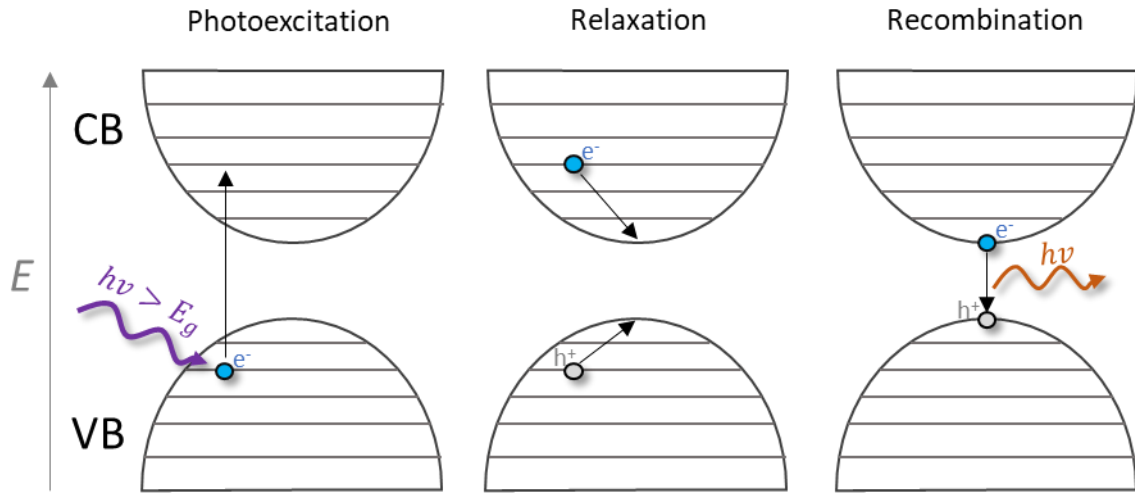


Fig.1.17 Schematic of the typical excitonic PL emission process in semiconductors.

As noted earlier, one of the most interesting features of MoS₂ is the large shift in the band structure when reducing layer number. Bulk MoS₂ is an indirect bandgap semiconductor and has a valence band maximum at the Γ point, comprising of out-of-plane *Mo* d_{z^2} orbitals and *S* p_z anti-bonding orbitals. Conversely, monolayer MoS₂ is a direct bandgap semiconductor where the direct bandgap is located at the K point in the BZ and comprises solely of combinations of in-plane *Mo* d_{xy} and $d_{x^2-y^2}$ which are localized in the middle of the MoS₂ structure, these bonds are largely unaffected by the changing layer number of the MoS₂. And so decreasing layer number has an outsized effect on the indirect gap at the Γ point, the K point is not as sensitive to layer number and therefore becomes the new highest energy point in the valence band, enabling a direct transition with the conduction band where the minimum is also at the K point.

This change in band structure causes the photoluminescence to be very prominent in monolayer MoS₂ at room temperature with a sharp decrease in intensity for subsequent layer thicknesses and no photoluminescence for the bulk form.¹⁵ A complicating factor for MoS₂ is the broken inversion symmetry of its 2H structure, MoS₂ has a hexagonal BZ and its lack of symmetry results in differing energy at the corners, Fig. 1.18. Resulting in a strong spin-splitting of the band at the K and K' point.¹⁰⁵ The splitting is of approximately 150 meV and is responsible for monolayer MoS₂ having a two-component PL structure.¹⁰⁵ The most prominent exciton is from the higher energy split band with an energy of ~ 1.85 eV (670 nm) this is called the A exciton of MoS₂, the exciton from the lower energy split band has an energy of ~ 150 meV above this at 2 eV (621 nm), it is known as the B exciton of MoS₂.

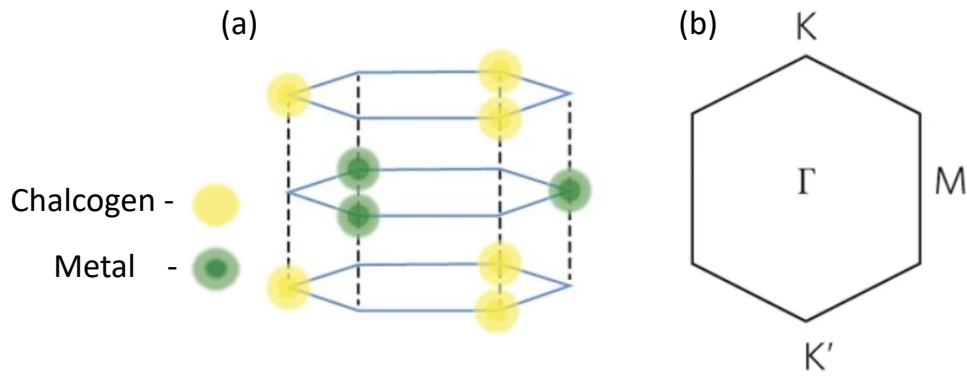


Fig. 1.18 (a) Structure of trigonal prismatic 2H TMDs (b) Corresponding first Brillouin zone with the high-symmetry points. Adapted from reference.¹⁰⁶

MoS₂ is often studied for its interesting and complex optical properties and features. Beyond the two excitonic resonances of the A and B excitons, MoS₂ can also display higher order excited excitons called trions¹⁰⁵ which are an exciton bound with an extra electron or hole and larger quasiparticles of two combined excitons called bi-excitons. While PL features from trions are commonly observed in MoS₂, bi-excitons are rarer occurrences requiring low temperatures to be observed.¹⁰⁷

PL of MoS₂ has been shown to be very sensitive to changes in the structure and environment. With the intensity of the PL emission, the PL peak energy, and the FWHM of the emission peak all being characteristic of the crystal quality.¹⁰⁸ Similar to Raman, MoS₂ PL is also known to be sensitive to temperature,^{109, 110} strain,^{100, 103, 111} dielectric,¹¹² defects,¹¹³ substrate,^{93, 114} and dopants.^{97, 115}

1.11 Scanning Probe Microscopy

As the layer number of TMDs has a significant impact on their properties, accurate measurement of their thickness can be essential. While it is often very feasible to identify monolayer TMDs due to their frequent dramatic change in properties at the monolayer limit, using tools such as PL and Raman, the most obvious method of course is to use atomic force microscopy (AFM), but this has its own complications.

AFM is the most prominent form of scanning probe microscopy and is a very common technique of characterisation for 2D materials whereby a physical probe is ran along the surface to acquire topographical information, presented in Fig. 1.19 It operates by rastering an atomically-sharp tip at the end of a cantilever, oscillating at a known frequency, across a surface

and measuring the deflection of the tip due to the forces between the tip and surface. Piezoelectric motors enable the precise, fine movement of the tip required.

The surface forces acting on the tip, and therefore cantilever, are measured by reflecting a laser off the end of the backside of the cantilever, any change in the AFM tip oscillation or height is then observed by a deflection of the laser reflection onto a photodetector.

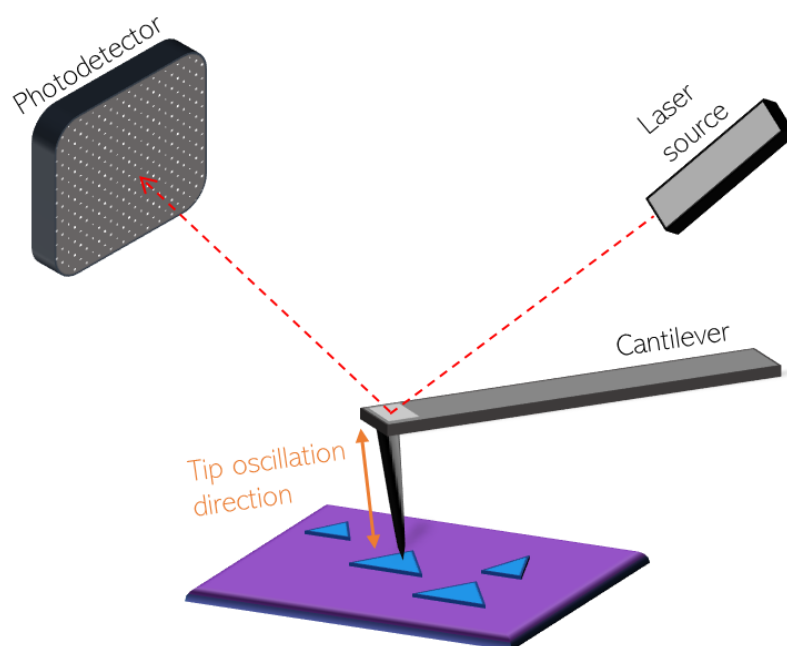


Fig. 1.19 Schematic of the typical atomic force microscopy apparatus in tapping mode.

AFM is commonly operated in one of two modes, contact or tapping. Contact mode involves touching the surface with the AFM tip and slowly pulling the tip across the surface, this causes the repulsive forces at the surface to change the height of the AFM cantilever correspondingly to changes in the surface topography. Tapping mode or intermittent contact mode is used exclusively in this work, and generally comprises oscillating the AFM tip at a fixed frequency during rasterization, this frequency is maintained by moving the tip away or closer to the surface, this change in height is measured. This allows a map of the topology of the surface to be built up. The surface interaction forces against the tip can be a mixture of van der Waals interactions, electrostatics, chemical bonds, magnetic and others.

These other forces can allow further information beyond topography to be measured. The relative attraction/repulsion of the tip between different materials on a surface can affect the phase of the tip oscillation. This change can also be measured and used to show changing material properties on a surface, although the specific material property responsible for the phase change cannot be measured due to the many contributions to it, such as stiffness and surface charge. Phase is often measured alongside the amplitude data which forms the topography map.

AFM is a very versatile technique and can operate in ambient, UHV, and in liquid. It is capable of atomic resolution at its most advanced and can reliably measure the topography of single layers of 2D materials and other high-aspect ratio materials.

While the ability of AFM to directly measure the topography precisely and indicate material differences on a surface is extremely valuable it is not without its difficulties. High-quality AFM imaging is often over very small areas $<100\text{ }\mu\text{m}$. While AFM can reliably determine the height of a 2D monolayer on a surface, it is not trivial with a number of complicating factors for fully accurate measurement. For example, sample and tip cleanliness are essential, if measuring mechanically exfoliated or transferred material there can be contaminants below/on top of the material or on the substrate. Substrate and material homogeneity can have a substantial effect on calculated heights if not accounted for accurately. Post-processing AFM data is often necessary to remove errors and deconvolute system contributions in the measurement, this opens the possibility for user error.

Beyond traditional AFM, modern SPM methods are expansive with a variety of modes of measurement possible. For example, this includes measuring the magnetic interaction across the surface with magnetic force microscopy (MFM), conductive AFM (C-AFM) where a conductive AFM tip can measure the conductivity of the surface by applying a voltage to the tip and measuring the current going between the tip and sample. Amongst these more exotic SPM techniques, Kelvin probe force microscopy (KPFM) is used briefly in this work, KPFM is used to measure surface potentials on a surface and therefore can measure the work function. KPFM measures the contact potential difference between the tip and the surface, when a freely oscillating tip is held above the sample the variations in the electric field cause current to flow in the tip. By measuring this current and knowing the work function of the AFM tip we can determine the work function at each point in the KPFM scan.¹¹⁶

1.12 Scanning Electron Microscopy (SEM)

This section is largely adapted from elements in the book by Joseph I. Goldstein et al.¹¹⁷ Scanning electron microscopy (SEM) is a very common method of imaging 2D materials due to its ability to resolve features far below the limit of optical microscopy. Unlike an optical microscope, an SEM operates by generating and focusing a beam of electrons through magnetic lenses onto a sample. The resolving power of an optical microscope is limited by the wavelength of light. Electrons travel with far smaller wavelength than optical light and their wavelength can be adjusted by changing their acceleration. The incident electron beam in SEM is generally operated with energies $\sim 1\text{--}30\text{ keV}$, in the work discussed in this thesis $\sim 3\text{ keV}$ was mostly used.

These electrons interact in several ways when encountering the sample, SEM generally uses either backscattered electrons (BSE), or secondary electrons (SE) to generate an image. An SEM rasters the electron beam relatively rapidly over an area and detects the electrons emitted from the sample, in the form of black and white intensity images collected generally on charge coupled device (CCD) detectors. Electrons penetrate into the sample proportionally to their energy, the dispersal of the electrons inside the material creates an interaction volume wherein emitted electrons can be generated.

BSE are those which are elastically scattered out of the sample by the electron fields or nuclei of the atoms in the sample. These BSE are collected by detectors placed by the electron source output. BSE have the highest energy of those measured and therefore have the highest penetration into the sample. The energy of the scattered electrons is related to a number of properties importantly including the atomic number of the material being measured, with higher atomic number atoms scattering more electrons, giving a more intense BSE signal. This allows SEM to differentiate between materials on a surface.

SE result from the inelastic interaction of the source electrons with the sample, this interaction causes the excitation and emission of electrons from the samples atoms. These SE are of much lower energy than BSE and are collected by a detector positioned near the sample and off to the side. Secondary electrons are arbitrarily limited to those $< 50\text{ eV}$ but $> 90\%$ of those emitted are $< 10\text{ eV}$. Due to their much lower energy, SE are emitted from a smaller depth than BSE and are therefore more surface sensitive. Unlike BSE, SE show a near insignificant atomic number dependence. The combination of increased surface sensitivity from the lower energy and the lack of element sensitivity make SE well suited for imaging the topography of a sample.

1.13 Present Study

The present study intends to consider a characterisation prioritised examination of the synthesis of several 2D TMD materials in order to broaden the knowledge of their analysis. Particular focus is paid to XPS data, with the intention of constructing a transparent understanding of the analysis of TMD XPS spectra. This was achieved by thorough examination of a variety of TMDs across many chemical environments

Chapter 2 will describe the instrumental and experimental details.

Chapter 3 will present the synthesis and typical characterisation methods and analysis of high-quality CVD monolayers of MoS₂.

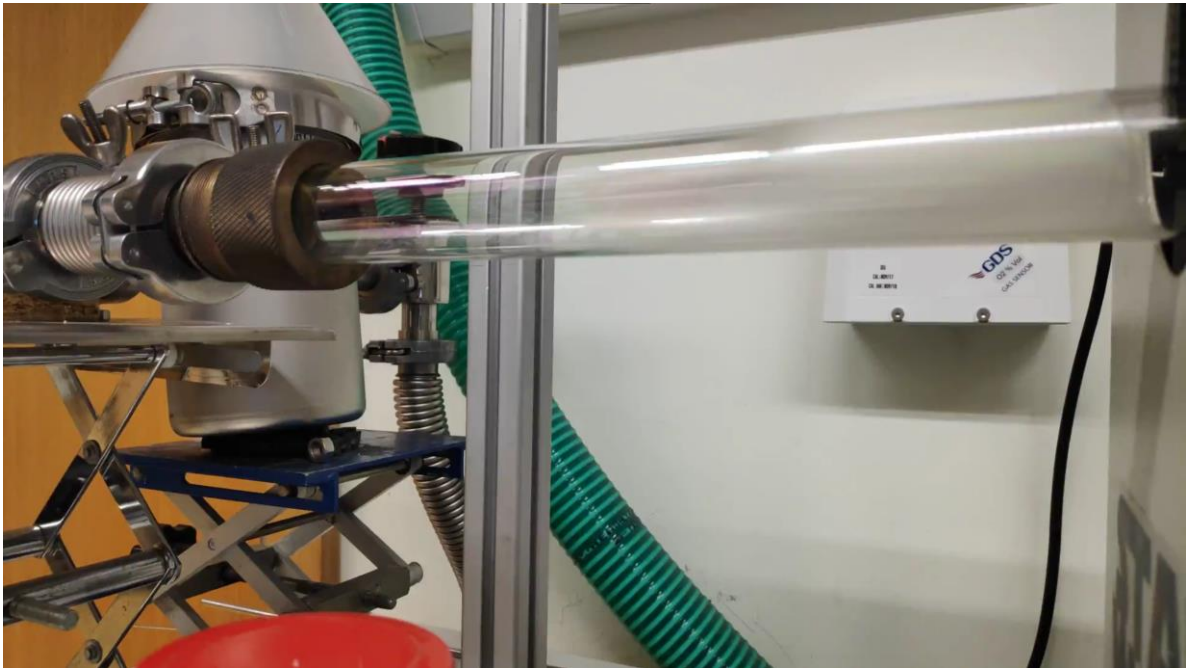
Chapter 4 will report the NH₃ plasma treatment of CVD MoS₂ and its subsequent effects on the material and methods to assess this.

In Chapter 5 the methods to understand and fit the XPS spectra of a wide range of 10 TMD materials are outlined, while highlighting the benefits of complementary characterisation methods.

Chapter 6 contains a study of methods to synthesise separately thin films of the two competing sulfides of platinum, alongside rigorous characterisation to differentiate between them.

Finally, Chapter 7 provides a summary and conclusion of all of the presented results.

2 -Experimental



The operational processes for the equipment and various techniques used throughout this body of work are provided here. The theory behind these techniques is largely contained in Chapter 1, except occasionally where it was deemed more suitable to be included here.

Chemicals used were supplied by Millipore Sigma unless specified otherwise and were used as received. All gases were supplied by BOC gases.

All materials synthesised in this work were grown on SiO₂/Si substrates, purchased from University Wafers and Dasom RMS. These consisted of 300 nm dry thermal oxide on Si(100) wafers. The wafers were split into suitable sample sizes by mechanical cleavage. These sample pieces will be referred to as SiO₂ substrates in this work and were rinsed in IPA and acetone directly before use to remove surface contamination.

2.1 Furnace Systems

The vapour phase deposition processes used extensively in this thesis can be broadly experimentally defined under two headings of chemical vapour deposition (CVD) and thermally assisted conversion (TAC).

These synthesis methods were similar, and all were performed in quartz tube furnaces. To minimise cross-contamination a separate furnace was used for each chalcogen examined. Sulfides and selenides were synthesised using similar methodologies in similar furnace systems. Telluride materials were synthesised through a modified process and were provided by Dr John McManus.

The majority of material synthesis methods detailed in this work utilise comparable methods, as such, the standard operational procedure will be described and the important variables for each specific material. These variables were

- The chalcogen
- TM precursor
- Growth substrate geometry
- Carrier gas composition
- Temperature of primary heating zone
- Temperature of chalcogen heating zone

- Chalcogenisation time
- Pressure

2.2 Synthesis Precursors

Solid phase chalcogen precursors were used throughout this work. These were either sulfur powder, selenium pellets (<5mm, >99.99% purity), or an electrodeposited Te film.

Two distinct types of TM sources were used for the synthesis processes here. A thin layer of TM oxide on a SiO₂/Si piece e.g. MoO₃, or a sputter deposited TM film.

The TM oxide thin layer was made from a solution dispersed TM oxide precursor. MoO₃ powder (>99.5% purity) was made up to an approximately 5 mg ml⁻¹ solution in HPLC IPA, with sonication in a sonic bath to ensure a uniform dispersion. 30µL of this dispersion was drop cast onto the SiO₂ substrates. Substrates were then annealed at 150 °C for 2 minutes to completely evaporate any remaining IPA from the surface. This process yields an uneven film of MoO₃ across the surface.

For sputter deposited TM precursors. TM targets were purchased from HMW-Hauner. TM films of Mo, W, or Pt were Ar sputter deposited onto SiO₂ substrates using a Gatan 682 Precision Etching and Coating tool (PECS). During deposition a quartz crystal monitor was used to monitor the rate with TM films, generally depositing at ~1 Å s⁻¹, the pressure in the chamber was approximately 5 × 10⁻⁵ mbar.

2.3 Standard Furnace Operation

Furnace operation was generally similar for each material synthesised here, and a standard operation will be provided with the variables specific to each material given in Table 2.1. Exceptions and variations from this standard process will be detailed and specified subsequently.

A two-zone quartz tube furnace was used, Fig. 2.1–2.2. Precursors and substrates were placed into ceramic crucibles and loaded into their respective positions in the furnace, with the chalcogen precursor placed upstream from the TM precursor and growth substrate. After loading both zones with the appropriate samples, the system was sealed and evacuated with a

rotary-vane vacuum pump, and 150 sccm of carrier gas, generally forming gas (90% Ar + 10% H₂), was introduced. This established a pressure of ~1 mbar (~0.7 torr) in the system.

The primary heating zone containing the growth substrate was then heated to the synthesis temperature for the material being grown, specified in Table 2.1. Once this temperature was reached, the secondary heating zone containing the chalcogen precursor was heated to melt the precursor and allow the carrier gas to carry chalcogen vapours towards the growth substrate. This reaction time varied for different materials e.g. 25 min for MoS₂, 120 min for MoSe₂. After the reaction time had elapsed, the carrier gas was changed to solely Ar gas and the secondary heating area cooled rapidly by moving the furnace away from the chalcogen crucible.

The substrates were then annealed for 20 minutes before the primary furnace was turned off and the samples cooled to room temperature before reopening of the furnace and sample retrieval.

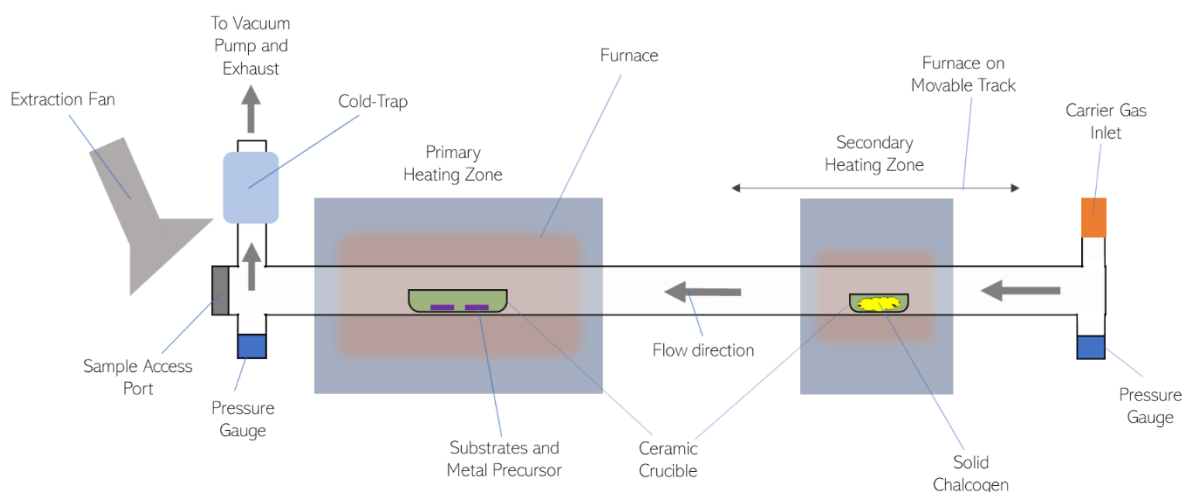


Fig. 2.1 Schematic representation of the two-zone quartz tube furnace systems used for synthesis of TMDs here.

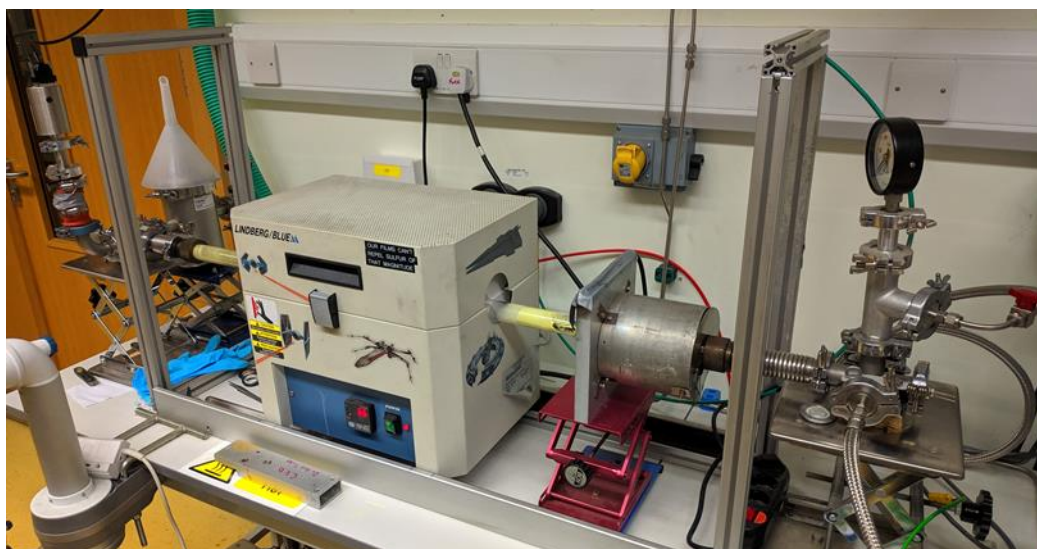


Fig. 2.2 Photograph of the two-zone quartz tube furnace system used for sulfur materials

While this general procedure was followed for synthesis of all of the materials used here, there were several changes for some materials which will be specified below.

2.4 CVD MoS₂

The CVD synthesis method here was previously developed by Dr Maria O'Brien, as described in the literature¹¹⁸. This method was used to synthesise mostly monolayer MoS₂. The notable difference between the CVD MoS₂ process and the TAC process was in the TM precursor and growth substrate geometry.

The CVD MoS₂ method utilised a microreactor geometry. A dropcast MoO₃ film was dispersed onto a SiO₂ precursor substrate. The clean growth substrate was then placed face-down onto the MoO₃ precursor substrate, this stack was then used in the standard process detailed above. This stack or sandwich geometry allows a sufficient amount of sulfur vapour to intercalate between the wafers and react with the vaporised Mo precursor to generate MoS₂. This MoS₂ then deposits as primarily monolayer crystals on the growth substrate.

2.5 TAC Materials

For TAC style synthesis of TMDs, the growth substrate is coated with a chosen thickness of sputter deposited TM, which is then directly converted to the TMD by reaction with the chalcogen vapour during the standard procedure. This process has been examined in detail previously.³⁰

2.5.1 TAC Tellurides

The three telluride materials, MoTe_2 , WTe_2 , and PtTe_2 were supplied by Dr John McManus using a modified TAC style method which has been detailed in literature.¹¹⁹⁻¹²¹ This is a one-zone quartz tube process wherein firstly a layer of TM was sputter deposited onto a SiO_2 substrate, Fig. 2.3. This TM layer was then covered with an electrodeposited layer of elemental Te. Te has a melting point far above the other chalcogens of 450 °C. The samples were annealed at temperatures of 450-600 °C, inside a series of nested crucibles, this maintained a higher partial pressure of Te during TMD synthesis. Importantly these crucibles were not sealed but were simple closed by the weight of their lids.

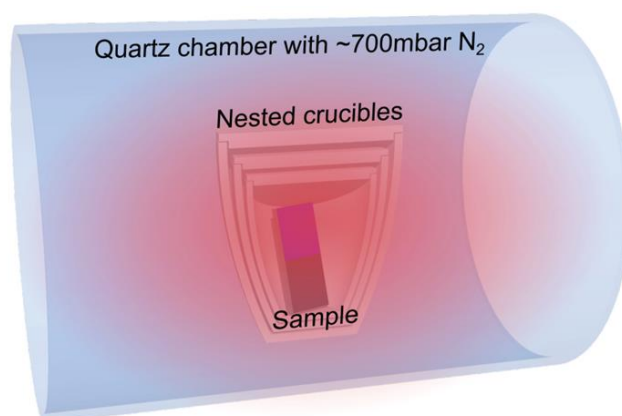


Fig. 2.3 Schematic representation of the quartz tube furnace system and nested crucibles used for synthesis of telluride TMDs. (courtesy of Dr John McManus)

2.5.2 Platinum Sulfides

The synthesis and characterisation of PtS_2 and PtS films is the focus of Chapter 6.

PtS films were synthesised using a standard TAC style process with sputter deposited Pt films and a synthesis temperature of 500 °C, see Fig. 2.4.

PtS₂ required several modifications to the standard procedure. In addition to using the standard sulfur furnace system, the following changes were implemented. Substrates were placed into a 17 mm diameter (2 mm wall) quartz tube with one open end. Additional sulfur powder was placed at the entrance of this tube. This tube was then placed into the primary heating zone of the quartz tube furnace with the open side facing upstream (into the direction of gas flow) and situated with the tube opening near the edge of the main heating zone. Vacuum pumping was manually throttled to maintain a pressure of ~200 mbar throughout the synthesis. When the substrates in the primary heating zone reached 500 °C the sulfur powder in the secondary heating zone was heated to 180 °C and maintained for 1 hour. After this, the forming gas was changed to 100% Ar and the furnace was then turned-off, lifted open, and air cooled to room temperature before samples were retrieved.

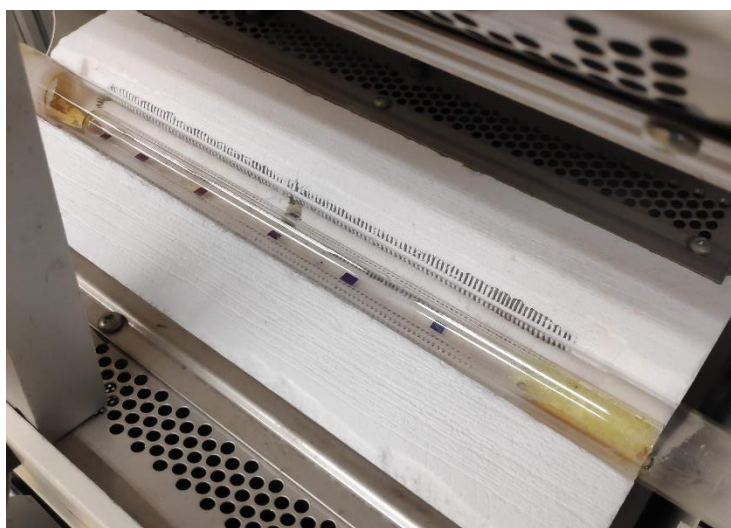


Fig. 2.4 Photograph of the internal quartz tube method used for PtS₂ synthesis

Table 2.1 List of the important variables and their values used for the synthesis of the materials studied in this thesis.

Material	Chalcogen Precursor	TM Precursor	System Geometry	Carrier gas	Primary Zone (°C)	Secondary Zone (°C)	Reaction Time (min)	Pressure (mbar)
MoS₂	S powder	Mo film	TAC	Forming	750	130	25	~1
CVD-MoS₂	S powder	Dispersed MoO ₃	Micro-reactor	Ar	750	130	20	~1
WS₂	S powder	W film	TAC	Forming	800	130	25	~1
PtS₂	S powder	Pt film	Internal Tube	Forming	500	180	60	200
PtS	S powder	Pt film	TAC	Forming	500	130	60	~1
MoSe₂	Se Pellets	Mo film	TAC	Forming	800	300	120	~1
WSe₂	Se Pellets	W film	TAC	Forming	600	300	120	~1
PtSe₂	Se Pellets	Pt film	TAC	Forming	450	300	120	~1
MoTe₂	Te film	Mo film	Nested Crucibles	Nitrogen	450	-	55	~700
WTe₂	Te film	W film	Nested Crucibles	Nitrogen	550	-	90	~700
PtTe₂	Te film	Pt film	Nested Crucibles	Nitrogen	450	-	180	~700

2.6 Treatments

2.6.1 Plasma

NH₃ plasma treatment was performed using a downstream plasma quartz tube system equipped with a 1000 W R³T TWR-2000T microwave radical generator (2.4 GHz). Samples were placed approximately 15 cm downstream from the generator output. During operation, the system was evacuated with a rotary vane pump and 100 sccm of NH₃ was injected into the system establishing a pressure of ~1.1 mbar. When the microwave generator was activated the pressure to approximately double to ~2.1 mbar. Samples were exposed to the plasma for a desired time before the generator and gas injector were turned off. The system was brought back up to ambient pressure by backfilling with N₂ to allow sample retrieval.

This method of plasma treatment generates a high density of downstream chemical radicals while reducing etching or ion bombardment effects by separating the location of radical

generation and acceleration from the sample. This maintains the high chemical reactivity of the plasma species while minimising physical effects.

2.6.2 Ambient thermal oxidation

Ambient thermal oxidation was used to investigate stability and to characterise degradation of TMD films. Samples were annealed on a VWR hotplate at up to 400 °C in a ~50% humidity controlled ambient environment, for 30 minutes at the specified temperature. This was paired with a secondary thermocouple to measure the surface temperature of the hotplate.

2.7 Characterisation

2.7.1 XPS

As was discussed in Chapter.1, XPS can be considered a technique of two equal halves, and this is reflected here in terms of the experimental procedure. First there is the measurement of XPS spectra using UHV equipment. Secondly there is the analysis and curve fitting of the XPS spectra.

2.7.1.1 XPS Measurement

Three XPS systems were used regularly throughout the course of this work. Fig 2.5 provides a rough summary of the most impactful benefits and disadvantages for each of the XPS systems. Each tool will be briefly introduced, and their core differences presented. All systems used here utilised various models of concentric hemispherical analysers (CHA). Al X-ray sources were used exclusively in this thesis.

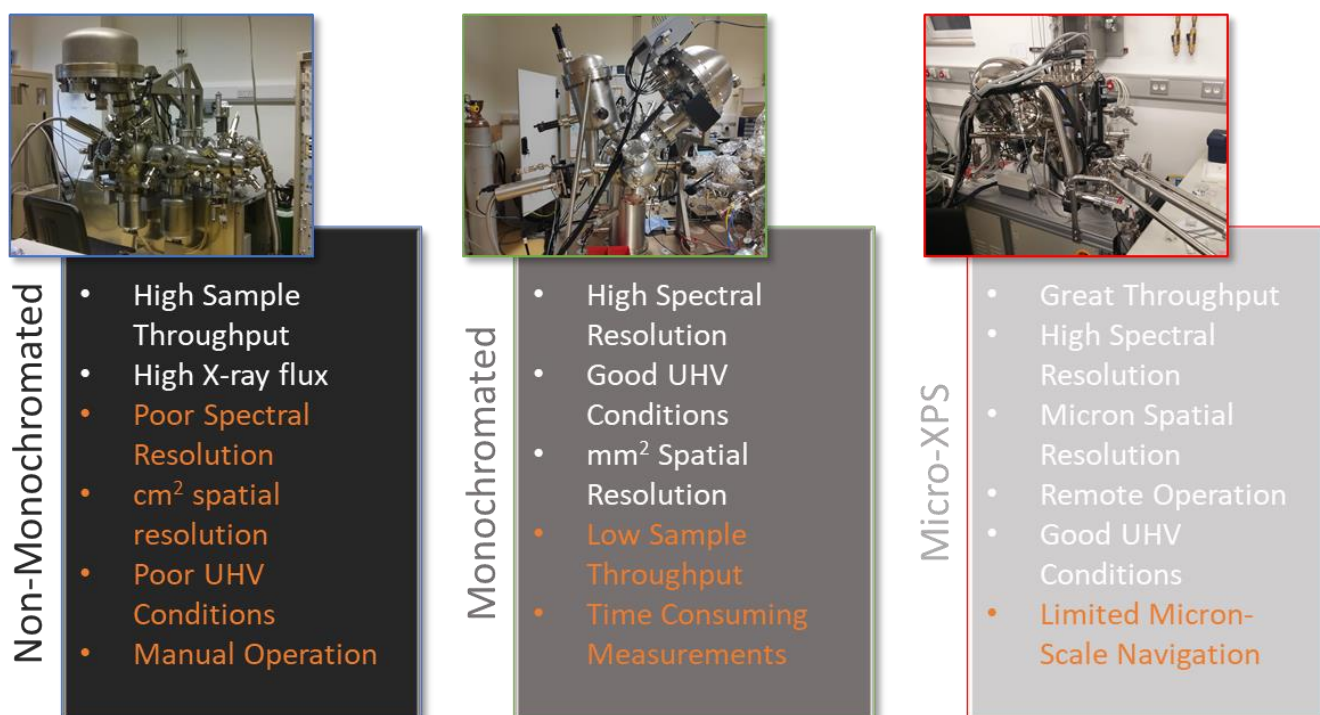


Fig. 2.5 Summary of the main benefits and disadvantages attributed to the three XPS systems used in this work.

Non-monochromated XPS

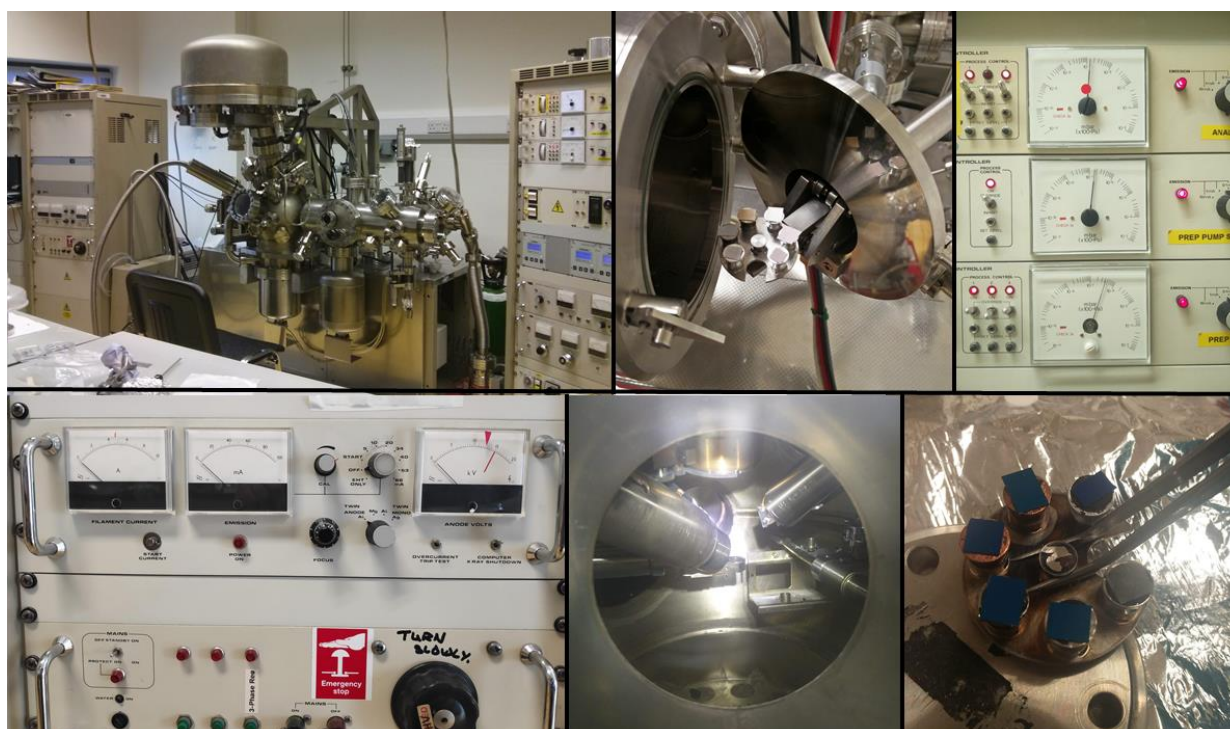


Fig. 2.6 Photographs of the non-monochromated XPS system, showing several components and aspects of the system.

The first system is a non-monochromated VG Scientific ESCAlab MKII system with a CLAM2 analyser and a PSP twin anode source (Al/Mg). The Al anode was exclusively used. I will refer to this tool as the “non-monochromated XPS”, Fig. 2.6.

This system is the oldest and least advanced XPS tool utilised in this work and serves well to illustrate the advances in XPS technology in recent decades. This tool is largely manually controlled with a series of wobble stick mechanical arms, and cable driven rails used to transfer a sample carousel with up to six samples between the internal chambers. Each sample is mounted using carbon tabs to an individual metal stub. After the sample carousel is loaded into the analysis chamber, these metal stubs must be individually removed from the carousel and placed into the single measurement holder.

Owing to the age of the system, the XPS source is controlled entirely with an analogue dial system and similarly the pressure gauges are analogue gauges. A benefit of this system and a common benefit of non-monochromated XPS sources is the high X-ray flux which can allow for very high XPS signal counts with short scan times, unfortunately this system has a comparatively poor UHV environment, with operating pressures of $\sim 10^{-7}$ - 10^{-8} mbar. This pressure regime largely negates the expected high-count rates provided by a non-monochromated XPS source. A low energy electron flood gun is used to compensate for surface charge build-up.

The system analyser was controlled with Thermo Scientific Advantage software. The analysis lenses used gave a measurement spot size of $\sim 1\text{cm}^2$. Survey spectra were taken with a pass energy of 200 eV and core-level spectra were generally acquired with 20 eV pass energy; this gives core-level scans a spectral resolution of ~ 1 eV.

Monochromated XPS

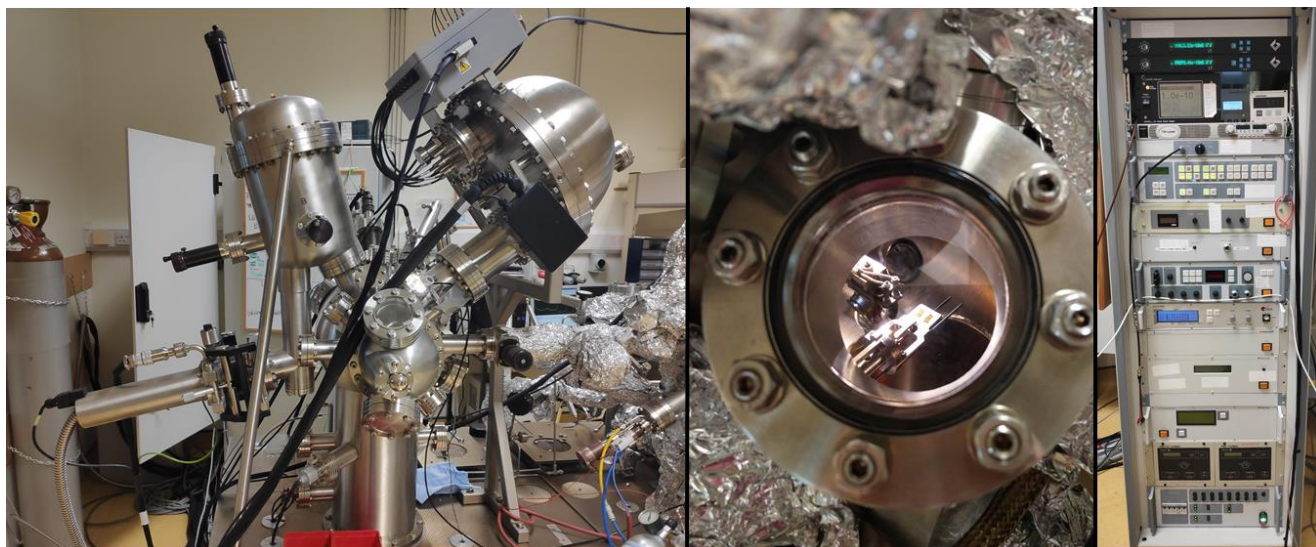


Fig. 2.7 Photographs of the monochromated XPS system, showing several components and aspects of the system.

The second system is a monochromated Scienta Omicron Multiprobe XP system with a EA 125 analyser. This system uses an Al anode and a quartz crystal monochromator to select the Al $K\alpha$ line at 1486.67 eV. I will refer to this tool as the “monochromated XPS”, Fig. 2.7.

This tool is significantly more modern than the non-monochromated system and achieves an operating pressure in the conventional 10^{-9} - 10^{-11} mbar range. Samples are mounted to an Omicron sample plate (approximately 1.5 X 1.8 cm) using carbon tabs or Cu foil. This is transferred between chambers using magnetically coupled linear drive transfer arms. The available area on each sample plate allows a maximum of two samples per plate. The system lenses can be adjusted to provide a spot size of $\sim 1\text{mm}^2$.

The spectra were acquired using Omicron software EIS software. Survey spectra were acquired with 100 eV pass energy and core-level scans were generally acquired with 15-20 eV pass energy. A low energy electron flood gun with tuneable energy was used to minimise surface charging.

To illustrate the improvement in spectral resolution between the monochromated system and the non-monochromated system the same sample of a dispersed MoO_3 film was measured with a 20 eV pass energy in both systems. These spectra are both fitted with two doublets, one from MoO_3 and the other from a sub-oxide MoO_{3-x} . While this component can be roughly detected and fitted using the non-monochromated system, the peak width, intensity, and peak shape is far more reliably fitted with the monochromated system. The measured FWHM of the MoO_3 main peak is 1.6 eV and 0.98 eV respectively for the two systems, illustrating the substantial benefit of a monochromated XPS source, Fig.2.8.

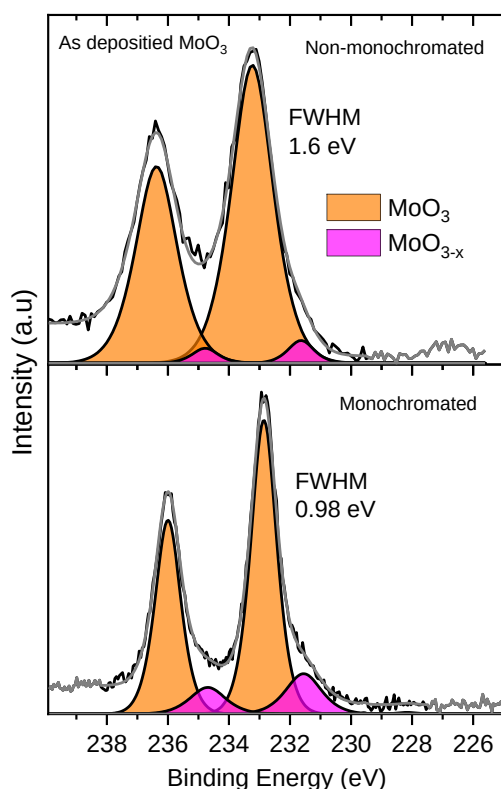


Fig. 2.8 Contrasting fitted XPS spectra of a MoO_3 sample acquired with the non-monochromated and monochromated XPS systems.

Micro-XPS

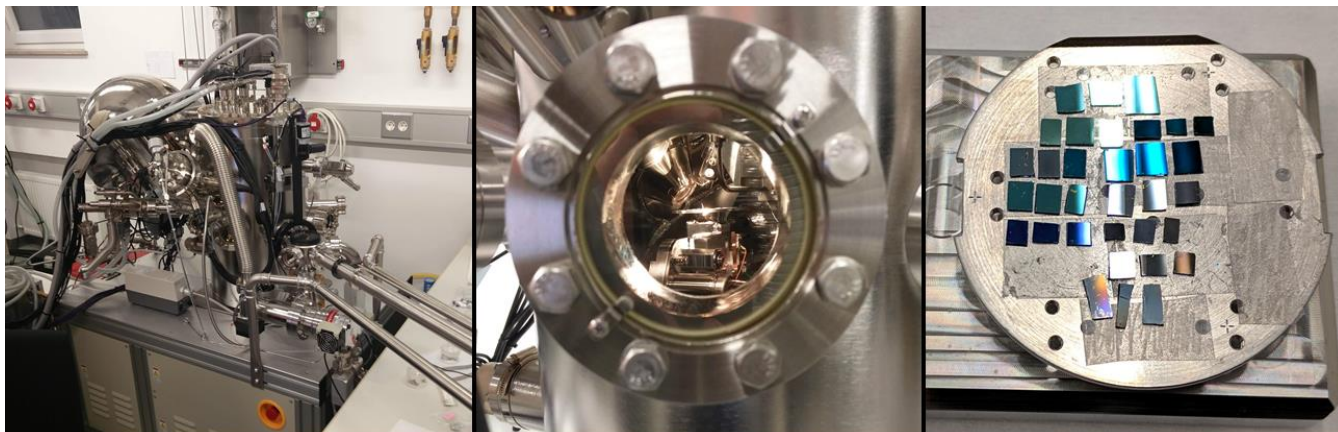


Fig. 2.9 Photographs of the micro-XPS system, showing several components and aspects of the system.

Finally, the third XPS system used here was a PHI VersaProbe III system. This system uses a monochromated micro-focused scanning X-ray source with the Al $K\alpha$ X-ray line. I will refer to this tool as the “micro XPS”, Fig. 2.9.

This is an advanced micro-XPS tool which has many benefits over older systems. The X-ray beam can be reduced to selected sizes between ~ 200 - $10\ \mu\text{m}^2$. This enables point spectra to be measured from a much smaller region of a sample than the previous systems, facilitating measurement of single crystals of TMDs. The controlled small X-ray spot size allows mapping XPS analysis by rastering the beam over a surface while acquiring the spectrum.

This system has a very high sample throughput. The bright X-ray source and highly sensitive detector facilitate a low number of scans to achieve adequate signal to noise for spectra acquisition. The system can use large sample mounts of up to 6 cm in diameter, this mount plate was covered with double-sided sticky tape and allowed a large number of samples to be loaded and examined simultaneously while maintaining UHV pressures of approximately 10^{-10} – 10^{-11} mbar.

An important but difficult to quantify benefit of this system is the relatively simple user experience. Many aspects of the XPS process are automated with the SmartSoft-VersaProbe software with simple to follow instructions provided by software when user input is required.

Beyond this, there are several other user experience advantages. A digital camera image is used to enable sample identification and measurement point selection. Multiple analysis tasks over many samples can be queued and will automatically be sequentially performed. Sample height is optimised per sample before spectral acquisition by automatically measuring background

count intensity for several steps of Z-position. A requirement of micro-XPS analysis is a more sophisticated charging compensation technique, here a dual-beam low energy electron flood gun and a low energy Ar^+ ion supply was automatically used to neutralise surface charge in the analysis region for each sample.

The non-monochromated, and monochromated XPS systems were both located in Trinity College Dublin, while the micro-XPS is located in Universität der Bundeswehr München. While I physically operated the micro-XPS system in person several times, the high level of automation also made remote operation possible. Samples for analysis were frequently shipped in inert atmosphere to Oliver Hartwig in Munich who loaded and unloaded the micro-XPS system with these samples. The automated and software-controlled elements of this system allowed me to effectively operate the system remotely with minimal issues.

Survey spectra were acquired with a pass energy of 112 eV and core-level spectra were generally acquired with a pass energy of 26 eV. To measure specific micron-sized regions on the sample surface another function of this tool was required. Scanning X-ray induced secondary electron imaging, alternatively called Scanning X-ray imaging (SXI), is used to generate an SEM-like image of the surface of the sample. SXI is performed by rastering the small X-ray beam over an area and measuring the intensity of photoelectrons generated at each point to build an image. This method is used to select areas or points for micro-XPS measurement.

To illustrate the utility of this tool, an example is given in Fig.2.10 of my measurement of an area of a sample with CVD-grown vertical heterostructures of MoS_2 monolayers with some overlayers of WS_2 grown on top, this sample was prepared by Lisanne Peters. The intensity of the Mo, S, and W XPS regions were mapped over an area of approximately $150\text{ }\mu\text{m}^2$ using the smallest XPS spot size of $\sim 10\text{ }\mu\text{m}^2$, this data was then combined into an elemental map in Fig. 2.10(a) where the various regions of substrate, MoS_2 , WS_2 , and the overlap of the materials can be seen. The same region is shown in the SXI image, Fig. 2.10(b). The XPS map confirms that heterostructures are present and with comparison to the optical microscopy image in Fig. 2.10(c) we can confirm the overlayers are WS_2 on MoS_2 .

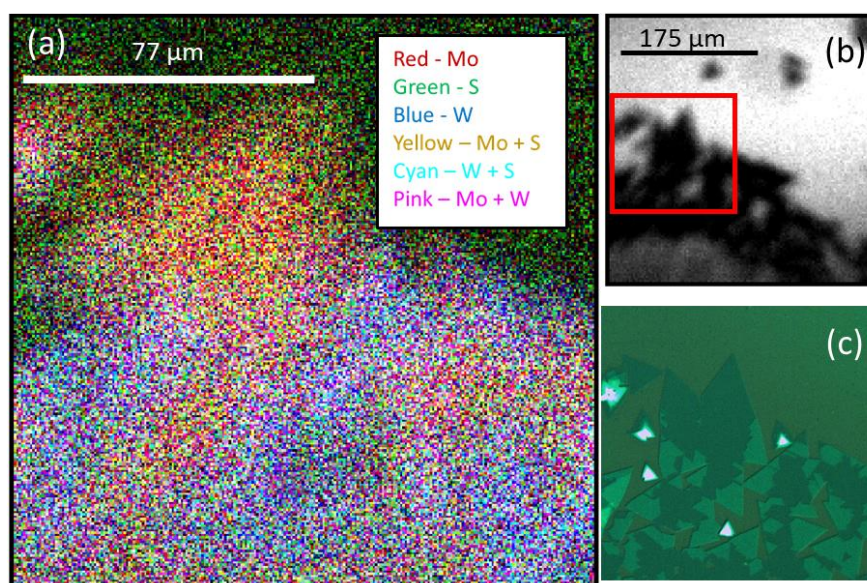


Fig. 2.10 (a) Elemental map of the MoS₂/WS₂ heterostructure sample acquired with the micro-XPS system. (b) SXI image showing the mapped region. (c) Optical microscopy image of the same area.

Regardless of the XPS system being used, XPS measurement required defining the parameters for each core-level region and the Survey spectrum for each sample. For standardisation and calibration purposes, a Survey, C 1s, and O 1s spectra were acquired for almost all samples measured in this thesis. Beyond these spectra, the specifics of the material or experiment were used to determine which other core-level regions should be measured. The energy range to acquire across for each core-level was determined by a combination of reference literature and an initial scan to determine approximately where a suitable background exists on either side of a spectrum. The most commonly changed parameter was the number of scans, and occasionally the pass energy. These two parameters can be adjusted to optimise for spectral resolution and/or the scan time when attaining suitable signal to noise for a spectrum.

The effect of increasing pass energy or number of scans for a spectrum is demonstrated in Fig. 2.11. A MoSe₂ sample was measured with 6 pass energies with 10 scans each in Fig. 2.11(a). Similarly, the sample was also measured for 6 different number of scans at a pass energy of 26 eV in Fig. 2.11(b). For each of these spectra a loosely constrained curve-fitting analysis was performed and the stoichiometry of the MoSe₂ calculated, this was to indicate the impact these parameters can have on the fitted data, particularly when fitting is not well implemented. The

approximately linear relationship between pass energy and the width of XPS peaks and their intensity is shown in Fig.2.11(c).

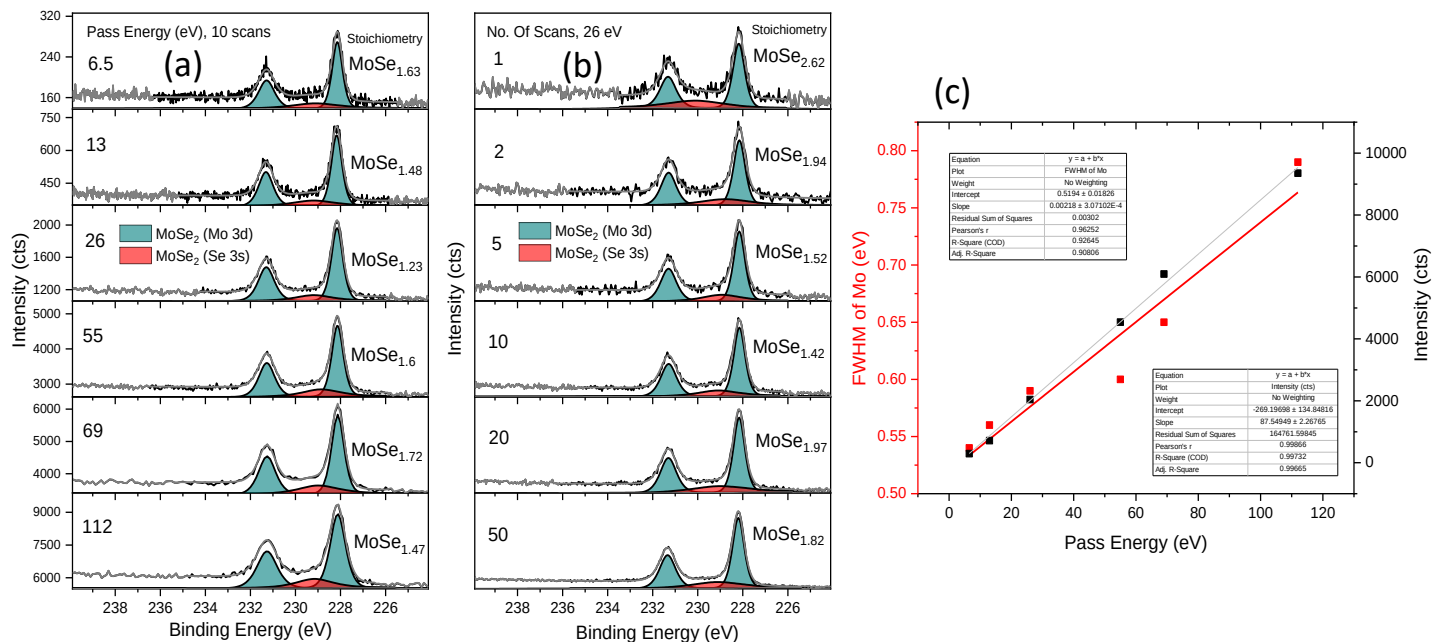


Fig. 2.11 Fitted XPS spectra illustrating the effect of pass energy (a) and the number of scans (b) on the acquired and fitted spectrum. (c) Plot of the FWHM and intensity of the fitted MoSe₂ peak against pass energy.

2.7.1.2 XPS Analysis

After measurement, all XPS data was imported into the software CasaXPS version 2.3 for analysis.

The standard curve fitting procedure used in this thesis for all XPS analysis is summarised below, while some important considerations, background information, limitations, and errors are previously discussed in section 1.8. A number of thorough curve-fitting guides now exist in literature which provide the remaining clarity, nuance, and exceptions not covered here.⁶⁵

The first step was to apply any charge correction if required. All acquired spectra were charge calibrated by referencing to the C-C C 1s peak at 284.8 eV, this was performed universally expect in scenarios where surface contamination or variable surface charging would result in nonsensical calibrated values. This process of charge correction has significant intrinsic error

for a multitude of reasons and can result in uncertainties in peak binding energies between 0.4 to 2.6 eV.⁷⁶

The Survey scan was then used for elemental identification of the sample. Any potential coincidental overlap of XPS components from different elements were noted at this point to minimise confusion when analysing core-level spectra.

Each core-level spectrum of interest was then fitted with appropriate backgrounds (as discussed in section 1.8.3), generally a Shirley type background was used here. While the error introduced by the background can be difficult to ascertain or control directly, the choice of starting and end-points for the background can have a large impact and was varied to observe any significant variations when applying a background.

The curve-fitting process for each core-level involved inserting peaks for each component in the spectrum and then suggesting a variety of parameters for this peak which were then automatically fitted onto the data using an iterative process by the software within user defined constraints. These parameters included the binding energy (position), peak shape (line shape), FWHM (width), and intensity/area.

If available, the core-levels were fitted by importing a previously used set of parameters with loose constraints and allowing the software to attempt to roughly match the components to the spectrum before further adjustment and optimisation.

If a material was being measured for the first time, a new set of parameters were created using appropriate peak arrangements (quantum number determined splitting and area ratios, and literature determined doublet splitting). It was generally at this step when the appropriate number of components in the spectrum would become apparent and these would be added until an approximately correct peak envelope was achieved.

It was essential to consider the validity for adding each new component as the software has no consideration of physics or chemistry and will fit as many components as the user inputs. This consideration included determining the chemical assignment for each component through reference to literature sources and by qualitative comparison across the measured core-levels. Consequently, all core-levels were analysed concurrently to minimise errors. An overreliance on reference peak positions when assigning each component can mislead due to the variability across the literature for these values. Therefore, when assigning peaks, priority was given to maintaining the qualitative consistency across the core-levels. If there was uncertainty in peak

assignment (e.g. multiple compounds in the literature potentially being the source) preference was given to anticipated likely results over strict adherence to reference values.

Similarly, constraints on peak position did not strictly adhere to reference values and instead sensible constraints when accounting for the various potential errors and factors such as noise, overlapping components, and possible charge transfer were used.

A fixed peak shape for each individual XPS system was generally used as there was a negligible variation between most peaks. This fixed peak shape was found by analysing and adjusting the Gaussian/Lorentzian mix for a single clear peak with a high signal to noise ratio, such as the O 1s of a clean SiO₂ substrate. The clear exception was for asymmetric peaks which were fit through a combination of reference values and manual refinement to greater match the data. Inaccurate peak shapes can contribute to error in a systematic way and lead to a greater mismatch with the raw data. In severe cases inaccurate peak shapes could potentially be incorrectly remedied by adding additional components to the spectrum which do not have an “real” source.

Implementing constraints on peak width/FWHM requires significant amounts of user interpretation and are a frequent source of error in the literature. Several factors affect the width of an XPS peak, such as the intrinsic lifetime of a core-hole which generally gives increasing peak width for $s > p > d > f$ orbitals. The various spectral peaks from the same material often have very similar peak widths as the chemical bonding environment of material has a large effect on the peak widths, therefore the peaks from one material should be fitted with similar constraints. Highly ordered materials (e.g. single crystals) will have narrower peaks than more disordered materials with higher bond diversity.

The fitting would then be gradually refined by adjusting the constraints. This was often an iterative process with each fitted core-level in the spectrum being compared to ensure qualitative consistency across a sample.

Quantification of the relative atomic concentration of different species using XPS can be complex to perform with high accuracy. Unless a very rigorous procedure is followed it can be more reliable to consider this a semi-quantitative analysis. Relative sensitivity factor (RSF) values for each core-level for each tool were provided by the manufacturers and were used to calculate stoichiometry of the TMD materials being measured. This was primarily to ensure a sensible peak fitting and peak assignment process had been performed.

The fitting was iterated upon until the curve fitting was consistent in both a qualitative and semi-quantitative manner, and that it closely matched the raw spectrum. Once this was achieved, the fitted spectrum was ultimately considered by a final reality check with expected experimental results for the sample and compared to good XPS literature examples to minimise errors in assignment or fitting.

2.7.1.3 XPS Data Presentation

The presentation of curve fitted XPS results is an important aspect of their utility. The high degree of user input in the results requires that the data is transparently presented to allow informed assessment and critique of the curve fitting implementation. Beyond transparency in data analysis, the legibility and clarity of presented XPS data should be considered to ensure that the interpreted information is clearly conveyed and can be understood by those with less familiarity with the technique. As previously mentioned, the role of XPS as a popular but often secondary characterisation method for TMD materials in the literature has resulted in several problematic issues. Improving the general presentation and readability of XPS data may aid in reducing misinterpretation in literature.

In this work fitted XPS spectra were presented here using Origin 2018 software. To improve readability, spectra were presented with background subtraction of the fitted components from the raw spectrum. To ensure the accuracy of the fitting implementation can still be determined the envelope of the fitted peaks is not subtracted and is presented alongside the raw spectrum.

An example of this is given in Fig.2.12 for the Mo 3d core level of MoTe₂. While both fitted spectra are acceptable in that scenario, a highly complex example region is presented in Fig. 2.12 (b) and(c). This region for a WTe₂ sample has overlapping sets of components from three separate core-levels. This yields 10 separate peaks corresponding to only three different materials, the differences in peak shape, peak width, peak area, and peak position can be easily determined using this method of presentation while the envelope confirms the alignment with the raw spectrum. All XPS spectra are presented in this style.

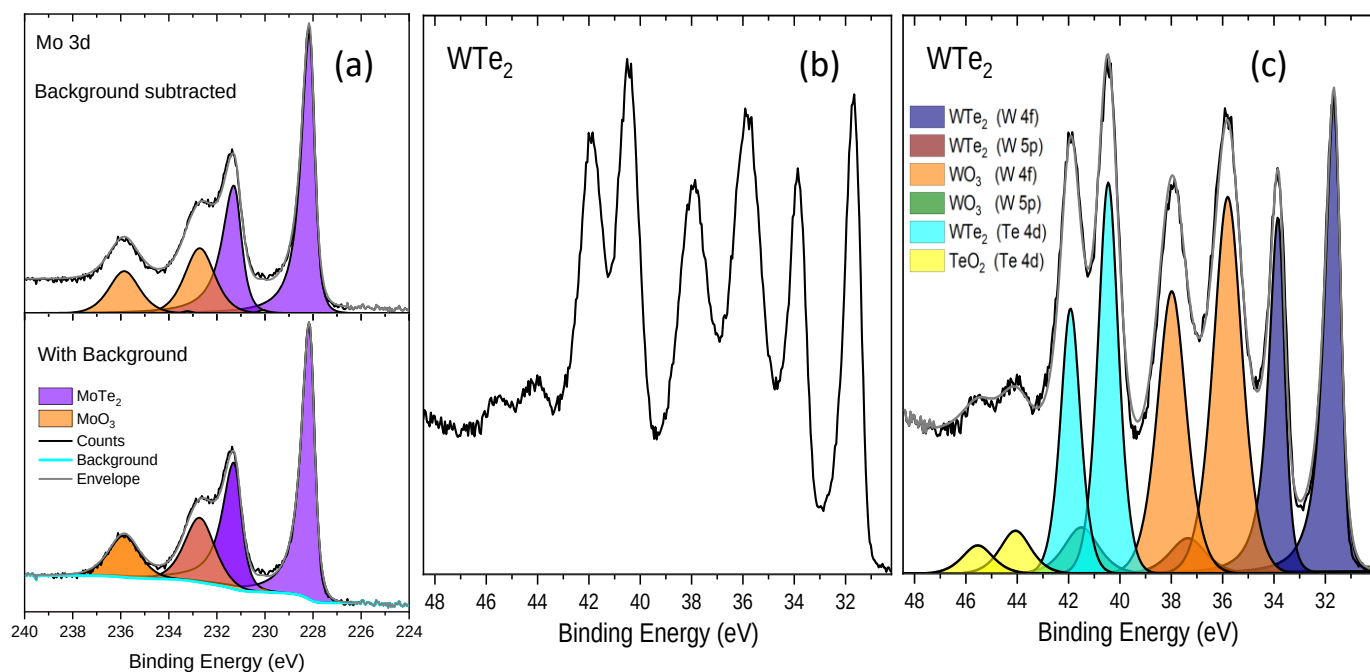


Fig. 2.12 (a) Fitted XPS spectra for a MoTe₂ sample showing the same data with and without background subtraction of the fitted components. The XPS spectrum of WTe₂ before (b) and after (c) fitting.

2.7.2 Raman

Raman spectra measurements acquired in this thesis were performed using WITec Alpha 300R scanning Raman spectrometers. Unless specified otherwise, measurements were taken using a 532 nm excitation laser at a power of <200 μ W with a spectral grating of 1800 lines/mm and a 100x microscope objective (0.95 numerical aperture, spot size $\sim$ 0.4 μ m). A minority of spectra were acquired with 633 nm and 405 nm excitation lasers using similar parameters. Spectra were acquired as averages of area maps or of line scans. Raman data was analysed using WITec Project FIVE 5.1 software.



Fig. 2.11 Photograph of the WITec Alpha 300R scanning Raman and PL spectrometer used in this thesis.

2.7.3 Photoluminescence

The same WITec Alpha 300R spectrometers and settings which were used for Raman spectroscopy were utilised for PL measurements also. With PL data analysed using WITec Project FIVE 5.1 software.

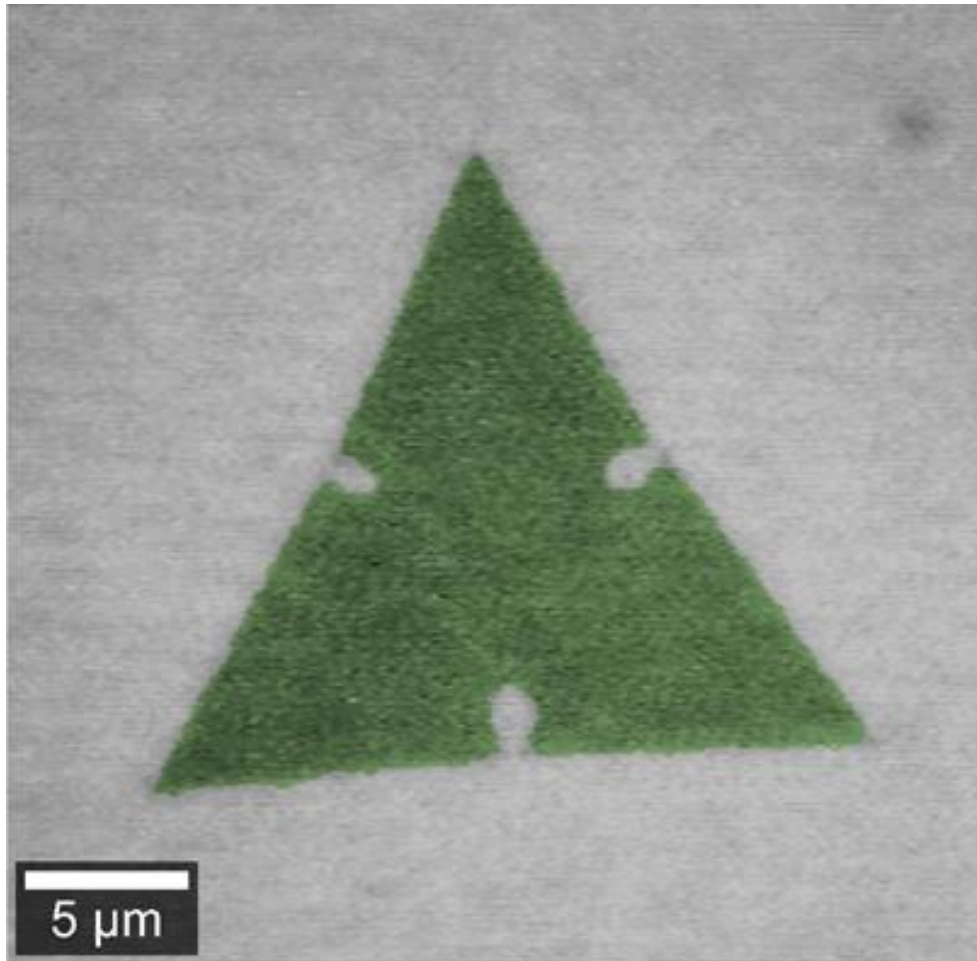
2.7.4 SPM

A Bruker Multimode 8 system was used for all SPM measurements in this thesis. The system was operated for AFM in ScanAsyst Air 146 mode with ScanAsyst Air AFM tips. KPFM measurements were performed by Katie O'Neill. All SPM data was analysed using Gwyddion software.¹²²

2.7.5 SEM

SEM images were acquired with the assistance of Dr John McManus using a Karl Zeiss Supra microscope, generally operating with a 3 kV accelerating voltage, 30 μm aperture and a working distance of $\sim 3\text{--}4\text{mm}$. Images were gathered using both the in-lens and secondary electron detectors. ImageJ software was used for limited processing of these images.

3 -Synthesis and Characterisation of Monolayer MoS₂



“An expert is a person who has made all the mistakes that can be made in a very narrow field.”

— Niels Bohr

3.1 Introduction

This chapter details the synthesis and typical characterisation methods of monolayer MoS₂ which was used extensively throughout the course of this thesis. A chemical vapour deposition (CVD) style technique is leveraged to grow large amounts of primarily monolayer MoS₂ across SiO₂ substrates. The synthesised material consists of an interesting variety of MoS₂ crystals with different sizes, shapes and other features which will be discussed. Raman, PL, and X-ray photoelectron spectroscopies were used to characterise the material in detail. Scanning probe and scanning electron microscopies were also used to briefly examine the morphology of the MoS₂.

CVD is one of the most scalable methods to synthesise large amounts of high-quality monolayer MoS₂ and thus it is an area where study is rapidly developing in the literature.⁴¹ The aim in this work was to produce large areas of high quality, primarily monolayer MoS₂ which can be then used in a broad range of analysis experiments and studies for specific applications.

Similar to graphene, initial experiments and fundamental studies of monolayer MoS₂ used mostly mechanically-exfoliated MoS₂. As the complexity of the experiments and the demand for 2D MoS₂ grew, the many limitations of mechanically-exfoliated MoS₂ became constraints. This led to demand for rapid advancements in other methods to isolate monolayer and few-layer MoS₂. As such, there now exists a plethora of different methodologies and techniques which are both effective and useful for generating MoS₂ samples in the various forms and environments needed for further experimentation. As discussed in Chapter 1 these include liquid-phase exfoliation in various solvents, and vapour-phase processes.⁴¹

Of these vapour-phase processes, there are different methods and aims for the different synthesis techniques e.g. from synthesis of very flat single-crystal monolayers on molten surfaces,⁴⁴ to full coverage synthesis of MoS₂ across sapphire³³ or electrically compatible substrates like SiO₂.³⁹ Likely the most common method, and also the one used here, monolayer MoS₂ has been made by a CVD process wherein sulfur and molybdenum precursors were heated upstream from the target substrate in a quartz-tube furnace. These elements react in the vapour phase causing MoS₂ crystals to nucleate and then grow laterally on the growth substrate. Even within the constraints of this form of CVD, there are many possible parameters which can affect the synthesis of monolayer MoS₂, e.g. growth substrate, temperature, pressure, time, choice of sulfur and molybdenum precursors, precursor phases, carrier gas and flow rate,

distance between precursors and substrate. This swath of parameters and different synthesis techniques has made CVD synthesis of MoS₂ and related TMDs a very dynamic research area.

3.2 CVD of MoS₂

The core methodologies and techniques utilised in the synthesis procedure of CVD MoS₂ here were developed and optimised previously by Dr Maria O'Brien.¹¹⁸ The experimental details of the synthesis process are described in Chapter 2, but the motivations behind the different aspects of the process and a rough summary of the procedure will be described here.

Many of the frequent commonalities seen in the literature for CVD of MoS₂ are also featured here. Solid-phase precursors in the form of sulfur powder and MoO₃, a two-zone quartz-tube furnace to independently heat the sulfur and molybdenum precursors, and a continuously pumped low-pressure system under a carrier gas flow. The most notable differences between the technique used here and many of the literature techniques relate to the configuration of the Mo precursor and the growth substrate in a microreactor setup, which is illustrated in Fig. 3.1.

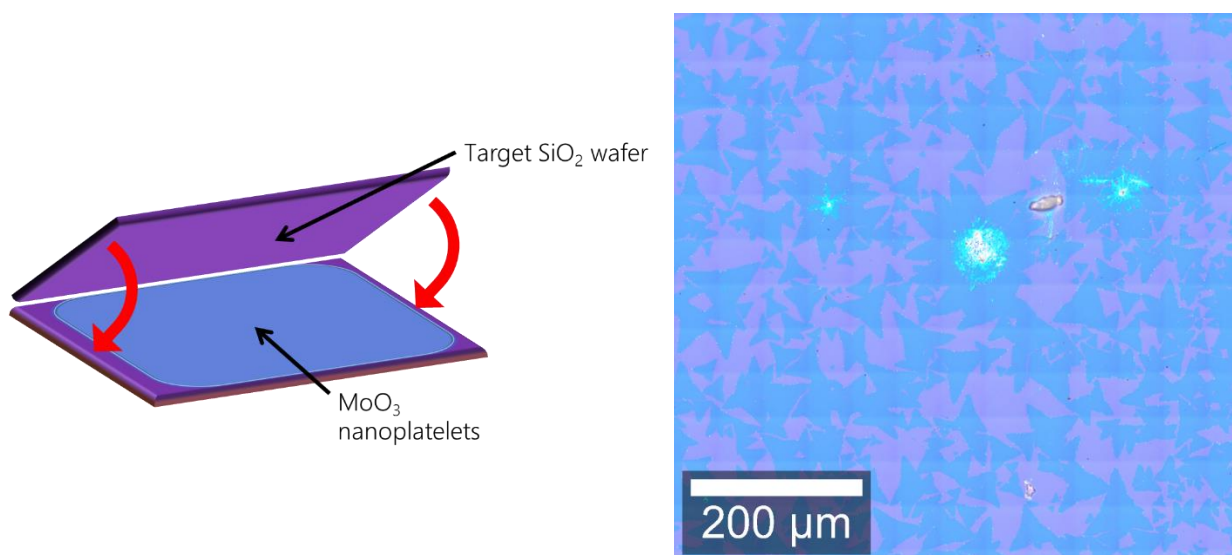


Fig. 3.1 (a) Representation of the “microreactor” used in the MoS₂ CVD synthesis process **(b)** Stitched optical image showing the large number of monolayer MoS₂ crystals on SiO₂.

Uncommonly, the Mo precursor of MoO₃ is dispersed into an IPA solution and then dropcast onto SiO₂/Si substrates at 150 °C, as the IPA quickly evaporates the MoO₃ is dispersed across

what is now referred to as the seed substrate. When cooled to room temperature, the target substrate, generally another SiO₂/Si wafer of ~1 cm², is placed face-down onto the seed substrate, as shown in Fig.3.1(a). This sandwich is then placed into a ceramic crucible at the main heating zone of the quartz-tube furnace for the synthesis of monolayer CVD MoS₂. The synthesis involves heating of the microreactor sandwich to evaporate the MoO₃. Once at the growth temperature of 750 °C, the microreactor leaves enough space for the mass excess of vaporised sulfur from the secondary heating zone to intercalate between the SiO₂ wafers and mix with the vaporised Mo precursors to generate MoS₂. MoS₂ crystals then grow across both the target and seed substrates, with large amounts of monolayer MoS₂ forming on the target substrate. The samples are sulfurized for 20 minutes, and then annealed without sulfur at the same temperature for another 20 minutes to ensure completion of the process, before cooling to room temperature and removing the samples.

This process yields a large number of MoS₂ crystals across the substrate, primarily monolayers. The synthesised material displays an interesting variety of MoS₂ crystals with considerable differences in size and shape over each individual sample and between runs, with isolated single crystals and also large-area stitched films common. Optical microscopy images of some examples of the variation in MoS₂ crystals seen over the surface are presented in Fig. 3.2.

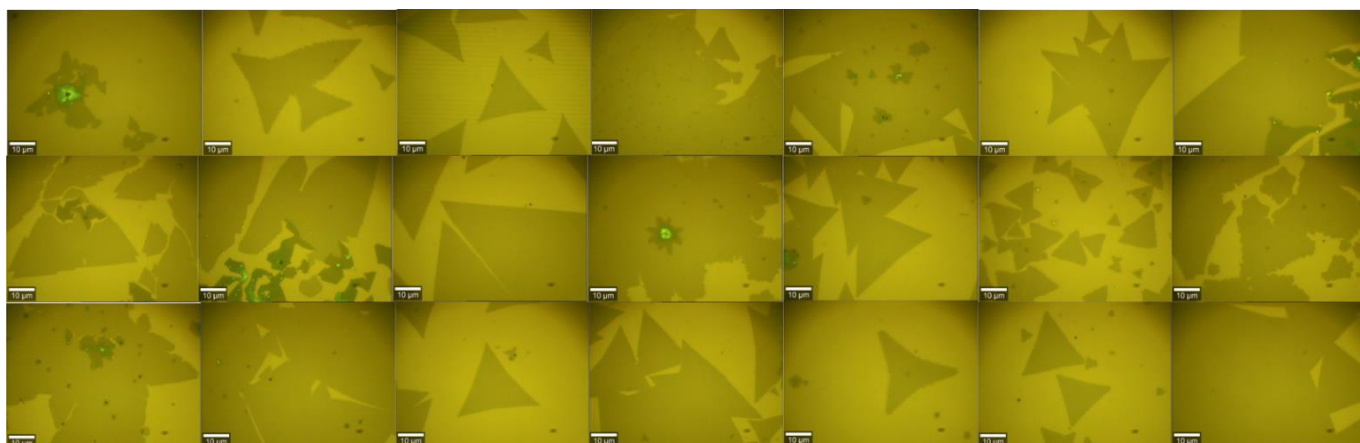


Fig. 3.2 Optical images displaying the diversity in MoS₂ crystals synthesised. Scale bar 10µm

MoO₃ dispersions were drop cast and the subsequent evaporation of IPA resulted in an uneven distribution of MoO₃ across the seed substrate. This distribution is often reflected in the patterning of the growth of the MoS₂ on the target substrate. The irregular MoO₃ distribution leads to a hyper local variation in the spacing between the Si wafers, and therefore in the

concentration of Mo and sulfur vapours across the microreactor. These features each contributed to the unpredictable and erratic coverage across each sample. Optical images of the full growth substrate of five MoS₂ samples after synthesis are displayed in Fig. 3.3, the variation in coverage is clear here, with the dark green colour corresponding to monolayer MoS₂ on top of the yellow coloured SiO₂ substrate. The circular pattern left by the evaporation of the IPA on the MoO₃ seed substrates can be seen mirrored on these growth substrates.

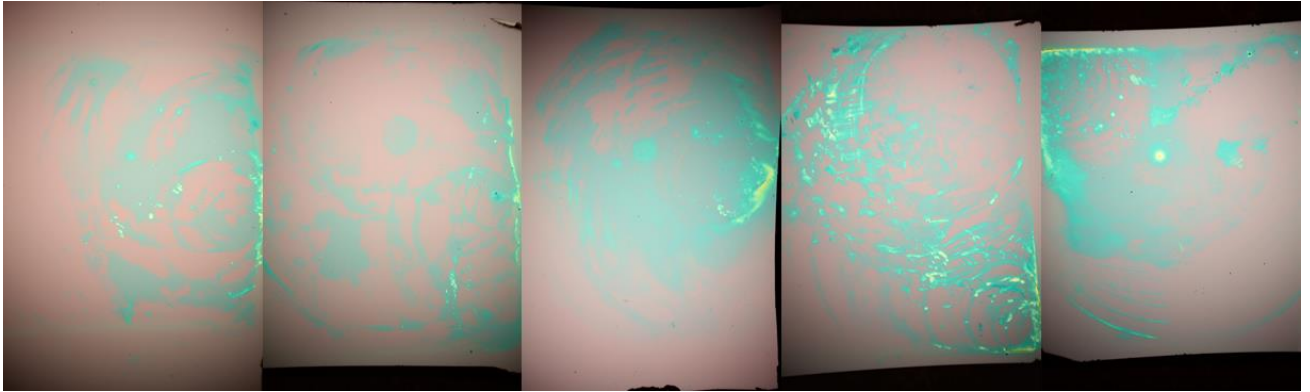


Fig. 3.3 Digital camera photographs of five MoS₂ growth substrates after synthesis displaying the variation in coverage. Samples are approximately 1 cm along their long axis.

Importantly, a highly consistent result of this method was in the synthesis of large amounts of monolayer MoS₂ as both individual isolated single crystals, and as large films of up to mm² in area. Beyond this, there is also consistent synthesis of regions showing MoS₂ with a variety of layer thicknesses and different shapes. This diversity across each individual sample opens up many opportunities of study, with the possibility to investigate many different aspects of MoS₂ crystals using only one sample.

3.3 Raman

Raman spectroscopy is almost certainly the most universal technique used in MoS₂ characterisation and is utilised heavily in this work. The rapid and non-destructive nature of Raman spectroscopy make it ideally suited for analysis of the CVD MoS₂ synthesised here due to the aforementioned variability in synthesis. As discussed in the introduction, the Raman modes of MoS₂ are highly characteristic of the state of the crystal with the E_{2g}^1 and A_{1g} Raman modes being greatly studied in the literature. As mentioned previously, while the Raman modes of monolayer MoS₂ are in fact the E' and the A'_1 , it is common practice in the literature to

neglect the changing symmetry with layer number and to refer to the Raman modes using bulk notation.

A typical optical image of CVD MoS₂ with a continuous layer of monolayer MoS₂ and two islands sitting atop this showing visible bilayer and thicker layers of MoS₂ is shown in Fig. 3.4(a), below. Mapping Raman spectroscopy was used here with the mapped area denoted with a red square. A 15x15 μm map with 5,625 individual point spectra of the intensity of the Raman modes of MoS₂ is shown in Fig. 3.4(b). This intensity map further resolves the different layers of MoS₂, the Raman spectra isolated from each of these layer regions, Fig. 3.4(c). The narrow Raman peaks with an average FWHM $\sim 3.5\text{ cm}^{-1}$ are characteristic of the high crystalline quality of the material.³³ The expected increasing intensity and increasing separation of the Raman modes with increasing layer number are also evident.⁴¹ As peak separation is often used in the literature to determine the layer number of MoS₂, the positions of the Raman peaks and their separation for each layer are given in Fig. 3.4(d). The monolayer peak separation of 21.5 cm^{-1} is larger than the commonly cited numbers of 18–20 cm^{-1} . This is most likely due to surface effects with SiO₂ which have been shown to affect MoS₂ Raman modes in this way,⁹³ it is also possible that growth effects such as strain contribute to this. The molecular vibrations corresponding to the MoS₂ Raman modes are shown as inserts in Fig. 3.4(c) with the A_{1g} mode of MoS₂ attributed to out-of-plane vibrations consisting of only sulfur atoms moving in the vertical plane. The E_{2g}^1 mode on the other hand is attributed to in-plane vibrations as the sulfur atoms and molybdenum atoms oscillate in the horizontal plane only.

Similar mapping of the PL intensity for MoS₂ and the corresponding spectra from each thickness region are given in Fig. 3.4(e)-(f). The dramatically higher intensity of the PL signal from the monolayers of MoS₂ are clear here, with all other layers having much reduced PL. This shows PL as being the simplest method to clearly differentiate monolayer MoS₂ from other layer numbers.

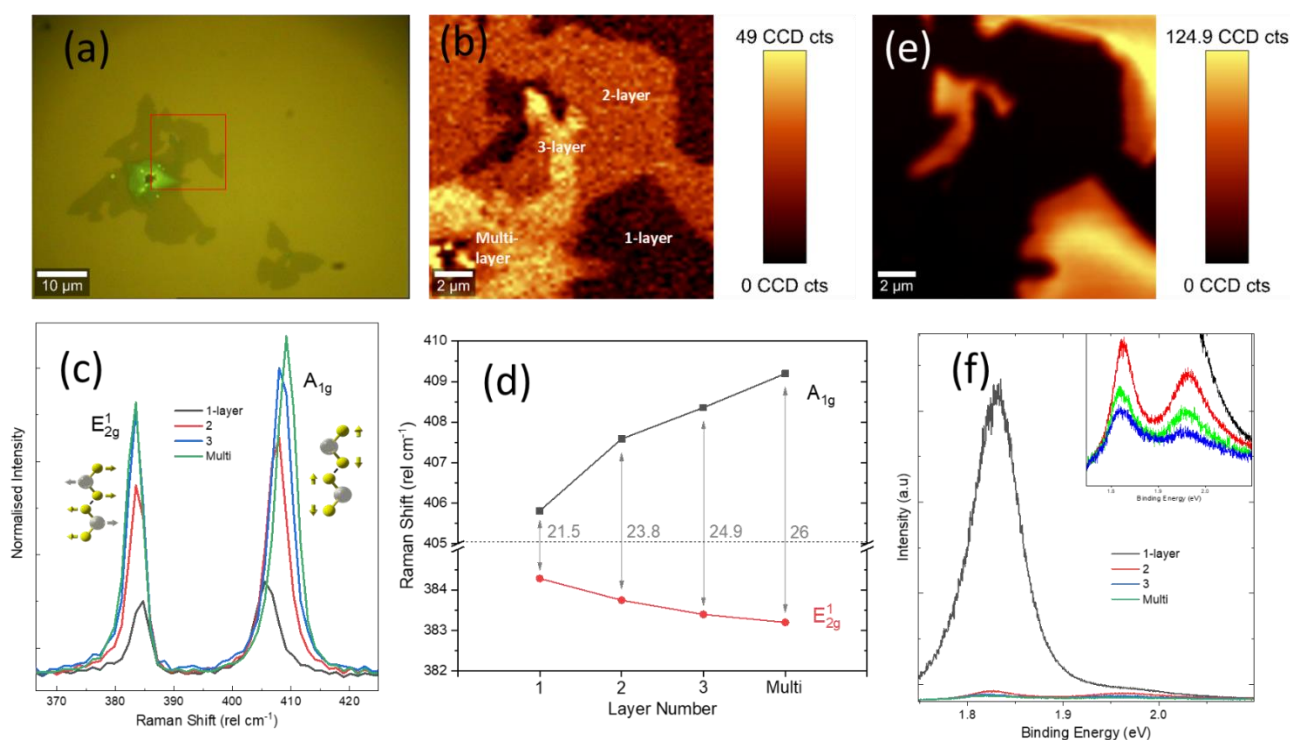


Figure 3.4 (a) Optical image of a monolayer film of MoS₂ with an island of thicker MoS₂ on top, red box indicating mapping spectroscopy area. (b) Intensity map of the Raman modes of MoS₂ (c) Raman spectra isolated from different layers of MoS₂, inset: molecular vibrations for the Raman modes. (d) Plot of the increasing separation of the Raman modes with layer number (e) Intensity map of the PL spectrum of MoS₂. (f) PL spectra isolated from the different layers of MoS₂, inset: zoomed-in spectra showing peaks for 2-, 3- and multilayer MoS₂.

Due to the variability in the MoS₂ growth, it is important that representative data is collected by taking averages over several samples and crystals. The averaged Raman spectra for monolayer and bilayer MoS₂ taken from 40 different samples measured over 4 years of syntheses and measurements is shown in Fig. 3.5(a).

The Raman peak positions of the MoS₂ A_{1g} and E_{2g}¹ modes for monolayer and bilayer regions are shown in Fig.5(b). The A_{1g} data shows a clear distinction between the two thicknesses, with an average Raman shift of 405.3 and 407.3 cm⁻¹ for monolayer and bilayer respectively. Comparatively, the E_{2g}¹ data is more mixed with substantial overlap in Raman shift. The monolayer is on average at a higher frequency, with a peak position of 384.4 cm⁻¹, compared to bilayer, which has an average peak position of 383.9 cm⁻¹. Together, these give the average

separation of the MoS₂ Raman modes as 20.9 cm⁻¹ for monolayer MoS₂ and 23.4 cm⁻¹ for bilayer, this is reflected in the averaged Raman spectra in Fig. 3.5(a). By graphing this same data, i.e. the position of the Raman modes, against each other as in Fig. 3.5(c) it can be observed that while there is substantial variation in the exact position of the clusters for each layer, there is little overlap, making differentiation between the layers clear when using Raman spectroscopy.

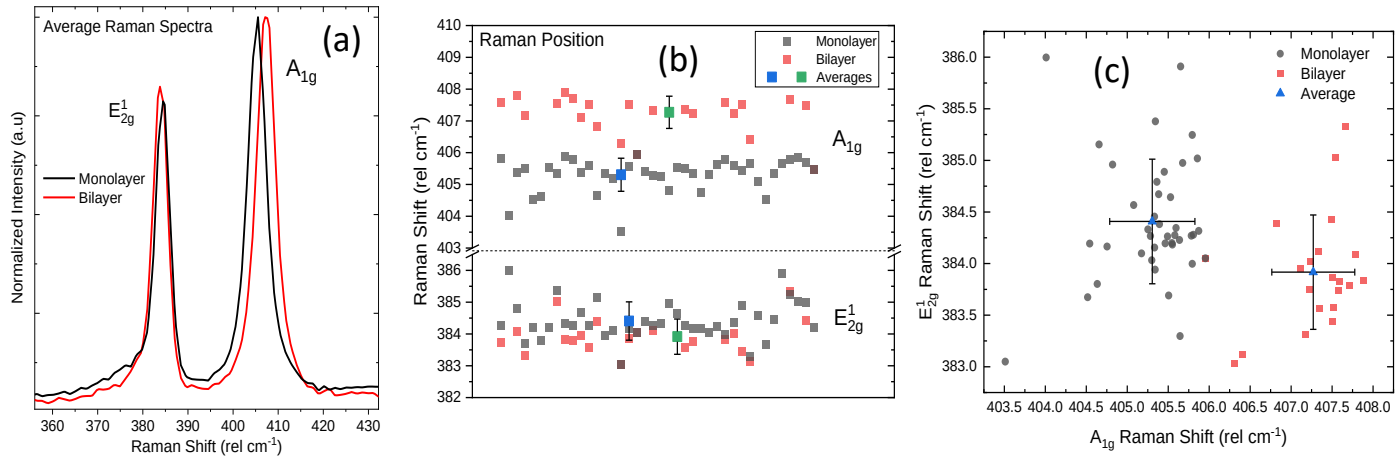


Fig. 3.5 (a) Averaged Raman spectra for monolayer and bilayer CVD MoS₂ from 62 spectra. (b) Plot of the peak position of the MoS₂ Raman modes for monolayers and bilayers from the same samples, as well as their averages with standard deviation. (c) Alternate Plot of the position of the MoS₂ Raman modes for monolayers and bilayers.

The strain induced during this CVD MoS₂ synthesis process has been investigated by a collaborator Siwei Luo, her findings indicate that the strain causes shifts in the Raman peaks around the perimeter of certain shapes of MoS₂ crystals.¹⁰² The Raman peak positions for dozens of spectra over the centre and perimeter regions of an as-grown strained monolayer crystal are reproduced in Fig. 3.6, this data contrasts with that in Fig. 3.5(b). From this it can be determined that while shifts of the A_{1g} peak of monolayer MoS₂ indicate changing thickness of the crystal, changes in the E_{2g}¹ are more indicative of strain effects. This aligns well with the understanding of the A_{1g} mode of MoS₂ being out-of-plane vibrations, and the E_{2g}¹ being in-plane vibrations.

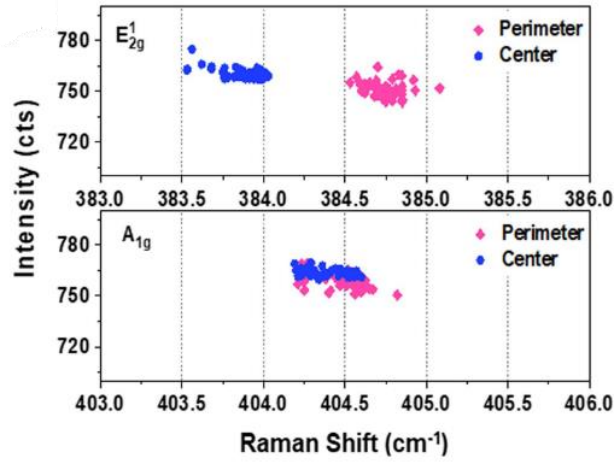


Fig. 3.6 Raman peak intensities plotted against the peak position in the centre (blue) and in the perimeter (pink) region of a CVD MoS₂ flake. Reproduced with permission from¹⁰².

3.4 Photoluminescence (PL)

One of the properties fuelling the high levels of interest in MoS₂ is its PL, which suggests potential suitability for numerous applications in the area of optoelectronics.¹⁶ As discussed in the introduction, the band structure of MoS₂ changes substantially when reducing layer number, particularly when transitioning to monolayer. Bulk MoS₂ has an indirect bandgap of ~ 1.3 eV, while monolayer MoS₂ has a significantly larger bandgap of ~ 1.8 eV, but of even more substantial significance is that this monolayer bandgap is a direct bandgap which increases the likelihood of PL.

The PL of MoS₂ is generally characterised by two excitonic emissions, the so called *A* exciton at ~ 1.8 eV and the *B* exciton at ~ 2 eV. MoS₂ features these two excitons due to spin-orbit splitting.¹⁰⁵ As discussed in the introduction, the band structure of MoS₂ changes substantially when reducing layer number, particularly when transitioning to monolayer. Bulk MoS₂ has an indirect bandgap of ~ 1.3 eV, while monolayer MoS₂ has a significantly larger bandgap of ~ 1.8 eV, but of even more substantial significance is that this monolayer bandgap is direct which increases the efficiency of PL. MoS₂ PL is highly complex with numerous factors other than layer number affecting the PL, these were outlined in Chapter 1 but include temperature, strain, dielectric, defects, substrate, and dopants. These factors can also influence the nature of the emission, with charged excitons, called trions ($2 e^- + 1 h^+$ or $1 e^- + 2 h^+$), commonly observed as well as more complex emissions such as biexcitons ($2 e^-, 2 h^+$).¹⁰⁵ These factors can influence

the peak position of the PL, the intensity, the FWHM, the lifetime etc. and therefore PL can be a very sensitive method to investigate the quality of pristine MoS₂ and any changes to this after treatments.

Similar to the Raman data, an average PL spectrum from monolayer MoS₂ is displayed in Fig. 3.7(a). The prominent peak at 1.836 eV is the *A* exciton, this is a typical energy for MoS₂ on SiO₂.^{123, 124} The secondary peak corresponding to the *B* exciton is at ~1.98 eV. The variability in the peak position of the *A* exciton is shown in Fig. 3.7(b) with a typical range between 1.83 and 1.85 eV. As was the case for the Raman spectra, the excitation power and the focus of the spectrometer optics influence the intensity of the acquired spectrum, this makes fair comparison between samples somewhat difficult. Representative spectra normalized to the intensity of the *A* exciton are shown in Fig. 3.7(c). The narrow range of peak position can be seen here, as can the difference in relative *B* exciton contribution, it was frequently observed that lower *B* exciton contribution was a feature of higher-quality MoS₂.

Extracting the data from these spectra can help make determinations about the CVD MoS₂ PL in general. Fig. 3.7 (d)–(f) illustrate a number of metrics obscured by the overlapping data in the spectra. By plotting FWHM against *A* peak binding energy in Fig. 3.7(d) the typical spread in values can be seen. An average value, as shown in Fig. 3.7(a), gives us a peak position of 1.836 eV with a typical FWHM of ~70 meV. This is a reasonable value for room temperature PL of CVD MoS₂ when compared to the literature,³³ with FWHM being the metric of quality most used in the literature. Another important aspect of (d) is the tight cluster of samples at ~1.835 eV and FWHM of ~60 meV, these are very high-quality emissions comparable to high-quality mechanically-exfoliated MoS₂, it was very common to synthesise samples consisting of a majority of MoS₂ with these values.

The relative intensity of the *B* exciton, in comparison to the *A* exciton is shown in Fig. 3.7(e) against the peak position of the *A* exciton. There is a broad distribution of data points but an overlapping cluster of data points at 1.83–1.84 eV and a relative *B* intensity of 5% are indicative of the same high-quality MoS₂ cluster seen in the previous graph. Finally, by comparing the relative *B* exciton intensity to the FWHM of the *A* exciton a near linear distribution of values indicating the relative contribution of the *B* exciton. This can also suffice as a rough benchmark of PL quality, similar to FWHM of the *A* peak. It is noteworthy that there is a large cluster of data points below 10% *B* exciton intensity, with a FWHM of ~60 meV, these are the high-quality samples.

This data validates using either FWHM of the *A* exciton, or relative *B* exciton intensity as quality metrics for PL spectroscopy of MoS₂, rather than peak position or intensity, allowing for very quick quality control of the synthesised MoS₂ to be performed using PL spectroscopy.

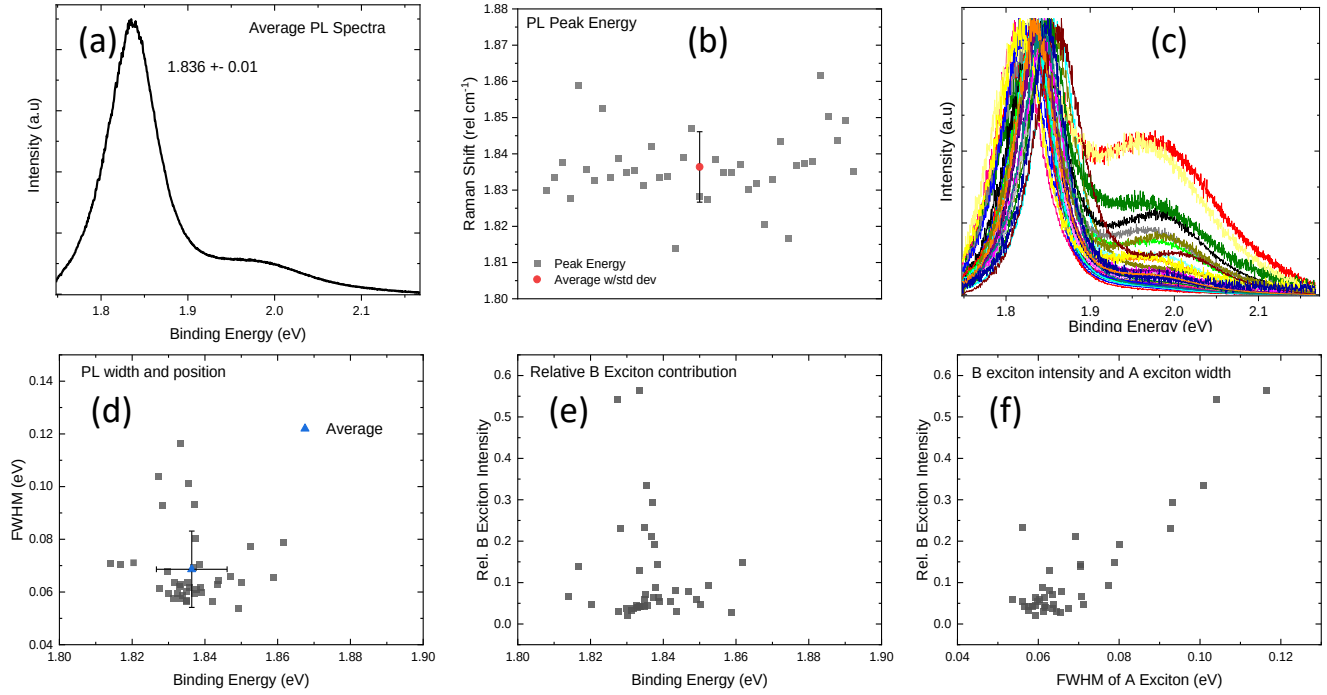


Fig. 3.7 (a) Averaged PL spectrum for CVD MoS₂ (b) Plot of the PL peak position for monolayer MoS₂ (c) Overlaid PL spectra from different MoS₂ samples (d) Plot of the PL width against peak position for the A exciton (e) Plot of the relative PL intensity of the B exciton compared to the A, against PL A exciton position (f) Plot of the relative PL intensity of the B exciton compared to the A, against PL A exciton FWHM.

PL of MoS₂ was found to be sensitive to the excitation laser power, with laser power >0.1 mW, as dictated by the spectrometer software and inbuilt power meter, resulting in an increase of FWHM and also the relative contribution of *B* exciton, presented in Fig. 3.8(a)-(b). Increased laser power would yield considerably higher signal intensity but would yield an unsteady signal as damage was being done to the MoS₂ crystal, this caused a shift in peak position to lower energy. Fig. 3.8(c)-(d) further illustrate the changes in peak width and peak position with increasing laser power, showing clear trends of wider peaks and lower peak position with increasing laser power. As a result, spectra were acquired using laser powers lower than 0.1 mW, or when no reliable method to measure laser power was accessible, at a point below where the spectra would change in width or position.

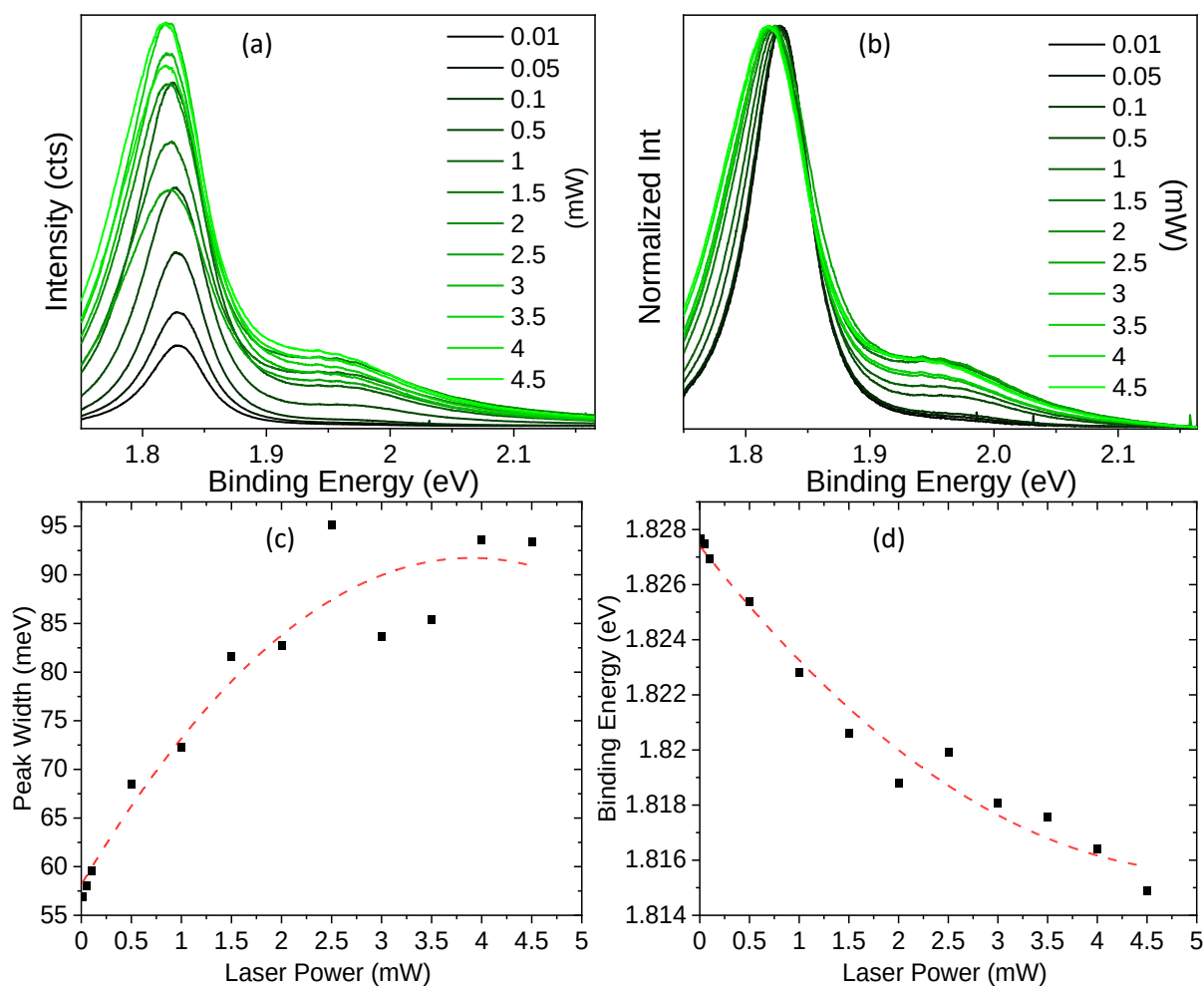


Fig. 3.8 (a) PL intensity spectra for monolayer MoS₂ acquired with different laser powers (b) Normalized spectra. (c) Graph of Peak Width (FWHM) against laser power. (d) Graph of Peak position against laser power .

When suitable laser power was used, PL spectroscopy of MoS₂ at room temperature was very sensitive to acquisition time. A region of pristine CVD MoS₂ the PL of which was measured continually over 10 minutes yielding an average spectrum as shown in Fig. 3.9(b). This spectrum illustrates typical behaviour consistent with the expected spectra in Fig.3.9(c) and demonstrates the intensity, peak position, and FWHM of the *A* exciton over time. From this figure it is clear that the peak position and FWHM change by negligible amounts across the measurement time, with a slight gradual narrowing of the *A* exciton is observed. Contrastingly, the intensity at no point reaches a steady state and is seen to quickly reach a clear peak in

intensity after ~ 1 minute before gradually decaying. Which further validates the use of FWHM as the primary benchmark of PL quality from MoS_2 .

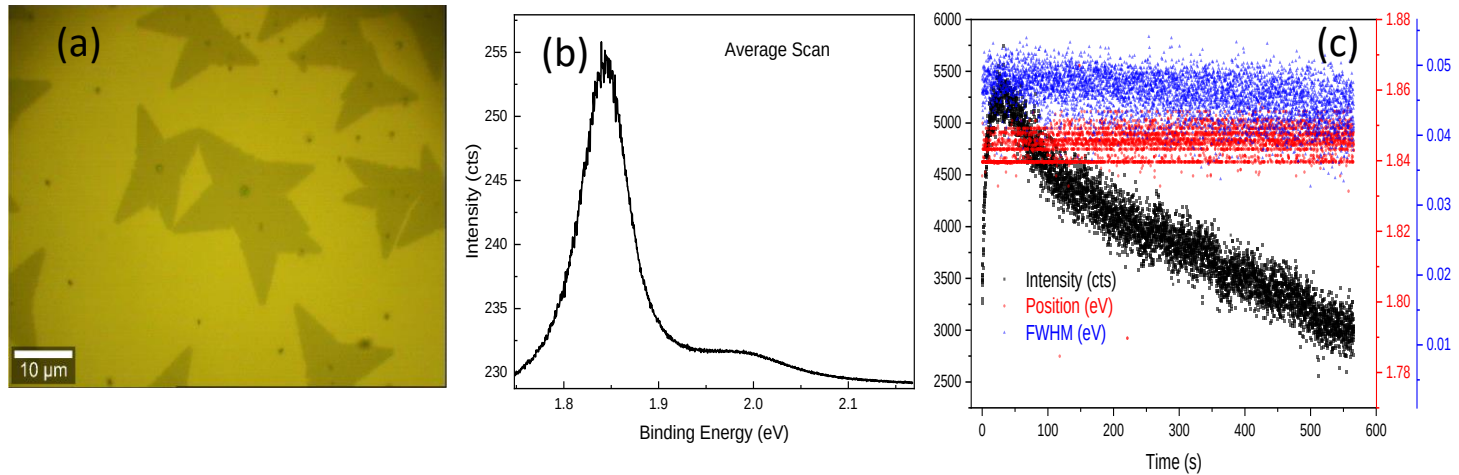


Fig. 3.9 (a) Optical image of CVD MoS_2 (b) Average PL spectrum acquired over 10 minutes (c) Overlaid plots of the PL intensity, peak position, and FWHM over 10 minutes of scanning.

The ability of PL spectroscopy to rapidly characterise MoS_2 is beneficial when using mapping spectroscopy as previously discussed for Raman spectroscopy. PL spectroscopy was found to be considerably more sensitive to local changes in the MoS_2 crystal than Raman, whereby PL mapping was shown to quickly visualise grain boundaries between MoS_2 crystals. Fig.3.10(a)-(c) present a CVD-grown monolayer film of MoS_2 , and the PL mapping data acquired across it. While optically there were no visible grain boundaries, the PL intensity map in Fig. 3.10(b) clearly revealed several, and the slight lowering of intensity at each boundary was also visible. Notably, there is also a marked increase in PL signal at the edge of the film, this is also the only region to show a clear change in peak position, this is consistent with strain effects seen at the edges of MoS_2 crystals.¹⁰²

Optical, Raman, and PL mapping data for two different MoS_2 films are portrayed Fig.3.10(d)-(f) and (g)-(i) and demonstrate the limited utility of Raman mapping to characterise the grain boundaries compared to PL. Some of the bountiful diversity in MoS_2 crystal interactions can also be seen with large regions around the GBs in Fig. 3.10(f) showing near zero PL signal, and a variety of intersections between different grains shown in Fig.3.10(i).

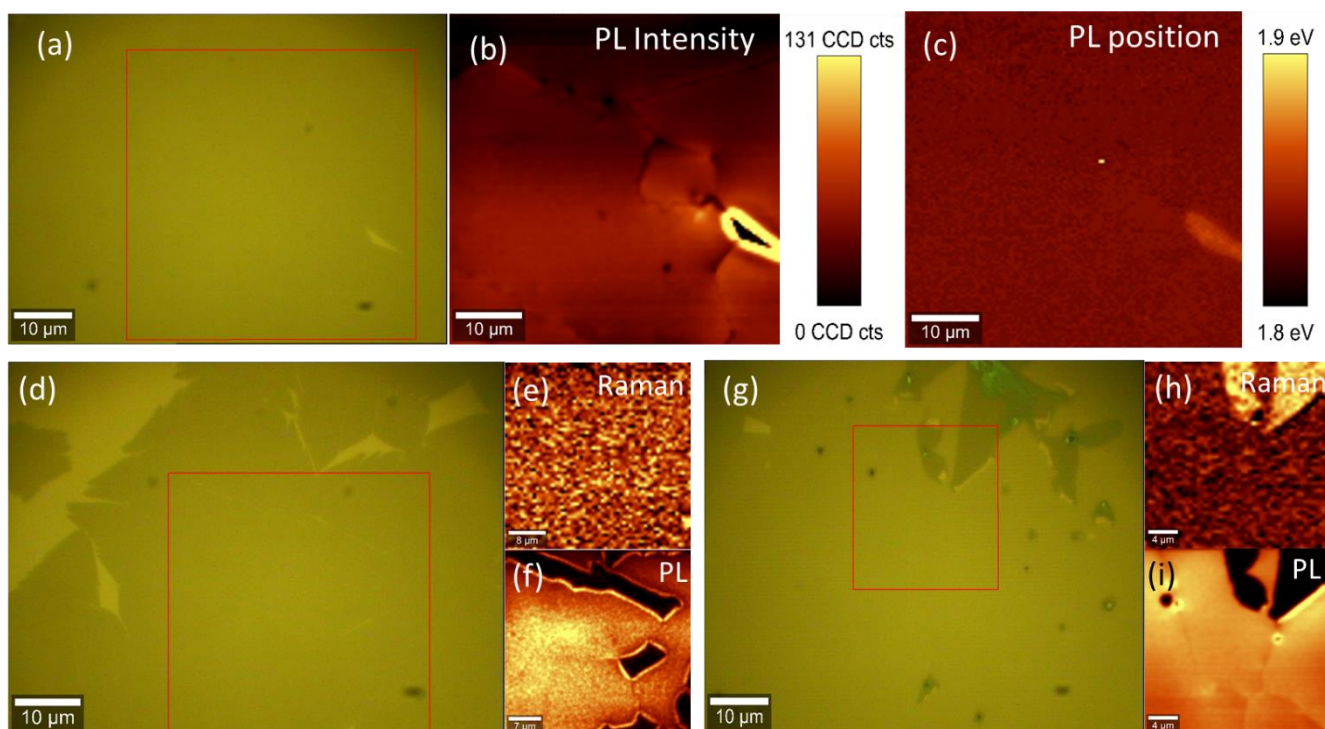


Fig. 3.10 PL maps of stitched MoS₂ films **(a)** Optical image of a stitched MoS₂ monolayer film, red box indicating the mapped area. **(b)** PL intensity map of (a). **(c)** PL peak position map of (a). **(d)** Optical image of a stitched MoS₂ monolayer film. **(e)** MoS₂ Raman peaks intensity map of area in (d). **(f)** PL intensity map of (d). **(g)** Optical image of a stitched MoS₂ monolayer film with thicker regions. **(h)** MoS₂ Raman peaks intensity map of (g). **(i)** PL intensity map of (g).

PL spectroscopy can also be used to assess the uniformity across MoS₂ crystals. An area of MoS₂ with many different crystal interactions, intersecting monolayer crystals, island-like growth on top of the monolayer, edges, etc is shown in Fig. 3.11. Optically this area bears resemblance to the region shown in Fig. 3.10(g), which was found to have a mostly uniform PL spectrum except at edges. Three PL maps were acquired over the area of Fig. 3.11(a). These three squares, labelled A, B, and C have their PL intensity maps displayed in Fig. 3.11 (b), (c), and (d) respectively. These PL maps show a lack of uniformity across the surface, with changes in intensity seen across the surface, not just bound to edge sites. While many of the previously shown PL maps of CVD MoS₂ have shown tightly constrained areas of varying intensity around defects, or edges, or grain boundaries, the regions here are much broader ~1–5 μm in width indicating a much higher diversity in crystalline properties.

The *A* region as shown in Fig.3.11(a) and (b) can be further analysed by both isolating spectra from regions of interest, and also by mapping other parameters beyond intensity. A map of the intensity of only the *B* -exciton region of the PL spectra is shown in Fig.3.11(e). This map is very similar to that of the *A* -exciton intensity in Fig. 3.11(b), with the one exception is the small bilayer region previously visible in the middle of the sample cannot be distinguished here. This is due to the *B* exciton intensity being very similar for both the monolayer and bilayer MoS₂, this map also shows a more uniform contrast over the surface. Next, analysis of the PL peak position across the mapped region in Fig.3.11(f), which shows the not uncommon shifting of the PL peak to higher energy positions at grain boundaries and at the crystal edge.¹⁰² Interestingly, ~4 μm in from the edge against the SiO₂, another parallel line of shifted PL energy is noted. Combined with the varying intensity seen previously in the intensity maps of this region, it can be hypothesised that this is a region with low crystallinity and disordered and/or defective MoS₂, leading to grain-boundary-like spectra. Mapping the PL peak width in Fig.3.11(g) it can be observed that generally the PL peak narrows along the edge regions when compared to the centre of the film.

The four points on the PL intensity map Fig.11(b), labelled 1–4 have their point spectra for PL and Raman spectroscopy displayed in Fig.11(h)–(j). Fig.11(h) shows the PL spectra from these points, and (i) shows the normalised intensity PL spectra, while (j) is the normalised Raman spectra at the four points. There are significant disparities in PL intensity, with the lowest intensity across the centre of the MoS₂ at point 1, this region also has a PL peak at ~1.83 eV which is the average energy seen for pristine MoS₂ but the lowest of the 4 points. The other 3 points have higher intensities PL but with corresponding increases in peak energies to between ~1.85–1.87 eV. The changes in the Raman spectra between the points are more subtle and are harder to discern due to Raman's lower signal when compared to PL at the same acquisition parameters. What can be determined from the Raman data is the change in the intensity ratio between the two Raman peaks, with point 3 having the highest PL intensity, PL energy, and highest Raman peak intensity disparity, these properties were often observed to occur at some edge and defect regions.

These characterisations act as examples of the frequent analysis and quality control performed on these samples to account for the diversity of the CVD MoS₂ synthesised by this method.

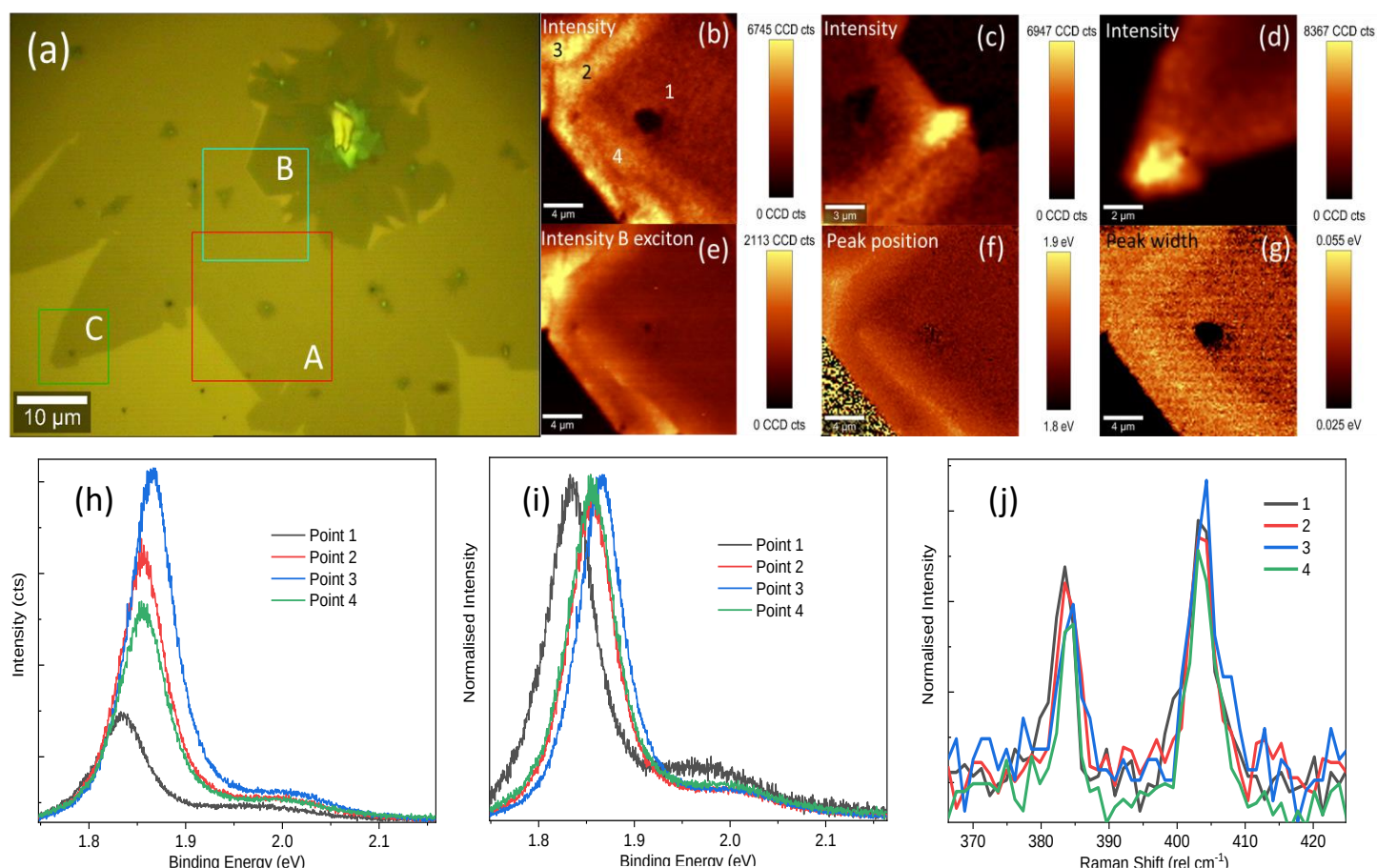


Fig. 3.11 PL spectroscopy analysis of a defective MoS₂ region **(a)** Optical image of a large stitched-together monolayer MoS₂ crystal with thicker regions. Areas A, B, C indicate areas of mapped spectroscopy. **(b)** PL intensity map of area A, with points 1,2,3,4 labelling regions point spectra were acquired from. **(c)** PL intensity map of area B. **(d)** PL intensity map of area C. **(e)** PL intensity map of the B exciton over area B. **(f)** PL peak position map of area B. **(g)** PL peak width map of area B. **(h)** PL spectra from the points highlighted in (b). **(i)** Normalised PL spectra from the points highlighted in (b). **(j)** Normalised Raman spectra from the points in (b).

3.5 XPS

XPS is one of the most powerful characterisation tools for 2D materials as it can be used to measure the chemical state of the atoms non-destructively. Due to this, XPS is a very frequently used technique across 2D-materials research. It is particularly common in synthesis works, to confirm the successful generation of the target material. As MoS₂ is the 2nd most common 2D

material in the literature, it could be anticipated that a consensus to have been reached on how to appropriately characterise and report its XPS spectra. However, this does not generally appear to be the case, with significant variations in the energy windows for spectra reported. The most commonly studied and reported XPS core-level regions for MoS₂ are the Mo 3d and S 2p. These were acquired for every sample measured as well as a C 1s for charge correction, and a survey spectrum for completeness.

The CVD MoS₂ synthesised here was examined using three separate XPS systems over the course of this work. These systems are discussed in Chapter 2, they are a non-monochromated XPS, a monochromated XPS, and a micro-XPS scanning system, each have different feature sets and advantages.

XPS spectra for CVD-MoS₂ samples acquired using all three XPS systems are shown in Fig.12. For simplicity each core-level region individually is discussed. Collected core-level spectra were rigorously and procedurally fitted according to procedures previously discussed. These spectra are presented by subtracting the fitted components from the raw measured spectra and the fitted ensemble envelope. This allows any deviations from the raw data to be seen while allowing the components and their shapes to be clear. The Mo 3d core-levels of MoS₂, are shown in Fig. 3.12(a). The spectrum was acquired across a wide region of ~223–240 eV. The reason for this is to include any likely or potential oxides or other components that may appear in the spectrum, and to ensure an adequate low signal region on both sides for background fitting. It is frequent in the literature to acquire and report only the region with the main TMD XPS component ~228–235 eV; however, not including an adequately wide spectral range can lead to incomplete conclusions or other mistakes.

This region has 3 sets of components in each of these spectra, the Mo 3d region for MoS₂ coincidentally overlaps with the S 2s region. The primary component in the spectrum is a doublet with Mo 3d _{5/2} at ~230 eV, this has a corresponding Mo 3d _{3/2} at ~233 eV as the Mo 3d has a spin-orbit splitting of 3.14 eV. This doublet corresponds to Mo⁴⁺, is attributed to MoS₂. There is also a second and more minor Mo 3d doublet corresponding to Mo⁶⁺ detected in each of these samples with Mo 3d _{5/2} at ~233 eV and Mo 3d _{3/2} ~236 eV. These were attributed to MoO₃, which is the most stable and commonly seen oxide in MoS₂. Lastly, there is a singlet peak from the S 2s at ~227 eV corresponding to MoS₂. From these representative XPS spectra it can be determined that MoO₃ is a common contaminant in the CVD MoS₂ here at levels ~15%

of all Mo atoms. It is not possible to determine if this is a by-product of the growth process or a result of the ambient exposure after synthesis.

The S 2p core-level region in Fig.3.12(b), was acquired over a range of ~158–175 eV. This allowed any oxide peaks to be detected as these could appear at any point across this range due to the many stable oxides of sulfur. For the S 2p, a simpler spectrum is observed with only one component, a doublet at ~162 eV. This corresponds to a sulfite (S^{2-}) state and this is attributed to the MoS_2 . The spin-orbit splitting of the S 2p is much narrower than the Mo 3d at 1.16 eV, and so the two peaks are discernible when the monochromated XPS systems are used. However, the non-monochromated XPS has significant overlap of the components. This can make determining the number of components more difficult and therefore increases the likelihood of inaccurate fitting of the data. The FWHM of the fitted S 2p $_{3/2}$ peak for the non-monochromated spectrum is 1.16 eV, this is ~50% wider than for the mono- and micro-XPS systems at 0.71 and 0.76 eV respectively. This same broadening of the peaks when using non-monochromated XPS was also observed for the Mo 3d, where the peaks are substantially broader than the others, with the FWHM of the MoS_2 Mo 3d $_{5/2}$ peaks for the non-mono, mono-, and micro- systems being 1.29, 0.73, and 0.78 eV respectively. The similarity in the width of these peaks with those of the MoS_2 component in the S 2p region lends credibility to this fitting model and is one of the many metrics that are important to observe critically in XPS.

The XPS spectra of the C 1s core-level and the survey region are given in Fig.3.12(c) and(d) respectively. Little attention was paid to the C 1s spectra beyond as a charge reference point. The C 1s for C-C bonds, the main peak in these spectra, was charge referenced to 284.8 eV. As discussed in Chapter 1 there are limitations to this and the correctness of this method of charge correction is contested due to its unreliability, nevertheless it is the accepted method in the literature and is applied uniformly across this work to foremost enable fairer comparison between samples.

The survey spectrum is populated by a number of peaks and components. As each element generally has several peaks in its XPS spectrum, a sample containing few elements can still provide a survey spectrum with many peaks. A survey scan is a near essential part of validating XPS results. Confirming which elements are present is important as contaminants can lead to incorrect conclusions being drawn if, for example, they have overlapping XPS core-level regions with the regions of interest. For these samples the elements present in a detectable amount are O, C, Si, Mo and S. For readability, the assignments for the peaks are given by

shading the area behind them. Not all features of these spectra are XPS core-level components, for example the peaks at ~ 1000 eV are attributed to the KLL Auger line of oxygen.

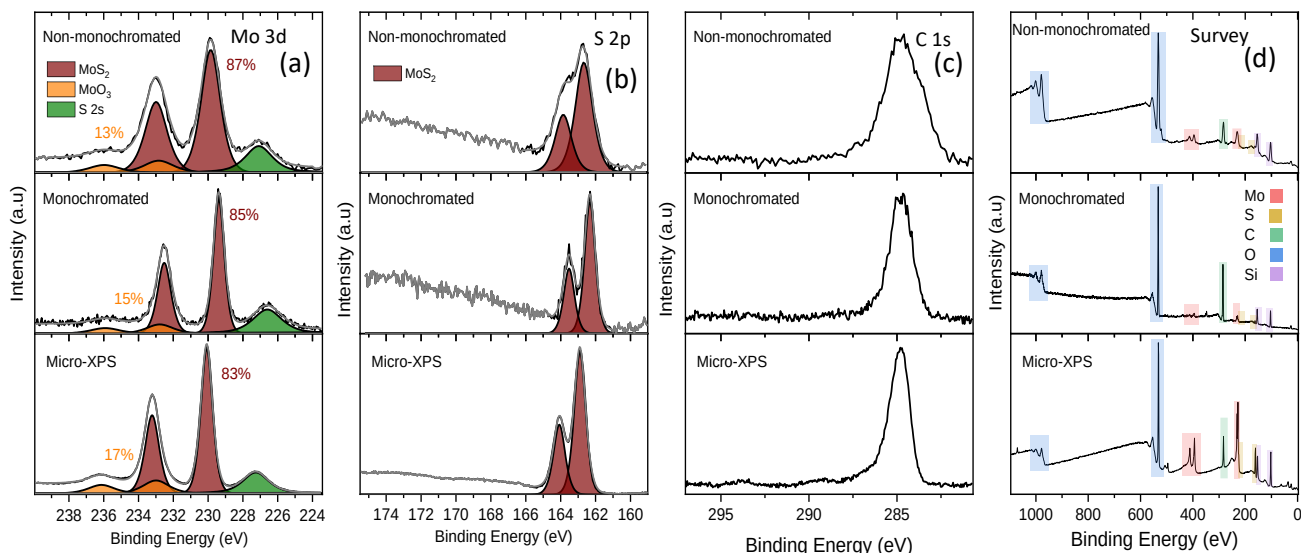


Fig. 3.12 XPS spectra of CVD MoS₂ taken using three XPS spectrometers **(a)** Mo 3d core-level **(b)** S 2p core-level **(c)** C 1s core-level **(d)** Survey region

One of the important differences in features amongst the three XPS systems used here is illustrated nicely by comparing the survey spectra. The non-monochromated, mono-, and micro-XPS systems have a scanning area of approximately 1 cm², 1 mm², and 100 μ m² for the spectra acquired here. For the first two systems, this leads to large-area averages being taken which include large amounts of bare SiO₂. The micro-XPS measures almost completely through a layer of MoS₂, resulting in a much higher amount of MoS₂ XPS signal in this survey scan. There are benefits and drawbacks to both approaches naturally, as collecting an average, or just the spectra for a specific crystal, can yield useful information.

3.6 Additional Characterisation Methods

Thus far, the use of Raman and PL in the reliable determination of monolayer MoS₂ have been discussed. Other methods such as AFM can alternatively be used to precisely determine layer

number and investigate the morphology of the MoS₂. However, correctly calibrating and post-processing AFM data can be more time and labour intensive than Raman and PL spectroscopy and so AFM was not used routinely for standardisation or quality control of this synthesis process.

Beyond solely AFM there is much potential in SPM methods to investigate the properties of CVD MoS₂. In particular for CVD MoS₂ samples, such as the ones generated in this thesis, with considerable diversity in crystals for each sample. As an example, a region of CVD MoS₂ with several different layer thicknesses was measured using standard AFM and also Kelvin probe force microscopy (KPFM), this can measure the work function of the surface using the contact potential difference between the scanning tip and the surface.

Fig. 3.13(a) and (b) show the AFM height and KPFM potential scans over the MoS₂, a region of the SiO₂ substrate can be seen in the upper right corner. The line profiles displayed on these images are shown in Fig. 3.13(c). Using this the stark contrast that KPFM can provide between the monolayer MoS₂ and the thicker bilayer region on top of it is observed. A higher potential on the monolayer MoS₂ and a sizable drop for increasing thickness is noted, consistent with the expected difference in work function due to the changing band structure of MoS₂.¹²⁵ KPFM also reveals more complex behaviour for the overlayer of MoS₂ in the lower left section of the scan. Here there is no notable change in height but a clear change in potential, likely related to some disruption in the coupling of the layer. The phase data for this map is provided in Fig. 3.13(d) this also shows the stark contrast between monolayer MoS₂ and the SiO₂ and also to the bilayer MoS₂. However, phase does not detect the divergent data for the crystal in the lower left section.

This example illustrates that while both AFM and KPFM are clearly capable of analysis of the surface morphology of MoS₂, and can distinguish different layers of MoS₂, they can also be employed to observe and investigate more complex behaviour not easily observable through other methods.

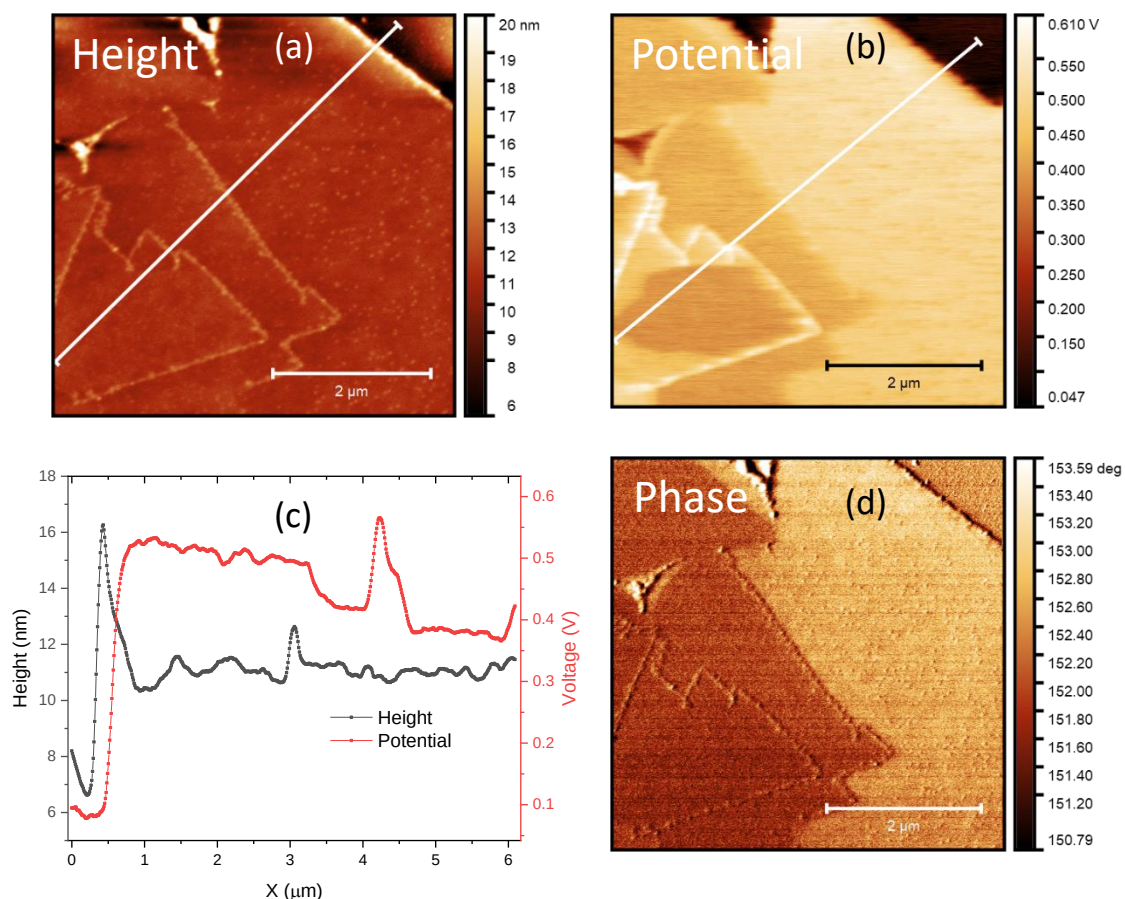


Figure. 3.13 SPM data for a CVD MoS₂ region with multiple layers **(a)** AFM amplitude map, with line profile. **(b)** KPFM surface potential scan, with line profile. **(c)** Line profiles over the AFM and KPFM scans. **(d)** KPFM phase map.

One of the other most common techniques in MoS₂ characterisation is SEM. SEM was used here as it is well suited for imaging the different crystal shapes and edges common to this CVD MoS₂ process. An SEM image of several CVD MoS₂ crystals as grown on SiO₂ is presented in Fig. 3.14. The high uniformity in contrast over the MoS₂ surface in this image further indicates the quality and consistency of the CVD MoS₂ used herein.

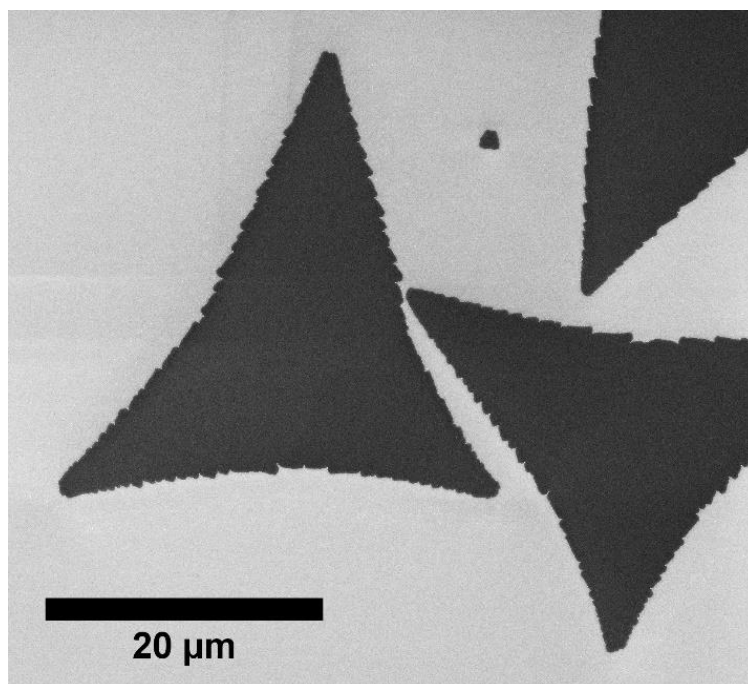


Figure. 3.14 SEM image of MoS₂ monolayers on SiO₂ using the in-lens mode.

3.7 Thermally Assisted Conversion (TAC) of MoS₂

CVD synthesis of MoS₂ was not the only method to generate MoS₂ used throughout this work. Alternatively, when high-quality monolayers of MoS₂ were not required for a particular use case, another method of MoS₂ synthesis was utilised, this and similar methods will feature prominently in later chapters.

As discussed in Chapter 1, TAC involved the direct conversion of a sputter deposited Mo film rather than vaporised MoO₃ as a Mo source. This method allowed uniform thickness films of MoS₂ to be synthesised over large areas and directly on a wide array of substrates, with the limitations being the quartz tube diameter for size and temperature compatibility for substrates.

The properties of films synthesised in this way have been examined in the literature and they were found to have small crystal grain size leading to a very high amount of grain boundaries.³⁰ Due to this low crystallinity and disordered surface, measuring the precise number of layers of MoS₂ can be difficult. For consistency, these samples are referred to by the thickness of the initial deposited Mo film which will expand after sulfurization.

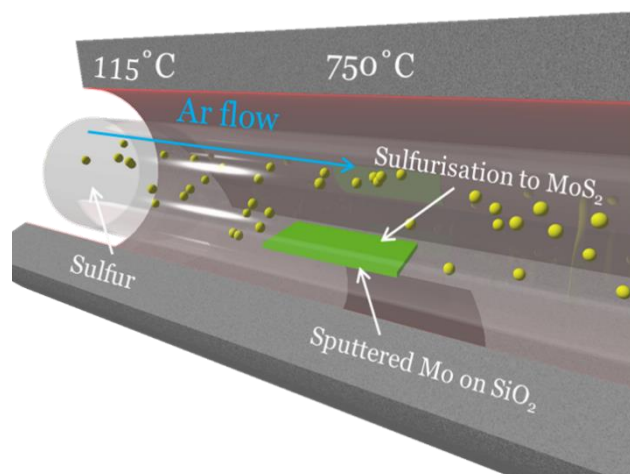


Fig. 3.15 Diagram of the TAC sulfurization process for synthesis of polycrystalline thin films of MoS₂. (courtesy of Dr. Christian Wirtz)

Three TAC films of MoS₂ (0.5, 1, 2 nm), a CVD monolayer of MoS₂, and a thick film of vacuum filtered liquid-phase exfoliated (LPE) MoS₂ produced using commercial MoS₂ powder are compared in Fig. 3.16. The LPE MoS₂ was produced and supplied by Dr J.B Boland. Optical microscopy in Fig.3.16(a) highlights the high uniformity across the TAC films. The large disparity in crystal sizes between the filtered LPE film and the CVD MoS₂ are also conveyed.

Comparing the Raman spectra from the films in Fig.3.16(b), several notable contrasts between the samples are observed. The three different thicknesses of TAC MoS₂ have significantly broader Raman peaks than CVD MoS₂ or the LPE MoS₂, indicating the expectedly lower crystallinity and lack of order in the MoS₂ prepared with this method. Further, the LPE MoS₂ peaks are much narrower, similar to the highly-crystalline CVD MoS₂, which indicates that the exfoliation process has not greatly damaged the MoS₂ itself. There is a clear difference in the separation between the different MoS₂ Raman modes across the samples, as shown in Fig. 3.16(c) with the CVD MoS₂ having the smallest gap of 21.3 cm⁻¹, while the TAC films show the expected trend of increasing Raman mode separation with film thickness of 22.8 cm⁻¹ for 0.5 nm, up to 24.3 cm⁻¹ for 2 nm. The thick film of LPE MoS₂ has the widest separation at 25.3 cm⁻¹, indicative of bulk-like MoS₂. From this it can be deduced that while TAC produces MoS₂ with poor crystallinity, it is effective at synthesising large-area few-layer MoS₂.

For very thin films of TAC MoS₂, such as the 0.5 nm sample, a PL signal indicating the formation of monolayer or few-layer MoS₂ is observed. Fig.3.16(d) compares the normalized PL spectra of the CVD monolayer and the TAC film. It is necessary to normalize the intensity as the same laser power was not used for both spectra acquisitions; regardless, TAC MoS₂ PL was consistently of much lower comparative intensity than that of high-quality CVD monolayer. The peak positions for the two spectra are 1.83 eV for CVD and 1.9 eV for TAC, this TAC peak is similar in peak energy to that occasionally seen for CVD MoS₂ at defective grain boundaries, this is consistent with the poor crystallinity being associated with the MoS₂ peak shifting to higher energies. As discussed previously, the FWHM of the PL peak and the relative intensity of the *B* exciton to *A* exciton were seen as consistent indicators of MoS₂ quality. The TAC film has a much broader PL spectrum with a FWHM of ~80 meV compared to that of CVD MoS₂ (~60 meV). The TAC film also has a substantially more intense *B* exciton compared to CVD MoS₂.

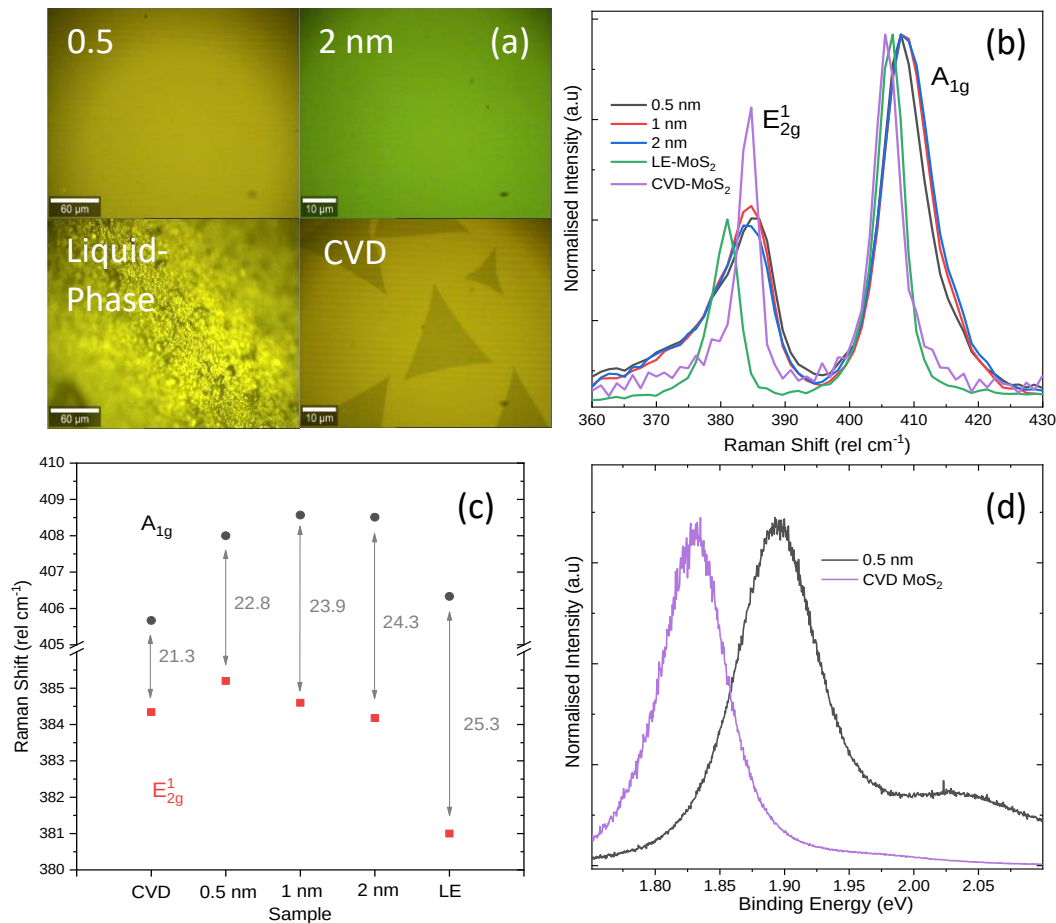


Fig. 3.16 Comparison of TAC, LE, and CVD MoS₂ (a) Optical images (b) Normalised Raman spectra. (c) Plot of the position of the MoS₂ Raman modes and their changing separation. (d) Normalised PL spectra for a 0.5 nm TAC film and from a CVD monolayer of MoS₂.

3.8 Conclusions

High-quality, largely monolayer films of MoS₂ were successfully synthesised on SiO₂ using the ‘microreactor’ CVD method outlined. It was found that there was significant variance in the MoS₂ growth across individual SiO₂ wafers and between growths, with variation in the size of MoS₂ crystals and the degree of coverage over the wafer. This may be caused by variation in MoO₃ distribution and consequently variation in the sulfur intercalation between SiO₂ wafers. This variation allows a broad swath of possible MoS₂ crystal configurations, e.g. isolated single crystal monolayers, various types of grain boundaries, stitched monolayer films, and terraced multiple-layer regions, to all be directly synthesised on electronics-compatible substrates. Given this diversity across samples, they were regularly characterised using Raman, XPS, and PL spectroscopies to confirm their quality and consistency.

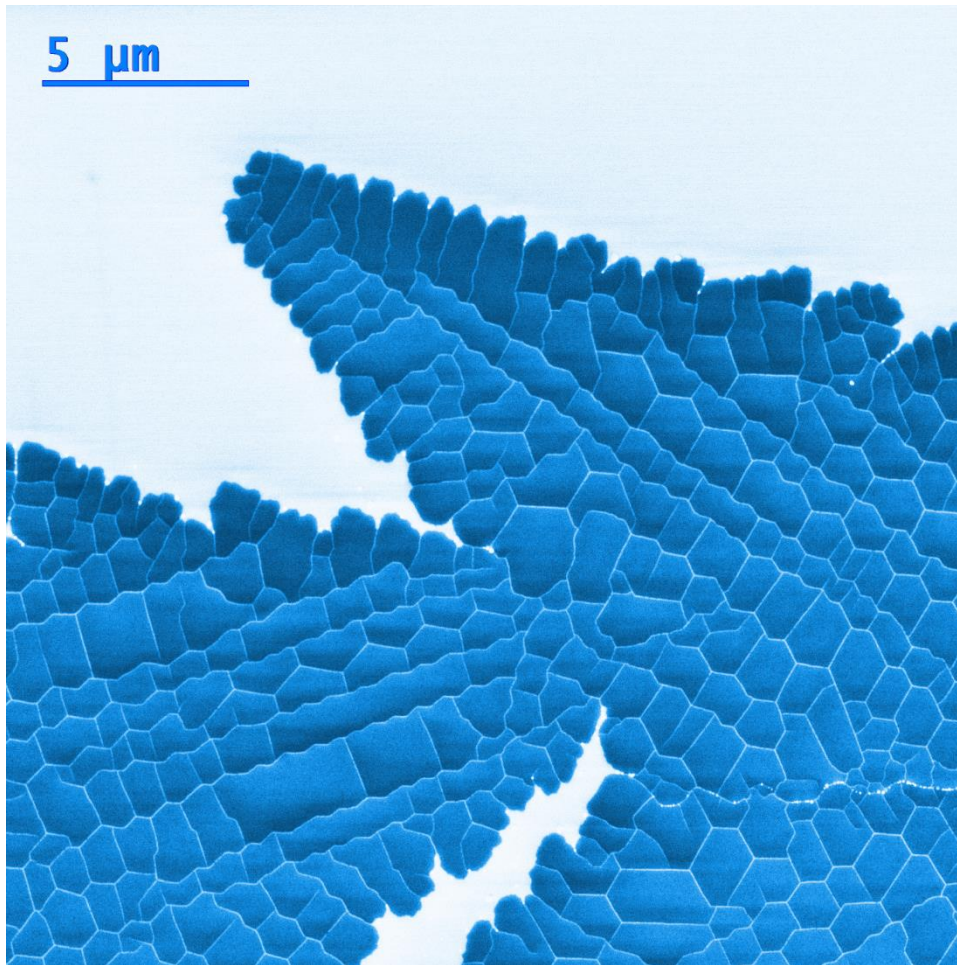
The utility of Raman spectroscopy and Raman mapping to differentiate between layers of MoS₂ was shown. Importantly by comparing a large number of monolayer and bilayer MoS₂ samples the average positions of the Raman peaks could be reliably determined, their average peak separation was found to be 20.9 and 23.4 rel cm⁻¹ respectively for CVD MoS₂ on SiO₂. The relative sensitivity of the monolayer MoS₂ Raman modes to changes in crystal environment were shown with the A_{1g} Raman mode having pronounced layer number sensitivity while the E_{2g}^1 has comparatively enhanced strain sensitivity. Raman spectroscopy was used to gauge the crystallinity of several MoS₂ samples including CVD, TAC, and an LPE film.

PL spectroscopy metrics were developed to quickly ascertain the quality of monolayer MoS₂ samples. An average CVD monolayer had a PL peak at 1.836 eV with FWHM of ~70 meV. A combination of low FWHM of the A excitation and low relative intensity of the B exciton were determined to be the most reliable indicators of PL quality. High quality samples were determined as those with <60 meV FWHM and <10% relative B exciton intensity.

The XPS measurement and fitting process for MoS₂ was discussed using spectra from three different XPS systems. A low level of MoO₃ was found to be a persistent contaminate in the CVD MoS₂ synthesised here.

Synthesis of MoS₂ by TAC was also introduced with the ability to generate large area, uniform, polycrystalline MoS₂ with the possibility for low enough layer numbers for PL emission.

4 -Effects of NH_3 Plasma Treatment on Monolayer CVD- MoS_2



“The single biggest problem in communication is the illusion that it has taken place.”

— George Bernard Shaw

4.1 Introduction

The fundamental properties and applications of pristine TMDs have increasingly been explored, methods to control and tailor these materials or their properties have grown in importance and popularity, these processes are referred to generally as functionalization. Functionalisation can be desirable to tune properties towards a specific function or application. As functionalisation is a broad umbrella term with regards to TMDs, an overview detailing the many of the common methods is supplied in Chapter 1.

Amongst these methods, plasma techniques are becoming very popular for 2D TMDs, as post-growth treatments for various purposes e.g. doping,¹²⁶ defect formation,⁵⁹ layer thinning,¹²⁷ etc. Plasma treatments are firmly established processes in industries such as semiconductor device fabrication, making it natural that they should be investigated and used to process 2D TMDs.

As MoS₂ is the preeminent TMD, it is not surprising that it is the TMD for which the effects of different plasmas have been most extensively studied. These have been shown to have a variety of effects on MoS₂. An important aspect when considering plasma treatments is that the properties of the plasma are determined by several factors, not just by the source gas. The method of generation, temperature, pressure, concentration, voltage differential, and exposure time are also among the important aspects which can have a major impact on the effect the plasma treatment has on the material. This variation in the effect the plasma treatment has on the material can be partially understood by considering the nature of the plasma as a collection of high-energy ions. Therefore, the effect they have can be summarised as a combination of both physical and chemical effects. The KE of the plasma ions, which are heavily influenced by temperature, will have a major contribution to their physical effects, with higher energies driving etching-like effects. These physical effects are also a property of the size and reactivity of the ions. Plasma treatment with ions of larger, less reactive elements such as Ar, will likely be dominated by these more physical effects. More chemically-reactive ions, for instance oxygen, are sensitive to the parameters of the plasma treatment with a diverse set of effects seen for oxygen plasmas generated in different scenarios as the relative physical or chemical activity is adjusted. For example, the effects of lower KE oxygen plasma are likely dominated by the chemical reactivity of the ions. These chemical/physical/physical and chemical effects become more complex for molecular plasmas or when a combination of gases are used. This is presented in Table 4.1, below, wherein a broad and incomplete selection of plasmas, and some of their varying effects when used to treat MoS₂, is provided.

Table. 4.1 A list of the effects of plasma treatment on MoS₂ using different gases.

Plasma	O ₂	Ar	N ₂	H ₂	Other
Effect	Form Mo oxides ¹²⁸⁻¹³⁰	Layer thinning ¹²⁷	Nitrogen substitution ¹²⁶	Formation of defects/vacancies ^{59, 131-133}	SF ₆ , CHF ₃ , CF ₄ , XeF ₂ Fluoridation. ¹³⁴ P-doping. ^{135, 136}
	Layer thinning ^{137, 138}	Phase change 2H->1T ¹³⁹	Induce strain ¹²⁶	Reduce oxides	
	Oxides as conduction channels ¹⁴⁰	Formation of defects/vacancies ⁶⁰	Work-function tuning ¹⁴¹		He Defect/ Vacancy formation. ¹⁴²
	Change contact properties ⁵⁸	Surface cleaning	P-type doping ^{126, 143}		
	Ambipolar devices ⁵⁸				

These are an example of the potential utility that many of these plasmas provide when treating MoS₂. Many of these plasmas have been shown to be extremely surface sensitive, dependent on the specifics of the experiment, with a monolayer of graphene being sufficient to prevent H₂ plasma from affecting a layer of MoS₂ below it.¹⁴⁴

To date, despite the growth in research in this area, ammonia plasma (NH₃) treatment of MoS₂ remains unexplored and is the inspiration for the work discussed in this chapter. The constituent elements in ammonia have both been studied separately for plasma treatment of MoS₂. H₂ plasma has been shown to be a reliable method to induce sulfur vacancies in MoS₂ by reducing the surface.⁵⁹ Separately, the effects of nitrogen plasma on MoS₂ were found to result in substitutional doping of nitrogen into the MoS₂ lattice by replacing sulfur.¹²⁶ Ammonia itself has been shown to dissociate into a variety of species when in plasma form. For NH₃ plasma, the ion composition is shown to vary significantly for different experimental parameters.¹⁴⁵⁻¹⁴⁹ Without direct measurement it is not possible to know the constituent ions formed in a NH₃ plasma or their relative proportions, which are both potentially subject to multiple experimental factors such as generator power, pressure, and generator type. It is likely that such a plasma

contains several species of N-H radicals such as NH_2^+ , NH^{++} , atomic nitrogen, and importantly H^+ .¹⁴⁵⁻¹⁴⁹

While some of the effects of the related plasmas of H_2 and N_2 have been explored, such as vacancy creation and nitrogen doping of MoS_2 respectively, their relative combination in NH_3 plasma introduces complexity. The crystal quality of MoS_2 being subjected to plasma treated is also likely to be an important factor given the roles defects, edges, and grain boundaries play in MoS_2 stability, and the layer dependency of MoS_2 properties.^{54, 150, 151} Direct treatment of MoS_2 with NH_3 gas has been investigated and found to show no reaction below 696 °C, above this temperature conversion to Mo_5N_6 was observed.¹⁵²

Functionalisation of MoS_2 via nitrogen doping has become a topic of interest in recent years with several works being published on the potential applications for catalysis,⁸¹ energy storage,^{79, 80, 153} electrochemistry,⁷⁷ and transistor doping.¹²⁶ The most common method reported in the literature for verifying nitrogen doping of 2D MoS_2 is through XPS analysis, which is frequently relied on as the sole method for measurement and verification of doping.¹²⁶

Chapter 1 section 2.1.3. details that there is a pervasive issue across a significant section of the nitrogen-doped- MoS_2 literature regarding this XPS analysis, with the majority of works containing critical XPS fitting errors. These errors are mostly related to mistaking all or part of a Mo-oxide XPS component, in the uncommonly studied Mo 3p orbital, as being a N-Mo component from the N 1s orbital. These errors jeopardise any quantitative measurement of the nitrogen doping of MoS_2 and may result in oxidation results being confused for nitrogen doping.

While high-quality fitted XPS characterisation of substitutional nitrogen doping into the MoS_2 lattice does exist in the literature,¹²⁶ the measured material is in a pristine state with no contamination from commonly encountered oxides or organic species. This unfortunately is not particularly applicable to application-focused research, of which a considerable amount of 2D MoS_2 research is dedicated. In contrast, the applications-focused nature of the literature likely contributes to a lower emphasis being given to the reliable characterisation of the starting material and the proposed doping experiments.

In this chapter, high-quality CVD-synthesised mostly monolayer MoS_2 with NH_3 plasma using a remote-plasma system for various exposure times is discussed. These films were then characterised thoroughly using a variety of methods including PL, Raman and XPS analysis. The changes in the morphology of the films were also analysed using both AFM and SEM.

4.2 Synthesis of CVD MoS₂

MoS₂ was synthesised on SiO₂ substrates through the CVD-like process described in Chapter 3. In Chapter 3, this process resulted in a large amount of MoS₂ crystals across the substrate, these vary in size, shape, and thickness. There was also a considerable amount of film formation with many individual crystals growing into each other forming large mostly monolayer films up to mm.²

The majority of the synthesised MoS₂ is formed as either isolated monolayers or as part of these extended films. As it is well known that defects are the most reactive sites in MoS₂ crystals,^{150, 151, 154} maintaining relatively consistent quality of the samples being used was important.

The natural variability in the CVD process used here, where samples show substantial variability run-to-run, necessitated that a quality metric be established to ensure MoS₂ of similar quality was used consistently throughout. PL spectroscopy was used as a time efficient and reliable method to analyse all of the samples to ensure homogeneity. Accordingly, CVD MoS₂ samples were only used for further analysis if they contained an adequate amount of monolayer MoS₂ and produced high-quality PL.

These high-quality PL monolayers of MoS₂ typically displayed intense PL with an *A* exciton peak at ~1.83 eV with a FWHM of ~50-60 meV. This PL signal is similar to high-quality exfoliated MoS₂¹⁶ and so this threshold was used to ensure relatively high-quality MoS₂ was used.

4.3 NH₃ plasma treatment of MoS₂

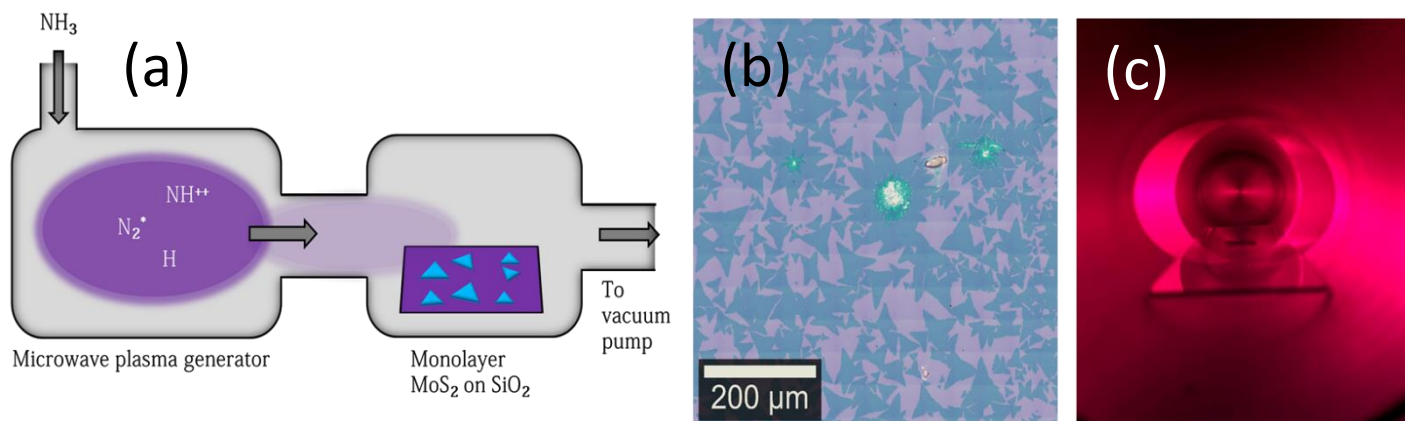


Figure. 4.1 (a) Schematic illustration of the NH₃ plasma treatment process used here. (b) Optical microscope image of the pristine CVD MoS₂ surface on SiO₂. (c) Photograph through a glass window of the NH₃ plasma treatment of MoS₂ in progress with the characteristic pink glow of NH₃ plasma.

For this study, a 1000 W microwave plasma generator fitted onto a custom quartz-tube furnace apparatus was utilised. MoS₂ samples were placed approximately 15 cm from the outlet of the plasma system, allowing some cooling to occur, reducing the high kinetic energy of the generated ions while maintaining the high chemical potential of the reactive species. An important step as it is well known that direct plasma treatments and ion bombardment can cause damage to the surface.¹²⁹ A representative diagram of the experimental set up is shown in Fig. 4.1(a). In this study this lower kinetic energy plasma is referred to as remote plasma, in reference to the distance travelled by the ions. The ions are also not accelerated towards the substrate nor is the flux so high that they are ablative.

The MoS₂ samples were treated with NH₃ plasma at a pressure of ~2.5 mbar for a variety of exposure times. The change in properties of the MoS₂ after plasma treatment was characterised using a variety of spectroscopies and microscopies. There are several benefits using CVD MoS₂ as the material here, *i.e.* it produces both a high-quality material and also a high monolayer content which yields PL. However, there are also drawbacks including the reproducibility of samples, crystal defects, and domain edges. Characterisation of ~1 nm thick crystals with lateral dimensions on the order of 100 μm has its own limitations and difficulties, and so the choice of suitable characterisation techniques is of utmost importance.

4.4 XPS

Micro-XPS is used throughout this chapter to analyse the changing chemical composition of the MoS₂ with NH₃ plasma time. Micro-XPS is particularly suited here as it has the ability to gather spectra from individual MoS₂ crystals. Generically, XPS systems gather spectra across an area on the order of mm². This larger area, bundled approach averages out results to obtain an overall characteristic spectrum, however, it ordinarily does not allow one to discriminate between individual 2D crystallites or different layers of a material due to the comparatively large X-ray spot size. Layer number is a core determinant of the properties of MoS₂, and as such is a very useful feature of micro-XPS. Numerous samples were tested using a variety of XPS equipment over the course of this study, the data presented in this chapter only reports data taken from a micro-XPS system. Monolayer MoS₂ was primarily of interest and while the XPS spot size of this system is capable of measuring $\sim 10\mu\text{m}^2$, the system tools for defining measurement regions are less capable of differentiating between MoS₂ crystals at this resolution.

The Phi-Omicron technology known as secondary X-ray imaging (SXI) is used to observe the surface on the scale of 100s of μm . As discussed in Chapter 2, this is a secondary electron measurement tool similar to SEM. The SXI images for three CVD MoS₂ samples with different NH₃ plasma exposure times is presented in Fig. 4.2. The pristine sample shows a high contrast with the underlying SiO₂ being white and the likely monolayer MoS₂ triangles appearing dark. The high contrast makes placing the measurement spot of $100\mu\text{m}^2$ on an area with a large monolayer MoS₂ contribution possible. A similar area but for a sample after 60 s of exposure to NH₃ plasma, is shown in Fig. 4.2(b). The contrast is noticeably lower here, making determination of the MoS₂ regions more difficult, however the regions of interest are discernible. It should be noted that there are a number of dark spots in all of the SXI images displayed. These dark spots are inherent instrumental artefacts and not surface features. Which add to the difficulty interpreting the images. A region of the sample which contains a large amount of MoS₂ after 180 s of NH₃ plasma, is shown in Fig. 4.2(c). The contrast observed in Fig. 4.2(c) between MoS₂ and SiO₂ is very low, if not imperceivable, particularly when considering the tool-related dark spots. Resulting in a more error-prone process when finding

a suitable region of MoS₂. However, thicker regions on the surface, such as in the top-left corner of Fig. 4.2(c), are still visible and can be avoided. Within these limitations, the 100 μm^2 spot size for these experiments was centred on a region of likely monolayer MoS₂.

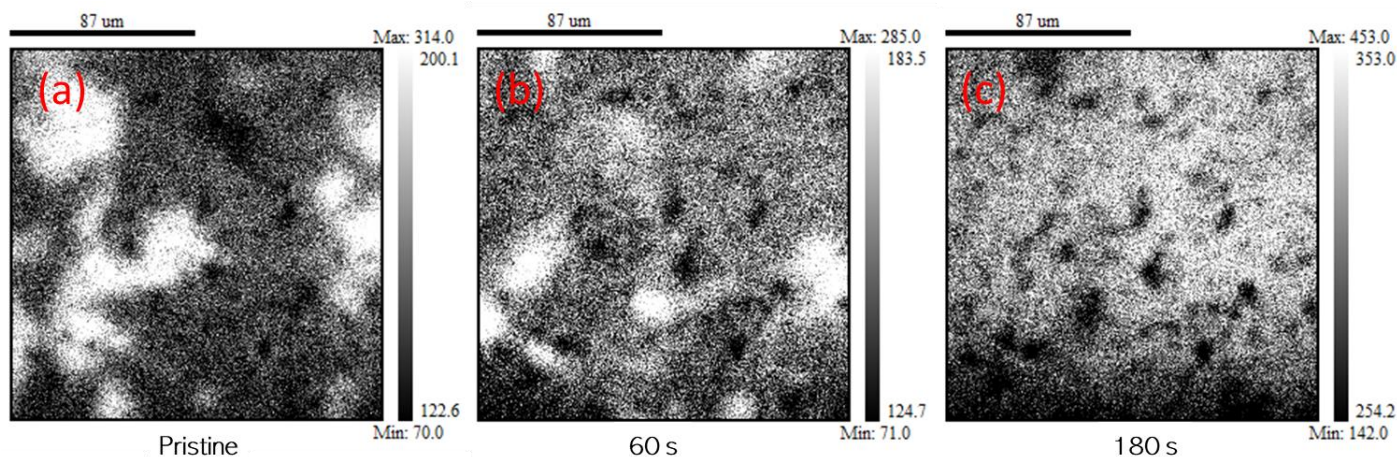


Figure. 4.2 Scanning X-ray imaging (SXI) images taken of the NH₃ plasma treated MoS₂ when determining 100 μm^2 regions for XPS measurement; **(a)** Pristine **(b)** 60 s plasma. **(c)** 180 s plasma.

Due to equipment availability and resource issues, samples were fabricated and plasma treated in Dublin before being transported in semi-ambient conditions over ~ 7 days to Munich where they were characterised with XPS. The degradation and/or stability of these samples before and after transportation will be discussed in a later section with a wider scope of characterisation.

The XPS spectra for 7 MoS₂ samples, treated with various NH₃ plasma exposure times, are shown in Fig. 4.3. The typical characteristic XPS core-level regions for MoS₂ are the Mo 3d (~ 230 eV) and the S 2p (~ 163 eV). Nitrogen is characterised in XPS by the N 1s (~ 400 eV), a complicating factor here is the coincidentally overlapping Mo 3p region (~ 395 eV). All spectra taken are gathered alongside a wide energy survey scan, an O 1s, and a C 1s core-level scan. The energy of the peaks is charge referenced to the position of the C 1s sp³ carbon peak at 284.8 eV. The characterisation of the three core-level regions for the untreated MoS₂ will first be briefly discussed before discussing the gradual changes as a result of NH₃ plasma treatment.

The Mo 3d region for pristine MoS₂ as shown in Fig. 4.3(a) displayed the characteristic line shape for MoS₂ with three main sets of components, the S 2s single peak at ~ 227 eV, the MoS₂ (Mo⁴⁺) doublet with Mo 3d_{5/2} at ~ 230 eV and spin-orbit splitting of 3.14 eV, and lastly the

MoO₃ (Mo⁶⁺) Mo 3d doublet with the 5/2 component at ~233 eV. This particular untreated sample had an extra, abnormal Mo 3d doublet with a 5/2 component at ~229.5 eV. This uncommon feature was attributed to defective MoS₂^{113, 155} likely formed *via* ambient degradation during transportation. It is not present in any of the other MoS₂ samples measured in this series or during the course of this study. The S 2p core-level region showed the typical single doublet state with S 2p_{3/2} at ~162.5 eV and a spin-orbit splitting of 1.18 eV.

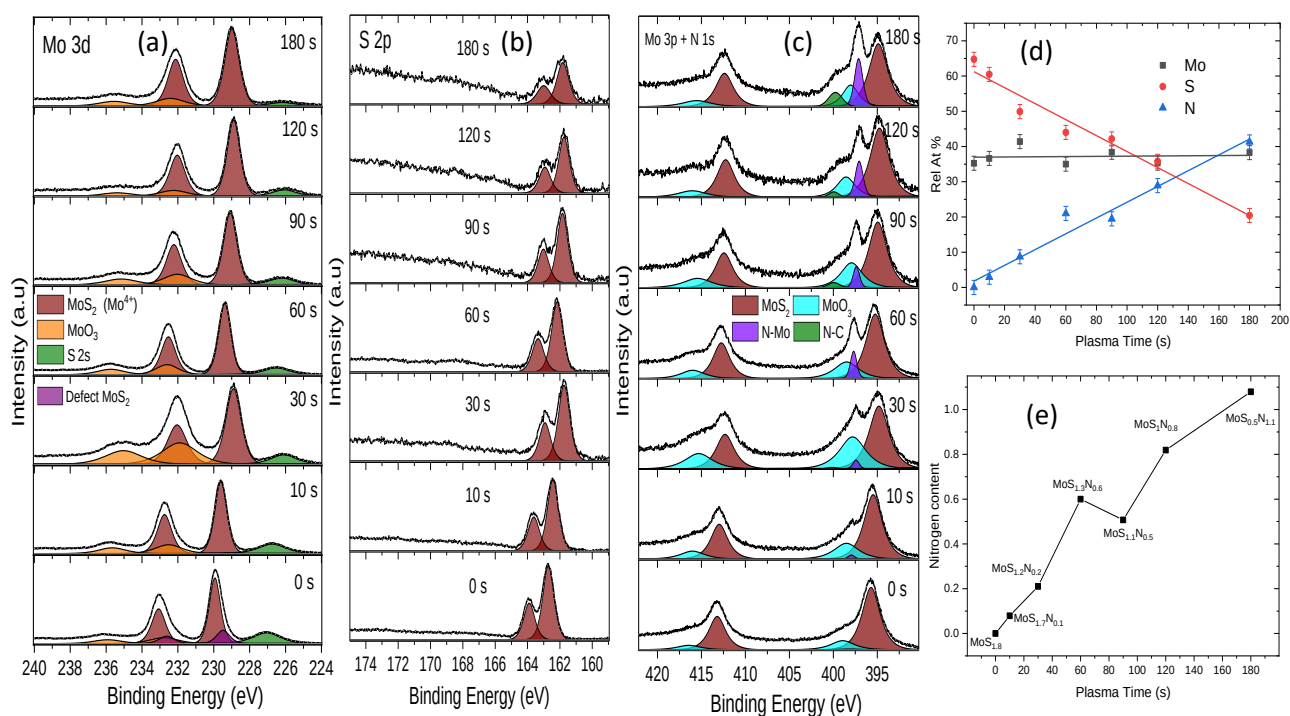


Figure 4.3 XPS core-level spectra for 7 MoS₂ samples after NH₃ plasma treatment, with three regions shown, (a) Mo 3d, (b) S 2p, and (c) Mo 3p + N 1s. (d) Graph of the relative atomic percentages of the doped MoS₂ components with plasma treatment time. (e) Changing stoichiometry of the N-doped MoS₂ with plasma time.

The Mo 3p and N 1s core-level region showed 2 sets of doublets for non-plasma treated MoS₂. The primary doublet attributed to MoS₂ has the Mo 3p_{3/2} component at ~396 eV with a large spin-orbit splitting of 17.5 eV. This large splitting often results in only the region around the 3/2 component being acquired in the literature. Due to the overlap in energy regions between the N 1s and the Mo 3p, it is essential that the entire range (390–423 eV) is measured to ensure a more accurate component analysis, this has frequently been omitted in literature.^{77, 79, 81, 141, 143, 153, 156-160} This oversight in literature has resulted in incorrect and misleading XPS fitting which has had a major impact on the conclusions in several of these works. It can be deduced

that the shoulder seen at ~399 eV is a Mo 3p component and not N 1s as it has a corresponding Mo 3p_{1/2} component at ~417 eV, this was attributed to MoO₃. All three core-level regions change with increasing exposure to NH₃ plasma, with a maximum duration of 180 s are shown in Fig.4.3.

Turning to the series of data for the Mo 3d region, this region showed a gradual broadening of the MoS₂ (Mo⁴⁺) component, with an increase in FWHM from 0.74 – 0.91 eV (shown in Fig. A5(b)) indicating increasing bond diversity. The MoO₃ (Mo⁶⁺) component did not show a significant trend, with a relatively consistent level of ~20% MoO₃ of the measured Mo atoms. An exception to this was the 30 s NH₃ plasma sample which had 40% MoO₃. Samples with NH₃ plasma treatment time around 30 s were observed to degrade more rapidly than those with longer treatment times, this will be discussed further at a later point.

Besides the Mo 3d, the other prominent XPS feature in this binding energy range is the S 2s, this component can be seen to noticeably reduce in intensity with increasing plasma time. This indicates a considerable reduction in the amount of sulfur in the material relative to molybdenum.

The S 2p region in Fig. 4.3(b) showed a commensurate reduction in intensity with no distinct new components appearing with increasing plasma time, a broad feature at ~168 eV could indicate a very low level of S⁶⁺ potentially from sulfite.

The most significant changes are seen in the combined Mo 3p + N 1s core-level region. Very quickly a new narrow component is observed at ~398 eV, which gradually increased with plasma treatment time. As there is no corresponding component in the Mo 3p_{1/2} region, this new feature must be a N 1s component. The relatively low binding energy of the peak is characteristic of N bound to a less electronegative element such as Mo. Alongside this, the energy position of the peak is consistent with literature values for a N-Mo bond,¹²⁶ thus suggesting that NH₃ plasma treatment is a suitable method to nitrogen dope MoS₂.

The Mo 3p MoO₃ component with Mo 3p_{3/2} at ~399 eV overlapped heavily with the other components of interest. The overlap could potentially cause confusion and ambiguity in terms of peak fitting unless the second half of the doublet is also acquired. Further, the overlap is an example as to why it is imperative to include both regions in the XPS measurement as excluding this would leave room for significant error. The Mo 3p MoO₃ mirrored the Mo 3d MoO₃ well, providing validity to the fitting model, as observed particularly for the 30 s sample with increased signal in both core-levels.

From 90 s of plasma treatment onwards, a second N 1s component appears at ~ 400 eV, this was attributed to nitrogen in an organic molecule. The origin of this was likely from a reaction of the plasma with the surface adsorbed carbon species incidentally present on these samples. This component also illustrated the significant energy shift for the N-Mo component compared to the N-C peaks.

The relatively narrow peak width of the N-Mo component indicated that it is in a highly ordered, likely crystalline, environment. A further confirmation of the hypothesis of nitrogen doping into MoS₂. To maintain qualitative consistency, a corresponding Mo-N bond in both the Mo 3d and Mo 3p core-level regions should also be observed. The presence of these components combined with the increasing bond diversity in the MoS₂ is the cause of the increased FWHM of the Mo 3d Mo⁴⁺ component. Setting specific fitting constraints, and assuming a ratio of N:Mo of 2:1, it is possible to include these Mo-N components into the spectrum. However, this method to include these components involved an excess of informed speculation. Instead, for a more accurate approach the widening component as transitioning from MoS₂ (Mo⁴⁺) to Mo⁴⁺ was assigned, and it was stated that they gradually become mixtures of Mo-S and Mo-N components. The splitting of these sub-components in the Mo 3d appears to be no greater than 0.4 eV.

It is noteworthy that the 30s plasma-treated sample was the only sample to show an increased level of MoO₃ compared to pristine MoS₂ even when all of the samples were transported and stored in identical conditions. This not only showed that this process does not oxidise the MoS₂, it indicated that the nitrogen doped MoS₂ has significant stability in semi-ambient conditions.

Increasing plasma time resulted in a gradual shift in the peak position of all of the MoS₂ components relative to the C 1s peak. The shift was indicative of a p-type doping effect, which had been previously observed for nitrogen doped MoS₂¹²⁶.

One of the most valuable aspects of XPS is the ability to compare the relative areas of different spectral components to calculate their quantities in the sample. By using this the changing stoichiometry of the measured monolayer MoS₂ crystals was monitored. The relative percentages of the MoS₂ components in the Mo 3d, S 2p, and the N-Mo component in the N 1s are shown in Fig. 4.3(d) These calculations gave a starting stoichiometry for pristine MoS₂ of MoS_{1.8}, CVD MoS₂ is frequently seen to be slightly sub-stoichiometric due to its many crystal edges, grain boundaries, and defects.^{10, 11, 46, 47, 108, 161} This, combined with the deterioration from substantial time in ambient conditions, alongside any errors in the fitting process, account

for the variance from perfect MoS₂. The trend line in Fig.4.3(d) displayed that with a relatively unchanging amount of Mo there was a significant reduction in sulfur with a corresponding increase in nitrogen in the MoS₂.

It is clear from Fig. 4.3 that the main outcome of the reaction between NH₃ plasma and MoS₂ was the gradual substitutional replacement of S atoms with N atoms in the MoS₂ lattice. The gradual increase in nitrogen atoms went to 41% of the MoS₂ crystal atoms for the 180 s sample. This high level of nitrogen goes far beyond traditional doping and shows that NH₃ plasma is an efficient means to create molybdenum-sulfur-nitrogen alloys. The changing stoichiometry of the monolayer crystals is shown in Fig. 4.3(e), with a clear progression in nitrogen alloying up to MoS_{0.5}N_{1.1}. NH₃ plasma is demonstrated here to be a fast method to introduce N into the MoS₂ lattice with several percent of the lattice's atoms being nitrogen after 10s, and the majority being so after ~3 minutes. This high level of nitrogen-sulfur substitution after a short time may make this process too rapid for very low-level doping traditionally seen in electronics applications. XPS is not ideally suited for analysing the low levels of doping common in classic semiconductor doping such as for silicon wafers, having ~1% of atoms sensitivity depending on factors such as the relative sensitivity of each element.

4.5 Raman

Once the gradual doping of nitrogen substitutionally into the MoS₂ lattice was confirmed by XPS, Raman spectroscopy was employed. to characterise MoS₂ to observe changes to crystalline properties.

Raman spectroscopy is one of the most universal techniques used for characterisation of 2D materials and MoS₂ in particular, it allows reliable measurement of the Raman modes of even monolayer crystals and has been heavily studied enabling layer thickness¹⁶², defect states^{97, 113}, crystallinity³⁰, doping^{97, 113, 163}, and strain^{100-103, 164} to all be frequently measured or indicated by changes in the Raman spectra alone.

The Raman spectrum of pristine monolayer CVD MoS₂ is discussed in Chapter3 and will be briefly recapped in this chapter. MoS₂ has three main characteristic peaks in the Raman spectrum when using 532 nm excitation. These are the E_{2g}^1 (~385 cm⁻¹), A_{1g} (~405cm⁻¹) and a

broad convoluted mode referred to as the $2LA(M)$ ($\sim 450\text{ cm}^{-1}$) these are routinely used to characterise MoS_2 .

The Raman spectra for individual monolayer MoS_2 crystals with different doses of NH_3 plasma is presented Fig. 4.4(a). After plasma treatment a number of significant changes are noticed. Namely, a reduction in the intensity of the MoS_2 modes, broadening of the components, and an increase in separation of the MoS_2 characteristic peaks. Further plasma resulted in the gradual complete loss of the typical Raman modes of MoS_2 . These changes occurred in conjunction with the formation of a minimum of three new features after plasma treatment. These three new features include a narrow component at Raman shifts just above the $2LA(M)$ mode of MoS_2 at $\sim 470\text{ cm}^{-1}$, as well as two broad features. The first between $\sim 250\text{--}270\text{ cm}^{-1}$ attributed to the $LA(M)$ mode of MoS_2 and the second mode at $\sim 350\text{ cm}^{-1}$ is currently unassigned. The Raman spectra showed that the high levels of nitrogenation of the MoS_2 achieved with NH_3 plasma caused a complete loss of the MoS_2 Raman modes in the monolayers. The preferential widening of the in-plane E_{2g}^1 mode over the out-of-plane A_{1g} mode, and the increasing contribution from the $LA(M)$, have previously been observed for ion-irradiated monolayer MoS_2 ⁹⁶, indicating that the MoS_2 structure is substantially damaged/alterd.

The Raman spectra of bilayer MoS_2 behaved markedly different. The Raman of regions of bilayer MoS_2 after plasma treatment, Fig. 4.4(b), showed that NH_3 plasma caused an initial splitting of the E_{2g}^1 Raman mode into two distinct modes, which also approximately halved the intensity, indicating one peak from each layer of MoS_2 . This behaviour has also been shown for bilayer MoS_2 with applied uniaxial strain of $>0.6\%$.¹⁶⁴ Progressively longer NH_3 plasma doses resulted in the appearance of the three new features for monolayer MoS_2 , the broad peaks at ~ 270 and 350 along with the peak at $\sim 470\text{ cm}^{-1}$. Unlike monolayer MoS_2 , alongside these new components there is still substantial Raman signal from MoS_2 , the intensity was greatly reduced but there was no significant broadening or complexity added to the MoS_2 peak shapes. The reduction in intensity of the MoS_2 peaks resulted in peak intensities similar to pristine monolayer MoS_2 .

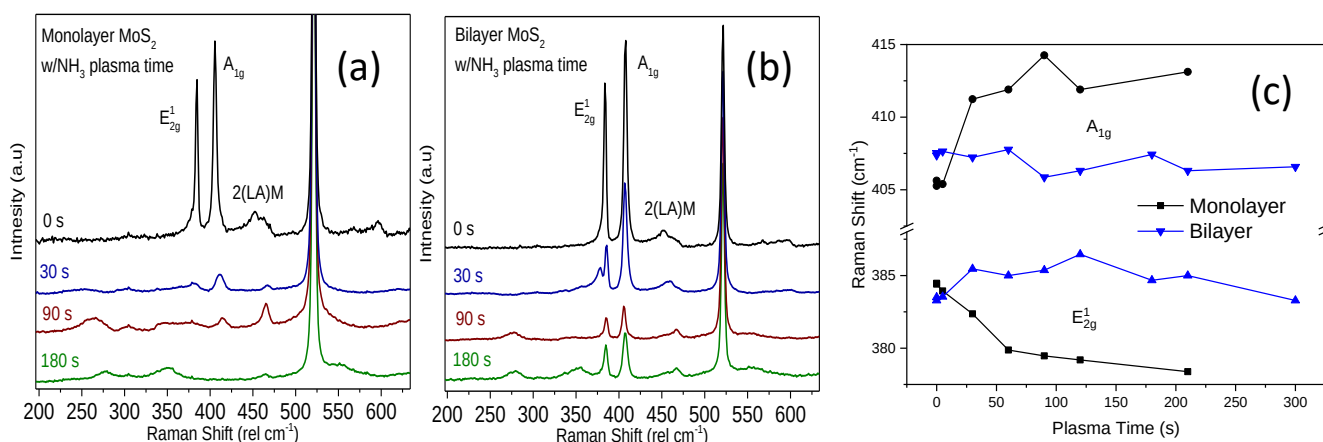


Fig. 4.4 Raman spectra of NH₃ plasma treated MoS₂ (a) Monolayer MoS₂ (b) Bilayer MoS₂ (c) Graph of the changing positions of the MoS₂ A_{1g} and E_{2g}¹ Raman modes for monolayer and bilayer MoS₂ with plasma treatment time.

The position of the centre of the peak for the A_{1g} and E_{2g}¹ modes of several monolayer and bilayer MoS₂ samples after different plasma doses is shown in Fig. 4.4(c). High uniformity was seen in the position of the peaks for pristine MoS₂ with monolayer MoS₂ having A_{1g} and E_{2g}¹ peaks at 405.5 and 384.4 cm⁻¹, and bilayer having these peaks at 407.5 and 383.4 cm⁻¹. This graph showed that NH₃ plasma treatment caused the monolayer Raman peaks to diverge quickly alongside the steady reduction in intensity seen in Fig. 4.4(a). Importantly, peak separation of the bilayer MoS₂ Raman peaks narrows substantially was also observed, even for very high plasma treatment times. The separation of the MoS₂ Raman modes is frequently used as a metric for determining layer number, with the bilayer MoS₂ displaying peak separations much more like monolayer than bilayer MoS₂ after plasma treatment. These results, coupled with the monolayer-like intensity seen in Fig. 4.4(b), indicates that the NH₃ plasma process is extremely surface sensitive, with only the top layer of MoS₂ being affected by the plasma. The bottom layer now emits Raman signal highly characteristic of monolayer MoS₂, suggesting complete decoupling of the layers vibrationally.

Low-frequency Raman spectroscopy can be used as a more reliable metric to determine layer number of TMDs than the traditional method of main Raman peak position or the separation of the peaks. The Raman peak separation as previously discussed can be affected by other factors

such as substrate⁹³, strain¹⁰⁰, doping⁹⁷ etc. While monolayers of MoS₂ do not have low-frequency Raman modes, bilayers do have such modes due to their symmetry and interlayer interactions. The Raman spectra for 7 separate samples treated for various times with NH₃ plasma, are shown in Fig. 5.5(a) and(b) and are consistent with those of Fig. 4.4. Gradual loss of MoS₂ Raman for the monolayer and formation of 2–3 new modes was observed. The bilayer Raman likewise is consistent and showed Raman features with these new plasma-induced components but also monolayer-like MoS₂ signal. The corresponding low-frequency Raman data for these samples is shown in. Fig. 4.5(c). The shear (SM) and layer breathing (LBM) modes for bilayer MoS₂ were distinct for the pristine and 10 s samples but beyond this dosage of plasma the low-frequency modes are lost. Further confirming the decoupling of the two layers, into a bottom layer of pristine monolayer-like MoS₂ and a top layer of heavily nitrogen-doped MoS₂.

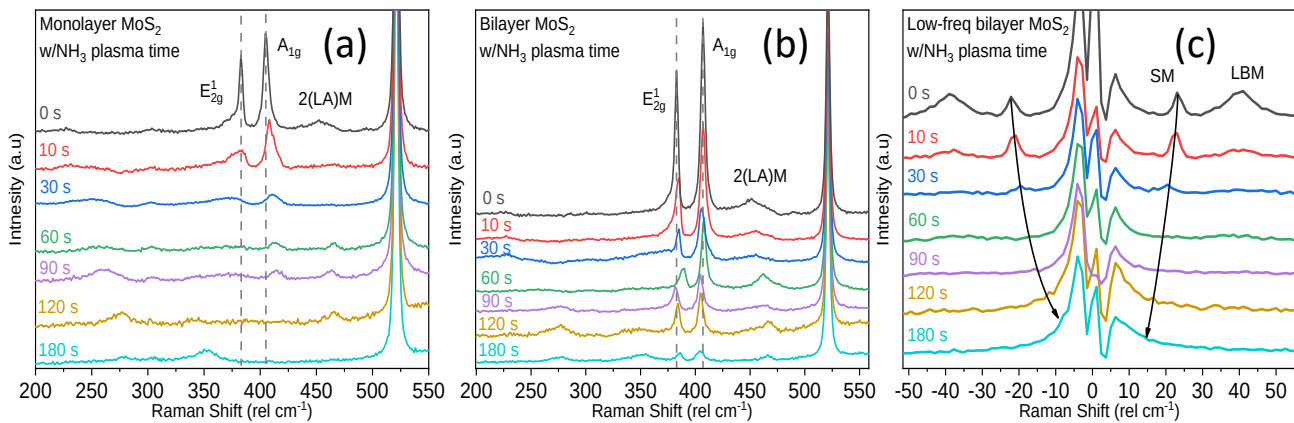


Figure. 4.5 Raman spectra of 7 MoS₂ samples after NH₃ plasma treatment **(a)** Monolayer MoS₂ **(b)** Bilayer MoS₂ **(c)** Low-frequency Raman signals from bilayer MoS₂ after NH₃ plasma showing the loss of interlayer vibrations.

Extending this process to include 3-layer MoS₂, and using longer plasma treatment times, the extent of the monolayer surface sensitivity of this process can be seen and is shown in Fig. 4.6. Monolayer MoS₂ showed the now expected behaviour up to 300 s of NH₃ plasma with complete loss of the MoS₂ Raman modes for this time. Bilayer MoS₂ also showed results consistent with the previous discussions.

3-layer MoS₂ showed a significant drop in intensity of the MoS₂ Raman modes after 120 s of NH₃ plasma with indications of the nitrogen-doped MoS₂ Raman signal at 470 cm⁻¹. After 300 s the MoS₂ Raman intensity was further decreased and the peak separation narrows, there was

also more easily distinguishable N-MoS₂ feature such as the peak at ~ 470 cm⁻¹. The low-frequency Raman showed a softening and shifting of the modes after 120 s and a complete loss of low-frequency Raman modes for 3-layer MoS₂ after 300s of NH₃ plasma. From this it can be deduced that while the process is extremely surface sensitive, for long durations, e.g. 300 s, the plasma gradually affects layers beyond the topmost one.

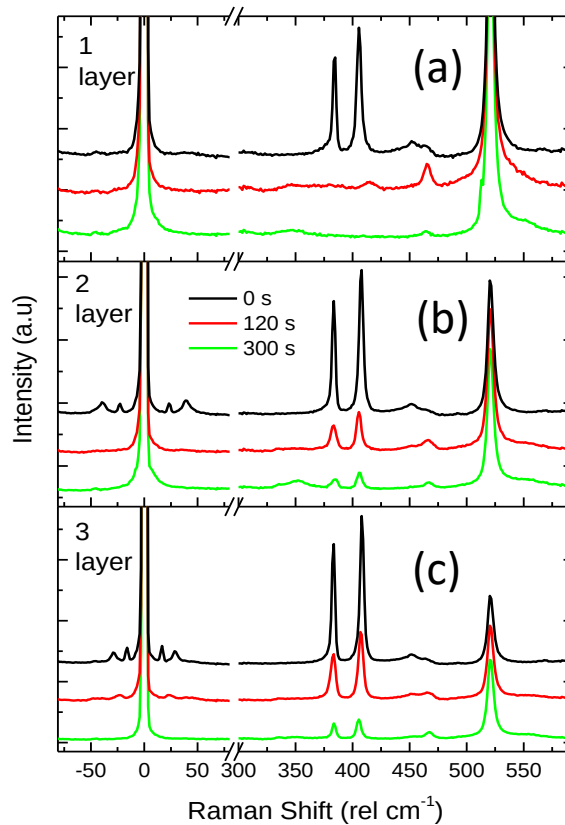


Fig. 4.6 Raman spectra of MoS₂ showing both low- and high-frequency regions before and after 120 s and 300 s of NH₃ plasma for **(a)** 1 layer, **(b)** 2 layer, and **(c)** 3-layer MoS₂.

4.6 PL

PL measurements is a common method to investigate the properties of monolayer MoS₂ as it has a direct bandgap giving rise to intense PL from two excitons. Similar to Raman, PL of MoS₂ is also sensitive to several factors including doping,^{97, 163} defects,^{113, 165, 166} substrates,^{93, 114} temperature,¹¹⁰ and strain.¹⁰⁰⁻¹⁰³

The monolayer pristine MoS₂ used has pronounced PL centred at 1.83 eV with a narrow FWHM of 50–60 meV, a contribution from the *A* exciton of MoS₂. This is a high-quality PL signal comparable to high-quality mechanically exfoliated MoS₂. A second, much lower component is centred ~1.98 eV, this broad feature is from the *B* exciton of MoS₂, caused by valence-band splitting.^{15, 167}

The PL spectra for 7 separate samples treated for various times with NH₃ plasma are presented in Fig. 4.7(A). A clear trend is observed wherein the NH₃ plasma resulted in the shifting of the PL peak to higher energy, up to a remarkable level of >2 eV, with shifts of ~250 meV seen here. This shifting peak was attributed as a single component from the *A* exciton of MoS₂ with a gradual shift, rather than the formation of a new photoluminescent feature at a different energy. The energy shift is alongside a general trend of increasing FWHM and a reduction in intensity when compared to pristine MoS₂.

A plot of the PL peak position for 76 different samples before and after plasma treatment with NH₃ is provided in Fig. 4.7(b), with an error bar showing the standard deviation of samples at each time, the full set of data can be seen in the appendix Fig.A6. The high variability and the logarithmic-like increase in peak binding energy can be plainly seen with a maximum energy ~2 eV. The variability in this data was likely related to the inherent variability in the synthesised MoS₂ with different sizes, shapes, density, coverages, and quality due to the run-to-run variation in the CVD process.

Samples with shorter treatment times, roughly <30 s, were observed to occasionally shift to lower binding energies before ultimately increasing in peak energy position. This was seen for the 10 s sample in Fig.4.7(a), wherein the *A* exciton was shifted to lower binding energies. The shift to lower energy can be caused by, for example, strain,^{101, 103} or oxidation.⁹⁷ In this scenario a potential cause of the lowering of the excitation energy was that the formation of sulfur vacancies happened prior to the nitrogen substituting into the MoS₂ lattice. These short plasma exposure times may enable the formation of more vacancies than fully substituted sites across the MoS₂ surface.

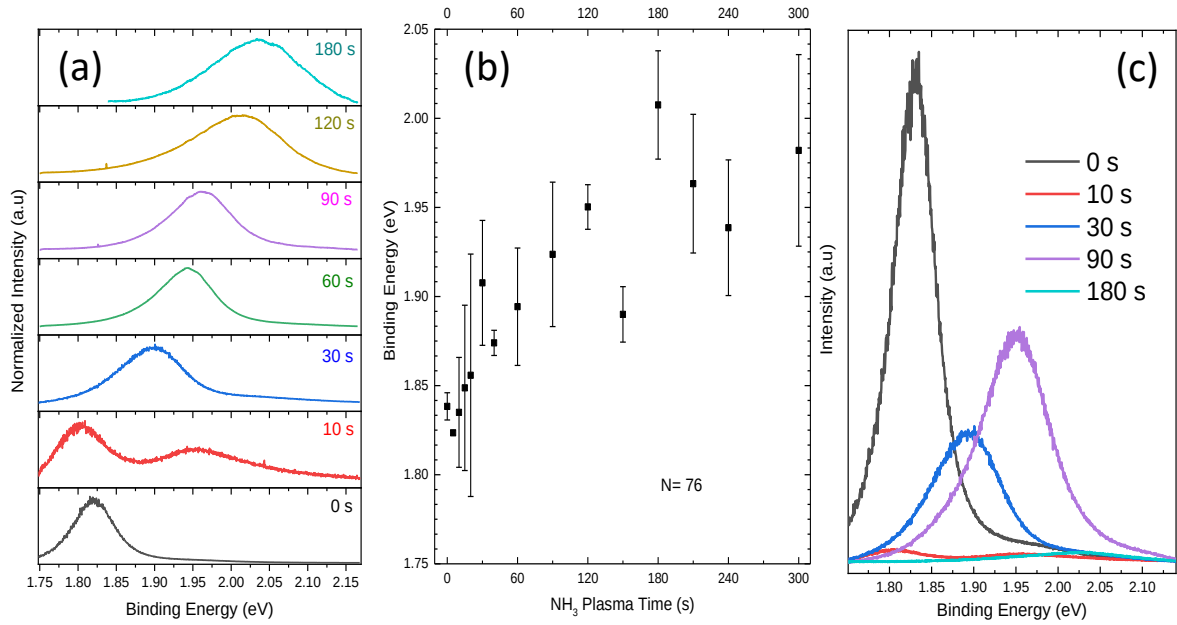


Fig. 4.7 (a) PL spectra for monolayer MoS₂ with increasing NH₃ plasma treatment time showing a gradual shift to higher energies. (b) Plot of the averaged PL peak position for monolayer MoS₂ for 76 samples after various amounts of NH₃ plasma (c) Overlaid PL spectra showing changes in intensity with plasma time.

Acquisition parameters influence the intensity of the acquired spectra substantially, primarily the focus of the combined PL/Raman microscope apparatus. The intensity of the PL spectra in this experiment were maximised during measurement by adjusting the microscope focus, to enable more reliable direct comparison of data. The non-normalized PL spectra for 5 monolayer MoS₂ samples after NH₃ treatment is presented in Fig. 4.7(c). The variance in PL peak intensity can be seen in this figure, the data are representative of the general trend observed for the PL of NH₃ plasma treated monolayer MoS₂. The intensity from the pristine peak was greatly reduced with initial plasma treatment, it then gradually increased to a new local maximum before further plasma results in the intensity decreasing.

As discussed in Chapter 3, intense, narrow PL is one of the best characteristics of MoS₂ and crystal quality. It is also one of the properties that make this material of such interest, MoS₂'s potential applications in optoelectronics in the monolayer form are well known.^{1, 168} Some tunability of the PL energy can be achieved through various methods, such as strain,¹⁶⁹ dielectric,¹¹² substrates,⁹³ doping,^{113, 115, 170} and defects.¹¹³ These effects have their limits with shifting MoS₂ PL energy, with shifts from these methods generally in the range of 100 meV and the majority shifting MoS₂ PL to lower binding energies. The method described thus far

showed a shift of the MoS₂ PL peak from 1.83 eV (678 nm) to over 2 eV (620 nm) potentially enabling new optoelectronics applications.

4.7 Raman and PL mapping

As discussed previously, the Raman and PL measurement tool used is also capable of mapping areas on the surface. Optical images of regions containing monolayer, bilayer, and thicker regions of CVD MoS₂ are shown in Fig.4.8(a) Alongside this are maps of the intensity of their Raman and PL modes. The averaged spectra acquired from these maps for the different MoS₂ layer number regions are shown in Fig. 4.8(e).

Looking first at the Raman and PL maps for pristine MoS₂ the Raman mapping allows the individual layers to be clearly distinguished with 1, 2, 3, and a multi-layer regions observed. PL mapping showed a very high contrast between the monolayer and other regions, with comparatively no emission from 2-layer and thicker. This PL map also showed how continuous the PL emission was across monolayer MoS₂ with changes in intensity happening with wide dispersions in intensity caused by longer range effects.

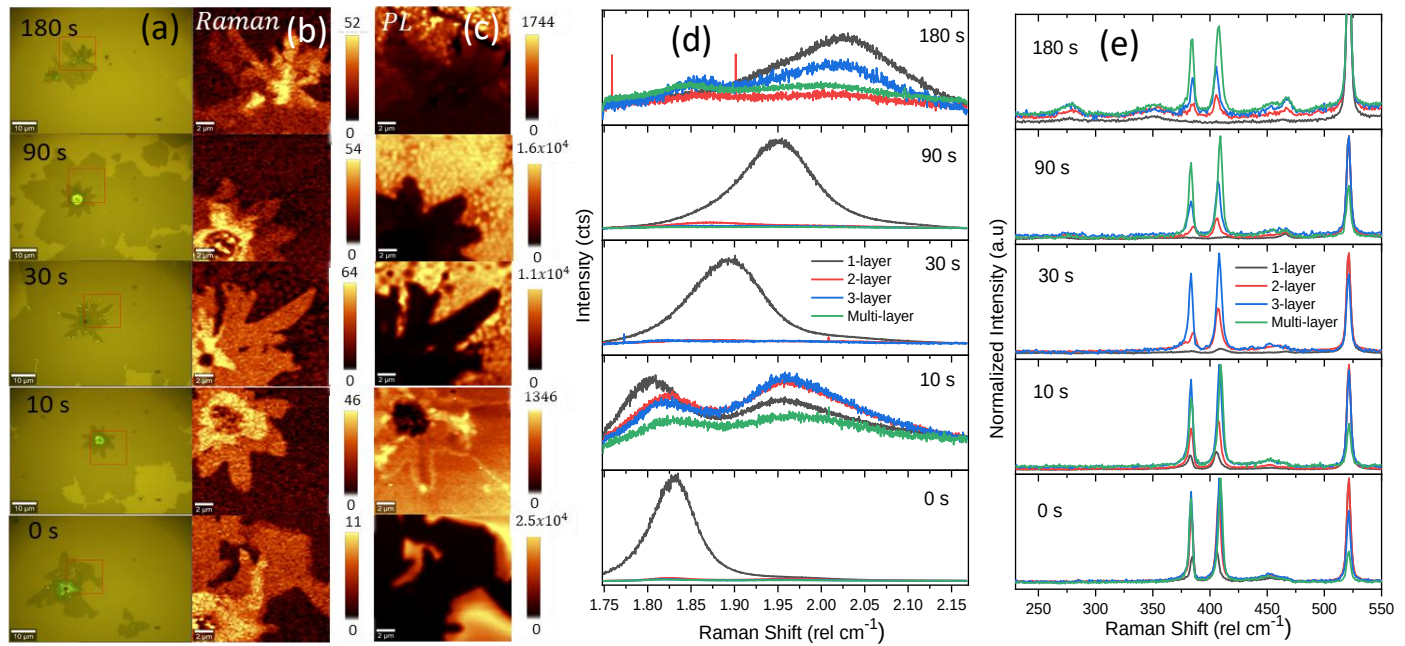


Fig. 4.8 Raman and PL mapping data of NH₃ plasma-treated MoS₂. **(a)** Optical images **(b)** Raman mode intensity maps **(c)** PL mode intensity maps **(d)** Corresponding PL spectra and **(e)** Raman spectra.

Looking at the maps for the respective increases in NH_3 plasma treatment time, we can see how the Raman maps do not generally show substantial changes after plasma treatment with the separate layers still distinguishable even for the longest exposure. This can be seen in the Raman spectra gathered from these maps in Fig. 4.8(e) with the now expected trend of a gradual loss of MoS_2 Raman modes especially from monolayer.

PL maps showed a more revealing set of images, after 10 s of plasma it was observed that the PL intensity from the monolayer plummets to similar levels to the rest of the MoS_2 layers while still maintaining its uniformity. This was also seen in the PL spectrum in Fig. 4.8(d). For the longer plasma treatments this intensity contrast is restored, with the monolayer clearly distinct from the other layers. Alongside this, the uniformity of the monolayer PL is dramatically changed with a fluctuating intensity and a mix of bright and dark spots in the intensity. This was seen for the remaining samples, with the intensity contrast reducing for the 180 s sample. The PL spectra from all layers thicker than monolayer did not show significant shifting of their limited PL. This is consistent with the proposed theory of the surface layer acting as a protective layer, further emphasising the surface sensitivity of this process. The individual PL spectra in Fig. 4.8(d) are all largely consistent with what has been discussed previously.

Resonant Raman spectroscopy

The Raman spectrum of MoS_2 is sensitive to excitation wavelength. After 532 nm, which is used extensively throughout the literature, 633 nm is likely the second most common wavelength in MoS_2 characterisation. 633 nm excitation yields resonant Raman spectra from MoS_2 due to the similar energy to bandgap transitions in MoS_2 , this presents a more intense Raman spectrum with a large number of peaks from second-order vibrations. 633 nm has added utility in that Mo oxides are more noticeable with this laser energy than at 532 nm. Inherently, Raman spectra are the relative Raman shift of the emitted light from the excitation frequency, while PL is emitted at a fixed energy given from the band structure of the material. This unfortunately means that for high-quality monolayer MoS_2 there is substantial overlap between the PL signal and the main MoS_2 Raman modes when using 633 nm excitation. This is shown in Fig. 4.9.

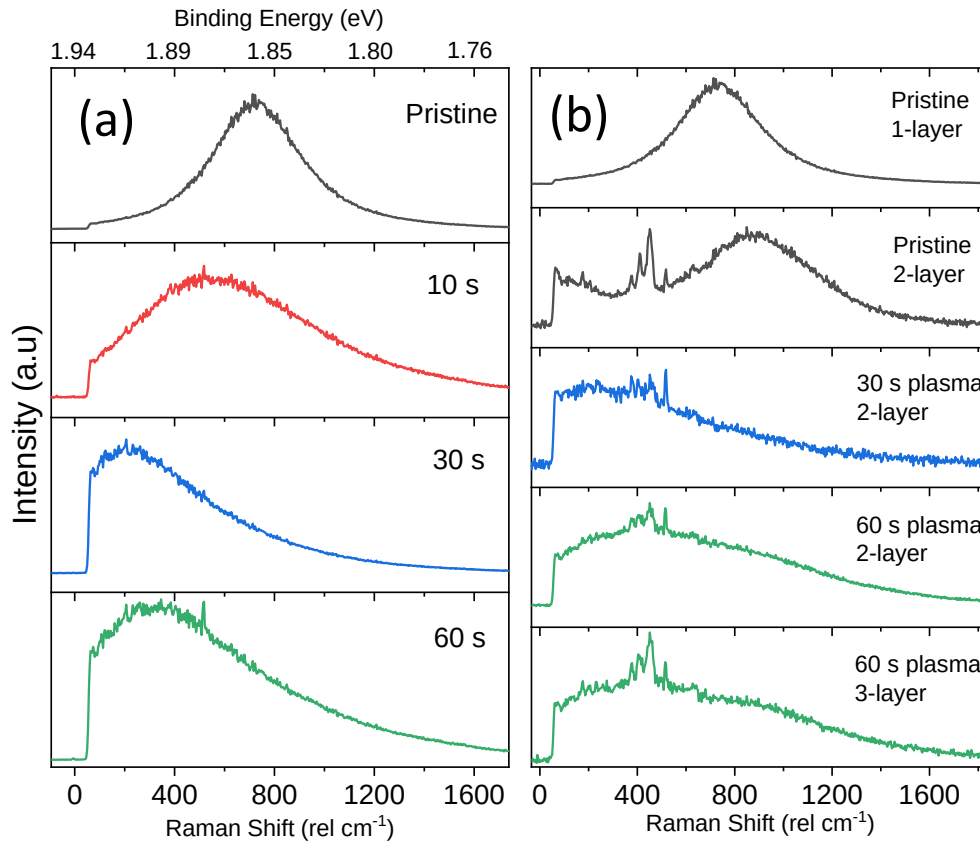


Fig. 4.9 Raman and PL spectra of MoS₂ using a 633 nm excitation laser. **(a)** Raman and PL of monolayer MoS₂ before and after several plasma treatment times, the intense PL signal obscures any Raman modes. **(b)** Raman and PL spectra of 1- and 2-layer MoS₂ before and after plasma treatment, the shifting PL peak obscures much of the Raman modes after plasma treatment.

The Raman and PL region for monolayer MoS₂ before and after NH₃ plasma treatment is shown in Fig. 4.9(a). The MoS₂ Raman modes were undiscernible due to the high intensity PL covering the ~ 400 rel cm⁻¹ region. After plasma treatment this becomes even more of a problem as the PL peak was shifted to higher binding energy, and therefore further overlaps with the Raman mode region, before being largely cut off due to the Rayleigh line filter.

The 633 nm Raman/PL spectra of bilayer and 3-layer MoS₂ are given in Fig. 4.9(b). While the Raman modes are more measurable, the overlap with the PL makes high quality data difficult to acquire and undermines any added utility of resonant Raman spectroscopy in this case.

Ambient Stability and Aging

XPS, PL, and Raman spectroscopy were the main characterisation methods used in this study and provided significant amounts of complementary information which gave insight to the nature of the material being analysed. With the effects of NH_3 plasma on MoS_2 in terms of XPS, Raman, and PL now in hand, it was possible to analyse the samples provided in Fig. 4.3 more thoroughly in terms of stability and degradation. The samples provided in Fig. 4.3. were transported in semi-ambient conditions over ~ 7 days after plasma treatment before XPS analysis.

The XPS data in Fig. 4.3 showed an uncommon defect feature for the pristine MoS_2 in the Mo 3d region, this was not present on the other samples measured. Raman spectroscopy of this specific sample before and after transport from Dublin to Munich, is given in Fig. 4.10(a). These spectra were very similar with the exception of an additional shoulder at $\sim 370 \text{ cm}^{-1}$ which can therefore be attributed to the defective MoS_2 as observed in XPS.

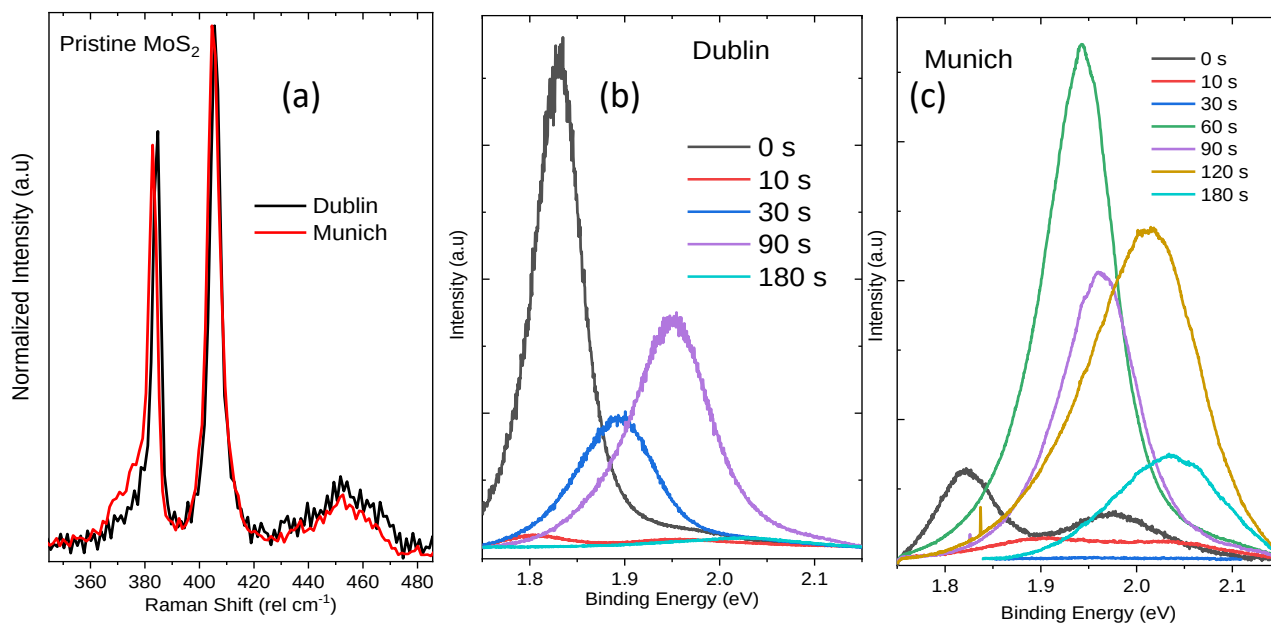


Fig. 4.10 Raman (a) and PL (b, c) spectra of a set of NH_3 plasma treated MoS_2 samples before and after transporting between Dublin and Munich.

The PL for the majority of the samples in this set were measured before and after transporting and are shown in Fig. 4.10 (b) and (c). The intensity of the PL spectra cannot be directly compared between Dublin and Munich due to differences in apparatus such as the method of laser power calibration. The most prominent changes between the two sets of data are for the

pristine and 30 s samples, both of these samples show substantially less intense PL after transport. This degradation is also observed in the Mo 3d XPS spectra with the defect peaks for pristine MoS₂, and the formation of a large amount of MoO₃ for the 30 s sample. Post plasma treatment these samples were all stored and transported together, suggesting that the MoS₂ with >30 s of NH₃ plasma treatment is more stable in semi-ambient conditions than <30 s plasma treated MoS₂ and even pristine MoS₂.

The stability over time of the material was investigated using Raman and PL after several months in an ambient pressure nitrogen storage box. The PL and Raman spectra of three samples are presented in Fig. 4.11. Pristine MoS₂ was measured and re-measured after 7 months of storage, different areas of the sample were chosen and still show almost identical Raman and PL as before. Similar measurements were made for plasma-treated MoS₂ after 2 months in storage. The 120 s and 300 s samples did not show any significant changes in PL or Raman after storage, indicating the stability of the doping and of the doped MoS₂ itself.

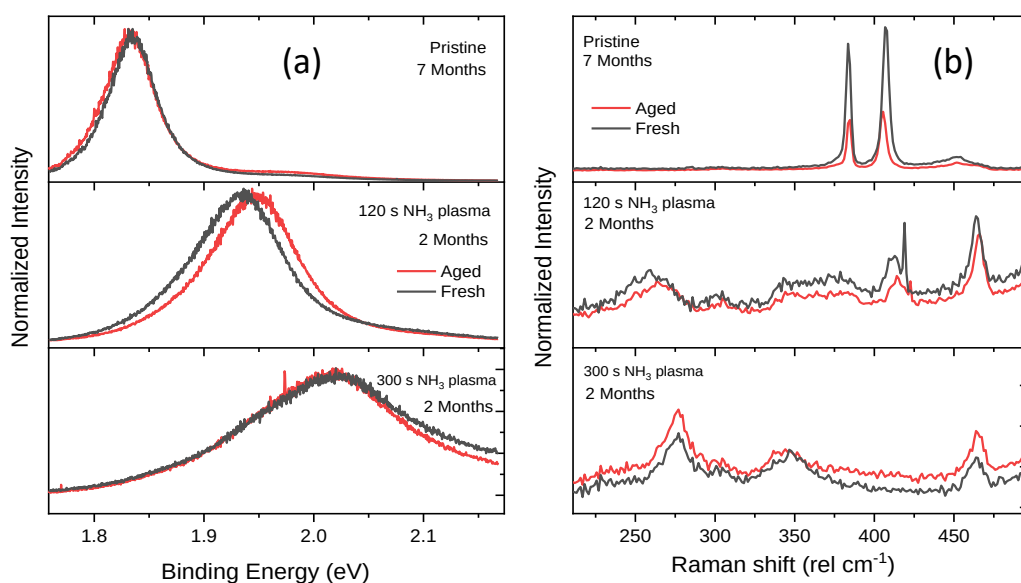


Fig. 4.11 Pristine and plasma treated MoS₂ spectra after aging in a nitrogen cabinet **(a)** PL **(b)** Raman.

4.8 Morphology

While remote plasma was used here to minimise the physical effects of high KE ions impinging on the MoS₂ while maintaining high chemical reactivity, structural damage or changes are still possible due to ion-bombardment effects. The characterisation methods up to this point also indicate potential structural and/or crystallinity changes.

The XPS components for MoS₂ show significant peak broadening with increasing plasma exposure time. While this is largely attributed to the increased bond diversity of the material due to nitrogen substitution into the lattice, XPS components of crystals also broaden with increasing defects.

Raman spectra are often used to verify the crystallinity of 2D TMDs, with sharp peaks representative of high uniformity in the crystal. MoS₂ here has shown large changes after plasma treatment, with broadening followed by a complete loss of the MoS₂ Raman modes with increasing plasma exposure time.

PL mapping of the MoS₂ after plasma treatment showed a fluctuating intensity with bright spots and pits in intensity, this may indicate changes to the surface morphology or structure. AFM and SEM were used to investigate the surface roughness and any morphology changes caused by the NH₃ plasma.

4.8.1 AFM

The changes resulting from NH₃ plasma treatment on monolayer MoS₂ regions as analysed by AFM is shown in Fig. 4.12. The 120 s image shows considerable change when compared to the pristine crystal with a series of flat plateaus and rolled-up edges across the previously uniform monolayer film. A longer duration of plasma exposure, as seen with the 300 s sample, it can be seen that ultimately the NH₃ plasma causes scrolling across the entire monolayer giving a field of roughly uniform nanoscrolls.

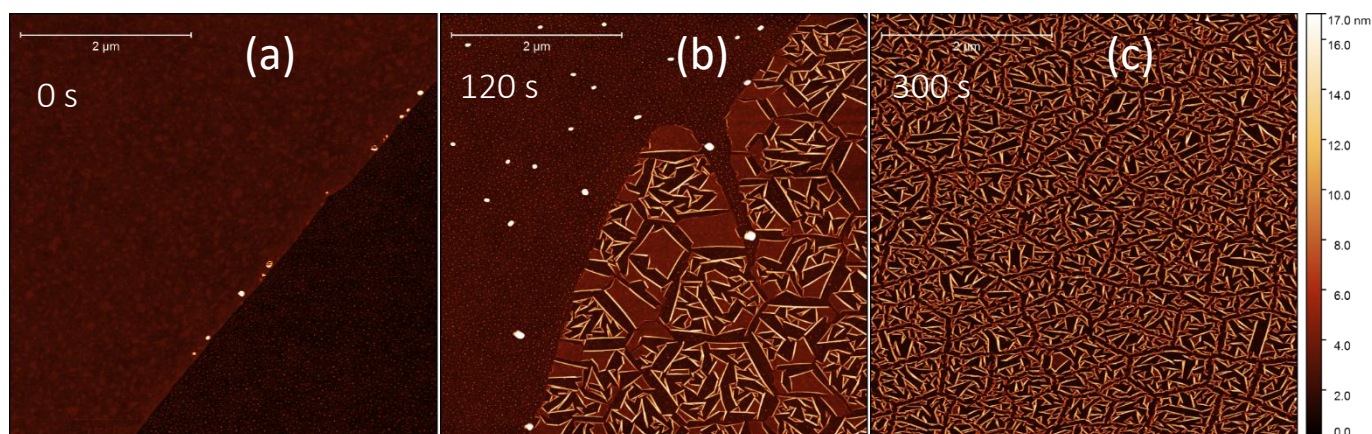


Fig. 4.12 AFM images of the changing surface of CVD MoS₂ after different NH₃ plasma treatment times. **(a)** pristine. **(b)** 120 s. **(c)** 300 s

To understand why and how NH₃ plasma causes this we need to understand the mechanism of sulfur-vacancy formation and nitrogen substitutional doping. It has been often stated since at least 1985 that the edges of MoS₂ are significantly more reactive than the basal plane.¹⁷¹ The logic for this is sound, in that the edges have unsaturated bonds for either S or Mo atoms. In this work we have found that these tears occur just as frequently across the basal plane as they do at edge sites. It is well known that both natural and synthetic MoS₂ harbour a multitude of defects.^{10, 32} When considering large crystals, the most common and relevant defect in these isolated MoS₂ crystals are sulfur vacancies. While the PL results indicate a high quality and uniformity across the basal plane of these crystals, there is a high likelihood that they contain several types of defects including many sulfur vacancies.

As the nitrogen doping occurs at these S vacancy points where it can access the Mo atoms, it contributes to an increase in compressive strain in the lattice.¹²⁶ Increasing doping, and therefore strain, results in tearing and subsequent rolling up of the torn crystal edges. These clusters of doping/defects appear to propagate along crystalline directions, resulting in a honeycomb like structure when viewed from above, as can be seen in Fig. 4.12. It has been calculated and observed that crack propagation along zig-zag edges is more energy favourable than the arm-chair direction for MoS₂.^{172, 173} Intersections of these cracks in the crystals here are often at 120° confirming that MoS₂ is tearing along crystalline directions. The plateaus formed in between these cracks do not show any increase in roughness with increasing plasma exposure time. In fact, the majority of them show a decrease in roughness from pristine MoS₂ as the plasma likely removes contamination on the surface.

Similar tearing and scrolling of MoS₂ has been observed in previous literature through Ar-ion bombardment and its resultant sulfur vacancies,⁶⁰ from rapid cooling of MoS₂ at rates up to ~300°C/min¹⁷², and from atmospheric air plasma.¹⁷⁴ Unlike this method with NH₃ plasma, these methods generally cause a high number of unstable sulfur vacancies which can then oxidise forming significant if not majority amounts of MoO₃ when exposed to ambient.

There is a great deal of uniformity of the scrolls formed in Fig.4.12, this is analysed in Fig. 4.13 showing the distribution in heights across each AFM image, with Fig.4.13(b) zoomed in to the scrolling region. This visualization of the AFM data can allow us to clearly see the different aspects of each data set. The pristine sample has two peaks, the SiO₂ substrate and the MoS₂ layer about 1 nm in separation consistent with the expected 0.7 nm height of monolayer MoS₂. The 120 s graph shows the reduction in coverage of the MoS₂ monolayer, the rolled edges and scrolls are only visible in the zoomed in region in Fig.4.13(b). After 300 s the monolayer MoS₂ is mostly absent with a small shoulder remaining due to the few plateaus in this image, the distribution of the nanoscrolls has tightened into a near Gaussian distribution, with a peak at approximately 7 nm and a range of ~ 3–12 nm. This demonstrates that NH₃ plasma treatment of MoS₂ can be used to form large areas of relatively uniform mixed chalcogen-nitride nanoscrolls.

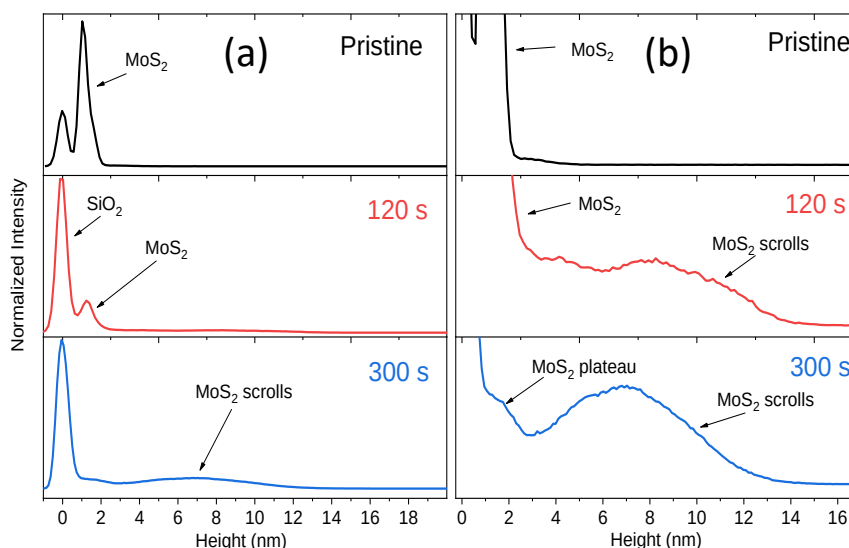


Fig. 4.13 Plot of the data points from the AFM images in Fig.12 with the substrate, MoS₂, and nanoscrolls visible by their separated heights. **(a)** full scale **(b)** zoomed into the nanoscroll region.

By comparing a PL map and an AFM image from similar regions of plasma-treated MoS₂ the strong correlation in the data is shown. Optical, PL, and AFM data of very similar MoS₂ after 60 s of NH₃ plasma showing both a monolayer and bilayer region is presented in Fig. 4.14. The mottled PL intensity of the MoS₂ monolayer corresponds with the scrolls and voids in the MoS₂ seen in AFM. With the dark spots in the PL likely from areas where the MoS₂ has rolled away. This is an example of the high utility of PL when characterising MoS₂ and demonstrates that PL mapping can be used to monitor the scrolling behaviour seen here.

Notably the bilayer region in both the PL and AFM does not show this same scrolling behaviour, it was noticed here that similar to the Raman, bilayer MoS₂ can withstand very high doses of NH₃ plasma before exhibiting similar behaviour to the monolayer.

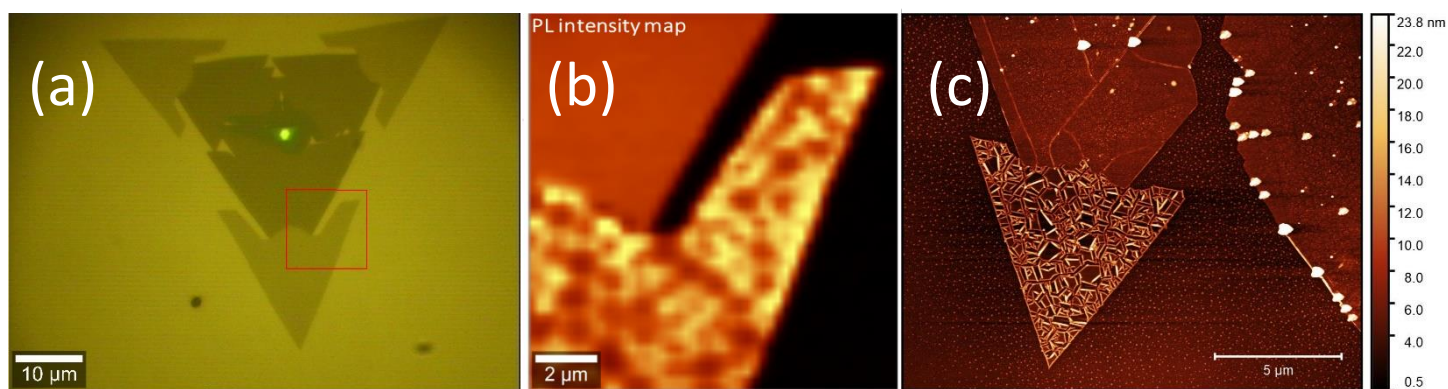


Fig. 4.14 Comparative images and maps of similarly plasma treated MoS₂ (a) Optical (b) PL (c) AFM.

4.8.2 SEM

The very high aspect ratio of the nanoscrolls formed during the NH₃ plasma process can make analysis with AFM difficult, and so SEM was also used to characterise the morphological changes of the MoS₂.

SEM images of four MoS₂ samples after different plasma exposure times are shown in Fig. 4.15. The SEM of the pristine MoS₂ crystals reinforces the uniformity and high-quality of the starting material, with no apparent contrast along the entire surface of the crystal. After plasma treatment the extensive tearing across the surface is evident with Fig.15(b) showing that across the entirety of the monolayer there are tears along crystalline directions. A contrast can be seen across many of the now individual MoS₂ plateaus between these cracks, this was attributed to contrast to charging from the electron beam as it scans across the image, but this also serves to illustrate the electrical isolation and separation of the facets.

Further plasma treatment in Fig. 4.15(c) continues with the expected trend where large parts of the surface has scrolled up, exposing the bare SiO_2 . For longer plasma exposure times we see complete scrolling across the monolayer surface, this scrolling results in a very low contrast in SEM, the insert in Fig.15(d) shows a zoom into the monolayer region and allows the confirmation of the presence of the nanoscrolls.

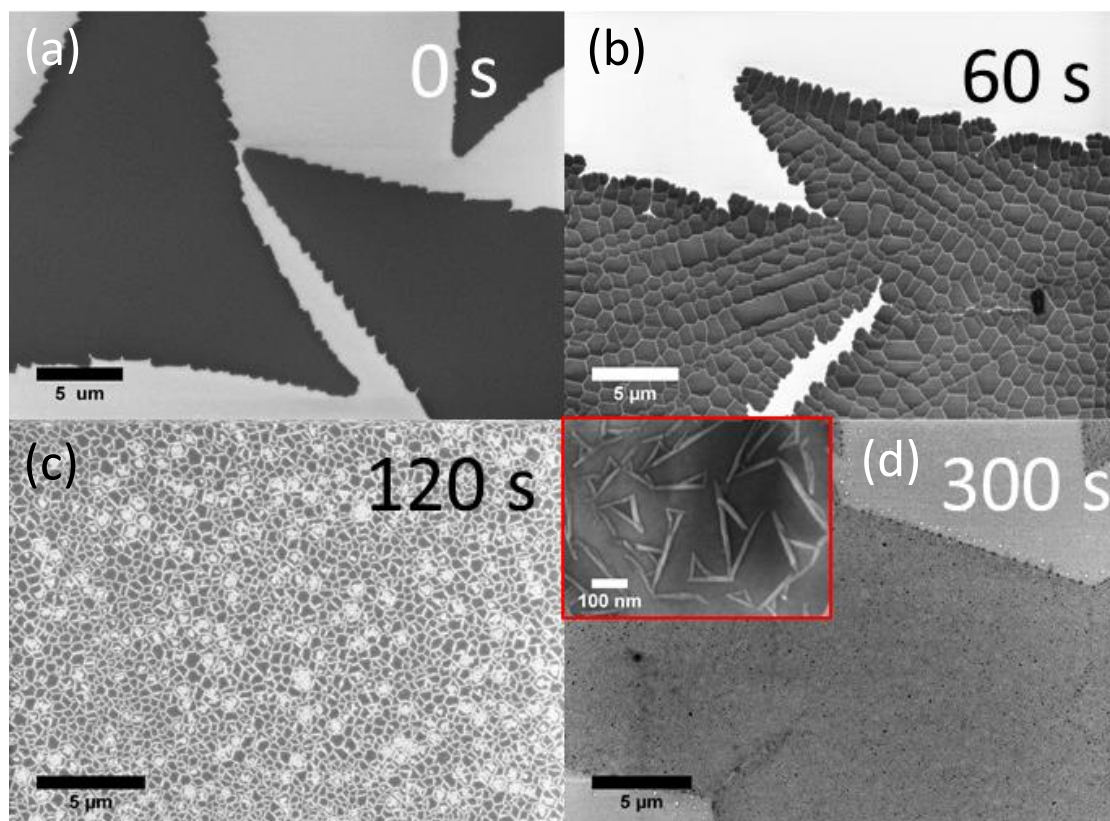


Fig. 4.15 SEM images of plasma-treated MoS₂ (a) Pristine (b) 60 s NH₃ plasma (c) 120 s NH₃ plasma (d) 300 s NH₃ plasma with insert of a higher magnification.

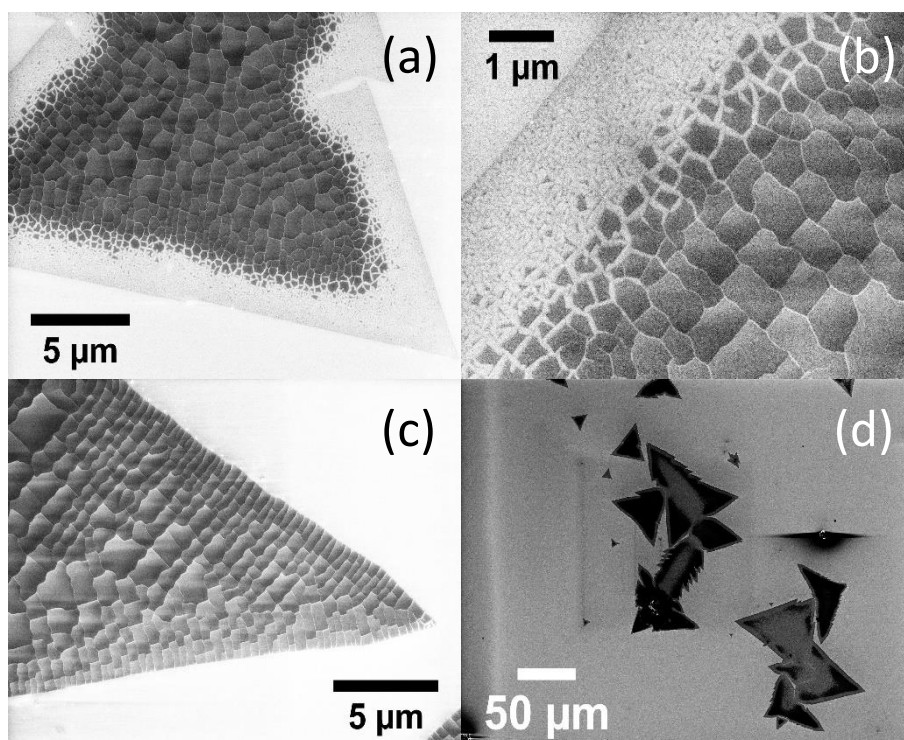


Fig. 4.16 SEM images of various crystals at several levels of magnification for a 30 s NH_3 plasma-treated MoS_2 sample.

Due to the previously discussed variation in the density, size, shape, and quality (from PL) of the MoS_2 crystals across some of the samples, some interesting phenomena are observed. SEM images of several MoS_2 monolayers from the same sample after 30 s of NH_3 plasma are shown in Fig. 4.16. In these images it is observed that for some of the crystals, scrolling happens from the edge-in almost exclusively (a) and (b), while others show widespread tearing but without any noticeable scrolling Fig. 4.16(c). A number of crystals with high contrast across their surfaces, are shown in Fig. 4.16(d) wherein the dark contrast is MoS_2 with widespread tearing but no scrolling, and the lighter grey regions of the crystals are almost entirely scrolled up. This suggests that properties of the individual MoS_2 crystals play an important role in the scrolling behaviour. This inconsistency, particularly at this plasma dosage of ~ 30 s, was also seen for the variability in PL peak shift in Fig. 4.7(b) previously. This variability is most likely due to non-uniform distribution of defects and grain boundaries during growth, altering the rate of nitrogen incorporation into the lattice.

4.9 Further observations

Aside from the so far detailed observations and characterisations of the typical effects of NH_3 plasma on CVD MoS_2 , A small number of other aspects to this process or the plasma-treated MoS_2 which were encountered during the experimental process are examined.

Transferred MoS_2

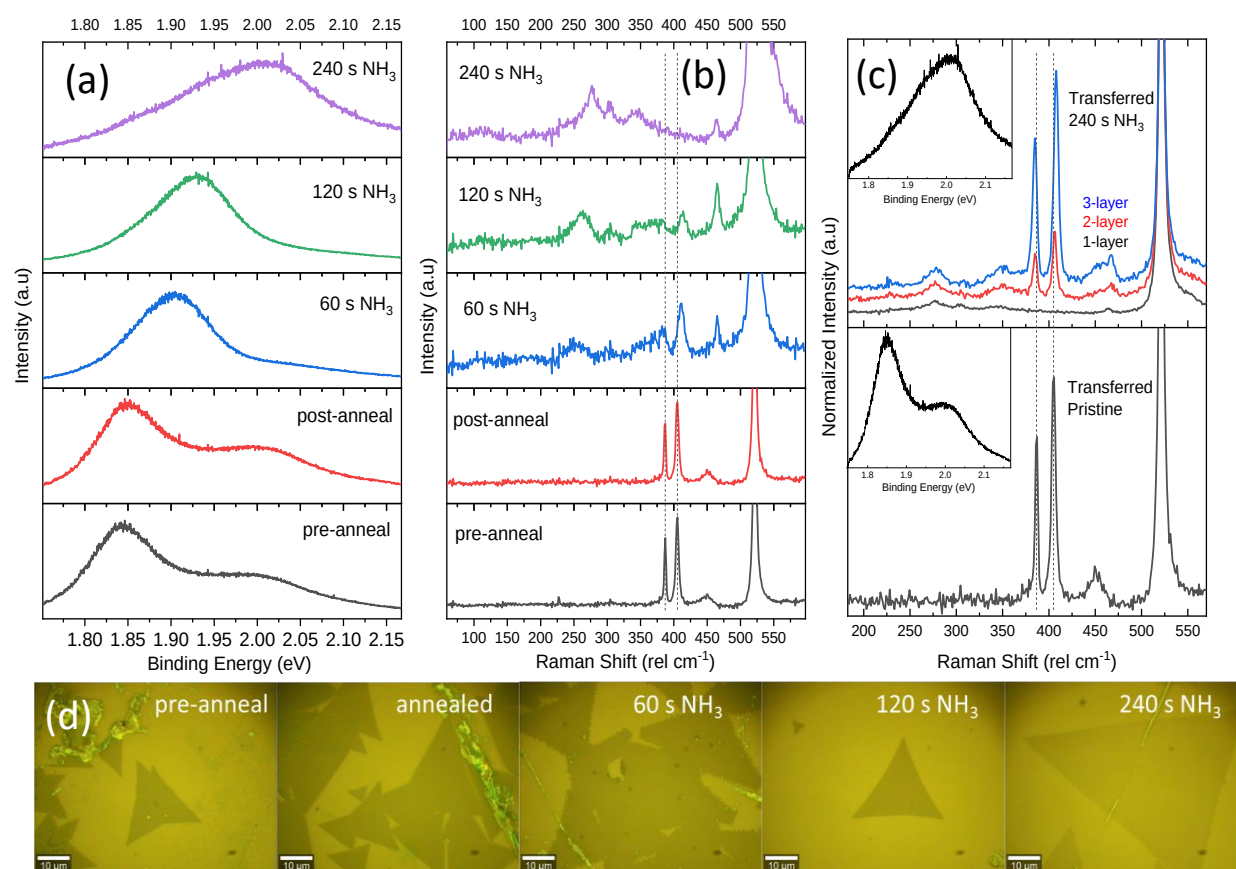


Fig. 4.17 (a) PL spectra for 5 transferred MoS_2 samples after various treatments. (b) Raman spectra. (c) Comparative Raman spectra for transferred pristine and 240 s plasma treated MoS_2 showing the effect on multiple layers, inserts of the monolayer PL spectra of each sample. (d) Optical microscopy images of the MoS_2 crystals measured.

For applications-focused research, MoS_2 is frequently transferred from the growth substrate onto a target substrate, a common method of doing this is by a polymer-supported wet-transfer method.

One of the effects of this is the MoS₂ is less bound to the new substrate than it was the growth substrate, this can change the properties and chemical reactivity of the crystal.¹¹⁵ Outside of this, the polymer-transfer process will introduce ripples in the material. These ripples would possibly allow relaxation rather than tearing, potentially necessitating a higher dose of plasma to achieve the same level of strain to induce tearing and rolling. Wet transfer may also leave behind residue on the substrate surface and on the MoS₂ itself which may slow the reaction with NH₃ plasma and passivate the surface sulfur atoms of MoS₂.

The difference that wet transfer may have on the susceptibility of monolayer MoS₂ to the effects of NH₃ plasma was briefly investigated. A number of MoS₂ samples were transferred onto clean SiO₂ substrates. These substrates were annealed in inert atmosphere to remove some of the polymer contamination on the surface, the samples were then treated for various amounts of time with the NH₃ plasma. The PL, Raman, and optical images of these treated samples are shown in Fig. 4.17.

The PL and Raman data for these transferred MoS₂ samples aligns with the results for as-synthesised samples, indicating that transferred MoS₂ behaves similarly, with an increase in PL peak position which fits the trend previously shown in Fig.7(b), and matching changes to the Raman spectra. Fig. 4.17(c) further validates this similar behaviour, showing the changes observed across multiple layers of transferred CVD-MoS₂ after 240 s of NH₃ plasma exposure compared with pristine transferred MoS₂.

Samples not shifting or folding

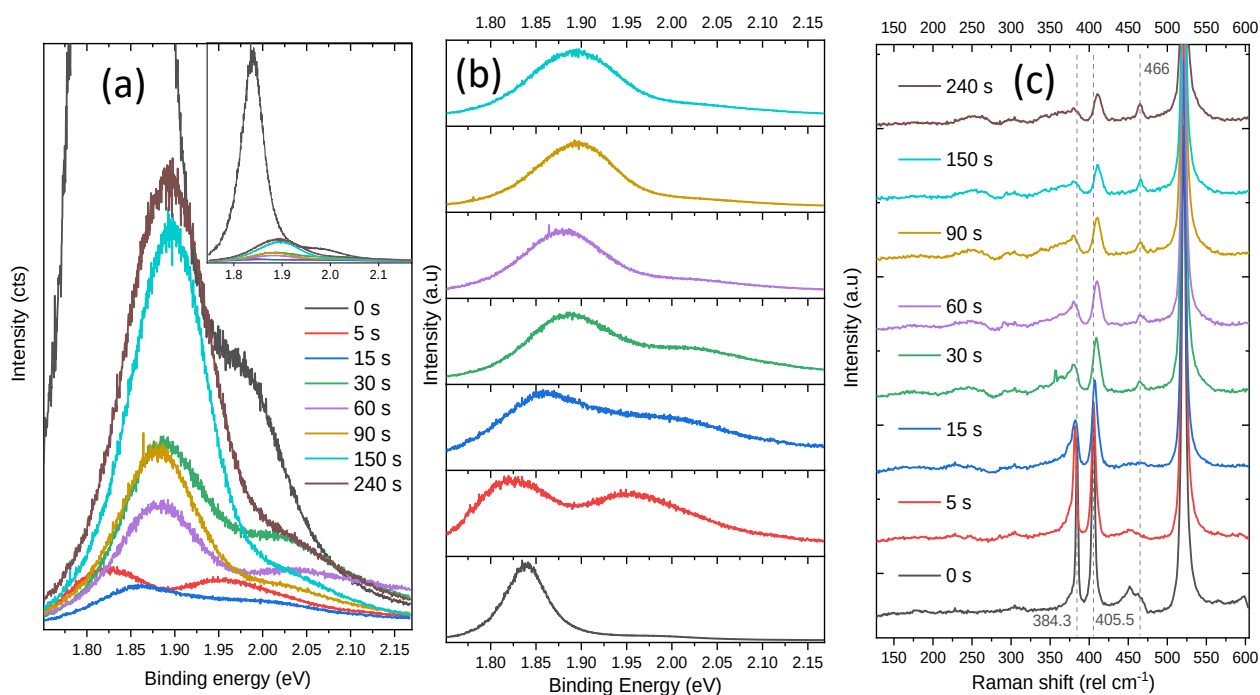


Fig. 4.18 Characterisation of 8 monolayer MoS₂ samples after NH₃ plasma treatment **(a)** PL spectra displaying the relative intensities, insert full scale showing the pristine intensity **(b)** PL spectra showing the small changes to PL energy **(c)** Raman spectra

Another peculiar phenomenon was that some batches of CVD-grown MoS₂ did not display any significant PL shift at even high plasma dosages. This was rarely observed but does further demonstrate the important role of the starting material, with some of this variability shown previously by SEM in Fig. 4.16. The PL and Raman spectra for a set of 8 samples which did not fully fit the routinely seen trend are shown in Fig. 4.18. There are changes in the PL intensity from the MoS₂ monolayers, but the PL peak does not shift >1.9 eV as was now expected. In contrasting, Raman spectroscopy Fig. 4.18(c) showed many of the features of NH₃ plasma treatment including, splitting and loss of intensity in the E_{2g}^1 mode of MoS₂, broadening and lowering of intensity of the A_{1g} mode, formation of a new peak at ~465 cm⁻¹, and the development of two new broad features around ~250 and 350 cm⁻¹. Unlike the previous samples, a complete loss of the MoS₂ Raman modes for the plasma times shown was not observed. The PL and Raman changes for these samples align with the gradual trend and changes previously seen, but for much lower plasma exposure times, with 240 s of plasma here being most similar to ~60–90 s of plasma when compared to all of the prepared samples. This

is potentially due to a lower number of defects in the starting material for this set of samples, resulting in a need for longer plasma time to get similar results.

NH₃ plasma of MoS₂ thin films

The adaptability of NH₃ plasma as a post-growth treatment was also briefly investigated for thin films of MoS₂ synthesised by the TAC method. This process yields large-area films of polycrystalline MoS₂ with small crystallite size (~10–100 nm) and a random orientation of these crystals. It would therefore be expected to start with a large number of exposed crystal edges and that strain will be less consequential. The XPS and Raman spectra with plasma treatment for two MoS₂ films with different starting Mo thickness are shown in Fig. 4.19. Similar to the CVD MoS₂ monolayers, 0.5 nm MoS₂ is doped with N-Mo after plasma treatment with a sharp peak appearing at ~398 eV in Fig. 4.19(c).

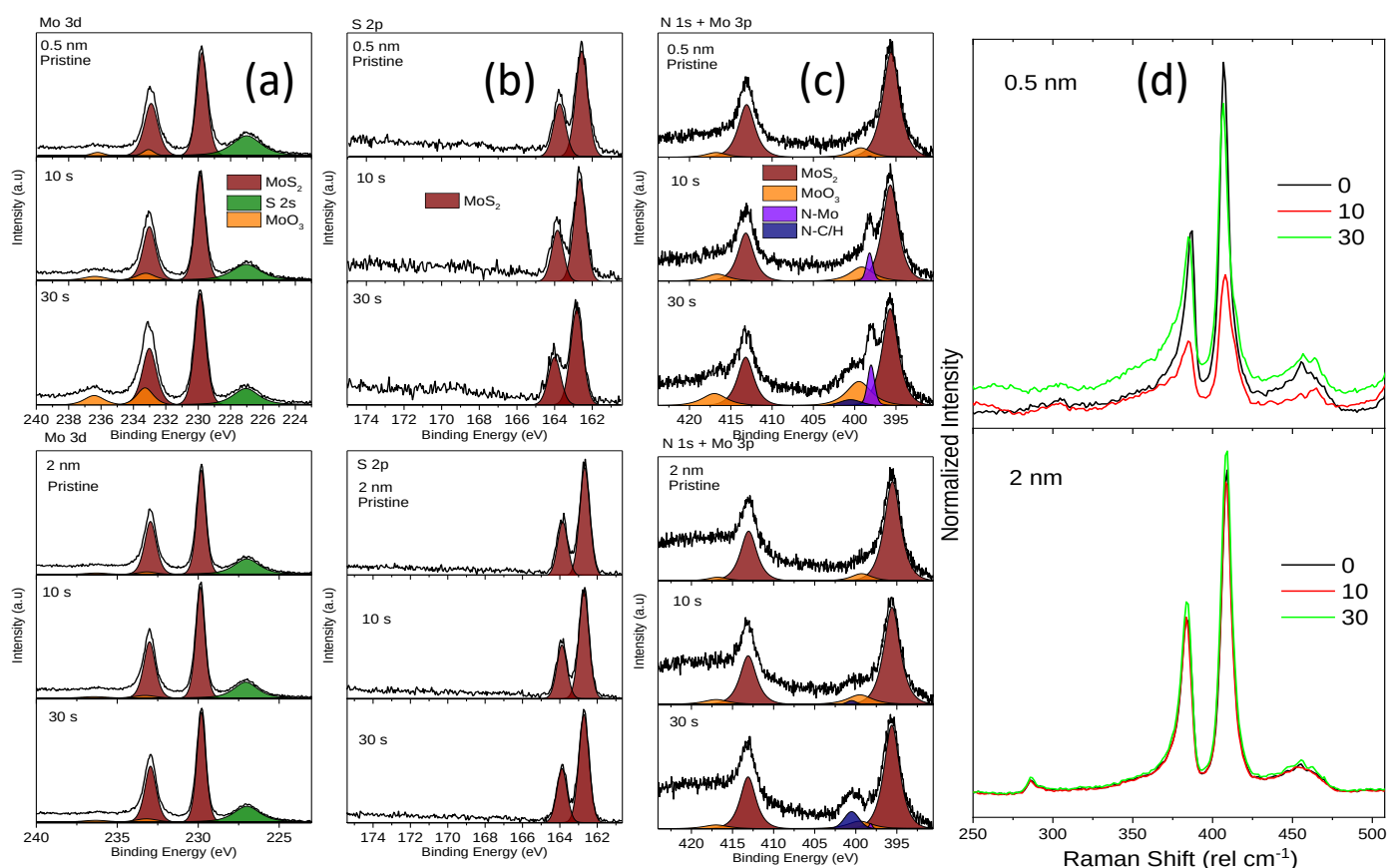


Fig. 4.19 XPS data for MoS₂ thin films after NH₃ plasma treatment (a) Mo 3d (b) S 2p (c) Mo 3p+ N 1s. (d) Raman spectra for the MoS₂ films

In contrast to this, the 2 nm film did not show a clear indication of N-Mo formation, with no N-Mo component observed instead there is formation of a clear N-C/H peak at ~401 eV. The Raman spectra from both films in Fig.19(d) have been normalized to the intensity of the SiO₂ Raman peak. Looking at the 0.5 nm film we can see that the now expected splitting of the E_{2g}^1 Raman mode of MoS₂ is seen here with increasing plasma time. A lower normalized intensity for the 10 s sample is now observed, this is likely as a result of inhomogeneity in the thickness of the 0.5 nm film across the substrate. For the Raman of the 2 nm film of MoS₂ there is no perceivable difference with increasing plasma time consistent with the XPS data.

Solvent washing

Cleaning of the surface of mono–few layer TMDs is an important aspect when considering any applications or during experimental design with any processing steps. Monolayers of MoS₂ on SiO₂ are susceptible to some delamination when using certain solvents to rinse and clean the surface of contaminants. Tearing or removal of crystals has been seen throughout this project when using H₂O to clean the surface of CVD MoS₂, and so IPA is the standard cleaning solvent. Allowing a drop of solvent to evaporate while sitting on the surface of a sample is now known to cause individual crystals to roll up into large scrolls.¹⁷⁵ That was replicated by dropping CH₃OH onto a CVD-grown MoS₂ sample and allowing the CH₃OH to gradually evaporate, Fig. 4.20 (a) and (b). It can be seen that the majority of the MoS₂ scrolled into many large rolls, the remaining surface MoS₂ is mostly unaffected. When the same process was repeated for CVD-grown MoS₂ after NH₃ plasma treatment, as in Fig. 4.20(c) and(d), a different result is noted whereby a small amount of the MoS₂ does form the large scrolls, in alignment with pristine MoS₂, though the majority of the surface monolayer MoS₂ quickly tears and scrolls into nanoscrolls similar to those observed for extended plasma treatment. This process for both the pristine and plasma-treated MoS₂ can be seen in several steps in appendix Fig.A7, and the video recording for both samples is accessible at <https://www.youtube.com/watch?v=CbobUfCupr8>. This is consistent with the postulated method of tearing and scrolling discussed previously, the increased numbers of dopants, defects and tears across the basal plane of the MoS₂ facilitates many further tears to form and expand when the added stress of the solvent is applied.

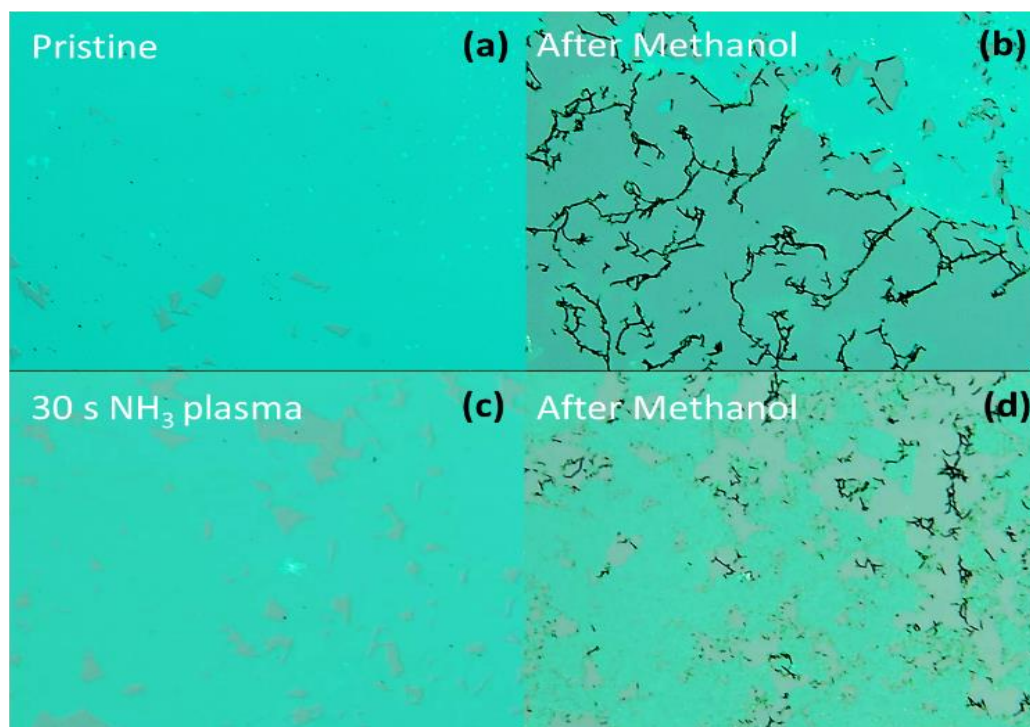


Fig. 4.20 Optical microscopy images of MoS₂ **(a)** Pristine MoS₂ **(b)** Pristine after methanol evaporation **(c)** MoS₂ with 30s NH₃ plasma **(d)** MoS₂ with 30s NH₃ plasma after methanol evaporation.

4.10 Conclusions

This chapter has explored the effects of NH₃ plasma on mono- and few-layer-CVD-grown MoS₂ through a variety of characterisation techniques. XPS analysis demonstrated that NH₃ plasma treatment resulted in the formation of covalent bonds between Mo and N atoms, by substitutional doping of nitrogen atoms into the MoS₂ lattice with removal of sulfur atoms. The doping level is proportional to the plasma treatment time. This allowed monolayer crystals with a stoichiometry of MoS_{0.5}N_{1.1} to be realised, showing that this process can achieve alloying with high amounts of nitrogen substitution. XPS analysis also served to clarify the identity and features of common components in the XPS spectra for nitrogen-doped MoS₂, these components are frequently confused in the literature.

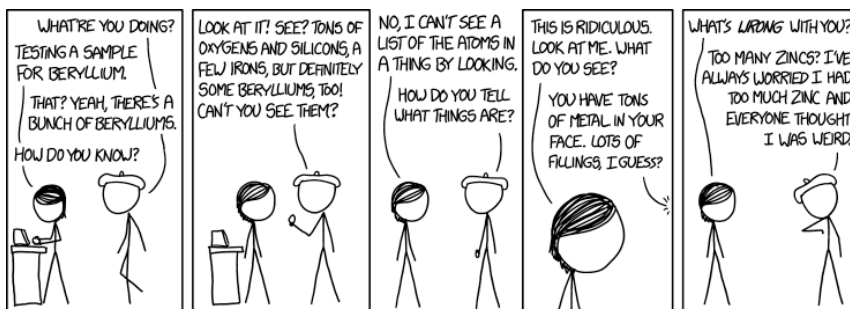
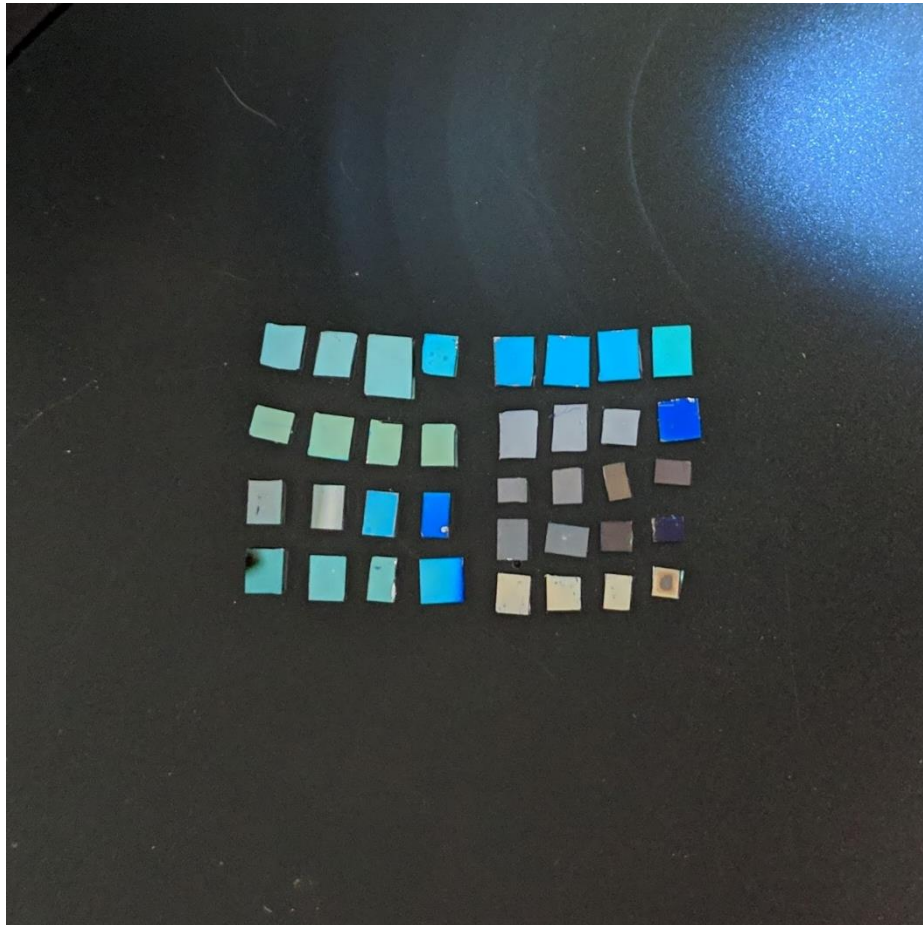
Beyond XPS, the many effects of NH₃ plasma on monolayer MoS₂ were examined using several of the most prevalent characterisation techniques in 2D materials research, this provides a deeper library of methods to characterise potential nitrogen doping of MoS₂.

NH₃ plasma treatment was found to have a pronounced impact on the PL emitted from monolayer MoS₂, with uncommon shifts of the PL peak to higher binding energies. The shifting of the PL energy was found to be both tuneable and largely stable over time, with shifts in the MoS₂ PL peak to over 2 eV (620 nm) achieved, representing a ~200 meV (70 nm) shift. The PL peak shift is a gradual shift of the energy of the A exciton to higher energies with increasing nitrogen doping, it is possible that the cause of the changing energy is bandgap widening of the MoS₂. It is not possible to determine here if this is due to an inherent bandgap of the MoS_xN_y alloys being synthesised, or if the peak shift is mostly a result of the strain and changing structure of the MoS₂, it may be a combination.

The extreme surface sensitivity of this process was observed using Raman analysis, with plasma-treated monolayers of MoS₂ losing the characteristic MoS₂ Raman modes. NH₃ plasma treated MoS₂ developed three new components in the Raman spectrum signifying extensive changes to the crystal structure. Bilayers of MoS₂ were found to transition to monolayer-like Raman signal after plasma treatment, indicating that the top-most layer is predominantly affected. Low-frequency Raman spectroscopy was used to confirm decoupling of the bilayer stack of MoS₂.

The substantial morphology changes caused by the compressive strain introduced into the lattice was examined with AFM and SEM, NH₃ plasma was found to create tears along crystalline directions across the MoS₂ surface. These tears gradually rolled into nanoscrolls, creating roughly uniform fields of mixed molybdenum sulfur-nitride MoS_xN_y nanoscrolls over the surface.

5 -Fitting and Analysis of the XPS spectra of TMD thin films



5.1 Introduction

The maturation of TMD synthesis procedures over the last ten years has naturally led to a shift from fundamental investigations of their properties towards studies focused on exploiting these properties for specific applications. The combination of applications-focused research and a healthy supply of research funding, the area of 2D materials has emerged as one of the fastest growing fields to date in modern material science, as illustrated in Figure 5.1, and encouraged research groups from a broad range of backgrounds to explore the utility of these materials in their areas of expertise. While generally positive, this broad interest has at times been detrimental to the quality of the characterisation of the TMD material itself.

In this chapter a wide array of TMDs are synthesised as thin films and are thoroughly characterised using a combination of XPS and Raman spectroscopy. This includes the sulfides, selenides, and tellurides of Mo, W, and Pt synthesised through a TAC process of metal films conversion on SiO₂. The synthesis process for thin films of telluride TMDs is more complicated due to several factors including increased safety concerns, due to this, these films are synthesised using a modified process whereby both the transition metal and tellurium are deposited on the sample before annealing. The specific experimental procedures for the synthesis of the TMD materials is described in Chapter 2.

As previously outlined, XPS fitting of the TMD materials is an often under discussed, yet essential part of a significant portion of 2D materials literature. The reasons for this lack of focus are many fold and corrective action in this field has been pleaded for by many of the world's foremost XPS experts.^{64, 68, 69, 72, 76}

In this chapter, the research focus was to acquire and rigorously fit the core-level XPS spectra for a large selection of TMD materials following common practice procedures and describe the accuracy as well as essential error entailed to an adequate degree. One of the most ubiquitous and useful techniques in 2D materials science is Raman spectroscopy, this same array of materials were measured using 3 different wavelength Raman lasers. This broad swath of TMD materials go from the most studied with large amounts of reference literature behind them e.g. MoS₂, WS₂ to the relatively unexplored e.g. PtSe₂, PtTe₂, with this work also including some of the first well-fitted XPS spectra and Raman spectra using uncommon excitation energies of several materials.

This spread in literature prominence for different TMDs is illustrated in Fig. 5.1 with the TMDs studied here grouped by chalcogen and their number of publications compared, with sulfides being >6x the number of the second largest grouping.

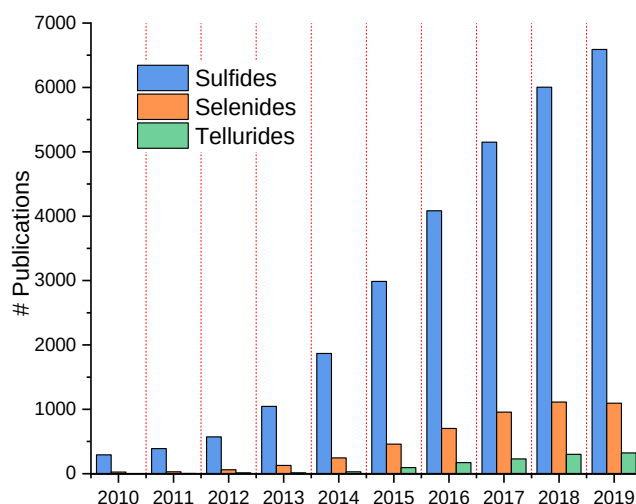


Fig. 5.1 Bar chart of number of publications per year for the 9 TMDs used here, grouped by sulfides, selenides, and tellurides. (Searched as Topic, Web of Science 2020)

As the primary purpose of gathering this data for a wide variety of the currently most studied TMDs is to improve the availability of high quality broadly applicable reference data, it was decided to also analyse the TMDs in various states of deterioration. To achieve this the thermal stability in air was investigated for each material by annealing at various temperatures in ambient conditions. This resulted in severe degradation and oxidation of the materials at various temperatures. As oxidation is the most common form of 2D material breakdown, the ability to measure and identify this using XPS and Raman is extremely useful as it is surprisingly common to not account for these oxides in literature even when collected spectra indicate their presence.

TMD thin films were synthesised, split into four pieces, three of the films were then annealed in a clean room atmosphere at 50% humidity for 30 minutes at the chosen temperatures, 150, 300, and 400 °C. All of the TMD films were then characterised through XPS measurements and subsequent Raman spectroscopy.

5.2 TAC Synthesis

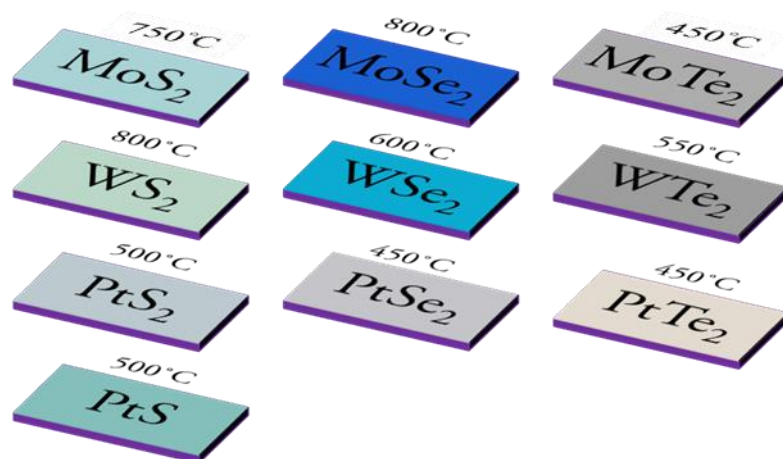


Fig. 5.2 Illustration of the 10 materials studied alongside their highest temperatures during synthesis

Specific experimental details of each synthetic process are given in Chapter 2, however the wide range of annealing temperatures, from 450–800 °C for these materials, are shown in Fig. 5.2

XPS characterisation of each film entailed measurement of their most relevant core-level regions, this varies per material but in general included, a TMD metal core-level (e.g. Mo 3d), a TMD chalcogen core-level (e.g. S 2p), the C 1s region, the O 1s region, and a survey spectrum across the full range of energies for that XPS system. Alongside XPS, Raman spectroscopy was heavily utilised for each of these samples. Raman spectra were measured for the most conventional excitation wavelength 532 nm (2.33 eV) as well as with 633 nm and 405 nm (1.96 and 3.06 eV) excitations.

This process yielded a minimum of 5 XPS spectra per sample, as there were 1 pristine and 3 annealed samples per material that makes 20 XPS spectra per material, with 10 different materials giving 200 measured spectra, the most useful for this work are overwhelmingly the TMD core-levels and so those will generally be the fitted spectra of interest. This reduces the number of essential spectra to 80 fully fitted, analysed and compared XPS spectra. Alongside this, 3 Raman spectra were acquired per sample resulting in 120 Raman spectra of interest.

Having 200 XPS and 120 Raman spectra of interest becomes an issue of data management and clarity. To manage this, the data will be broken into sections. First, the XPS fitting parameters and Raman of the unannealed “pristine” material will be discussed for each individual TMD material. The thermal stability and oxidation results will then subsequently be discussed with comparison of the materials in each chalcogen grouping.

Charge correction and compensation is an essential aspect to XPS spectroscopy, as discussed in detail in section in Chapter 1. The main impact that charge correction and charge referencing have on XPS spectra is on the energy position of the components. The most common methodology in charge correction is to shift the C-C (sp^3) component to ~ 285 eV, here the chosen value is 284.8 eV. This method is imperfect,⁷⁶ but is widely accepted as the common practice. A potential issue with this method arises if there is poor electrical contact between the measured carbon material and the TMD material. This could result in significant error in the quoted energy position of the TMD components. This is not to say that the peak position numbers should be discounted entirely, but to acknowledge that there is potential error present and that a variation in the literature values for specific components can often be attributed to this.

Another aspect of XPS analysis of TMD materials lacking consistency and accepted values is the energy windows to measure and report for the specific core-levels. This can result in important information being missed or misinterpreted e.g. a common oxide being left outside the measured window and its contributions therefore being missed, examples of these errors in the literature are outlined previously in Chapter 1.

One interesting feature of the TMDs are their varying structures and properties, a number of these and some characteristic information for each material are given in Table.1. While there is not much structural diversity among the most common TMDs, with many adopting either the trigonal prismatic ‘2H’ structure or the octahedral ‘1T’ structure in their most stable forms, there are several less common structures, particularly for the telluride materials. It is possible to synthesise different structures directly, e.g. $MoTe_2$ is frequently cited as being synthesised in either the semiconducting 2H phase or the metallic 1T’ phase^{176, 177}. As 1T’ is the only phase obtained here, the quoted information in Table.1 and the acquired spectra are specifically pertinent to the material used here. Full structural information and representations are provided in the appendix in Fig.A1-3

Table.1 Material properties and characterisation features for the 10 materials studied here.

Material	MoS ₂	WS ₂	PtS ₂	PtS	MoSe ₂	WSe ₂	PtSe ₂	MoTe ₂	WTe ₂	PtTe ₂
Bandgap (bulk/monolayer) eV	1.3 / 1.9 ¹⁶	1.4/ 2 ¹⁷⁸	0.25/ 1.8 ¹⁷⁹	1.36 ¹⁸⁰	1.1/ 1.6 ¹⁷⁸	1.2/ 1.7 ¹⁷⁸	Semimetal/ 1.2 ¹⁷⁹	Semimetal ¹¹⁹	Semimetal ¹²¹	Metallic/0.9 ¹⁷⁹
Structure	Trigonal Prismatic ¹⁶	Trigonal Prismatic ¹⁷⁸	Octahedral ¹⁷⁹	Tetragonal ¹⁸¹	Trigonal Prismatic ¹⁷⁸	Trigonal Prismatic ¹⁷⁸	Octahedral ¹⁷⁹	Monoclinic / Distorted Octahedral ¹¹⁹	Orthorhombic/ Distorted Octahedral ¹²¹	Octahedral ¹⁷⁹
Phase	2H	2H	1T	-	2H	2H	1T	1T'	T _d	1T
Space group	P6 ₃ /mmc	P6 ₃ /mmc	P $\bar{3}$ m1	P4 ₂ /mmc	P6 ₃ /mmc	P6 ₃ /mmc	P $\bar{3}$ m1	P2 ₁ /m	Pmn2 ₁	P $\bar{3}$ m1
Point group	D _{6h}	D _{6h}	D _{3d}	D _{4h}	D _{6h}	D _{6h}	D _{3d}	C _{2h} ²	C _{2v} ⁷	D _{3d}
Main Raman Modes	A _{1g} , E _{1g} , E _{2g} ¹	A _{1g} , E _{1g} , E _{2g}	A _{1g} ¹ , A _{1g} ² , E _g	B _g	A _{1g} , E _{1g} , E _{2g}	A _{1g} , E _{1g} , E _{2g}	A _{1g} , E _g	A _g , B _g	A ₁ , A ₂ , B ₁ , B ₂	A _{1g} , E _g
XPS regions (binding energy eV)	Mo 3d 223-239, S 2p 159-173	W 4f 30-45, S 2p 158-173	Pt 4f 68-82, S 2p 159-173	Pt 4f 68-82, S 2p 159-173	Mo 3d 224-240, Se 3d 51-62	W 4f 30-45, Se 3d 51-61	Pt 4f 69-82, Se 3d 51-62	Mo 3d 224-240, Te 3d 569-591	W 4f 30-48, Te 3d 569-591	Pt 4f 68-82, Te 3d 569-591

5.2.1 TMD Sulfides

5.2.1.1 MoS₂

Molybdenum disulfide is by a significant margin the most studied TMD. Both the XPS and Raman spectra of MoS₂ are widely reported in the literature. As is the case with many of these materials, the existence of well described literature does not automatically result in high-quality characterisations becoming consistently reported across the field.

The most frequently studied and reported XPS core-level regions for MoS₂ are the Mo 3d (~230 eV) and S 2p (~160 eV). The Mo 3d region has a coincidental overlap with the S 2s core-level, this can lead to potential confusion and incorrect fitting.

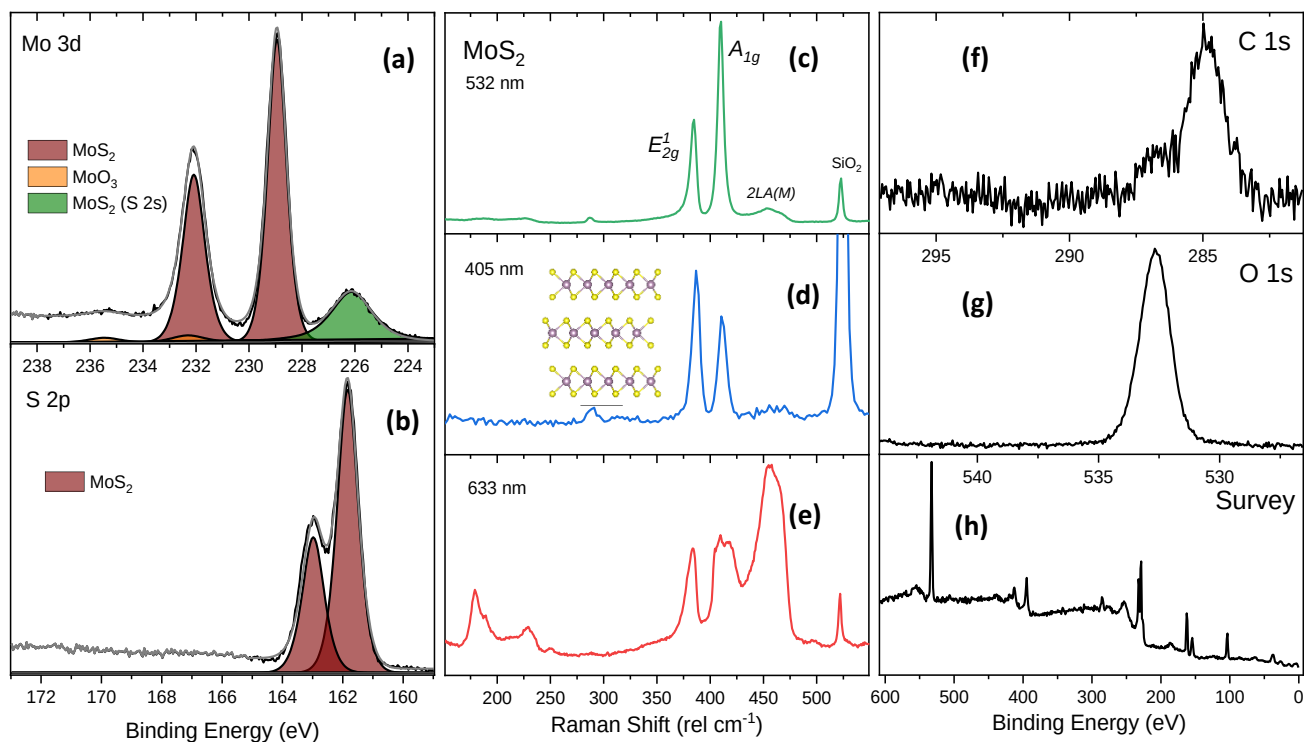


Fig.5.3 Peak-fitted XPS spectra of the Mo 3d **(a)** and S 2p **(b)** core-levels. Raman spectra of MoS₂ acquired with 532 nm **(c)** 405 nm **(d)** and 633 nm **(e)** excitation energies with insert of the MoS₂ structure. XPS spectra of the C 1s **(f)**, O 1s **(g)** and survey **(h)** regions.

Table.5.2 Details of the XPS fitting for MoS₂ core-levels

Mo 3d	MoS ₂	MoS ₂ (S 2s)	MoO ₃	S 2p	MoS ₂
Position (eV)	228.94	226.12	232.32	Position (eV)	161.84
Peak shape	GL(60)	SGL(60)	GL(60)	Peak shape	GL(60)
FWHM (eV)	0.83	1.84	1.46	FWHM (eV)	0.81
Mo %	96.1	-	3.9	S %	100

An appropriate measurement region for the Mo 3d, to include both the commonly occurring Mo 3d components and those from the S 2s, is determined as ~222–240 eV. The XPS spectra of the as-synthesised material in this study in this energy region are shown in Fig.5.3(a). There are three distinct components fitted in this region.

The major features will be discussed, going from the low to high binding energy side of the figure. The first is S 2s at 226.1 eV, this is fitted most accurately with an SGL(60) line shape, a sum Gaussian-Lorentzian line shape, this shows increased Lorentz-like features with a reduced peak height. The most important component is the MoS₂ Mo 3d doublet, with a peak separation of 3.14 eV, and the *Mo 3d_{5/2}* at 228.9 eV. The FWHM of 0.83 eV is an indicator of the high crystallinity and therefore high uniformity in the environment of the Mo⁴⁺ atoms in the MoS₂ and can be used as a comparative baseline to indicate crystallinity or disorder. It should be noted however that this is subject to parameters such as pass energy as outlined in Chapter 2.

The *Mo 3d_{5/2}* of the most common stable oxide, MoO₃, is at 232.3 eV and therefore overlaps with the MoS₂ *Mo 3d_{3/2}*, the presence of MoO₃ can be immediately observed without fitting if the measured region includes the MoO₃ *Mo 3d_{3/2}* at ~235.5 eV, not including this can lead to misinterpretation, misrepresentation and inadequate fits.

The chalcogen core-level used for MoS₂ characterisation is the S 2p. Unlike for the Mo 3d region, there is generally no overlap between the TMD and the common oxide components for sulfur, this can regularly result in the reported XPS region being too narrow to confirm the purity of the material as oxide are outside the measured region, the measured region here is ~159–173 eV. While it is very common to see low levels of molybdenum oxides in MoS₂, the same is not true for trace sulfur oxides. There is only one doublet detected in this region corresponding to MoS₂, with the *S 2p_{3/2}* at 161.8 eV with a peak separation between the *S 2p_{3/2}* and *S 2p_{1/2}* of 1.16 eV.

Raman spectroscopy of MoS₂ is a well-developed area of the literature. As with most TMDs a ~532 nm excitation wavelength is most used for characterisation of MoS₂. Alongside this, 405 and 633 nm lasers are also used here.

As mentioned in Chapter 1 terminology regarding the symmetry, point groups, and Raman modes of the TMD materials as they are reduced in layer thickness towards monolayer can be

troublesome, e.g. bulk-like, even, and odd layer numbers of MoS₂ possess different symmetries and therefore have different point groups and Raman modes. Common practice is to simply use bulk terminology for the material and their Raman modes unless specifically necessary to not. That convention is followed here.

The typical Raman spectra for MoS₂ with the different excitations are shown in Fig. 5.3(c), the characteristic modes of MoS₂ are the E_{2g}^1 and the A_{1g} at ~ 384 and 410 rel cm^{-1} respectively, the separation of these modes can be used to indicate layer thickness with a lower than 20 rel cm^{-1} separation generally indicative of monolayer. The Raman signal here is characteristic of bulk-like MoS₂ as previously seen for TAC films.¹⁶² Another common feature of the MoS₂ Raman spectrum is the broad component at $\sim 460 \text{ rel cm}^{-1}$ this is attributed to phonon interactions and is assigned as $2LA(M)$, as it involves 2 longitudinal acoustic phonons from the edge of the Brillouin zone at the M point¹⁶². Similarly, to XPS, the width of the Raman peaks is indicative of the crystallinity and uniformity of the structure, with the Raman peaks here for TAC MoS₂ substantially broader than the corresponding peaks of CVD MoS₂ in Chapter 3.

Excitation at 405 nm shows very similar features to the 532 nm, with the E_{2g}^1 and A_{1g} peaks being prominent. There is also an inversion in relative intensity with the A_{1g} now being lower in intensity than the E_{2g}^1 is due to a resonance effect at 532 nm.¹⁸²

Further, excitation at 633 nm (1.96 eV) provokes a substantially different spectrum, this is due to wavelengths in this region generating a resonant Raman spectrum from MoS₂ resulting in additional peaks. The energy proximity to the direct bandgap of MoS₂ for this excitation wavelength is the cause of this resonance. The relative lowering of intensity attributed to the first-order Raman modes (E_{2g}^1 and A_{1g}) and significant increase in second-order Raman features is a well know occurrence.^{183, 184}

5.2.1.2 WS₂

The regions of interest for XPS analysis of WS₂ characterisation are the W 4f (~33 eV) and the S 2p (~160 eV) and the resultant data is presented in Fig. 5.4.

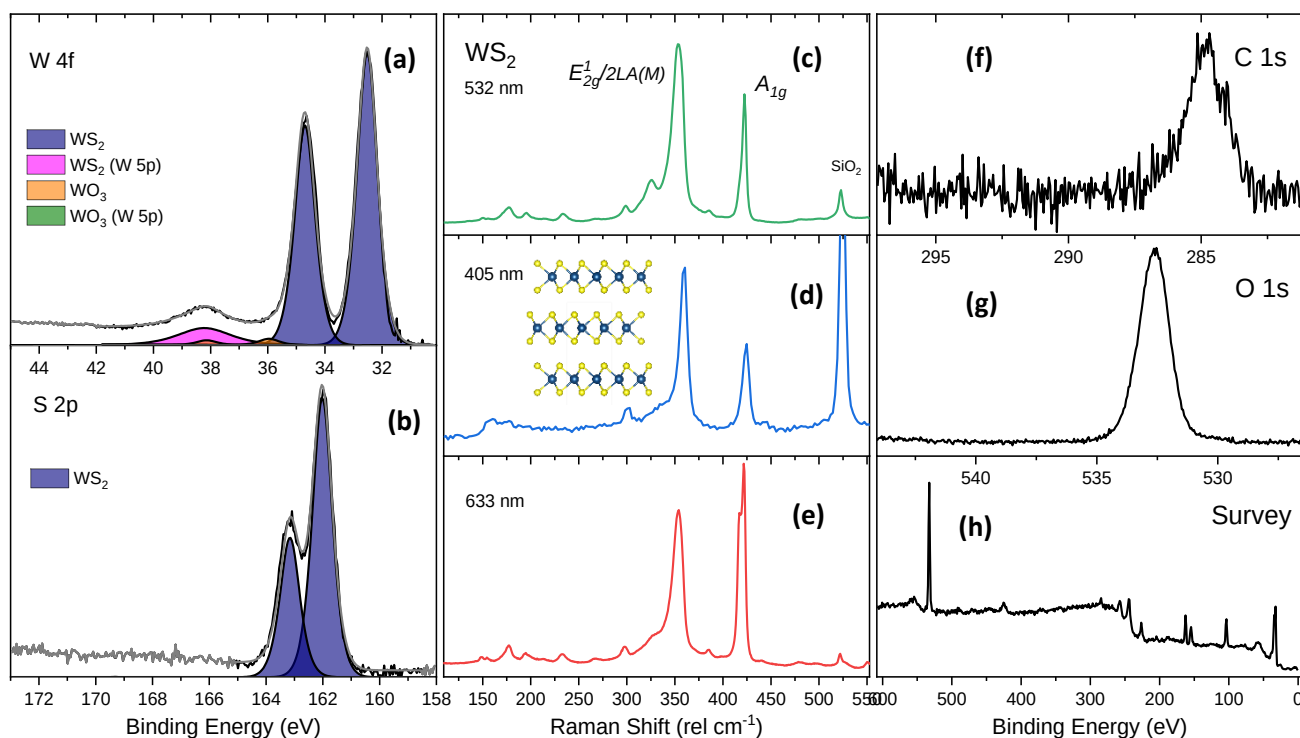


Fig. 5.4 Peak-fitted XPS spectra of the W 4f **(a)** and S 2p **(b)** core-levels. Raman spectra of WS₂ acquired with 532 nm **(c)** 405 nm **(d)** and 633 nm **(e)** excitation energies with insert of the WS₂ structure. XPS spectra of the C 1s **(f)**, O 1s **(g)** and survey **(h)** regions.

Table 5.3 Details of the XPS fitting for WS₂ core-levels

W 4f	WS ₂	WS ₂ (W 5p)	WO ₃	WO ₃ (W 5p)	S 2p	WS ₂
Position (eV)	32.52	38.22	35.96	41.69	Position (eV)	162.02
Peak shape	GL(60)	GL(60)	GL(60)	GL(60)	Peak shape	GL(60)
FWHM (eV)	0.83	2.15	0.82	3.5	FWHM (eV)	0.81
W %	98	-	2	-	S %	100

The W 4f core-level region is the most commonly studied W level in XPS characterisation due to the relative intensity of the core-level and the significant shifts in binding energy position with chemical environment. An appropriate energy window to measure the W 4f was determined to be ~30–45 eV. It has a coincidental overlap with the $W\ 5p_{3/2}$, the splitting of this core-level is large enough that only the $5p_{3/2}$ is located in this window. Fitting and accurately accounting for the $5p_{3/2}$ components in complex W XPS spectra can be difficult and a significant source of error or confusion if poorly accounted for.

The results of the XPS measurements on the WS₂ film made in this work are illustrated in Figure 5.4. Three separate components were measured in this region, all of them fitted with a GL(60) peak shape, a W 4f doublet corresponding to WS₂ with the $W\ 4f_{7/2}$ at 32.5 eV and a peak splitting of 2.18 eV. The WS₂ has its corresponding $5p_{3/2}$ at 38.2 eV. There is a very low level of oxide present in the form of WO₃, with its $W\ 4f_{7/2}$ at ~36 eV. The WO₃ also has its corresponding $5p_{3/2}$ component, but this is below the detection limit here.

Similar to MoS₂, the S 2p core-level region is used for characterisation. The same practice of using a wide energy window (~158–173 eV), to ensure that any oxides present are detected, is followed here. As was also the case for MoS₂, there are no other detected components besides the WS₂ S 2p, with the $S\ 2p_{3/2}$ at 162 eV.

The Raman spectra of WS₂ with the three excitation wavelengths are shown in Fig.4(c–e). Excitation energies in the region of 532 nm are the most common for WS₂ characterisation and so that will be discussed most fully. WS₂ has the same 2H symmetry as MoS₂ and similarly, the E_{2g}^1 and A_{1g} Raman modes are the most prominent for WS₂ also. 532 nm Raman spectroscopy of WS₂ is significantly more complex than MoS₂ as it has a high number of second-order peaks, the most significant is the $2LA(M)$ which overlaps with the E_{2g}^1 resulting in a broad double component feature at ~ 350 rel cm⁻¹. For few-layer WS₂ the ratio of A_{1g} to $2LA(M)$ can be used to identify monolayers, with an exceptionally pronounced $2LA(M)$ component present in monolayer WS₂ due to resonance effects¹⁸⁵.

The Raman spectra of the WS₂ film acquired using a 405 nm excitation laser shows some clear differences from that acquired with the 532 nm. There are markedly fewer second-order peaks as this excitation is off resonance, this is most pronounced in the significantly lower contribution of the $2LA(M)$ resulting in a mostly separated E_{2g}^1 at ~ 355 rel cm⁻¹.

Finally, the 633 nm excitation spectrum shows a similar number of second-order components to the 532 nm. The most unique feature in this spectrum is multiple peak nature of the A_{1g} at ~ 420 rel cm⁻¹, unlike the single peak structure for the other wavelengths. This has been seen in cases where the excitation energy is close in energy to the A exciton energy in WS₂, it is proposed this multi-peak structure is a result of the A_{1g} component from the distinct layers giving varying frequency Raman components¹⁸⁶.

5.2.1.3 PtS₂

To date, PtS₂ is a very rarely studied TMD in the literature, this is in part due to the relative difficulty in synthesis of PtS₂ films. The synthesis of this material and its nuances will be discussed thoroughly in Chapter 6.

As a result of the lack of study into this material there is little high-quality characterisation present in the literature. In particular, XPS and Raman spectra of thin films of PtS₂ have rarely been discussed in detail.

XPS of PtS₂ focuses on the regions of the Pt 4f (~72 eV) and the S 2p (~160 eV), the resultant data is shown in Fig. 5.5 and Table 5.4, below.

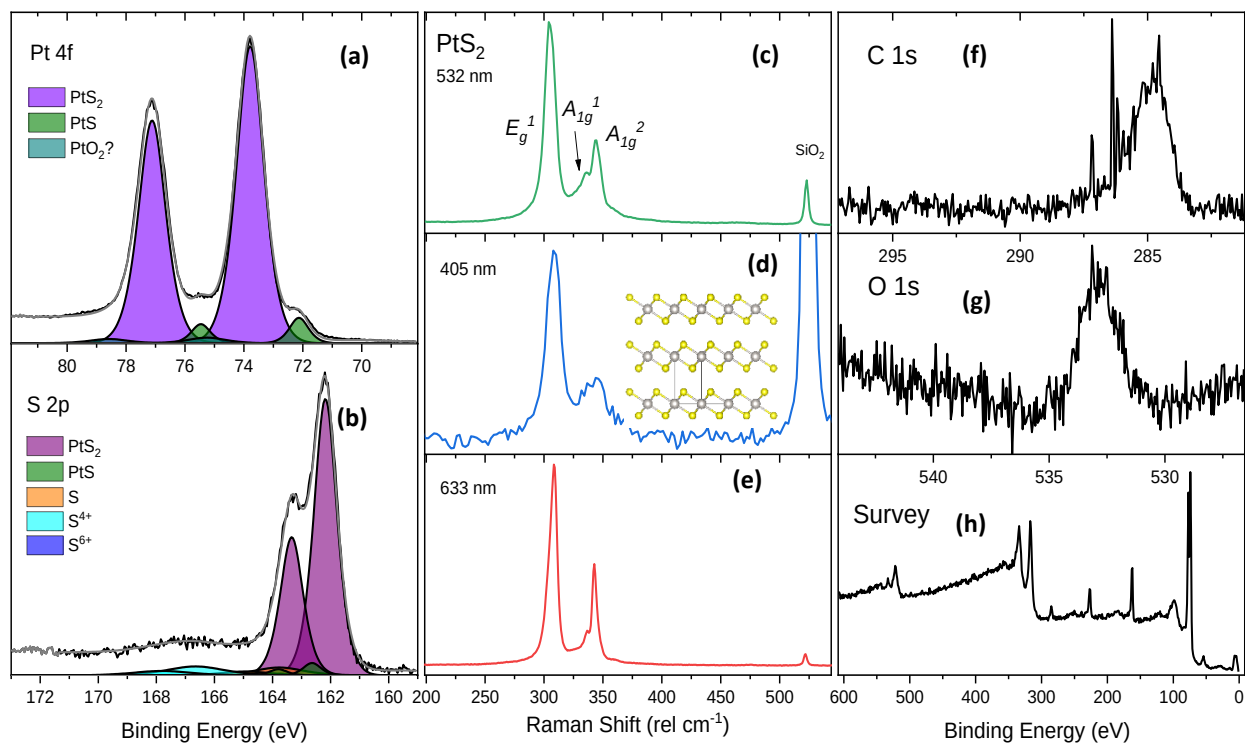


Fig. 5.5 Peak-fitted XPS spectra of the Pt 4f **(a)** and S 2p **(b)** core-levels. Raman spectra of PtS₂ acquired with 532 nm **(c)** 405 nm **(d)** and 633 nm **(e)** excitation energies with insert of the PtS₂ structure. XPS spectra of the C 1s **(f)**, O 1s **(g)** and survey **(h)** regions.

Table.5.4 Details of the XPS fitting for PtS₂ core-levels

Pt 4f	PtS ₂ (Pt ⁴⁺)	PtS (Pt ²⁺)	PtO ₂ ?	S 2p	PtS ₂ (S ²⁻)	PtS (S ²⁻)	Elemental S	S ⁴⁺
Position (eV)	73.79	72.13	75.26	Position (eV)	162.18	162.64	163.78	166.65
Peak shape	GL(60)	GL(60)	GL(60)	Peak shape	GL(60)	GL(60)	GL(60)	GL(60)
FWHM (eV)	1.09	0.76	1.50	FWHM (eV)	0.93	0.72	2	2.35
Pt %	92.1	5.5	2.4	S %	84.7	3	5.3	7

The appropriate energy window for measurements of the Pt 4f core-level here was 68–82 eV.

One of the complications in the synthesis and the characterisation of PtS₂ is the relative stability of PtS and its frequent presence in PtS₂. This can be a significant source of error during analysis.

XPS fitting of the Pt 4f core-level is an underdeveloped area of the literature and is an ongoing area of research which will be discussed more thoroughly in Chapter 6. There were three chemical states detected in the Pt 4f region. Going from low to high binding energy, the first doublet at 72.1 eV is attributed to Pt²⁺ in the form of PtS, it is found to be a common contaminate in PtS₂. This component can be potentially misattributed to Pt metal due to the similar expected peak positions, the symmetric line shape of this component is a clear sign against this, as Pt metal has an asymmetric XPS line shape.

The main PtS₂ component is found at 73.8 eV in this work, with a peak splitting of 3.33 eV.

A third feature is fitted at 75.3 eV, this has been tentatively attributed to a Pt oxide, most likely PtO₂¹⁸⁷. The exact fitting and peak identification of this component is up for some debate due to its consistently low area and significant overlap with both of the other *Pt 4f* states fitted here. Evidence indicating the high probability of this being PtO₂, will be explored more closely for PtSe₂ at a later point.

The energy window for measuring the S 2p region is ~159–173 eV for PtS₂. The S 2p region of PtS₂ is also markedly underexplored in the literature and is described in more detail in Chapter 6 due to its complexity.

Four separate chemical states were identified during deconvolution in this region. Going from low to high binding energy they are the $S\ 2p_{3/2}$ for PtS₂ at 162.2 eV, then the $S\ 2p_{3/2}$ for the low level of PtS at 162.6 eV. Unlike the other sulfide TMDs low levels of elemental sulfur were identified at $S\ 2p_{3/2}$ 163.8 eV and a S^{4+} species at 166.7 eV, this is likely from a sulfite species.

The Raman spectra of PtS₂ are shown in Fig.5.5 (c)-(e). As thin films of PtS₂ are at the moment not studied to the same extent as other TMDs there is not a clear consensus in the literature of the most appropriate excitation wavelength for Raman spectroscopy of PtS₂.

PtS₂ has a distorted octahedral or 1T structure and a D_{3d} point group. There is no significant difference between the Raman spectra acquired with the different excitation wavelengths, and so the discussion will focus on the 532 nm spectrum. There were three intense Raman modes from PtS₂, the most intense being the E_g^1 at 305 rel cm⁻¹. The second main PtS₂ mode is the A_{1g}^2 at 344 rel cm⁻¹ this has ~40% the intensity of the E_g^1 mode in these films. Some complications arise due to the third component, the A_{1g}^1 at 336 rel cm⁻¹. From the XPS analysis it is known there exists a low level of PtS in the measured material, PtS has its main Raman component at 335 rel cm⁻¹ which tightly overlaps with the A_{1g}^1 of PtS₂ this is a source of some potential error but may also serve as a method to identify PtS contamination in the material via Raman spectroscopy.

Additionally, there is a shoulder to this 532 nm Raman spectra at ~360 rel cm⁻¹, it is currently unassigned in literature and determination of this is beyond the scope of this thesis. Using a 405 nm Raman laser yields a significantly lower intensity Raman signal than for 532 nm, it is difficult to ascertain any significant changes in features to the spectrum beyond this. The lowering of intensity and broadening of the components makes any assignment of the heavily overlapping peaks less accurate.

The 633 nm Raman spectrum has a high intensity and shows significantly narrower Raman modes than for the previous wavelength. This shows the three previously discussed components clearly, the separation of the E_g^1 and the A_{1g}^1 also narrows from 39.7 to 34 rel cm⁻¹ when comparing the 532 and 633 nm Raman spectra respectively.

5.2.1.4 PtS

The PtS/PtS₂ system is unique among the materials analysed in this work as it the only TMD which preferentially forms a mono-chalcogenide over a range of common synthesis conditions. The synthesis and characterisation of PtS will also be a central focus of Chapter 6, and so the central aspects of characterisation are discussed herein.

PtS is not a layered material; it has a tetragonal structure as shown in Appendix- Fig.A1. It is therefore markedly different than any of the other materials looked at here, its importance in the characterisation of PtS₂ and the limited amount of characterisation literature of PtS in general elevate the necessity to include PtS here.

XPS of PtS follows the same practice and parameters as that of PtS₂ focusing on the regions of the Pt 4f (~72 eV) and the S 2p (~160 eV). The resultant data is presented in Fig. 5.6 and Table 5.5, below.

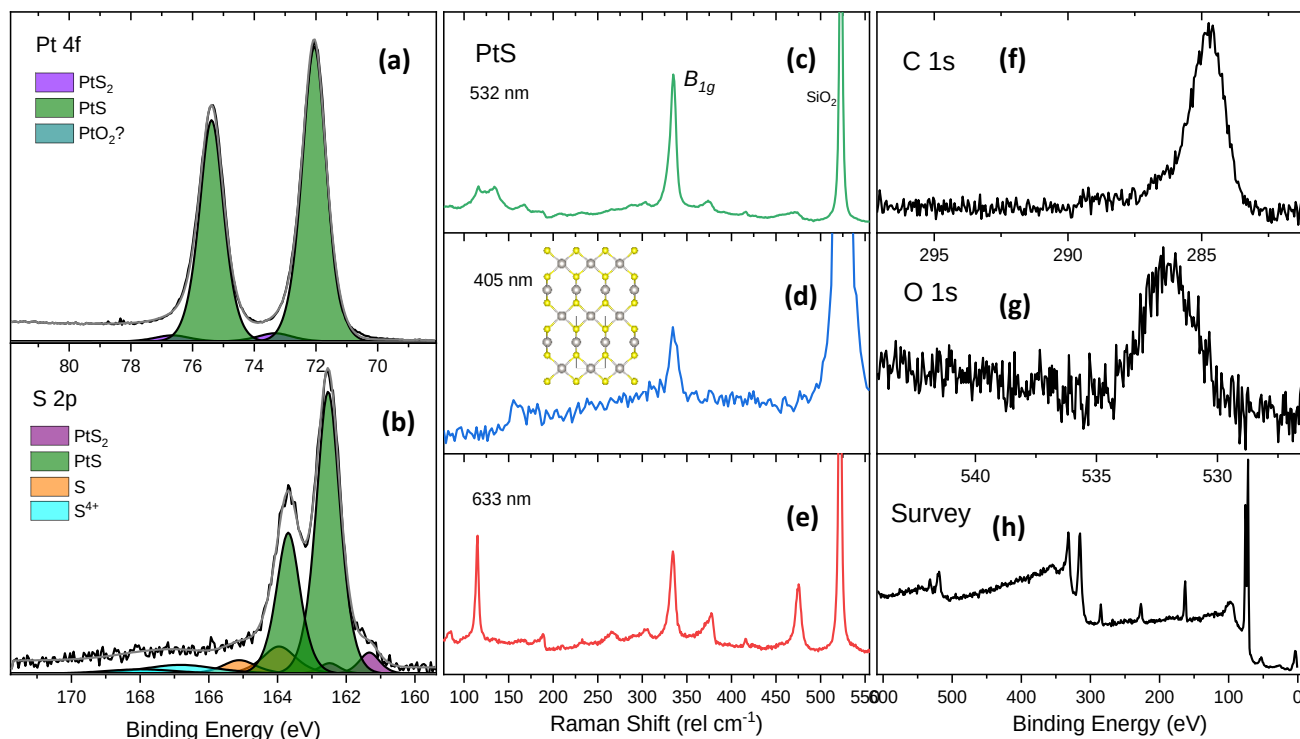


Fig 5.6 Peak-fitted XPS spectra of the Pt 4f (a) and S 2p (b) core-levels. Raman spectra of PtS acquired with 532 nm (c) 405 nm (d) and 633 nm (e) excitation energies with insert of the PtS structure. XPS spectra of the C 1s (f), O 1s (g) and survey (h) regions.

Table 5.5 Details of the XPS fitting for PtS core-levels

Pt 4f	PtS (Pt ²⁺)	PtS ₂ (Pt ⁴⁺)	PtO ₂ ?	S 2p	PtS (S ²⁻)	PtS ₂ (S ²⁻)	Elemental S	S ⁴⁺
Position (eV)	72.05	73.33	-	Position (eV)	162.53	161.33	163.95	166.83
Peak shape	GL(60)	GL(60)	-	Peak shape	GL(60)	GL(60)	GL(60)	GL(60)
FWHM (eV)	0.92	1.36	-	FWHM (eV)	0.81	0.7	1.15	2.5
Pt %	96	4	-	S %	76.9	5	10.6	7.5

As illustrated in Fig 5.6(a) the Pt 4f core-level is measured between ~68–82 eV. Two sets of Pt 4f doublets were fitted in this spectrum with a dominant *Pt 4f*_{7/2} PtS peak at 72.1 eV.

A high energy shoulder is fitted with the *Pt 4f*_{7/2} at 73.3 eV and is attributed to PtS₂. The low intensity of this component and its overlap with the PtS components can make it difficult to assign. However, by quantitative comparison with the S 2p spectrum, the relative area of the PtS₂ *S 2p*_{3/2} can be used to more accurately fit and determine that the high-energy shoulder in the Pt 4f spectrum must be PtS₂.

The recommended energy window for the S 2p core-level was ~159–172 eV. The PtS spectrum measured here is noticeably similar, in terms of components, to the PtS₂ S 2p spectrum. There were four distinct chemical states fitted in the spectrum. Going from low to high binding energy there were, a small PtS₂ component with *S 2p*_{3/2} at 161.3 eV. Further, the main PtS *S 2p*_{3/2} is fitted at 162.5 eV with an 0.81 FWHM. A substantial elemental sulfur component is fitted at 164 eV. And a broad feature with *S 2p*_{3/2} at 166.8 eV is assigned to a S⁴⁺ species, likely in the form of a sulfite as discussed for PtS₂.

Raman spectroscopy of thin-film PtS is a little studied area in the literature. As a result of this, the complex aspects of these Raman spectra are not currently understood and an in-depth theoretical study would be required in order to determine these modes.

Looking first to the 532 nm Raman of PtS in Fig.5.6 (c) the largest peak in the spectrum is from the SiO₂ substrate, indicative of the significantly lower Raman signal generated by PtS in contrast to the TMDs measured previously, all of which gave much stronger Raman signal for similar films.

The most prominent Raman component and the only commonly reported component of the PtS Raman spectrum is the major feature at ~ 330 rel cm⁻¹, this is a combination of two modes, the majority contribution is the B_{1g} mode at 335 rel cm⁻¹ with a shoulder from the E_g at ~ 326 rel cm⁻¹ ¹⁸⁰.

A large number, approximately 10, of low intensity features are spread throughout the spectrum, these are likely to be from a combination of first order and second order Raman features, due to the limited literature in this area, these are currently unassigned.

The 405 nm Raman spectrum of PtS yields very little information due to the low intensity Raman signal at this excitation. The expected main component is clearly present at 334 rel cm⁻¹. The feature at ~ 150 rel cm⁻¹ is due to the spectrometer cut off.

Interestingly the Raman spectrum of PtS using 633 nm excitation wavelength yields a substantially different spectrum than the other two lasers. Unlike the previous spectra there are at least four prominent Raman peaks from PtS in this spectrum. The B_{1g} mode at 334 rel cm⁻¹ and three other currently unreported and unassigned modes at 115 rel cm⁻¹, 375 rel cm⁻¹ and 475 rel cm⁻¹. Many of the unassigned low-intensity features observed in the 532 nm excitation spectrum are detectable in this spectrum also. The presence of only some of these peaks in both spectra is likely due to resonance effects caused by the different wavelengths.

5.2.2 TMD Selenides

5.2.2.1 MoSe₂

MoSe₂ is amongst the most highly studied TMDs, it is prepared here in a similar fashion to MoS₂ films.

The XPS regions of interest for MoSe₂ are the Mo 3d (~ 230 eV) and the Se 3d (~ 55 eV), and the resultant data is shown in Fig. 5.7 and Table 5.6, below.

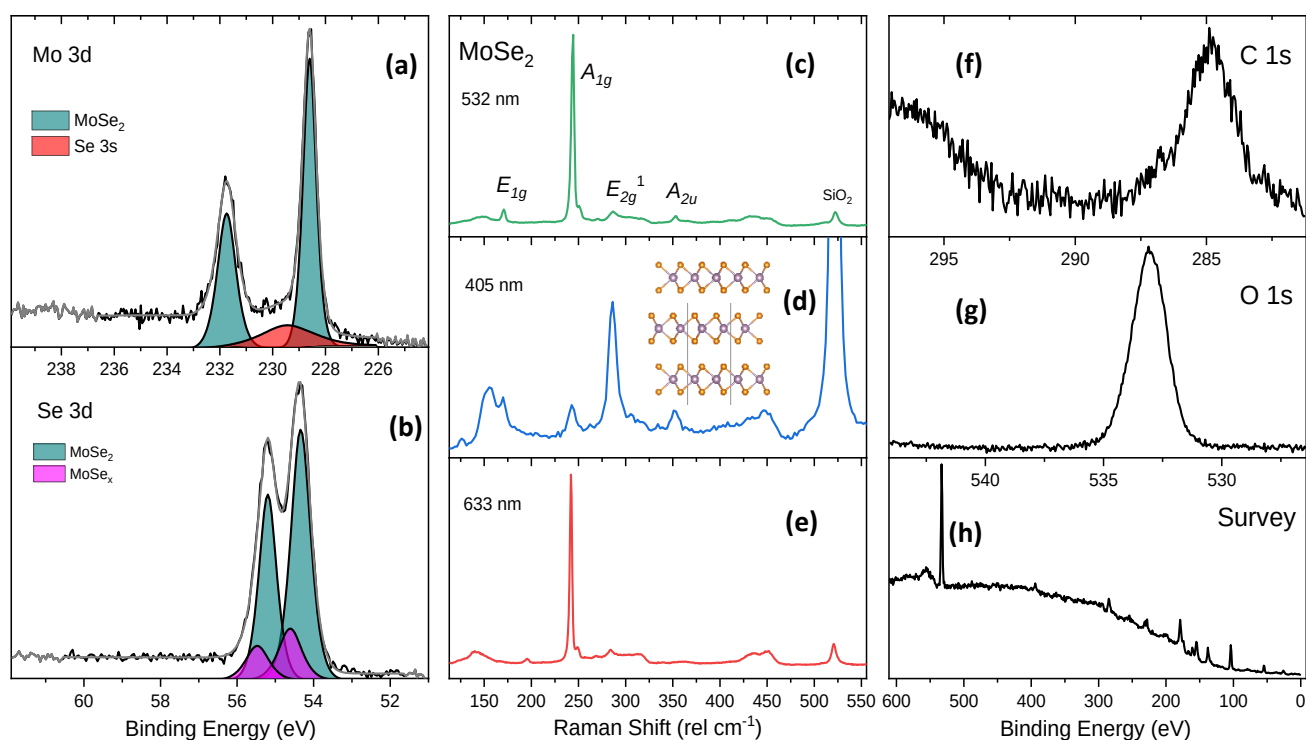


Fig 5.7 Peak-fitted XPS spectra of the Mo 3d **(a)** and Se 3d **(b)** core-levels. Raman spectra of MoSe₂ acquired with 532 nm **(c)** 405 nm **(d)** and 633 nm excitation energies with insert of the MoSe₂ structure. XPS spectra of the C 1s **(f)**, O 1s **(g)** and survey **(h)** regions.

Table 5.6 Details of the XPS fitting for MoSe₂ core-levels

Mo 3d	MoSe ₂	MoSe ₂ (Se 3s)	Se 3d	MoSe ₂	MoSe _x
Position (eV)	228.6	229.44	Position (eV)	54.34	54.61
Peak shape	GL(60)	SGL(60)	Peak shape	GL(60)	GL(60)
FWHM (eV)	0.92	2.4	FWHM (eV)	0.6	0.71
Mo %	100	-	Se %	80.5	16.5

As was the case for MoS₂, and all other Mo containing materials discussed in this thesis, the Mo 3d core-level, is used during XPS characterisation of MoSe₂. The recommended energy

window is similar at 224–240 eV. Three components were fitted in this spectrum, the main Mo 3d doublet has the $Mo\ 3d_{5/2}$ at 228.6 eV, which has a spin-orbit splitting of 3.14 eV for the $Mo\ 3d_{3/2}$. A significant complication in the $MoSe_2$ Mo 3d spectrum is the presence of the coincidentally overlapping Se 3s core-level. The Se 3s overlaps with both of the $MoSe_2$ components which can easily lead to confusion and inaccurate fitting. Here the Se 3s is at 229.4 eV.

The Se 3d is measured between 51–62 eV, shown in Fig. 5.7(b). The Se 3d core-level is fitted here with two doublets, the main $MoSe_2$ Se $3d_{5/2}$ at 54.3 eV, a high binding energy shoulder is resolved by including a second doublet with Se $3d_{5/2}$ at 54.6 eV. The spin-orbit splitting of the Se 3d being 0.86 eV results in significant overlap of these components, opening up the possibility for error in fitting.

This second doublet seen in Fig. 5.7(b) is attributed to a sub-stoichiometric $MoSe_x$ species, this is difficult to unambiguously assign and could potentially be from an undetermined SeO_x species. To be qualitatively consistent there should be a corresponding $Mo\ 3d$ $MoSe_x$ feature, which is not observed here. This may be explained by the $MoSe_2$ and $MoSe_x$ overlapping to a high degree, in that scenario it would be expected to see the $MoSe_2$ $Mo\ 3d$ peaks fitted with wider FWHM than its corresponding Se 3d component, that is the case here (0.92 and 0.6 eV) lending credence to the assignment of the secondary Se 3d species as $MoSe_x$. A similar overlapping high binding energy shoulder is found for all 3 selenides measured here; it is also commonly seen in the literature.^{30, 188} The peak position of this extra component varies for each TMD material, this within error, makes the assignment of oxide unlikely as there should be negligible change in SeO_x peak position between the different TMDs. Not including this sub-stoichiometric TMD component when calculating the stoichiometry of the selenide TMD materials yields significantly divergent results compared to the other TMDs. Together these arguments leave a $MoSe_x$ species as the most likely assignment.

A further complicating feature of selenide XPS is the overlap of the C 1s core-level (~285 eV) and the Se Auger peaks at ~ 287 and 299 eV. As charge referencing was used against the C-C C 1s at 284.8 eV, there is significant potential for increased error. This is one of the many potential issues with C 1s charge correction as previously discussed.

Raman spectroscopy of $MoSe_2$ is a mature area of research with well resolved spectra reported from at least 1980.¹⁸⁹

MoSe₂ has the same structure as MoS₂, that is the 2H, trigonal prismatic structure. The point group is D_{6H}. The 532 nm Raman spectrum of MoSe₂ has four prominent modes, the E_{1g} , A_{1g} , E_{2g}^1 , A_{2u} at 170, 244, 286, 352 rel cm⁻¹ respectively. There are a number of other modes of lower intensity, as they are not relevant here discussion of these is left to previously published works in the literature.^{190, 191}

The 633 nm excitation Raman spectrum of MoSe₂ is similar to the 532 nm, the most notable changes being the lower relative signal from the E_{1g} and A_{2u} peaks.

The 405 nm excitation Raman spectrum of MoSe₂ is complex and noticeably different from the 532 nm spectrum. The most prominent change is the dramatically lower intensity of the A_{1g} mode and the increase of the previously diminutive E_{2g}^1 . It has previously been postulated this is likely due resonance effect with the C exciton of MoSe₂^{190, 191}.

5.2.2.2 WSe₂

WSe₂ is the most widely studied of the selenide TMDs in the literature, likely due to its typically p-type or ambipolar conductivity in contrast to mostly n-type for other TMDs.¹⁹² The XPS regions of interest are the W 4f (~33 eV) and the Se 3d (~55 eV) and their resultant data is shown in Fig. 5.8 and Table 5.7, below.

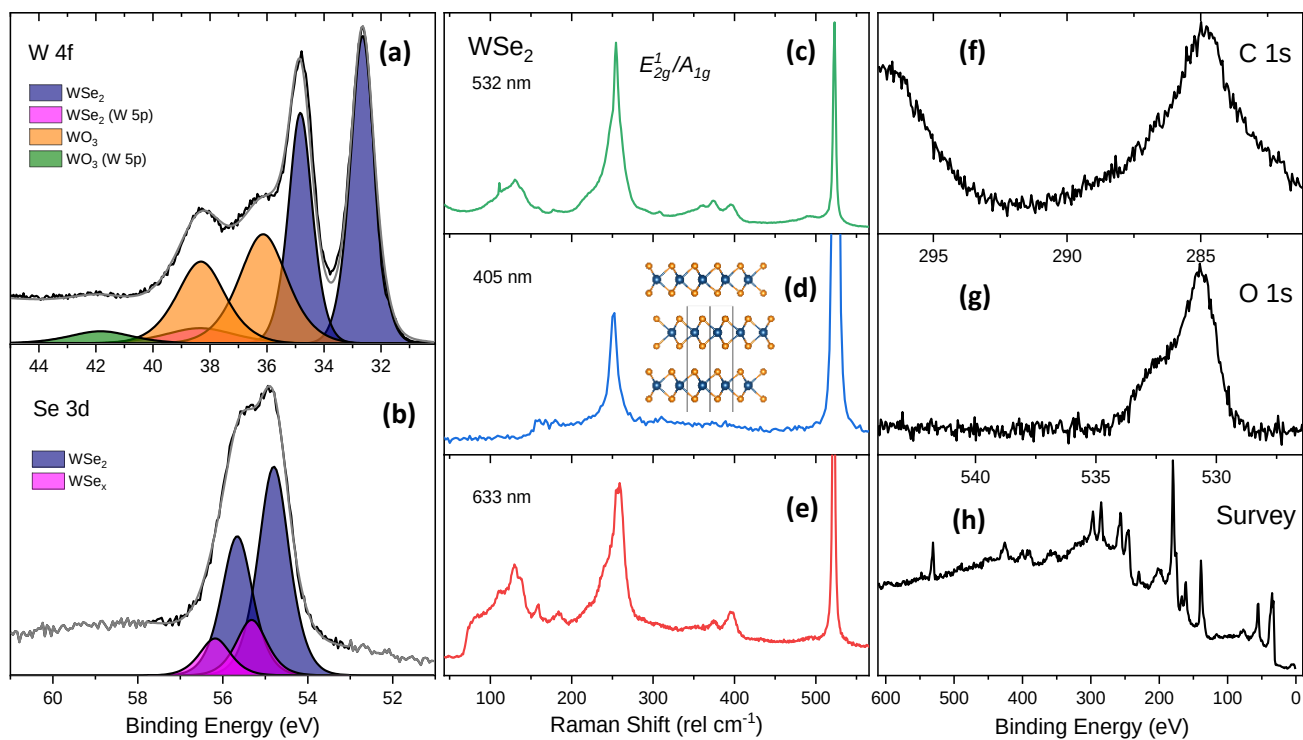


Fig. 5.8 Peak-fitted XPS spectra of the W 4f **(a)** and Se 3d **(b)** core-levels. Raman spectra of WSe₂ acquired with 532 nm **(c)** 405 nm **(d)** and 633 nm **(e)** excitation energies with insert of the WSe₂ structure. XPS spectra of the C 1s **(f)**, O 1s **(g)** and survey **(h)** regions.

Table 5.7 Details of the XPS fitting for WSe₂ core-levels

W 4f	WSe ₂	WSe ₂ (W 5p)	WO ₃	WO ₃ (W 5p)	Se 3d	WSe ₂	WSe _x
Position (eV)	32.65	38.35	36.13	41.83	Position (eV)	54.8	55.32
Peak shape	GL(60)	GL(60)	GL(60)	GL(60)	Peak shape	GL(60)	GL(60)
FWHM (eV)	0.99	2.9	2	2.62	FWHM (eV)	0.85	0.85
W %	58.15	-	41.85	-	Se %	79	21

As was the case for the WS₂ the energy window for the W 4*f* is ~30–45 eV. WSe₂ is fitted here with six components from only two chemical states of W. The main WSe₂ W 4*f*_{7/2} is fitted at 32.6 eV with a 2.18 eV spin-orbit splitting for the W 4*f*_{5/2}. The corresponding W 5*p* component is fitted at 35.4 eV.

There is a significant amount of WO₃ measured in this spectrum, ~40% of W atoms, with the W 4*f*_{7/2} of WO₃ fitted at 36.1 eV with a corresponding W 5*p* at 41.8 eV. Due to the complete overlap of the WO₃ W 4*f* components and the WSe₂ W 5*p*, it can be difficult to accurately account for all of the individual components in this spectrum. Nevertheless, by fixing the ratio of W 4*f*_{7/2} area to W 5*p* area, and finding a fixed binding energy separation, these overlapping components can be accounted for. This required referencing a W 4*f* spectra with little oxide, in this work the WS₂ examined previously was chosen. Accordingly, these parameters for the W 5*p* area were found to be (W 4*f*_{7/2} × 0.148) and the position was found to be W 4*f*_{7/2} + 5.7 eV. It is important to note that the FWHM of this W 5*p* component could not be as simply restricted in this way without significantly increasing the error in respect of the raw dataset.

The Se 3*d* region is measured similarly to MoSe₂ with a recommended region of ~51–61 eV. Similar to the MoSe_x discussed for MoSe₂, the WSe₂ Se 3*d*_{5/2} is fitted at 54.8 eV with the WSe_x component at 55.3 eV. WSe₂, as with all of the selenide TMDs, there was a higher potential error in the specific binding energy assignment of each peak due to the overlap of the C 1*s* and a Se Auger.

The Raman spectra for WSe₂ are shown in Fig.8 (c-e). WSe₂ has the 2H structure and as such the spectrum is dominated by the *E*_{2*g*}¹ and *A*_{1*g*} Raman modes. For WSe₂ these are at very similar frequencies resulting in an intense convoluted peak.

Multiple excitation wavelength Raman of WSe₂ has been well examined in the literature^{193, 194}. The 532 nm excitation Raman spectrum of WSe₂ has a peak for the combined *E*_{2*g*}¹ and *A*_{1*g*} modes at ~254 rel cm⁻¹. This large complex peak also contains contributions from second order modes, a major contribution from the 2*LA*(*M*) centred at ~260 rel cm⁻¹ which shows strong layer dependence¹⁹³, and another second order peak at ~242 cm⁻¹. There is a general lack of discussion of the broad features at ~ 130 rel cm⁻¹ in the current literature, this complex convoluted structure of multiple features is difficult to assign. The remaining features are the results of a variety of second order components.

Raman excitation at 405 nm of WSe₂ yields a simpler spectrum with a reduced number of visible components likely due to this excitation being further from resonance. The contribution from the 2LA(*M*) is greatly reduced in this spectrum resulting in a far narrower main peak ~254 rel cm⁻¹. Conversely, the 633 nm Raman spectrum has a relatively larger contribution from the 2LA(*M*) resulting in a broader main Raman feature.

5.2.2.3 PtSe₂

PtSe₂ is particularly interesting as it has only recently been studied for its 2D and thin film properties.^{38, 195, 196} Given its recent development there is a sparse but increasing amount of literature with high-quality characterisation of this material.

The XPS regions for PtSe₂ characterisation were the Pt 4f (~74 eV) and the Se 3d (~33 eV) and their resultant data is illustrated in Fig. 5.9 and Table 5.8, below.

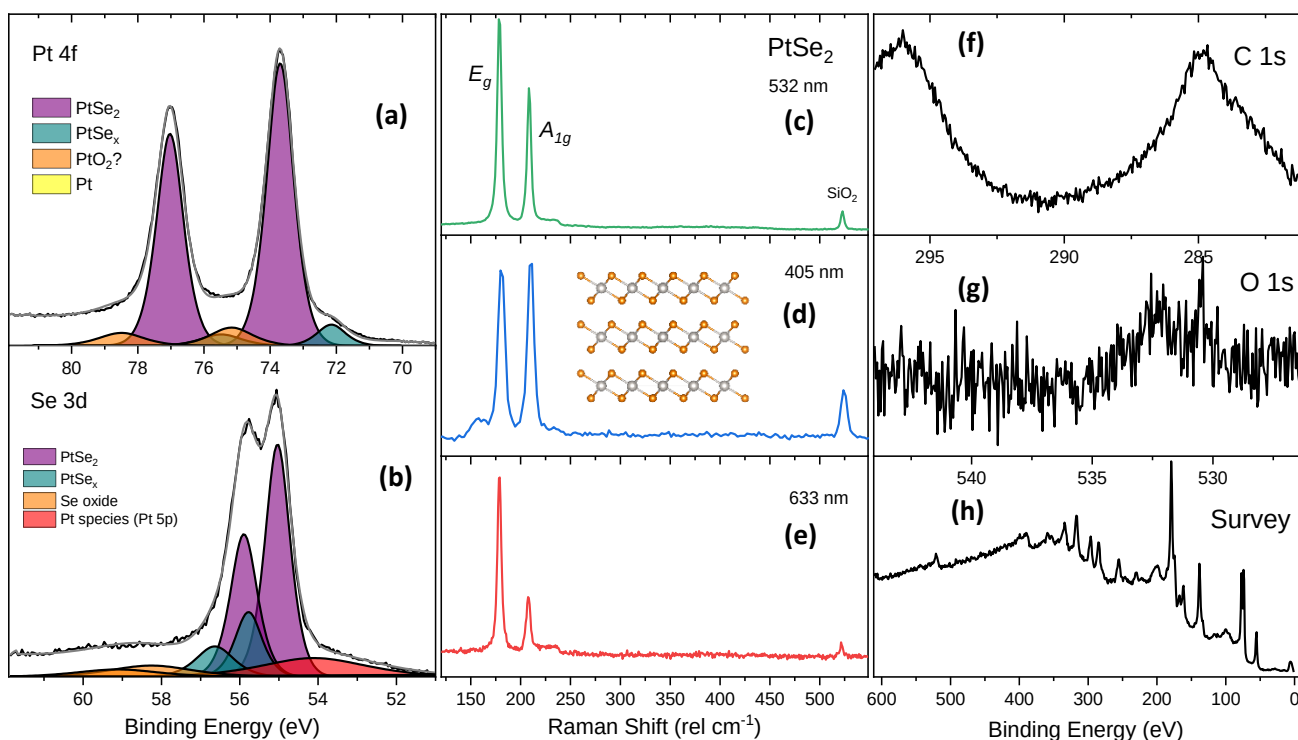


Fig. 5.9 Peak-fitted XPS spectra of the Pt 4f (a) and Se 3d (b) core-levels. Raman spectra of PtSe₂ acquired with 532 nm (c) 405 nm (d) and 633 nm (e) excitation energies with insert of the PtSe₂ structure. XPS spectra of the C 1s (f), O 1s (g) and survey (h) regions.

Table 5.8 Details of the XPS fitting for PtSe₂ core-levels

Pt 4f	PtSe ₂ (Pt ⁴⁺)	PtSe _x (Pt ²⁺)	PtO ₂ ?	Se 3d	PtSe ₂	PtSe _x	Se oxide	Pt 5p
Position (eV)	73.7	72.15	75.17	Position (eV)	55.03	55.77	58.33	53.67
Peak shape	GL(60)	GL(60)	GL(60)	Peak shape	GL(60)	GL(60)	GL(60)	GL(60)
FWHM (eV)	0.96	1.02	1.5	FWHM (eV)	0.77	0.82	2.5	2.62
Pt %	84.6	6.8	8.6	Se %	73.4	18.6	8	-

The PtSe₂ *Pt 4f* XPS core-level has similar issues to the PtS₂ region, in that there are several examples of inaccurate fitting of XPS in the literature.

The energy region for measuring the PtSe₂ *Pt 4f* was ~69–82 eV. This region was fitted with three *Pt 4f* doublets, as seen in Fig 5.10. The first doublet of *Pt 4f*_{7/2} is at 72.2 eV, attributed to a sub-stoichiometric PtSe_x state. The presence of a somewhat correlated PtSe_x component in the *Se 3d* spectrum increases confidence in this assignment. The symmetric nature of this peak indicates that it is not Pt metal, though this could potentially be a PtO_x component.

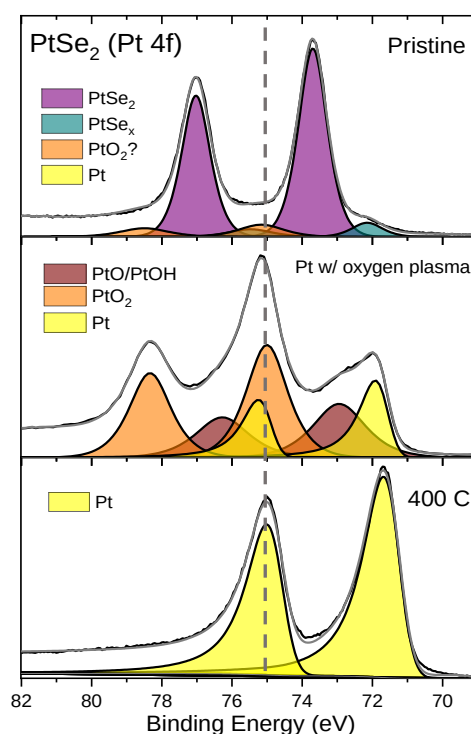


Fig 5.10 A comparison of three Pt 4f XPS spectra. Showing Pt metal, plasma oxidised Pt metal, and PtSe₂ spectra.

The PtSe₂ *Pt* 4 $f_{7/2}$ is fitted at 73.7 eV with 3.33 eV splitting. The third component is attributed to PtO₂ with *Pt* 4 $f_{7/2}$ at 75.2 eV.

In an attempt to verify that this chemical state is a Pt oxide, a Pt metal film was exposed to an oxygen plasma. A comparison of the Pt 4f spectrum for PtSe₂, the oxygen plasma treated film, and a Pt metal film is provided in Fig. 5.10. In Fig. 5.10 it can be seen that after oxygen plasma the film has two clear new chemical states, one with *Pt* 4 $f_{7/2}$ at ~73 eV and the other at ~75 eV, these are attributed to a Pt(II), likely PtO, and also to a Pt(IV) attributed to PtO₂. Similar oxide states are seen in many of the Pt TMDs measured here. This indicates that the *Pt* 4 $f_{7/2}$ component at 75.2 eV for PtSe₂ was correctly assigned to a PtO₂ state.

The Se 3d core-level region was measured here between ~51–63 eV. The Se 3d region for PtSe₂ is the most complex of the Se 3d regions examined in this chapter. This core-level is fitted with seven components corresponding to four chemical states.

A major complication in this material is the coincidental overlap of the *Pt* $5p_{3/2}$ with the low binding energy side of this spectrum, fitted here at approximately 53.7 eV. The *Pt* $5p_{1/2}$ is not included here as the spin orbit splitting of the *Pt* $5p$ is 24 eV. This then allows the *Se* $3d_{5/2}$ for PtSe_2 to be assigned and fitted at 55 eV. The *Se* $3d_{5/2}$ corresponding to the previously discussed PtSe_x state is fitted at 55.8 eV. The broad feature at ~59 eV is tentatively assigned here to an undetermined Se oxide at 58.3 eV.

Owing to the relative nascency of PtSe_2 as a material of interest for 2D TMDs, Raman spectroscopy is an area with rapidly advancing understanding for the specific nuances of thin film PtSe_2 . PtSe_2 has the octahedral 1T structure shared by all of the Pt TMDs measured here. This gives it a D_{3d} point group. The 532 nm excitation Raman spectrum of PtSe_2 matches very closely with the literature and shows the two prominent modes at 178 and 209 rel cm^{-1} , these are the E_g and the A_{1g} respectively. The shoulder at ~233 rel cm^{-1} is from a combination of the A_{2u} and E_u longitudinal optical modes.¹⁹⁶ These modes are sensitive to the film thickness with sharper peaks for lower thicknesses and a near absence of this mode for bulk samples.¹⁹⁶

While the 405 nm excitation Raman spectrum of PtSe_2 maintains the two intense Raman modes at similar frequencies to the 532 nm, the ratio of these peaks is significantly different. The A_{1g} mode is now slightly more intense than the E_g . Due to a low signal-to-noise ratio, it is difficult to ascertain if the broad feature at ~233 rel cm^{-1} is present in this spectrum also. An apparent feature at ~156 rel cm^{-1} appears for this wavelength, this is not a Raman feature and is simply a result of the spectrometer cut-off and can be seen at this position for all of the 405 nm spectra.

The Raman spectra taken with 633 nm excitation is mostly similar to the 532 nm spectrum with the exception of the peak intensity ratio between the E_g and A_{1g} modes which shows a lower contribution from the A_{1g} mode.

5.2.3 TMD Tellurides

5.2.3.1 MoTe_2

Telluride TMDs are, as of the time of writing this thesis, by a wide margin the least studied of the TMDs compared to sulfides and selenides. This is partly due to the increased complexity of their synthesis and, also, the potentially more hazardous synthesis due to the toxicity of Te.¹⁹⁷

The XPS regions for MoTe_2 characterisation are the Mo 3d (~230 eV) and the Te 3d (~573 eV) and their resultant data is illustrated in Fig. 5.11 and Table 5.10, below.

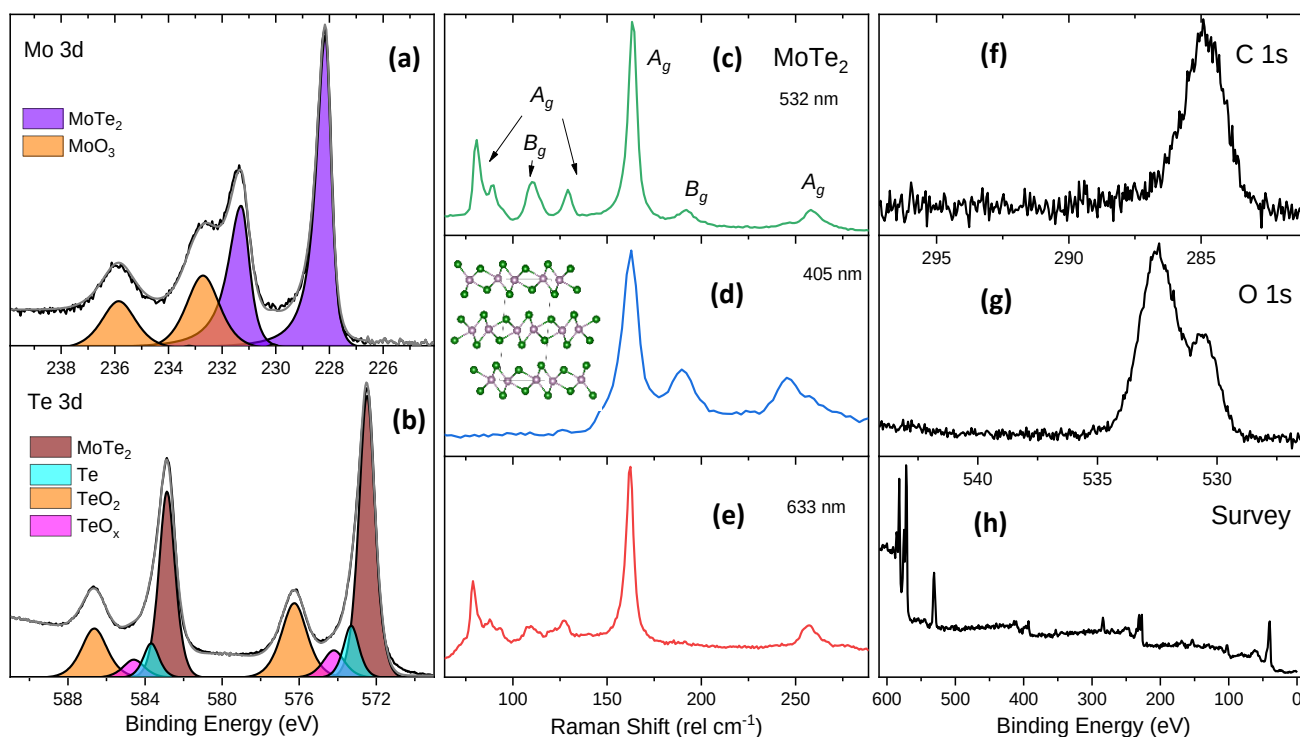


Fig. 5.11 Peak-fitted XPS spectra of the Mo 3d (a) and Te 3d (b) core-levels. Raman spectra of MoTe_2 acquired with 532 nm (c) 405 nm (d) and 633 nm (e) excitation energies with insert of the MoTe_2 structure. XPS spectra of the C 1s (f), O 1s (g) and survey (h) regions.

Table 5.9 Details of the XPS fitting for MoTe₂ core-levels

Mo 3d	MoTe ₂	MoO ₃	Te 3d	MoTe ₂	TeO ₂	Elemental Te	TeO _x
Position (eV)	228.15	232.71	Position (eV)	572.47	576.26	573.18	574.1
Peak shape	LA(1.1, 2.3, 2)	GL(60)	Peak shape	GL(60)	GL(60)	GL(60)	GL(60)
FWHM (eV)	0.52	1.46	FWHM (eV)	0.95	0.139	1.10	1.44
Mo %	70.1	29.9	Te %	58.5	22.1	13.6	5.8

Fig. 11 (a) shows the 1T' MoTe₂ Mo 3d core-level spectrum, this is measured between 224–240 eV. This region is fitted with two doublets from two chemical states, MoTe₂ is the only Mo TMD to not have overlapping XPS core-levels from the chalcogen. The MoTe₂ *Mo 3d*_{5/2} component is fitted at 228.2 eV, importantly this doublet is asymmetric, through a trial-and-error process this shape is found to be best fitted by an asymmetric LA(1.1, 2.3, 2) line shape. As discussed in Chapter 1, this asymmetry indicates the film is metallic in nature.

The second doublet corresponds to the commonly observed MoO₃ and the *Mo 3d*_{5/2} is fitted at 232.7 eV.

The Te 3d core-level region is measured between ~570–593 eV. The high spin-orbit splitting of this core-level of 10.38 eV necessitates this wide energy window. This region is fitted with four doublets, these will be described from low to high binding energy. The *Te 3d*_{5/2} for MoTe₂ is fitted at 572.5 eV, the significantly higher FWHM of this compared to the MoTe₂ *Mo 3d*_{5/2} component is due to the asymmetric peak shape of the Mo 3d component and the large difference in binding energy. An elemental Te component is fitted with *Te 3d*_{5/2} at 573.2 eV. A sub-stoichiometric Te oxide, called TeO_x, is fitted at 574.1 eV. The rationale for the fitting of this component requires comparison across the three telluride TMDs measured here, as well as the spectral data from the different anneal temperatures. The most common Te oxide TeO₂ has *Te 3d*_{5/2} fitted here at 576.3 eV.

The Raman spectra of the 1T' MoTe₂ are shown in Fig.5.11 (c)-(e). A complication of the spectra for MoTe₂ and the other tellurides is the relatively low Raman shift of the characteristic Raman modes ($\sim 50\text{--}300\text{ rel cm}^{-1}$). This can make accurate characterisation partially dependant on the low-frequency range of the spectrometer. The 532 and 633 nm wavelengths here were able to characterise all of the peaks in this range, the 405 nm had a higher spectrometer cut-off of $\sim 140\text{ rel cm}^{-1}$, therefore limiting the number of peaks resolvable.

1T' MoTe₂ has the low symmetry point group C_{2h}^2 giving it numerous low-frequency modes. The high level of complexity relative to the other TMDs has resulted in telluride TMDs being a less settled science and there is still some debate as to the assignment of modes. The work by Song et al.¹⁹⁸ will serve as the basis for the majority of this limited Raman study.

Seven Raman peaks are measured in the 532 nm Raman spectrum in Fig. 5.11 (c), five of these at $\sim 80, 89, 129, 164,$ and 258 rel cm^{-1} are assigned the A_g symmetry, the remaining peaks at ~ 111 and 192 rel cm^{-1} are assigned the B_g symmetry.

The impact of the Rayleigh scattering filter on the 405 nm spectrum cuts off the peaks below the main A_g peak, leaving only the 164 and 258 rel cm^{-1} peaks for the A_g symmetry. The 192 rel cm^{-1} B_g feature is maintained with this excitation wavelength and appears to show a higher relative intensity than for 532 nm.

Moreover, the 633 nm spectrum shows a similar spectrum to the 532 nm with a couple of exceptions. The 192 rel cm^{-1} B_g Raman peak is no longer detected. The Raman modes between $85\text{--}150\text{ rel cm}^{-1}$ are all significantly broader with further intersection of the peaks making accurate assignment more difficult.

5.2.3.2 WTe₂

The main characteristic XPS regions for WTe₂ are the W 4f (~33 eV) and Te 3d (~573 eV). Their resultant data is illustrated in Fig. 5.12 and Tables 5.10–5.11, below.

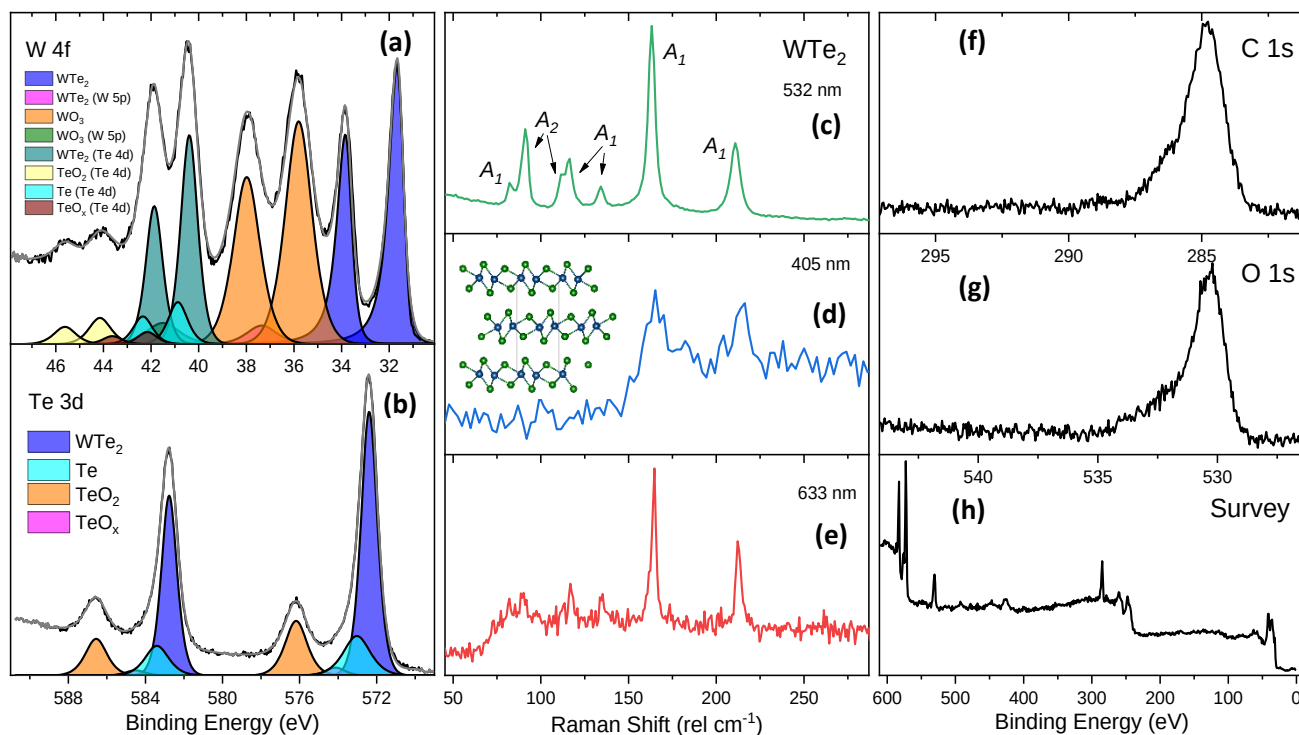


Fig.5.12 Peak-fitted XPS spectra of the W 4f **(a)** and Te 3d **(b)** core-levels. Raman spectra of WTe₂ acquired with 532 nm **(c)** 405 nm **(d)** and 633 nm **(e)** excitation energies with insert of the WTe₂ structure. XPS spectra of the C 1s **(f)**, O 1s **(g)** and survey **(h)** regions.

Table 5.10 Details of the XPS fitting for the W 4f core-level

W 4f	WTe ₂	WTe ₂ (W 5p)	WO ₃	WO ₃ (W 5p)	WTe ₂ (Te 4d)	TeO ₂ (Te 4d)	Te (Te 4d)	TeO _x (Te 4d)
Position (eV)	31.65	37.35	35.80	41.50	40.40	44.15	40.87	42.15
Peak shape	LA(1.3,2.5,11)	LA(1.3,2.5,11)	GL(60)	GL(60)	GL(60)	GL(60)	GL(60)	GL(60)
FWHM (eV)	0.61	1.48	1.33	1.64	0.84	1.08	0.95	0.95
W%	44.2	-	55.8	-	-	-	-	-

Table 5.11 Details of the XPS fitting for the Te 3d core-level

Te 3d	WTe ₂	TeO ₂	Elemental Te	TeO _x
Position (eV)	572.39	576.18	573.03	574.14
Peak shape	GL(60)	GL(60)	GL(60)	GL(60)
FWHM (eV)	0.98	1.34	1.64	1.17
Te %	63.7	18	16	2.3

In regard to XPS characterisation, WTe₂ is notably the most complicated of the TMDs discussed in this thesis due to the overlap of the W 4f, W 5p, and the Te 4d core-level regions. Due to this, it was found that measuring between ~30–48 eV allowed for the most appropriate fitting. This region, as shown in Fig. 5.11, is fitted with fourteen components from just five different chemical states.

Going from low to high binding energy these were, the WTe₂ W 4f_{7/2} at 31.7 eV, fitted with an asymmetric peak shape. Through trial and error this was most accurately described by a LA(1.3, 2.5, 11) line shape. The corresponding W 5p component used the fixed parameters described for WSe₂ and was fitted at 37.4 eV.

There is a prominent oxide contribution in the as measured material in the form of WO_3 with its $W\ 4f_{7/2}$ fitted at 35.8 eV and its $W\ 5p_{3/2}$ at 41.5 eV.

Turning to the Te 4d components, these are subject to heavy overlapping of components. Accurate fitting of these components required comparative analysis with the Te 3d region. Four sets of doublets were fitted for the Te 4d with spin-orbit splitting of 1.47 eV. The WTe_2 $Te\ 4d\ 5/2$ is fitted at 40.4 eV. The second doublet is attributed to an elemental Te component with $Te\ 4d\ 5/2$ at 40.87 eV. The most common oxide of Te, TeO_2 , is significantly shifted from the other peaks and is fitted with $Te\ 4d\ 5/2$ at 44.2 eV. A low intensity component is found with $Te\ 4d\ 5/2$ at 42.2 eV, this is attributed to a sub-stoichiometric oxide of Te, called TeO_x here.

The Raman spectra of WTe_2 at the three excitation wavelengths is given in Fig.11(c–e). WTe_2 has the C_{2v}^7 point group, it has 12 atoms in the unit cell giving rise to a number of Raman modes. Similar to MoTe_2 , the Raman of WTe_2 is quite complex and has not been as extensively studied as other 2D TMDs. The assignment of the Raman peaks in this chapter is based on several recent works.^{121, 199, 200}

The 532 nm excitation spectrum has seven clearly discernible component peaks. Five of these were related to an A_1 symmetry, with peaks at ~ 82 , 116, 134, 163, and 211 rel cm^{-1} . The other two modes are from an A_2 symmetry and are at ~ 91 , and 112 rel cm^{-1} .

The 405 nm spectrum is of limited utility as the modes below 150 are cut off. The low signal-to-noise ratio leaves the A_1 peak at 163 rel cm^{-1} and the A_2 peak at 211 rel cm^{-1} as only partly discernible.

Using 633 nm excitation spectra here also suffered from a low signal-noise ratio. Accounting for this, little substantial difference from the 532 nm spectrum can be distinguished.

5.2.3.3 PtTe_2

PtTe_2 is metallic in the bulk form and has been artificially synthesised since at least 1897²⁰¹. The Pt 4f (~ 73 eV) and the Te 3d (~ 573 eV) core-levels were used for characterisation of PtTe_2 . The resultant data are illustrated in Fig. 5.13 and Table 5.12 below.

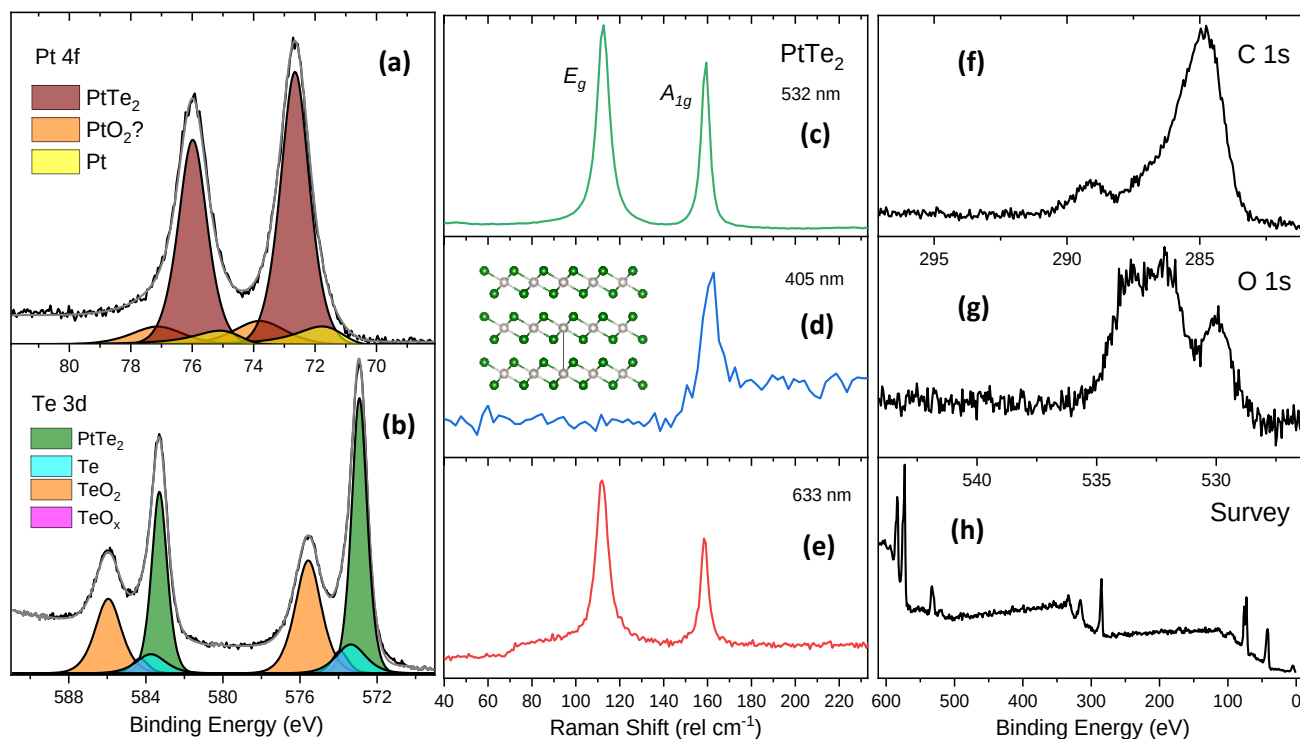


Fig. 5.13 Peak-fitted XPS spectra of the Pt 4f **(a)** and Te 3d **(b)** core-levels. Raman spectra of PtTe₂ acquired with 532 nm **(c)** 405 nm **(d)** and 633 nm **(e)** excitation energies with insert of the PtTe₂ structure. XPS spectra of the C 1s **(f)**, O 1s **(g)** and survey **(h)** regions.

Table 5.12 Details of the XPS fitting for PtTe₂ core-levels

Pt 4f	PtTe ₂	Elemental Pt	PtO ₂ ?	Te 3d	PtTe ₂	TeO ₂	Elemental Te	TeO _x
Position (eV)	72.65	71.30	73.80	Position (eV)	572.92	575.57	573.36	573.92
Peak shape	GL(60)	LA(1.2,85,70)	GL(60)	Peak shape	GL(60)	GL(60)	GL(60)	GL(60)
FWHM (eV)	1.11	1.5	2	FWHM (eV)	0.95	1.59	1.80	0.97
Pt %	77.7	10	12.3	Te %	50.8	35	10.1	4.1

The measured energy window for the Pt 4f here is ~68–82 eV. This region is fitted with six components from three chemical states. Unlike for the other Pt containing TMDs, an asymmetric *Pt* 4f_{7/2} peak is fitted at 71.3 eV and is attributed to Pt metal. It is not determined if this is the result of unconverted starting material or was a product of degradation of the material prior to the XPS measurements. The *Pt* 4f_{7/2} corresponding to PtTe₂ was fitted at 72.7 eV. A broader low energy doublet provisionally assigned as PtO₂ is also fitted with the *Pt* 4f_{7/2} at 73.8 eV.

The Te 3d core-level region is measured between ~569–591 eV. This region is measured to include eight components from four chemical states of Te. These are largely similar to those described for the other TMD tellurides discussed previously. The *Te* 3d_{5/2} for PtTe₂ was fitted at 572.9 eV. The elemental Te and TeO_x components were fitted at 573.4 and 573.9 eV respectively. The most common Te oxide, TeO₂ was fitted at 575.6 eV.

The Raman spectra of PtTe₂ are given in Fig. 5.13(c)-(e). Unlike the other tellurides studied, PtTe₂ is isostructural with its corresponding sulfide and selenide TMDs. It has a 1T structure²⁰² giving the *D*_{3d} point-group symmetry and corresponding Raman modes, and therefore a significantly simpler Raman spectrum than the other 2 tellurides.

The 532 nm Raman spectrum shows two clear peaks, these are the *E_g* mode at ~112 rel cm⁻¹ and the *A_{1g}* mode at ~159 rel cm⁻¹. As was the case for the other telluride TMDs, the 405 nm Raman spectrum is of much lower utility as much of the region of interest is below the cut-off. Lastly, the 633 nm excitation Raman of PtTe₂ shows the same two Raman modes present for 532 nm excitation at very similar frequencies.

5.2.4 Stoichiometry

One of the most common uses of XPS in 2D materials literature is to measure the stoichiometry of the material. While XPS is one of the few methods through which this is possible, it is not a trivial process. As previously discussed in Chapter 1, factors including the transmission function, relative-sensitivity factors, sample cleanliness, sample thickness, etc. in combination with key fitting choices each can have significant impacts on any calculated stoichiometry. Due to these factors accurate measurement of material stoichiometry is most applicable to experiments in ideal conditions with very high-quality material in pristine environments.

Intentionally the XPS analysis of 2D TMDs presented here used materials which have been exposed to ambient and have surface contamination, defects, and are partially oxidised, this reflects more accurately many of the XPS spectra seen in the literature for these materials.

Due to their all-surface nature the properties of 2D materials can be affected by variations in their stoichiometries- defects, vacancies, adatoms are all well known to be common occurrences. While it can be tempting to draw significant conclusions from XPS-determined stoichiometry, the error in these calculations can often be greater than any real variation from ideal stoichiometry in the material. However, this does not mean that XPS-calculated stoichiometry is not worthwhile or valuable in non-ideal conditions, semi-quantitative analysis of the stoichiometry serves a key role when validating the XPS fitting for a material.

The calculated stoichiometry from the XPS of the nine TMD materials discussed thus far in this chapter are presented in Fig. 5.14. An average stoichiometry of 1.92 with standard deviation of 0.13 gives an indication of the typical error in these calculations. I would consider the PtS₂ calculated stoichiometry of 1.69 to be the only one clearly indicating a definitive variation, for PtS₂ in particular this is likely a combination of the presence of PtS and the significantly more complex S 2p XPS core-level, the multiple overlapping components lead to inherently higher potential error in analysis.

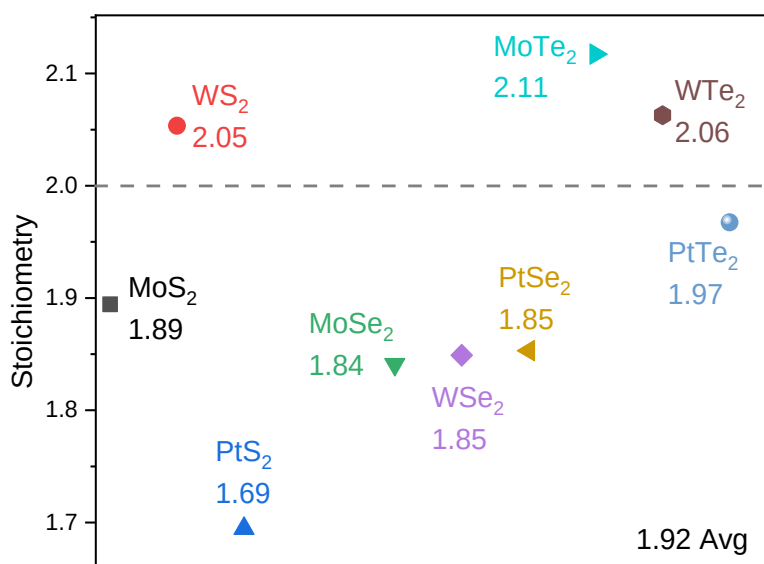


Fig. 5.14 Calculated stoichiometry values for the as synthesised TMD films

5.3 Thermal Stability and Characterisation of TMDs

An effective method to detect and assign the various features of an XPS spectrum for a material is to analyse a series of data which can help to differentiate between components and indicate their origin e.g. oxide or TMD. This method to improve the quality and reliability of the data is used in the work herein. This method can be expanded to not only improve the fitted XPS spectra of all the thin-film materials measured here but to also provide a better understanding of the oxidation tendencies of the materials. Together this can serve as a chance to further expand the library of TMD XPS data.

To achieve consistency in this experiment, individual samples of each material were separated into 4 pieces with 3 of these annealed in air for 30 minutes in 50% humidity at one of three temperatures, 150, 300, and 400 °C, respectively. Optical images of the samples are presented in Fig. 5.15 and further optical microscopy images are shown in Appendix Fig. A8. Despite the relative simplicity of this experiment, it can yield a significant amount of new information on the in-air stability of these materials and the most likely degradation pathways. This is achieved by examining changes in the XPS and Raman spectra of the materials at each of the temperatures.

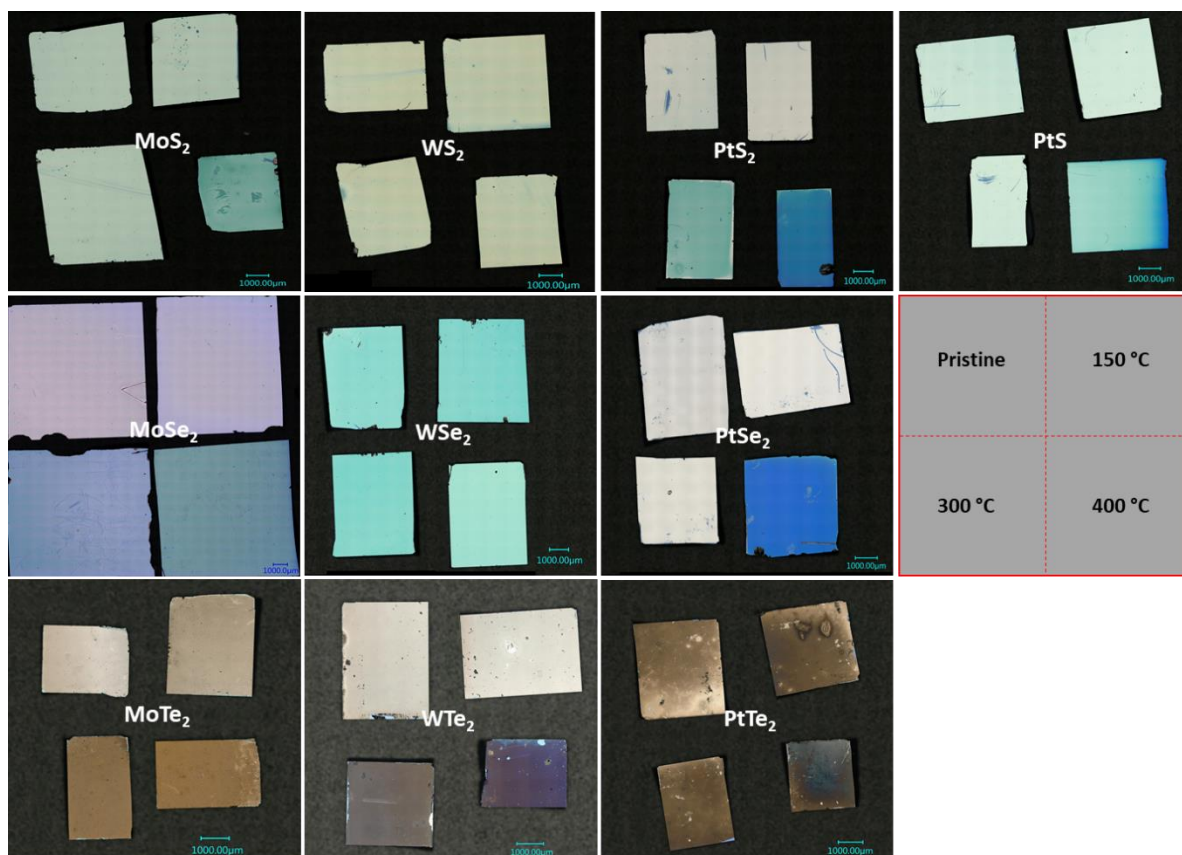


Fig. 5.15 Optical images of the 10 materials showing the changes in surface appearance after ambient annealing at 150, 300, and 400 °C.

The high volume of data generated by this section provides the greatest insights when viewed comparatively, and so the XPS and Raman data for each set of TMDs, categorized by chalcogen, will be displayed together (e.g. comparison of MoS₂, WS₂ and PtS₂). New insights can also be gained by comparing this data by transition metal (e.g. comparison of MoS₂, MoSe₂ and MoTe₂), this will be shown and discussed subsequently.

Due to the large number of figures in this study, two data presentation decisions were made. Firstly, the XPS spectra of the C 1s, O 1s, and survey region for all the materials are not included in this chapter but are instead presented in appendix Fig. A9. Secondly, the assembled Raman data is displayed closely together for each material to aid in direct comparison. This can hinder the readability of the finer details in some spectra. Consequently, all of the Raman spectra are also displayed individually in Appendices A8–11, grouped by Raman excitation energy which can be referred to if further clarity is required of any individual spectrum.

5.3.1 Transition Metal Sulfides

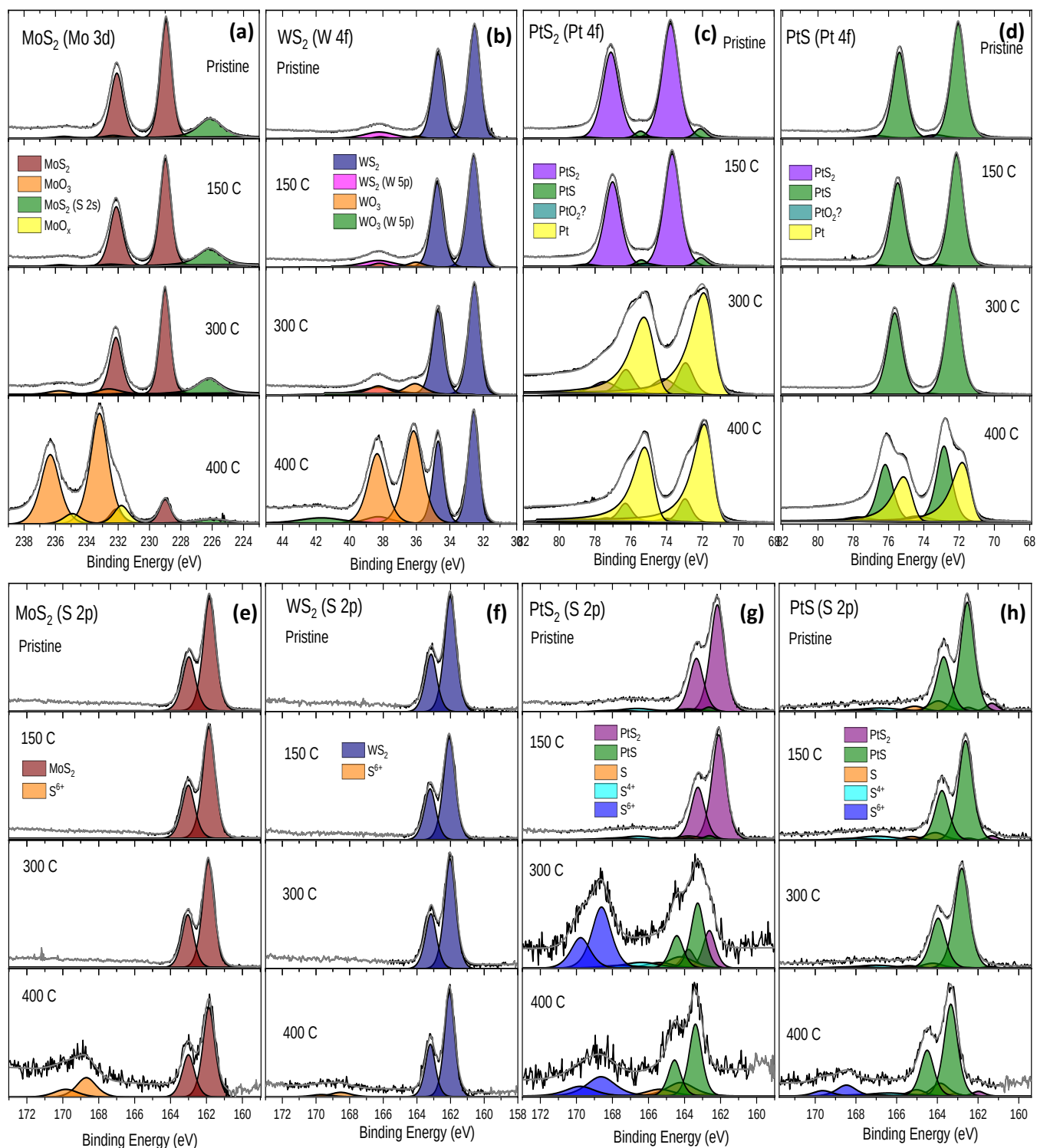


Fig. 5.16 XPS spectra for the sulfide materials showing multiple annealing steps. Transition metal core-levels (a)-(d) and S 2p core-levels (e)-(h) from each material.

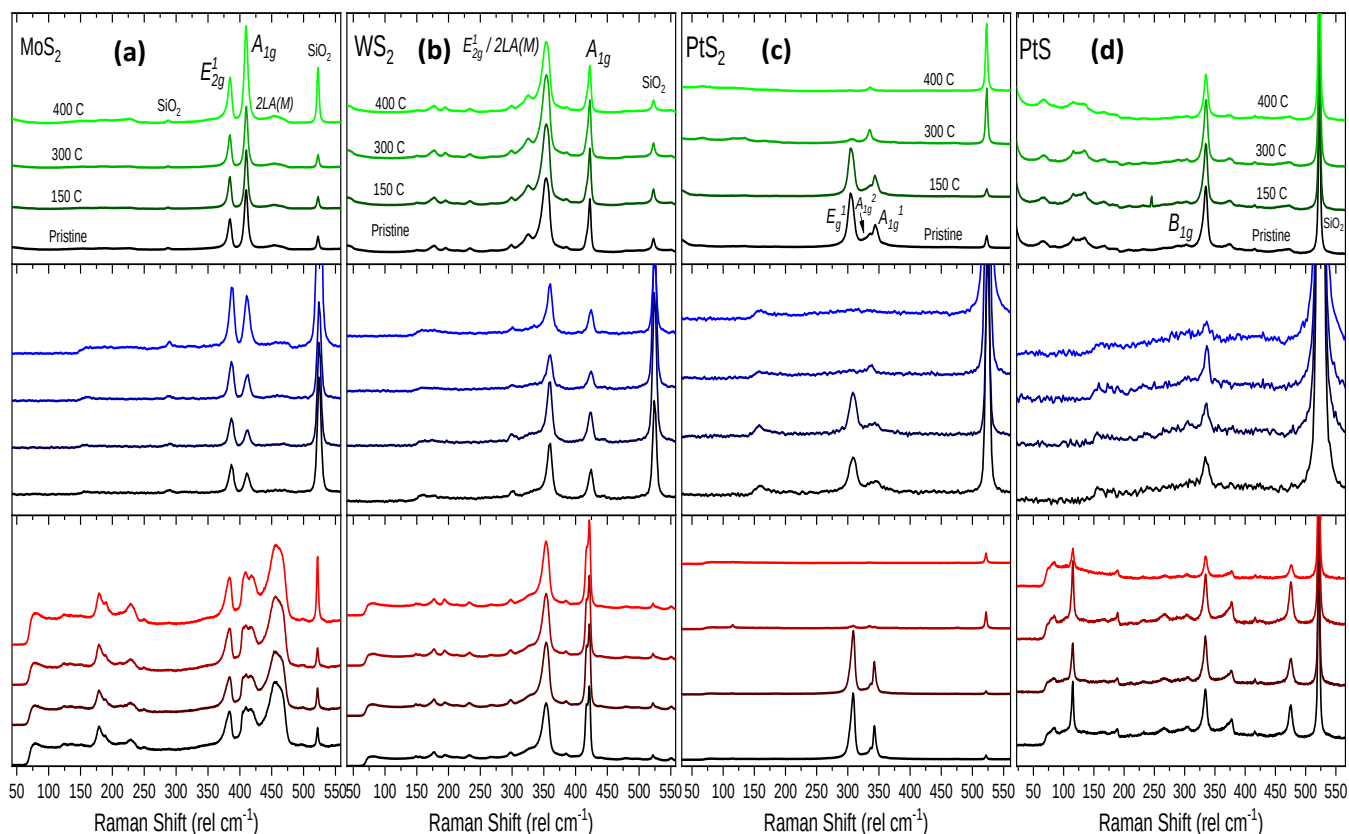


Fig. 5.17 Raman spectra for the sulfide materials after each anneal acquired with three laser excitation energies, green for 532 nm, blue for 405 nm, and red for 633 nm. MoS₂ **(a)** WS₂ **(b)** PtS₂ **(c)** PtS **(d)**

The XPS spectra for the previously discussed MoS₂ *Mo 3d* and *S 2p* core-levels are presented in Fig. 5.16 (a)-(e), respectively. The *Mo 3d* and *S 2p* show significant stability up to 300 °C where there is an increase in MoO₃ to ~10%. This indicates that we have passed the threshold for oxidation, aligning with reports in literature of this occurring at ~290 °C in ambient.²⁰³ There are no signs of oxidation in the S 2p core-level region up to 300 °C, indicating that the sulfur lost from the oxidation of MoS₂ is being lost to the ambient during the anneal or alternatively being lost to the vacuum during pump-down prior to the XPS measurement.

Both spectra following annealing at 400 °C show pronounced oxidation with only 10% of the surface molybdenum atoms being in the MoS₂ state. The majority of the oxidation is through the formation of MoO₃, a secondary oxide labelled as MoO_x forms at some stage between 300–

400 °C, this is fitted at ~232 eV, this oxide has been previously observed but a conclusive assignment is difficult²⁰⁴.

The S 2p region develops an oxidation-induced component in the 400 °C spectra at ~168.7 eV, attributed to S^{6+} , likely in a sulfate molecule. This oxide component only accounts for ~30% of the surface sulfur, with the remaining 70% being MoS_2 . This indicates that sulfur oxide formation is a secondary process in MoS_2 degradation. This compositional information can be seen in Fig.18 with the change in calculated amounts of TMD and oxide show as a line graph.

The Raman spectra of MoS_2 at three excitation wavelengths are shown in Fig.17(a). Looking at the 532 nm spectrum first, it is noteworthy that the MoS_2 Raman spectrum is almost imperceptibly changed with increasing anneal temperature with no oxide peaks present. The starkest change in the spectrum is seen after the 400 °C anneal, but only in the changing relative intensity of the SiO_2 Raman peak at ~520 $rel\ cm^{-1}$ when compared to the MoS_2 Raman modes.

While the XPS data makes it clear that the surface of the MoS_2 film is largely oxidised after the 400 °C anneal, the Raman data tells us that there is still an amount of pristine-like MoS_2 which has been undisturbed. The difference between penetration depth for Raman and XPS allows us to gain an understanding of both the surface and substrate facing sides of the film, with XPS measuring the first few nm's of the surface while Raman is generally probing through the entire thin film of TMD. The substantial oxidation shown in XPS and the relative increase in intensity from the SiO_2 in the Raman indicates a thinning of the MoS_2 film.

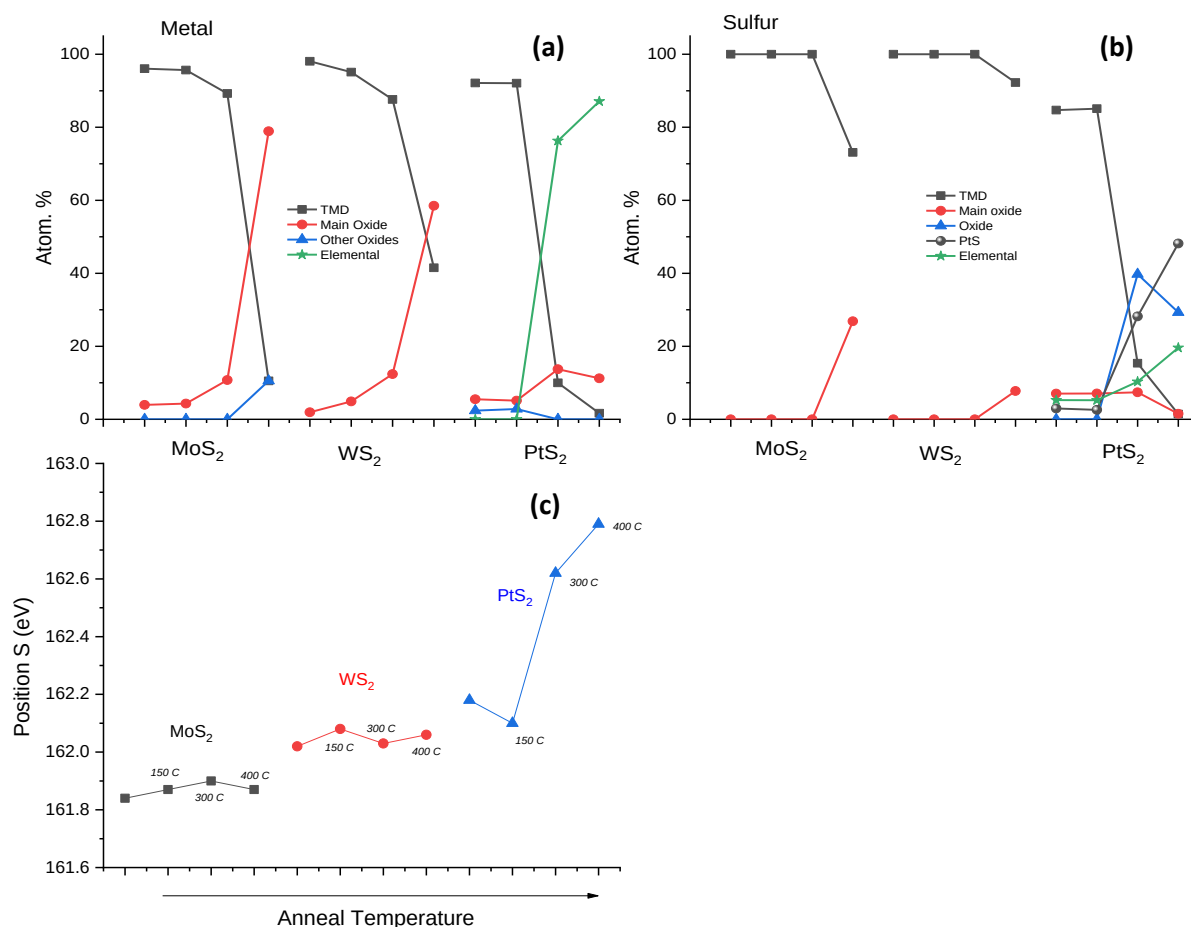


Fig. 5.18 Chemical composition from XPS for the transition metal (a) and S 2p (b) XPS core levels. Binding energy position of the S 2p_{3/2} for each sulfide (c).

The results of ambient thermal oxidation of WS₂ are similar to those of MoS₂. XPS of the W 4f core-level for WS₂ films, Fig.5.16(b), shows very little oxide formation on the surface up to 300 °C, with only ~12% of W atoms in the WO₃ chemical state. At 400 °C the WS₂ film now has 60% WO₃ surface oxide, this makes WO₃ the least oxidised of any of the TMDs measured here after the 400 °C anneal. The different electron affinities of the transition metals result in a shifting of the S 2p component, this is shown in Fig.5.18(c). Similarly, the S 2p shows no major changes until 400 °C where a second component at ~168.5 eV appears, this low intensity component only accounts for ~8% of the surface sulfurs, indicating the unlike for the TM the majority of sulfur is lost from the sample before measurement in XPS due to oxidation.

The Raman spectra of WS₂ show no distinctive changes after annealing at any temperature for the three excitation wavelengths used here. The relative intensity of the SiO₂ signal is mostly unchanged, indicating there is not substantial thinning or broad lowering in film quality, this further indicates the remarkable stability of the WS₂ film in this extreme environment.

An important impact of this data is the disconnect of the Raman and XPS data for both WS₂ and MoS₂. Many reports utilising these materials, which are not characterisation-focused reports, solely rely on one characterisation technique to determine TMD nature and quality, primarily Raman spectroscopy. This is clearly unsatisfactory for thin films where a minimum of two complementary characterisation techniques are necessary before any determinations of quality can be realistically made. In certain circumstances it may be mostly satisfactory for characterisation of monolayer films, but even in that case a single characterisation technique can result in mischaracterisation.

The results for PtS₂ and PtS show that these are notably more reactive materials. After annealing at 150 °C there is no change for either PtS₂ or PtS, in either the Raman or XPS. PtS is stable after the 300 °C anneal with the only change being a reduction in the amount of impurities including PtS₂ detected in the S 2p XPS region. PtS₂ shows substantial instability after this 300 °C annealing step with the composition of the film changing completely. The Pt 4f region shows that now ~75% of the surface Pt atoms have been decomposed into elemental Pt. Interestingly, the second largest contribution in this film is now attributed to a PtS state, with only ~10% of PtS₂ remaining.

The S 2p region also shows this change with a large PtS state accompanied by a shoulder from the PtS₂, contrasting with the results for the other sulfide films there is a large S⁶⁺ component formed here. The Raman spectrum of the 'PtS₂-' sample is transformed with the single peak of PtS at ~335 rel cm⁻¹ the most prominent feature of the spectrum now. This indicates that Pt oxides are not favourable in this scenario of ambient thermal oxidation, formation of Pt metal and reduction to PtS are the primary degradation pathways.

The sample annealed at 400 °C shows a continuation of this process for the PtS₂ film with all of the remaining PtS₂ being converted to PtS or Pt metal, the S⁶⁺ contribution is lower than for 300 °C. The Raman signal for this film is now very low in intensity as this high temperature results in some degradation of even the relatively stable PtS formed from the initial PtS₂ film. The line shape of the post-400 °C Raman spectra for PtS₂ and PtS are included in Appendix Fig.A11–A14, the striking similarity of these Raman spectra is apparent and reinforces the hypothesised process of PtS₂ converting to PtS with annealing. The XPS spectra for PtS after the 400°C anneal firmly establish it as being one of the more thermally stable materials investigated, with an approximate 50/50 split of the Pt region being PtS and Pt metal. The S 2p region changes with oxidation to include a minor component of S⁶⁺ similarly to PtS₂.

5.3.2 Transition Metal Selenides

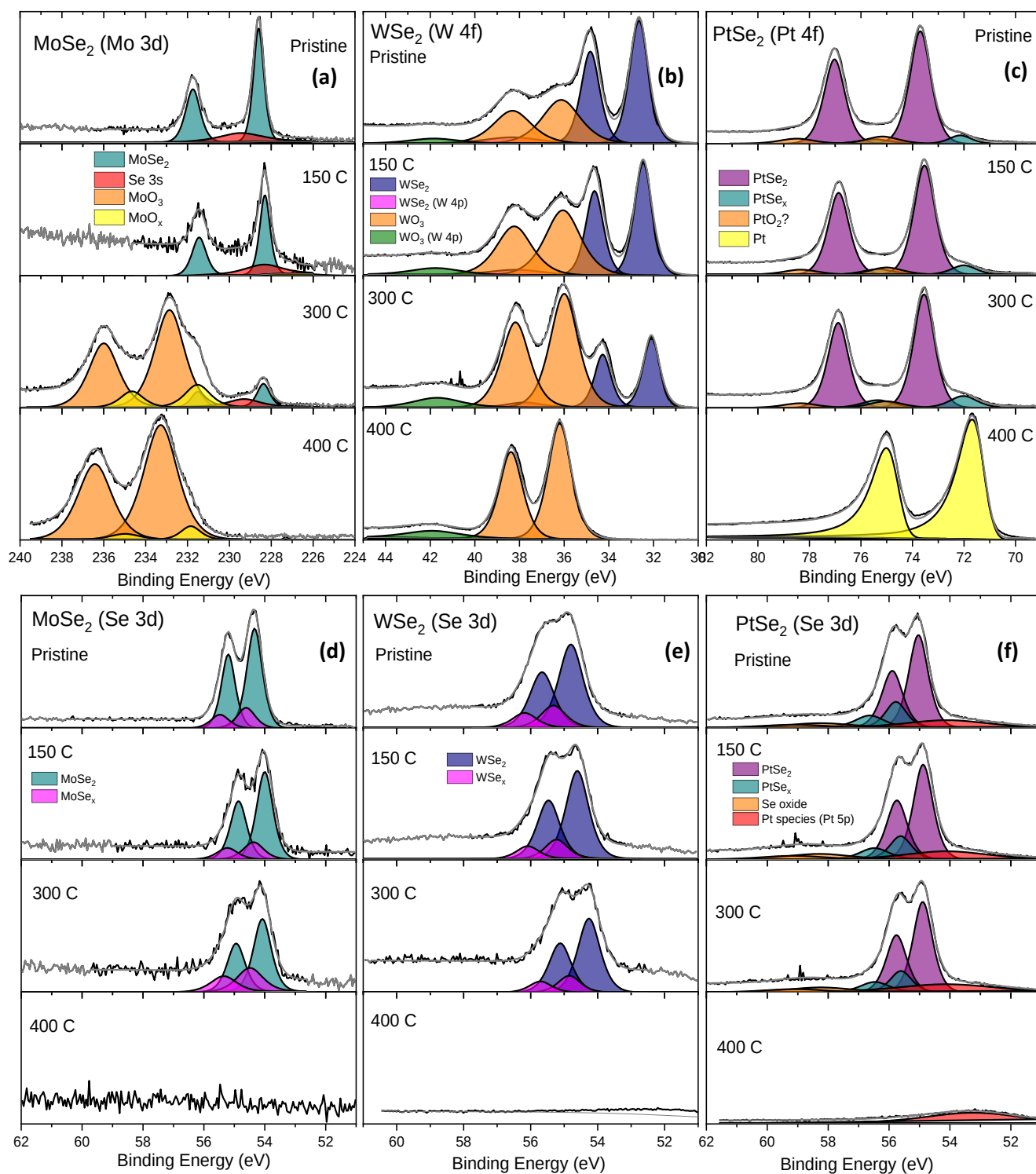


Fig. 5.19 XPS spectra for the selenide TMDs showing multiple annealing steps. Transition metal core-levels (a)-(c) and Se 3d core-levels (d)-(f) from each material.

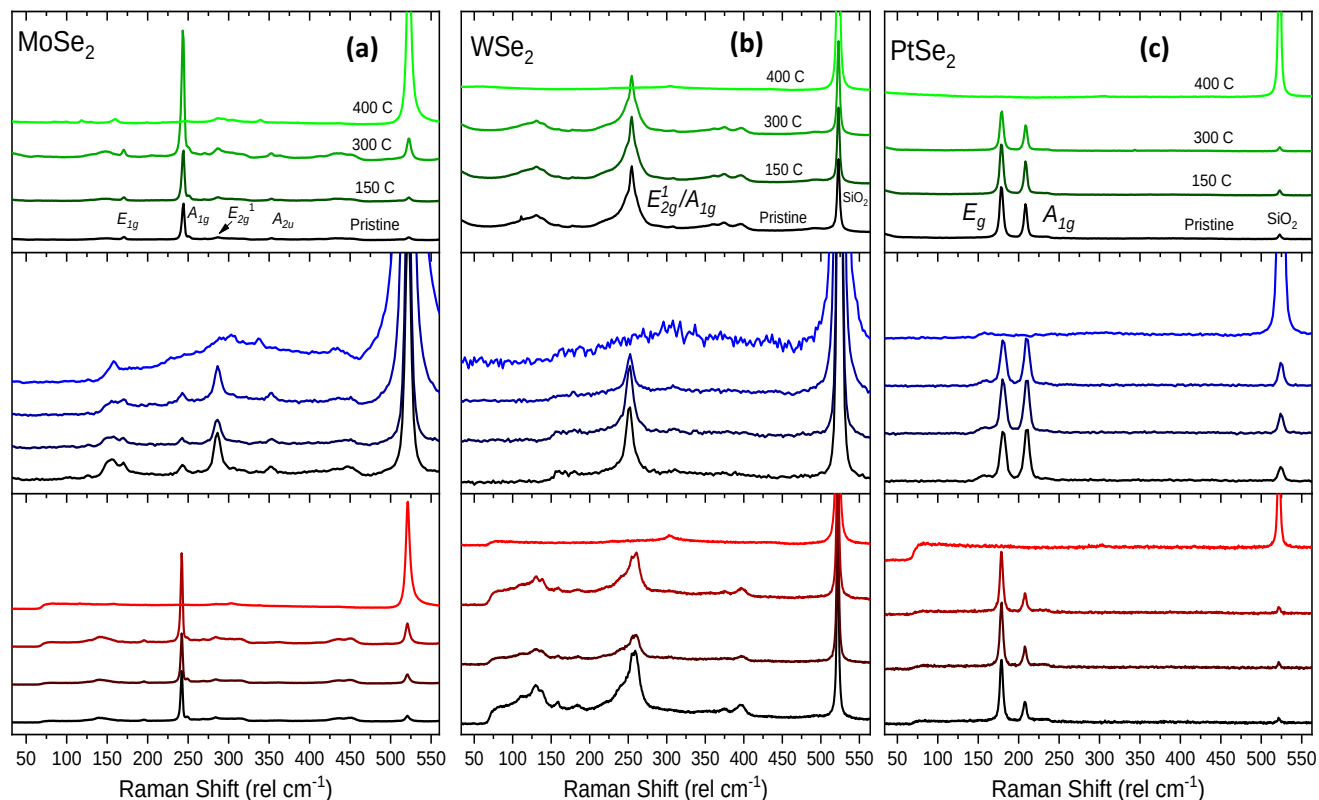


Fig. 5.20 Raman spectra for the selenide TMDs after each anneal acquired with three laser excitation energies, green for 532 nm, blue for 405 nm, and red for 633 nm. MoSe₂ **(a)** WSe₂ **(b)** PtSe₂ **(c)**.

The thermal stability of the TMD selenides is compared in Fig.5.19 and Fig.5.20, with the changing composition of the samples compared in Fig. 5.21. The Mo 3d and Se 3d XPS core-levels for MoSe₂ are shown in Fig. 5.19 **(a)-(d)**. MoSe₂ shows no formation of any oxides after 150 °C annealing in air indicating stability up to this point.

Annealing at 300 °C results in a very large amount of oxide generated, with only ~8% of the Mo atoms being in the form of MoSe₂. Two prominent oxides are formed, MoO₃ at ~233 eV and an unidentified oxide, likely the same one present in 400 °C annealed MoS₂, at ~232 eV. The corresponding Se 3d spectrum shows no sign of any new chemical states but shows broadening of the XPS peaks by ~15% when compared with the pristine material indicating a growing bond diversity and a lowering of crystallinity as Se leaves the TMD.

The results after 400 °C annealing reveal that MoSe₂ is in no way stable at this temperature with no trace of MoSe₂ remaining. The Mo 3d region consists of only the two oxides previously discussed, with the MoO₃ increasing in relative amount, indicating its greater stability than the unidentified oxide. The Se 3d region shows no Se atoms remaining, again this could either be due to the annealing itself causing loss of Se into the atmosphere or the products of annealing not being UHV compatible.

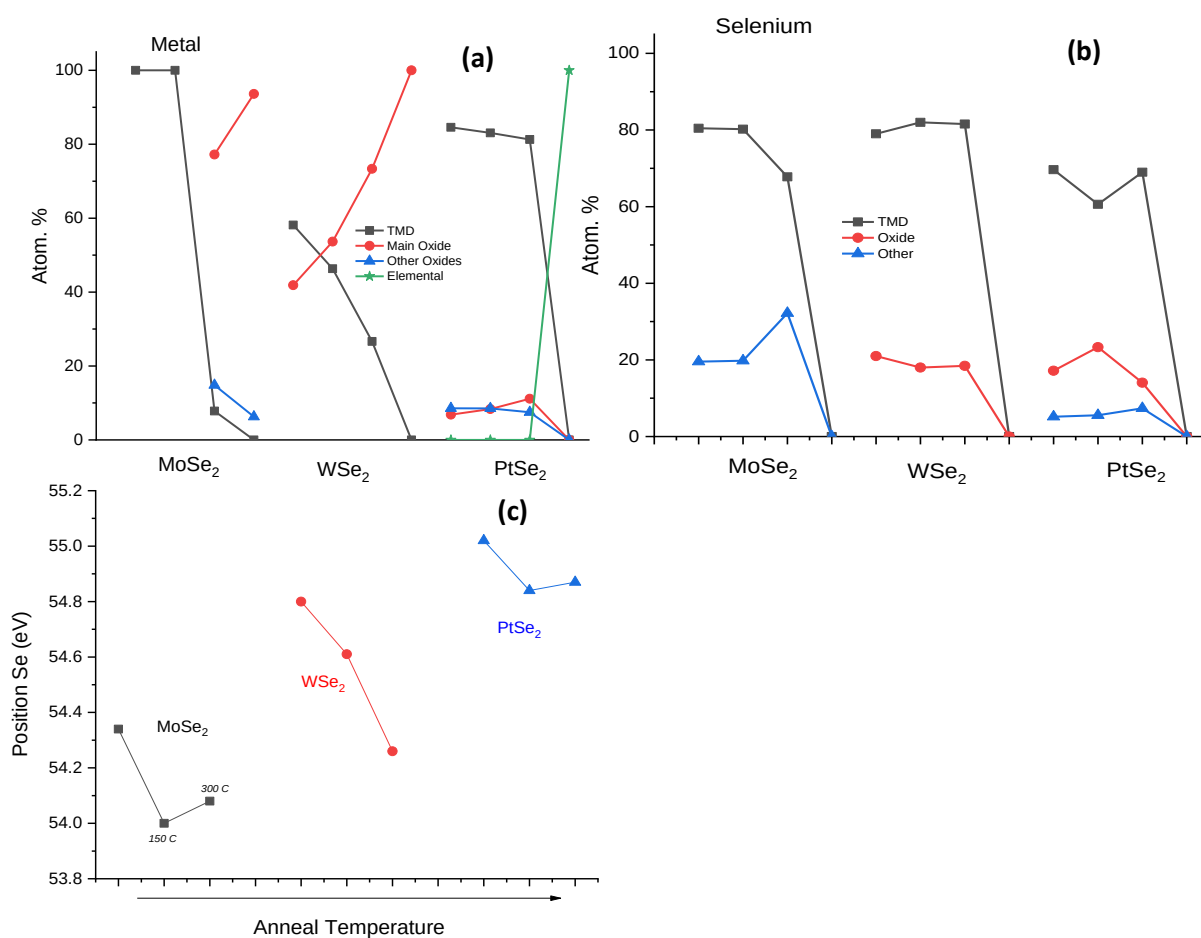


Fig. 5.21 Chemical composition from XPS for the transition metal (a) and Se 3d (b) XPS core levels. Binding energy position of the Se 3d_{5/2} for each sulfide (c).

Raman analysis of these films confirm the loss of MoSe₂. There were only very minor changes in the spectra for all excitation wavelengths up to the 300 °C anneal. Consistent with the XPS data, there is a loss of MoSe₂ Raman signal at 400 °C. Several new Raman peaks appear at this step, the most prominent peaks are at ~119, 160, 287, 304, and 339 rel cm⁻¹. These peaks are known to correspond to orthorhombic MoO₃, confirming the XPS conclusions²⁰⁵. This draws a

sharp contrast between the sulfides and the selenides wherein the 400 °C anneal causes oxidation of the surface layers of sulfide TMDs, but selenide films are completely oxidised at this temperature, showing the general higher stability of the sulfides.

The pristine WSe₂ sample measured here was found to be substantially oxidised on the surface before annealing, this starting oxide complicates any definitive statements on material stability can still serve to portray the most likely degradation pathway with annealing. XPS analysis of WSe₂ shows a clear trend with a gradually decreasing amount of WSe₂ with a corresponding increase in WO₃ up to 300 °C. A notable gradual shift to lower binding energy is observed in the Se 3d indicating a potential p-type doping as a result of oxidation.

Similar to MoSe₂, there is no WSe₂ remaining after annealing at 400 °C. The W 4f after 400 °C only has signal pertaining to WO₃ remaining, the FWHM of this $W\ 4f\ 7/2$ narrows substantially across annealing steps with a change from 2 -> 1.86 -> 1.47 -> 1.22 respectively with increasing anneal temperature.

PtSe₂ shows the highest thermal stability of any of the selenide materials studied here. The *Pt 4f* and *Se 3d* show marginal change for ambient anneal temperatures up to 300 °C, this indicates a relatively high stability. The limit to this is found to be between 300 and 400 °C as both of the XPS core-levels show the complete loss of PtSe₂ after annealing at 400 °C, this is consistent with the other selenides. Unlike the other materials, Pt TMDs do not form oxides during ambient annealing but Pt metal.

Further, the Raman spectra of PtSe₂ is consistent with the XPS data and shows that there are very minor changes to the spectra after 300 °C but a complete loss of PtSe₂ Raman signal after the 400 °C anneal.

5.3.3 Transition Metal Tellurides

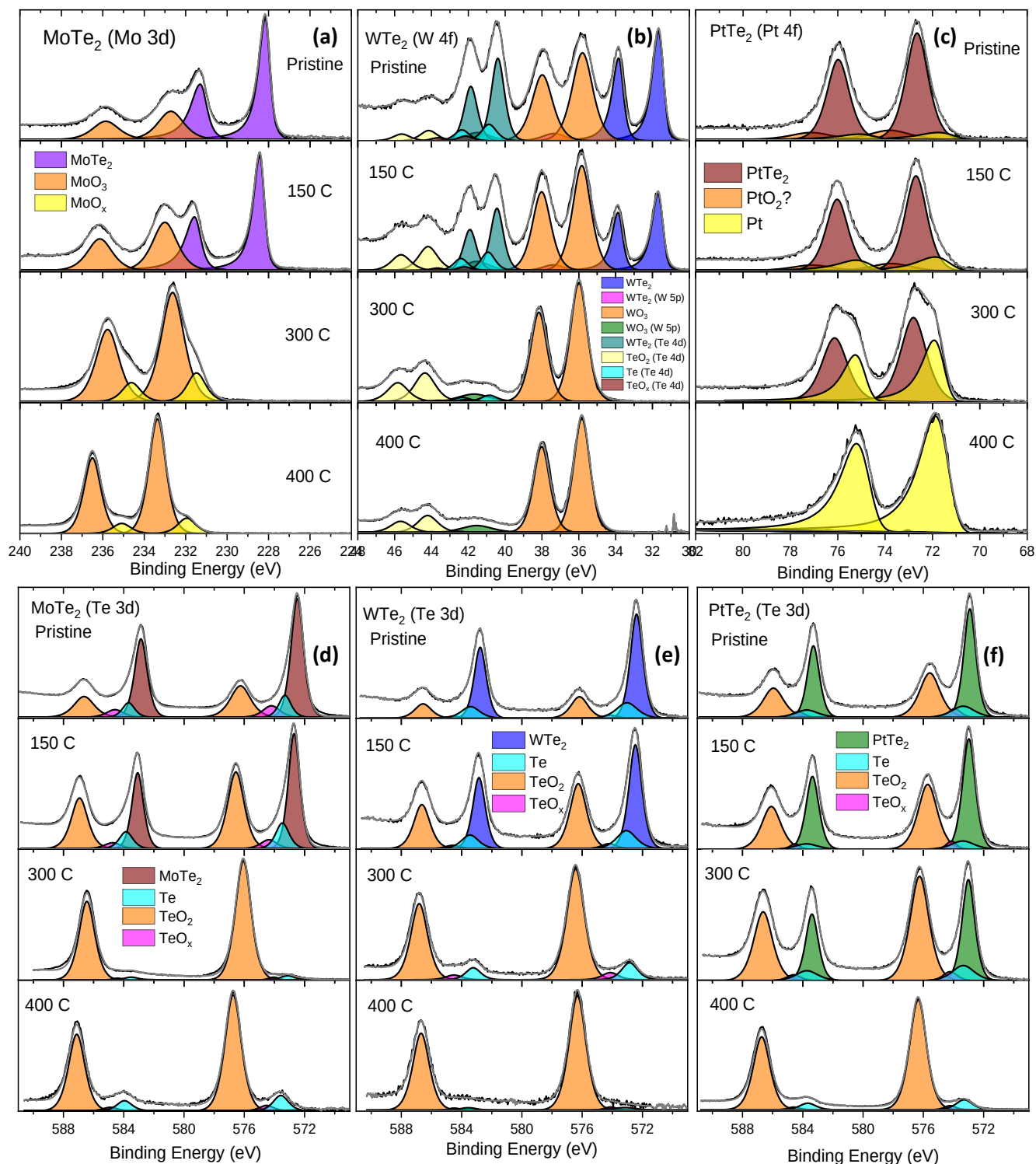


Fig. 5.22 XPS spectra for the telluride TMDs showing multiple annealing steps. Transition metal core-levels **(a)-(c)** and Te 3d core-levels **(d)-(f)** from each material.

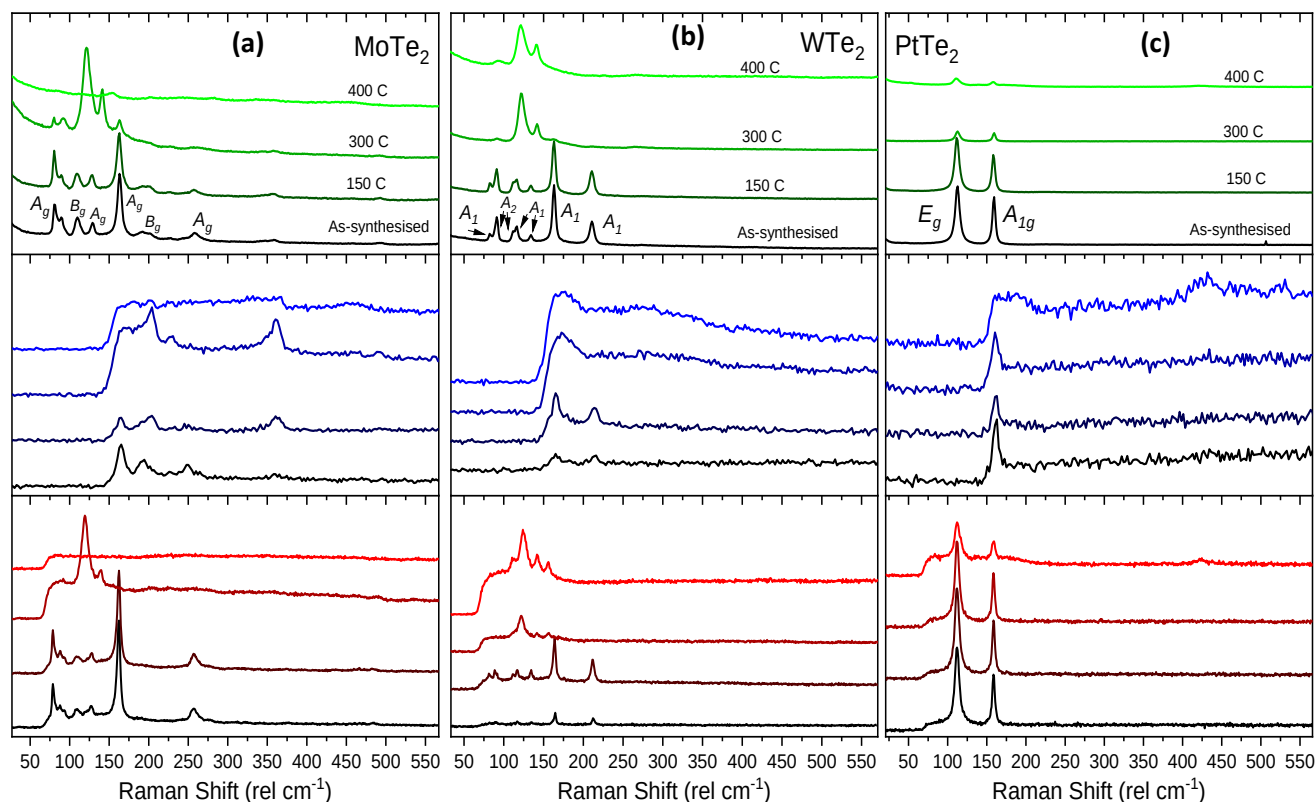


Fig. 5.23 Raman spectra for the telluride TMDs after each anneal acquired with three laser excitation energies, green for 532 nm, blue for 405 nm, and red for 633 nm. MoTe₂ **(a)** WTe₂ **(b)** PtTe₂ **(c)**.

Characterisation of the thermal stability and ambient oxidation of the telluride TMDs is relatively unexplored. The XPS and Raman data for MoTe₂ films is given in Fig. 5.22(a)-(d) and Fig. 5.23 (a)-(c) with the changing composition of the samples compared in Fig. 5.24. It can be seen in the XPS data that a similar trend to MoSe₂ is observed for the *Mo 3d* core-level. The pristine film contained ~30% of the surface Mo atoms as MoO₃, there is a gradual increase with each anneal temperature to show a low level of ambient thermal stability. Correspondingly to the other Mo TMDs, MoO_x is formed for the 300 and 400 °C anneal temperatures. All of the MoTe₂ XPS signal is absent after the 300 °C anneal in the *Mo 3d* region.

The *Te 3d* XPS core-level for MoTe₂ shows consistent results with a complete loss of MoTe₂ signal after the 300 °C anneal. The relative amount of TeO₂ increases for each anneal temperature. XPS signal from elemental Te and TeO_x are found to persist across all anneals with consistently low relative amounts.

The Raman spectra from these films, shown in Fig. 5.23 (a), reveal an interesting picture and highlight substantial change across the annealing steps. As a result of the different synthesis procedure for the telluride TMD films, these films show greater surface roughness, which is further increased by the annealing experiments conducted here. This increased roughness can hamper the averaging process used during the Raman measurements, resulting in greater variability in the results than for the other TMD films. This can contribute to erroneous conclusions when the Raman is analysed in isolation, again showing the major benefit of complementary characterisation. The 532 nm excitation Raman spectra for MoTe_2 show a loss of the majority of the MoTe_2 characteristic modes after the 300 °C anneal. New modes with pronounced peaks at ~ 121 and 141 rel cm^{-1} appear and these are consistent with previous reports of decomposition of MoTe_2 films, with the majority of works assigning these peaks to Te rather than TeO_2 .²⁰⁶

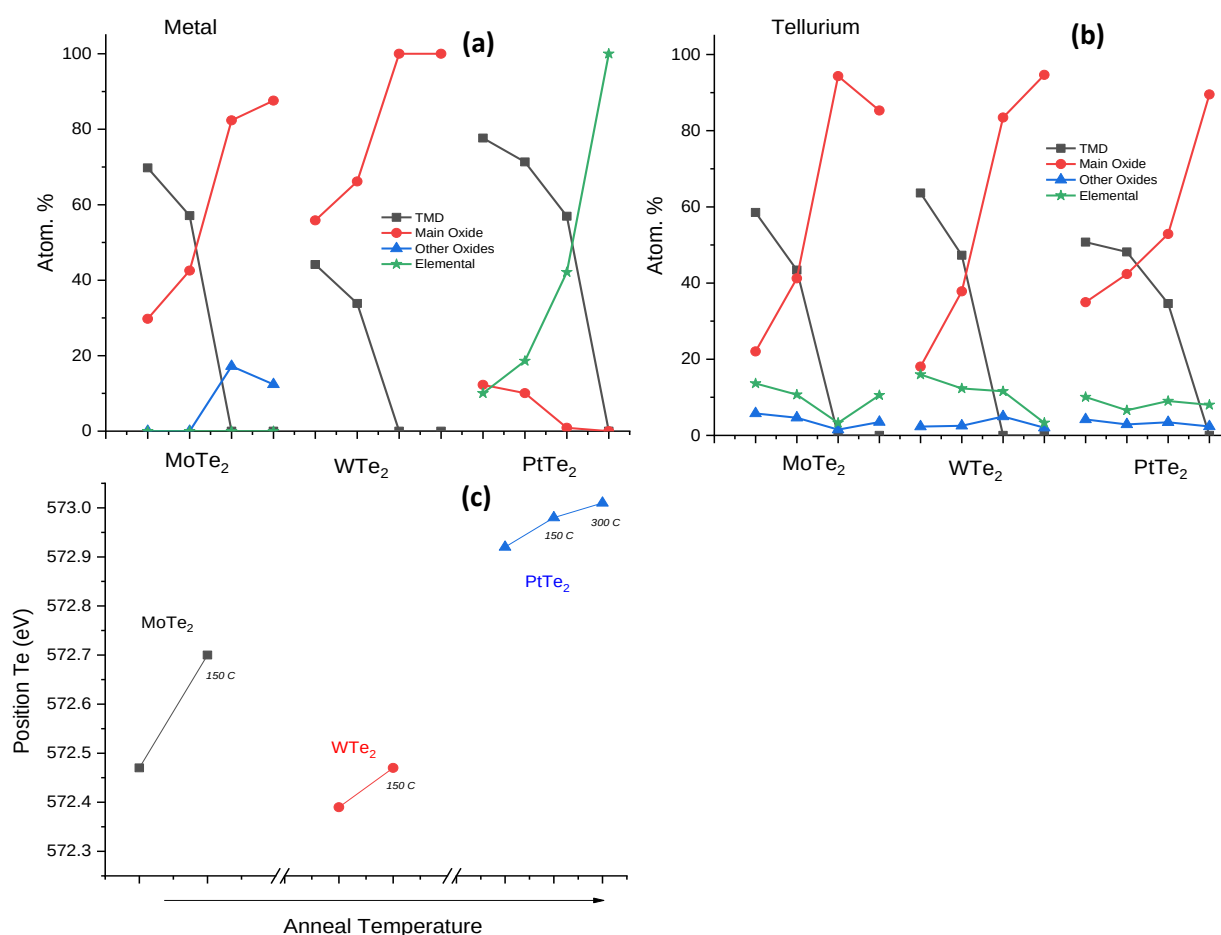


Fig. 5.24 Chemical composition from XPS for the transition metal (a) and Te 3d (b) XPS core levels. Binding energy position of the Te 3d_{5/2} for each sulfide (c).

Raman spectra acquired using 405 nm excitation show a substantially different spectra with the appearance of two narrow intense peaks at ~ 286 and 337 cm^{-1} . These are currently unassigned but from the XPS are expected to originate from Te oxides. The spectrum further evolves after the 400°C anneal with the three Raman peaks in this spectrum being of similar position to the modes seen in the 532 nm excitation spectrum.

The 633 nm Raman spectra show largely similar results to the 532 nm, with a complete loss of MoTe_2 signal after the 300°C anneal and formation of the Raman peaks corresponding to Te.

Ambient thermal stability of WTe_2 shows appreciably similar results to MoTe_2 , which firmly establishes the trend of Mo and W TMDs being chalcogen limited in their stability.

The $W 4f$ core-level is the literature standard when characterising W materials, this region also contains the $W 5p$ adding to its complexity. The region is further complicated in WTe_2 due to the coincidental overlap of the $Te 4d$ core-level. This necessitates a wide energy window fitted with twelve components. A set of directly comparable XPS spectra with an expected trend of oxidation greatly enhances the reliability of the XPS fit. Similar to MoTe_2 , a reduction in the amount of TMD is noticed and an increase in oxide content, in this case WO_3 , for the 150°C anneal. There is no remaining TMD signal after the 300°C anneal, and the 400°C anneal leaves WO_3 and TeO_2 as the only states detected on the surface.

The $Te 3d$ core-level is the primary characteristic XPS region for tellurium compounds and is shown in Fig. 5.22 (e). This shows a remarkably similar trend to the $Te 3d$ of MoTe_2 with the exception of the 400°C spectrum showing only TeO_2 remaining rather than a combination with Te.

Raman analysis of the degradation of WTe_2 follows a similar trend to MoTe_2 , with minor changes up to 150°C . Anneals above this temperature give spectra dominated by Te. The disparity between the Raman and XPS results of the 400°C annealed film - XPS indicating the presence of TeO_2 while Raman indicates amorphous Te - highlights once again the benefits of using multiple complementary analysis techniques. The disparity may be due to sampling depth differences between the two spectroscopies.

As was the case for the selenides, the platinum TMD, PtTe_2 shows the highest thermal stability of the three telluride materials studied here. The $Pt 4f$ core-level shows a small increase in the proportion of Pt metal in the film after 150°C annealing, this indicates that either this is the primary route of degradation, or that the only UHV compatible product is through the formation

of Pt metal rather than through oxide formation. As any small oxide particles may be lost during vacuum pumping. After the 300 °C anneal, the PtTe₂ film has a substantial Pt metal signal equivalent to ~40% of measured Pt atoms. Despite this, the film is still majority PtTe₂ indicating significantly higher stability than the other telluride films that had no TMD detectable after this anneal. It is likely that 300 °C is near the upper thermal limit for PtTe₂ in ambient as the surface is fully Pt metal after the 400 °C anneal. The *Te 3d* core-level provides data consistent with the Pt 4f, showing a large amount of PtTe₂ is present up to the 300 °C anneal and only Pt metal and TeO₂ above this temperature.

As previously discussed, PtTe₂ has a less complex Raman spectrum compared to the other telluride TMDs and as the primary degradation route appears to be to elemental Pt this carries through to the post-anneal spectra. There are no new Raman peaks observed after any of the anneals but there is a noteworthy change in intensity after the 300 °C anneal with a large drop in the Raman signal from PtTe₂. This is likely due to thinning of the film and formation of Pt metal on the surface. Interestingly, there is a clear PtTe₂ Raman signal still apparent after 400 °C even though the XPS clearly shows the surface is entirely Pt metal and TeO₂. This result is similar to the results for the MoS₂ film, suggesting that after the 400 °C anneal the surface is fully oxidised but there is still PtTe₂ present beneath the surface layers.

5.4 XPS Spectra of TMDs by Transition Metal

Another valuable angle of comparison for this data is to compare the TMDs when grouped by their transition metal rather than their corresponding chalcogen. As these materials are all characterised with the same XPS metal core-levels the data can be compared using just one region.

To maximise the usefulness of these figures, the different TMDs will be arranged vertically, with increasing anneal temperatures on the horizontal axis, as illustrated in Fig. 5.25. Comparing the TMDs vertically highlights the differences or similarities in XPS peak positions.

5.4.1 Mo TMDs

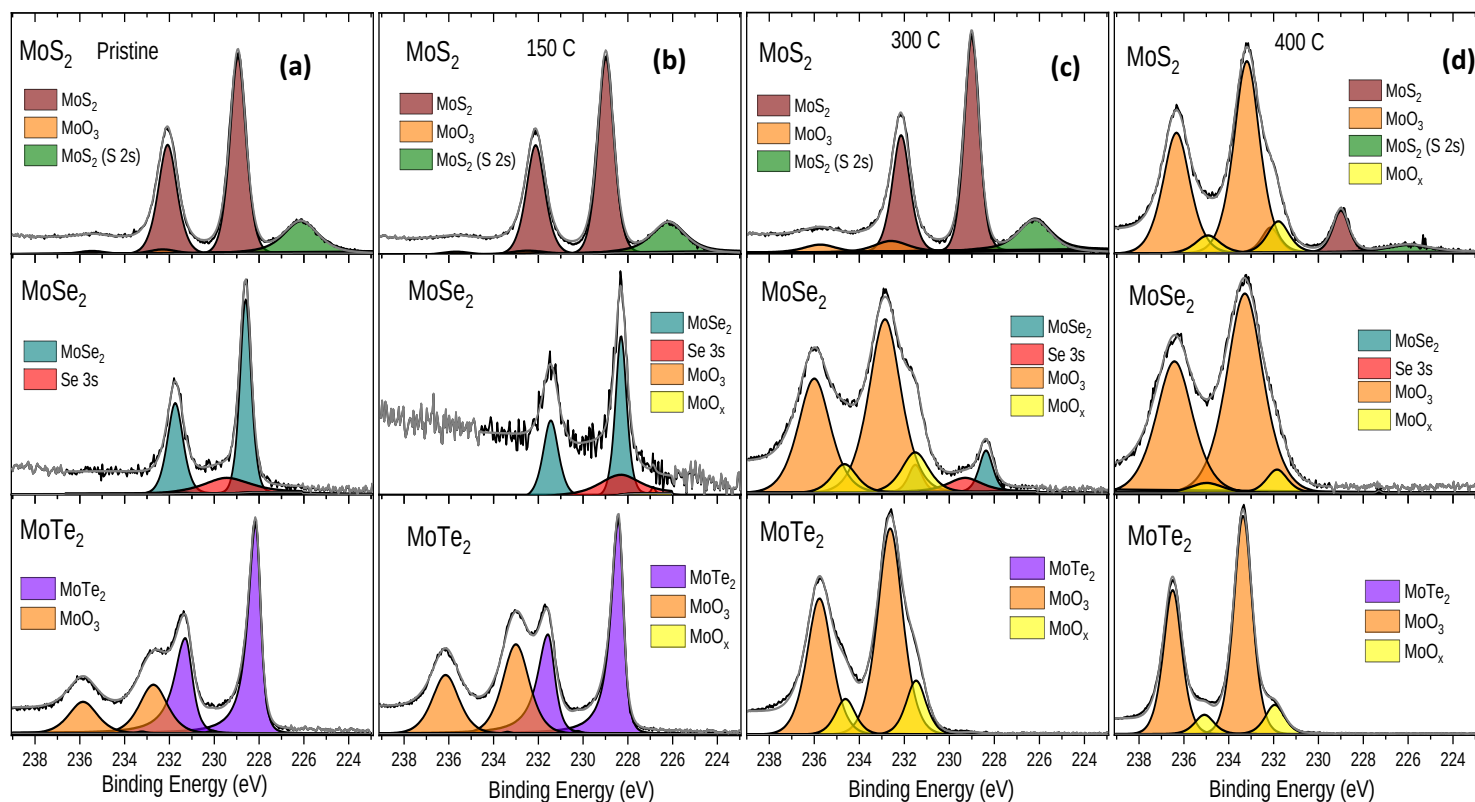


Fig. 5.25 Mo 3d XPS spectra for the molybdenum TMDs showing multiple annealing steps. Pristine (a), 150 °C (b), 300 °C (c), 400 °C (d).

Fig. 5.25 presents the Mo 3d region for MoS₂, MoSe₂, and MoTe₂, respectively. The difference in TMD peak position for the starting materials is clear here with a trend of decreasing peak binding energy position going sulfide > selenide > telluride. This is in-line with the trend in their electronegativities and is displayed further in Fig. 5.26, below. MoS₂ and MoSe₂ have coincidentally overlapping core-levels with their respective chalcogens in the S 2s and Se 3s complicating their spectra.

The difference in purity of the starting material is also clear, with MoTe₂ having ~30 % oxide while MoS₂ and MoSe₂ have negligible amounts. The relatively narrow FWHM of the MoSe₂ TMD peaks indicates a lower diversity of bonds and therefore a higher crystallinity than the other two materials, but the asymmetry of the MoTe₂ is complicates comparison.

Looking at the 300 °C dataset the significant difference in stability between the three materials are observed, with MoS₂ showing only a minor presence of MoO₃. MoSe₂ on the other hand is heavily oxidised on the surface, showing the formation of two oxides, a majority presence of MoO₃ as well as a minor oxide that it is not easily assigned. The MoTe₂ sample also has both of these oxides but no TMD is detected, which continues for the 400 °C anneal, with MoS₂ also now being predominantly oxidised showing the presence of both observed Mo oxides.

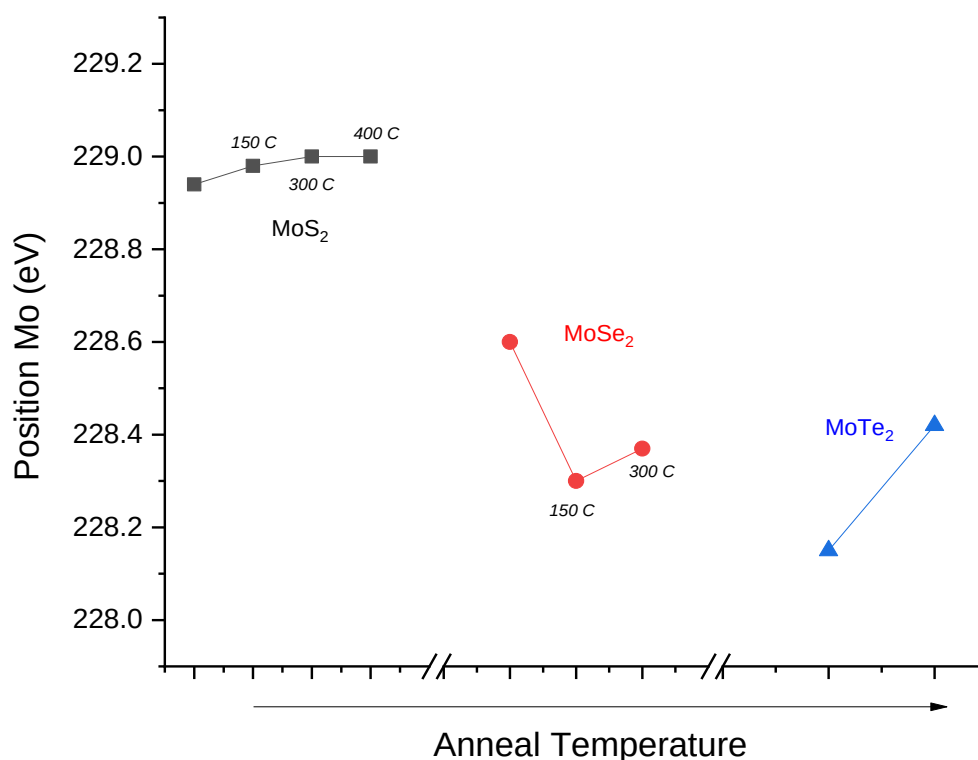


Fig. 5.26 Binding energy position of the Mo 3d_{5/2} for each TMD.

This analysis illustrates the relative thermal stability of these Mo TMDs. MoTe₂ has a significant amount of oxide in the starting material, which likely makes it more susceptible to further oxidation. This is also a sign of MoTe₂'s significantly lower ambient stability in general. These results present MoO₃ as the primary product in the decomposition of Mo TMDs, a sub-oxide at ~232 eV is also formed in much lower amounts. A clear stability hierarchy of sulfide > selenide > telluride is also demonstrated for TMD films.

5.4.2 W TMDs

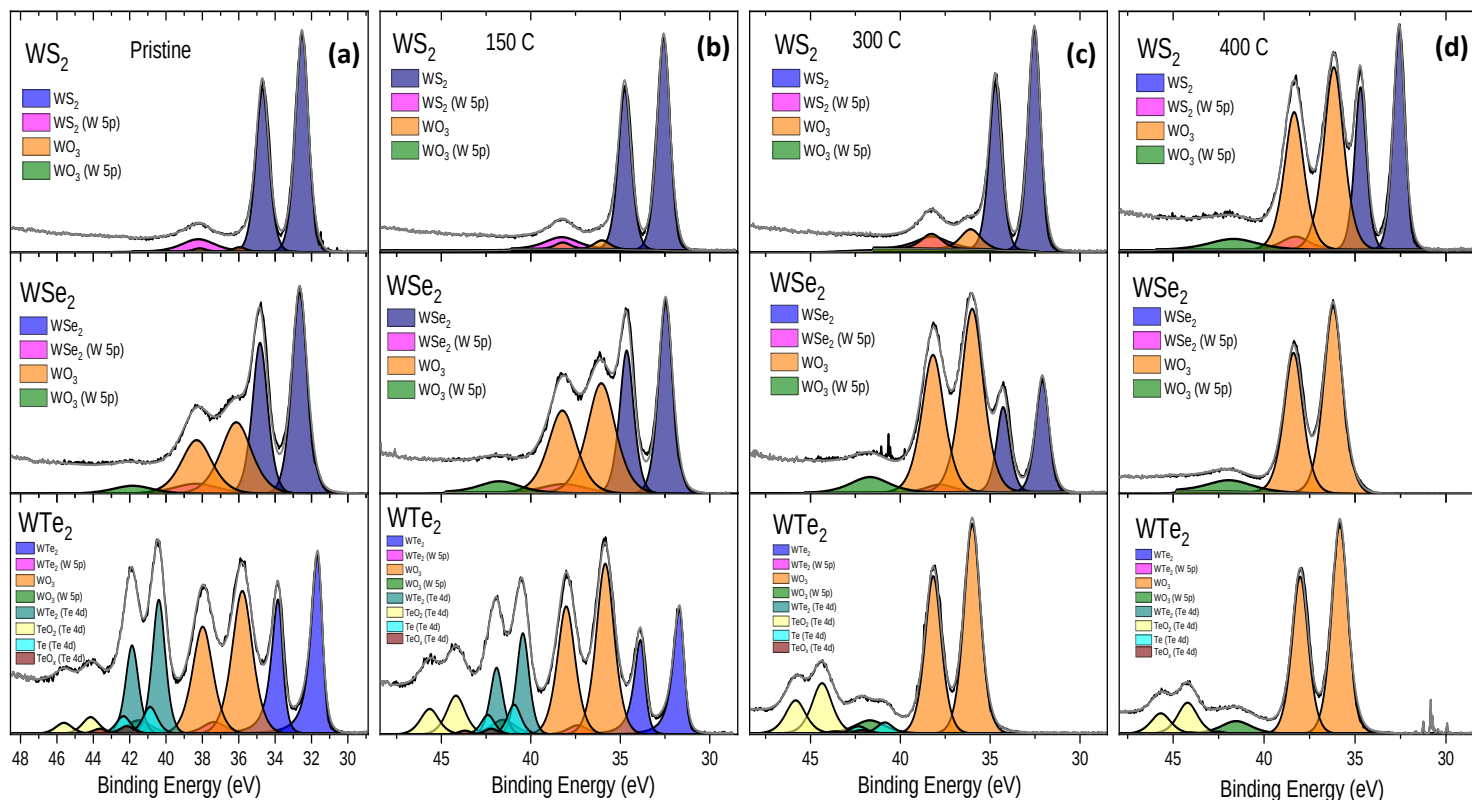


Fig. 5.27 W 4f XPS spectra for the tungsten TMDs showing multiple annealing steps. Pristine (a), 150 °C (b), 300 °C (c), 400 °C (d).

Fig.27 shows the W 4f core-level region of WS₂, WSe₂, and WTe₂ as-grown and after annealing at each temperature. All three of the materials have WO₃ present in their pristine or as-grown state, albeit as a very minor component in the case of WS₂. The WTe₂ spectrum, as previously discussed, is significantly more complex due to the presence of the overlapping Te 4d peaks. Unlike the Mo TMDs, the trend in peak position for the W TMDs is not as clear for the pristine samples, as seen in Fig. 5.28. This may be a result of charge-correction errors or a result of doping or charging from the oxide component in the films.

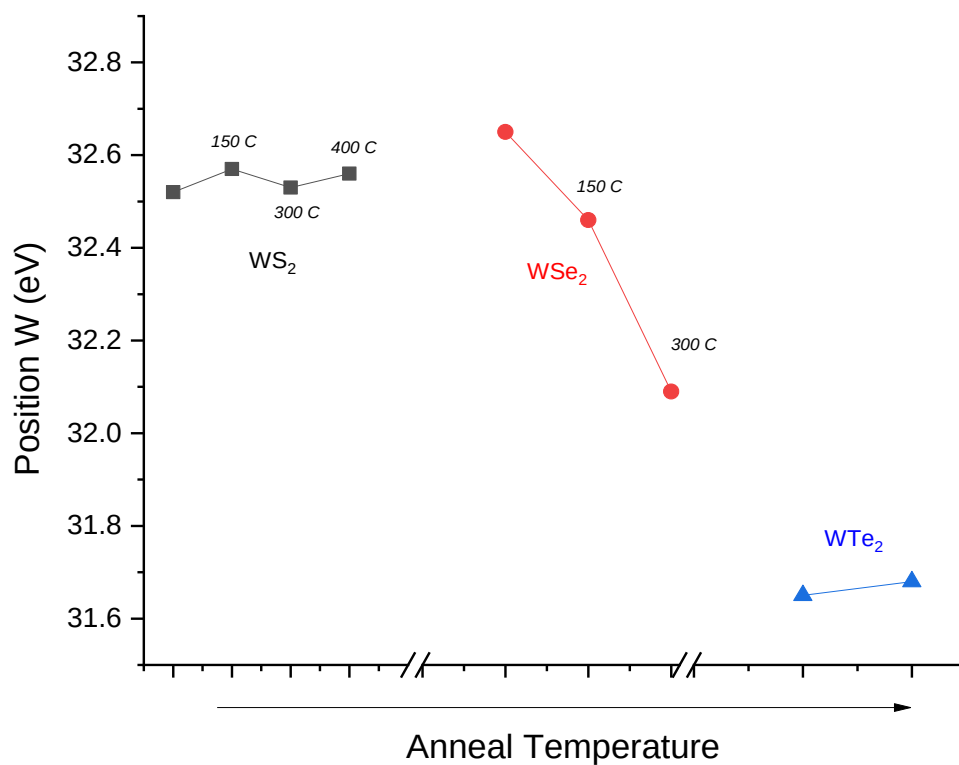


Fig. 5.28 Binding energy position of the W 4f_{7/2} for each TMD.

Analysis of the 300 °C annealed samples displays similar stability results to the Mo-based TMDs. The sulfide is only partially oxidised, while the selenide is heavily oxidised, and there is no TMD remaining on the WTe₂ film surface. Notably, after the 400 °C anneal, the WS₂ is still only 60% oxidised while the other materials are fully decomposed. For all three, WO₃ is the only W oxide detected and appears to be the primary decomposition product.

5.4.3 Pt TMDs

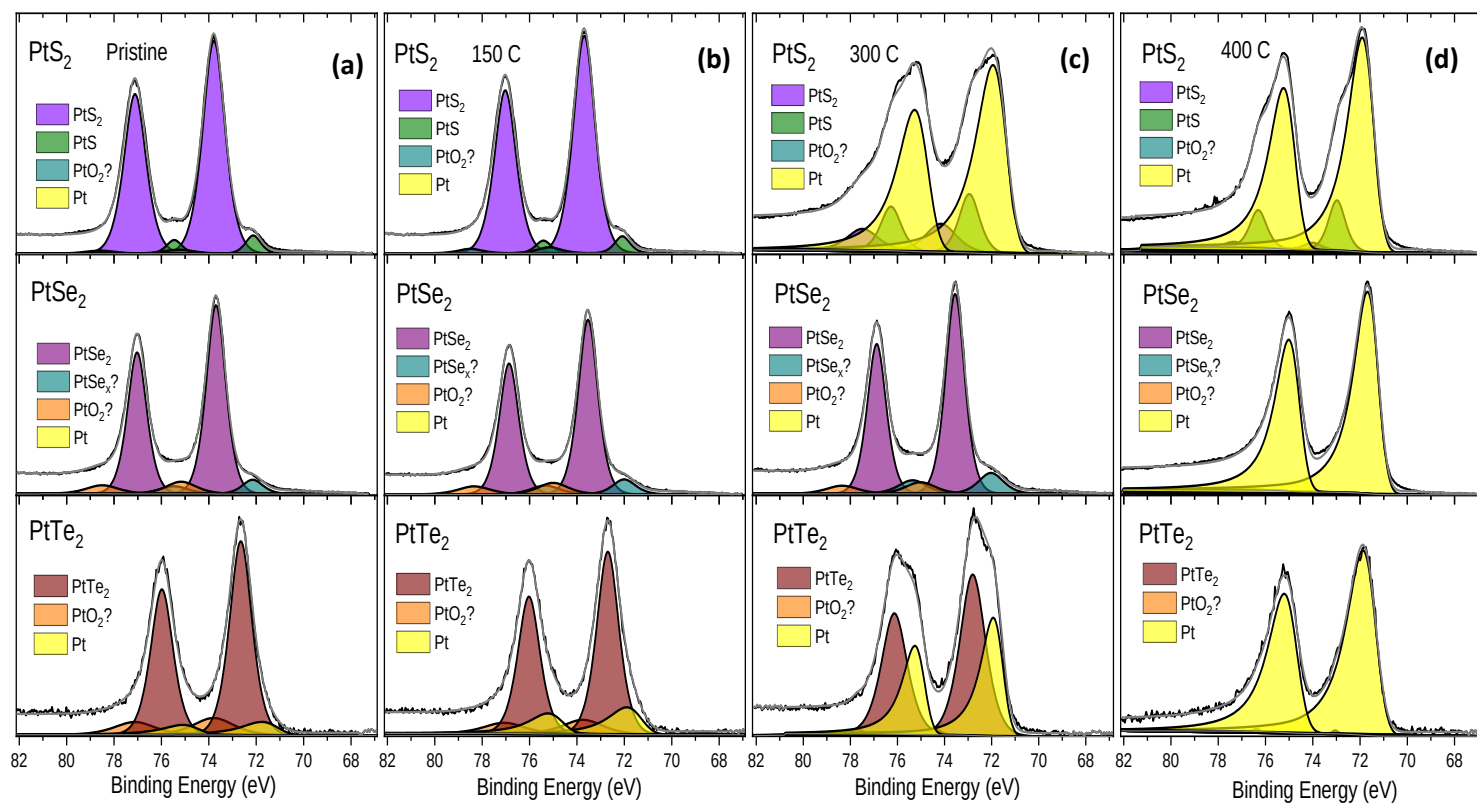


Fig. 5.29 Pt 4f XPS spectra for the platinum TMDs showing multiple annealing steps. Pristine (a), 150 °C (b), 300 °C (c), 400 °C (d).

The Pt 4f core-level region of the three Pt TMDs, PtS₂, PtSe₂, and PtTe₂ are presented in Fig. 5.29. The binding energy position of the TMD peaks again aligns well with the relative electronegativities of the constituent chalcogens with sulfide having the highest binding energy and telluride the lowest, see Fig. 5.30. As previously discussed, the Pt 4f core-level region for Pt TMDs is one of the least discussed in the literature and therefore is underdeveloped in identification of the likely components for the various materials.

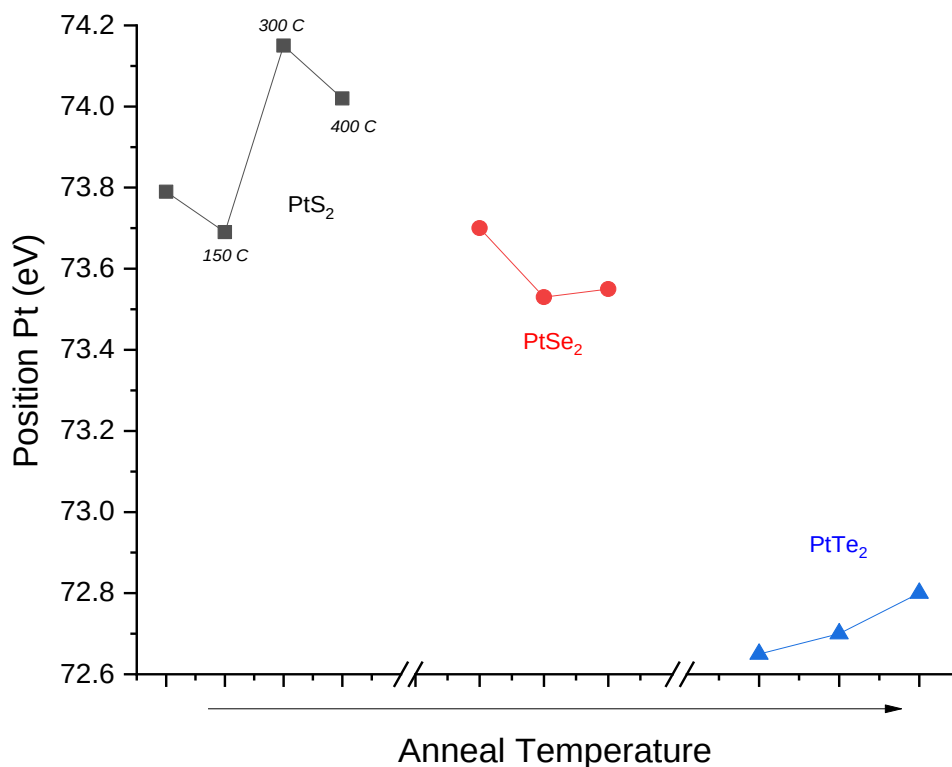


Fig. 5.30 Binding energy position of the Pt 4f_{7/2} for each TMD.

All three Pt-based TMDs examined thus far have complex spectra with multiple components. After the various anneals, there is an oxide component present for both PtSe₂ and PtTe₂, while PtTe₂ was found to also contain Pt metal, distinctive due to its asymmetric peak shape. Looking at the 300 °C annealed samples we can see that, in contrast to the Mo and W based TMDs, in this case PtS₂ is the least stable of the Pt TMDs. As previously mentioned, this is likely due to the relative stability of PtS. PtSe₂ shows marked stability amongst the Pt TMDs with negligible changes up to 300 °C. After 400 °C all of the Pt TMDs have decomposed, with PtS₂ maintaining a small PtS signal. It is noteworthy that all of the Pt TMDs have subsequently degraded to Pt metal instead of any oxide unlike the other TMDs studied. The rarity and low stability in ambient of Pt oxides is a known aspect in Pt catalysis.²⁰⁷

5.5 Conclusions

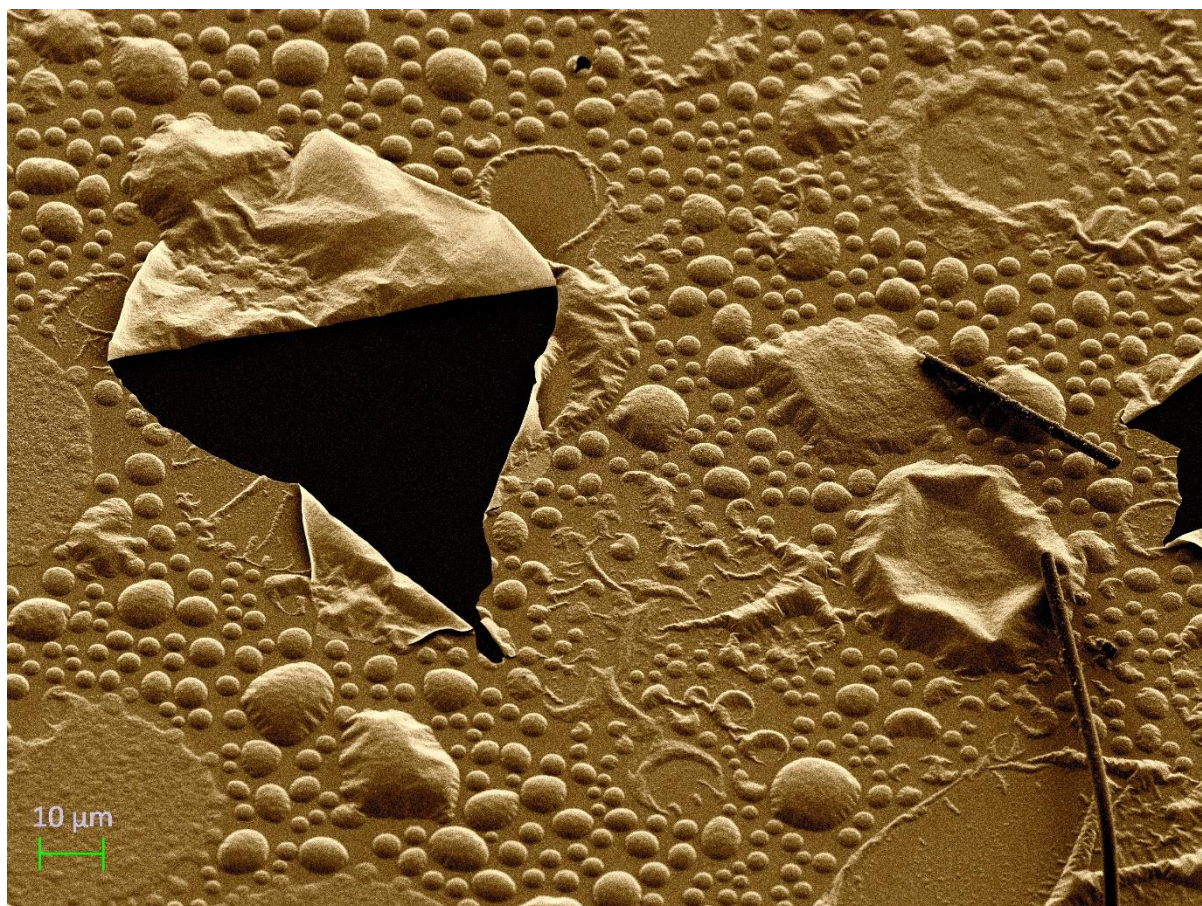
This chapter set out a coherent methodology to understand and fit the XPS spectra of a wide range of TMDs. Ten transition metal chalcogenides were synthesised through conversion of pre-deposited metal films on SiO₂. These include the sulfides, selenides, and tellurides of Mo, W, and Pt, together these encompass the vast majority of materials studied in modern TMD literature. Raman spectroscopy, using multiple excitation wavelengths, was presented alongside the XPS analysis to complement, verify, and improve the characterisation of each material.

The well-known utility of XPS leads to its prevalence in TMD characterisation. However, proficient measurement and interpretation of XPS data are complex tasks with significant room for error and misinterpretation. Consistency in interpretation was provided here in a clear, thorough and broadly applicable manner. The specific parameters for XPS measurement and curve-fitting of each material were discussed individually, including the specific intricacies for each core-level. To expand on the utility of this data as a resource, the TMD films were examined with the same techniques after several ambient annealing steps. This caused the gradual degradation of the films, indicating their ambient stabilities. Importantly this annealing experiment provides a trend of evolving XPS and Raman spectra for each material, which can be used to greatly improve the accuracy and confidence in the XPS fitting.

Beyond this, forced degradation of the TMD material allowed many of the most common features that may appear in the XPS spectra of the various TMDs to be illustrated and examined in detail, this can be significantly more useful as reference information than a pristine spectrum. Furthermore, the essential benefits of complementary characterisation were clearly demonstrated with the combination of XPS and Raman providing a considerably more accurate understanding of the state of the material than either technique in isolation partly due to the differences in measurement depth.

This wide library of data assembled in this work allows the comparison of the degradation of the different films through the lens of either the transition metal or the chalcogen. Accordingly, it can be qualitatively concluded that the stability of the TMDs follows the general trend of sulfides > selenides > tellurides. Analogously it appears the stability of TMDs grouped by transition metal is platinum > tungsten > molybdenum. A standout exception to this is PtS₂, as one of the least stable TMDs with regard to ambient annealing, this is due to the higher stability of the monosulfide in this case.

6 -Synthesis and Characterisation of Platinum Sulfides



“I apologize for such a long letter - I didn't have time to write a short one.”

— Mark Twain

6.1 Introduction

The interest in 2D TMD materials has rapidly increased over the last decade due to their varied and layer-dependent properties. As the more commonly studied TMDs such as MoS₂ and WSe₂ have been gradually explored in terms of fundamental properties and applications, interest has increased towards isolating and synthesising 2D forms of other less common TMDs. A prominent example are the group-10 TMDs, particularly PtSe₂. There exists a long history of studies of group-10 TMDs,²⁰⁸ which have risen to a point of prominence recently thanks to their impressive theoretical electronic-transport capabilities.^{38, 196, 209} These, in turn, have expanded the focus given to the other Pt chalcogenides (or Pt-based TMDs), PtS₂ and PtTe₂.^{202,}
210

Similarly to previously explored materials in this thesis, due to the popularity and rapid pace of development in the field of 2D TMD materials, occasionally the due diligence in terms of accurate and refined characterisation of the TMD material itself is overlooked in order to focus on more forward-looking aspects such as fabrication of electrical devices or electrochemical applications. Resulting in a lack of coherency within literature for the platinum sulfides in particular. Indeed, for the two most common sulfides, PtS₂ and PtS, several publications report conflicting identification of synthesised materials.^{83, 88, 211-213} These publications are largely reliant on the near ubiquitous techniques of Raman and XPS analysis, however, as discussed in Chapter 5 both techniques have their own particular limitations and can be subject to misinterpretation. The majority of the confusion found in the literature regarding the platinum sulfides stems from the competing nature of the mono- and disulfide materials, and the very limited amount of literature. Similar issues with competing sulfides have been encountered for tin sulfides where thorough comparative characterisation was needed to provide clarity.²¹⁴

There is an interesting history to the synthesis of both of these platinum sulfides which has strong connections to materials' science in Ireland. Edmund Davy (cousin of Humphry) published the first paper on the synthesis of both sulfides of platinum in late 1812,²¹⁵ the next year he would go on to become a professor of Chemistry in the Royal Cork Institution²¹⁶ and would proceed onto the Royal Dublin Society and Royal Irish Academy for the rest of his career, he was notably a founding member of the Chemistry Society of London which would go on to amalgamate into the Royal Society of Chemistry(RSC).²¹⁷

Davy was the first to recognize the utility of combining both Pt and S in an evacuated tube and heating at high temperature, he used this to synthesise PtS. A distillation setup combining an

ammonium chloride of platinum and sulfur powder over mercury yielded PtS₂. Both materials were analysed using rudimentary characterisation methods including by taste and smell. PtS₂ was found to be thermally stable in anaerobic environments but to degrade quickly under ambient annealing.²¹⁵ Much of the work discussed in this chapter can, to a certain extent, be regarded as a sequel to this foundational work in platinum sulfide synthesis.

A naturally occurring form of PtS known as cooperite was first described in 1928 by Richard A. Cooper,²¹⁸ it is a significant platinum ore and therefore many of the publications concerning platinum sulfides are mineralogical in nature.²¹⁹⁻²²³ The long history of misidentification between the platinum sulfides is present in this work wherein Cooper originally proposed that the cooperite material described had the formula PtS₂, cooperite was quickly re-ascribed as being PtS.²²⁴ PtS₂ is not known to form naturally, indicating a thermodynamic preference for PtS.

While PtS has benefited from more attention, its study has been confined to the lens of mineralogical investigation, it has generally not been investigated or characterised wholly in the manner which modern 2D materials typically are, with only few exceptions.^{180, 225}

Recently PtS has been observed to have several interesting properties including ultrafast saturable absorption and peculiar thickness-dependent surface states for a non-layered material.¹⁸⁰ PtS undergoes a pressure-induced phase change at ~3 GPa to the PdS structure P4₂m.¹⁸¹ PtS also has been shown to be one of only a handful of materials which possesses negative linear compressibility, meaning the structure expands along one direction when compressed uniformly.^{226, 227}

PtS₂ has garnered recent attention in part due to its predicted properties. PtS₂ is the only Pt-based TMD which is semiconducting in bulk.¹⁷⁹ This material has a strong layer-dependent bandgap variation with a change of the indirect bandgap from 0.25-1.6 eV when going from bulk to monolayer.¹⁷⁹ PtS₂ is predicted to have strongly-bound excitons in the monolayer form²²⁸ and a calculated monolayer electron mobility of up to ~3900 cm² V⁻¹ s⁻¹²⁰⁹, with FET devices delivering room-temperature electron mobility of 62.5 cm² V⁻¹ s⁻¹ and a 10⁶ on/off ratio.²²⁹

The majority of recent PtS₂ experimental studies have employed material synthesised by CVT methods, which can then be exfoliated to give individual 2D crystals. While this can result in high-quality material, it is not guaranteed, with PtS contamination being a common occurrence.^{212, 229-232} The main disadvantages of using CVT-style methods to synthesise and

isolate 2D materials are that they are time consuming, labour-intensive and also inherently unscalable. Further, while PtS₂ and PtS have both been synthesised *via* CVD methods,^{180, 233, 234} robust metrics and characterisation to confirm the quality and purity of these materials are noticeably absent. Though the Raman spectrum of few-layer PtS₂ has been studied in several works, it is an area with many unexplored aspects.²²⁹⁻²³² The catalogue of PtS Raman is poorer, with only a few works providing any insight into the features of the complex spectrum,^{180, 220} with some published PtS Raman spectra incorrectly claiming to be PtS₂ adding to the confusion. High-resolution XPS spectra of these materials are provided in several pieces of literature,^{88, 212, 235-237} unfortunately there exists little to no peak-fitted deconvolution of these materials that holds up to best-practice scrutiny.

This chapter aims to develop robust synthesis procedures using relatively simple methodology to synthesise high-purity thin films of both PtS and PtS₂ by the TAC method. Both platinum sulfides are rigorously characterised using Raman and XPS to better the understanding of the important aspects of their spectra. The stability of these films and the ability to convert PtS₂ into PtS are also investigated.

6.2 Synthesis

Owing to a combination of the complex competing nature of both platinum sulfides, the limited pre-existing Raman and XPS literature for both materials, and also for clarity of discussion, the optimised synthesis parameters for high purity films of both materials will first be introduced and the Raman and XPS spectra of these resultant materials are then examined. Following this, the investigated synthesis parameters and their role in the process are discussed.

6.2.1 PtS Synthesis

Polycrystalline films of PtS were synthesised using the TAC procedure previously described for other TMDs³⁰ detailed in Chapter 2. A Pt metal layer was deposited onto a substrate, typically SiO₂/Si, by sputtering and then placed into a two-zone quartz-tube furnace with sulfur powder in the secondary zone as shown in Fig. 6.1(b). Annealing the Pt film at 500 °C under forming gas (90% Ar/10% H₂) at a pressure of ~1 mbar for 1 hour generated uniform films of PtS.

6.2.2 PtS₂ Synthesis

Polycrystalline films of PtS₂ were synthesised using a modified design inspired by the work of Wu *et al.*²³⁴ Using the same two-zone quartz tube furnace as for PtS, the Pt metal film was placed inside an internal open-ended quartz tube in the main heating zone. The opening of this internal tube, at the edge of the hot-zone, was loaded with sulfur powder as a second local sulfur source and the opening placed against the direction of flow, as shown in Fig. 6.1(a). Annealing at 500 °C under forming gas and a pressure of ~200 mbar for 1 hour generated uniformly converted films of PtS₂.

The effects of synthesis temperature and initial Pt film thickness on the resulting TMD film were investigated for both materials. For simplicity, to differentiate between films they are referred to in this study by their initial Pt metal film thickness. The expansion factor when sulfurizing Pt films to PtS has been shown to vary depending on starting thickness.¹⁸⁰ It has previously been shown that a similar process for PtSe₂ resulted in an approximate quadrupling of film thickness after conversion.⁴⁰ An advantage of such synthesis methods was the ability to synthesise films on a variety of substrates. PtS₂ and PtS films were synthesised on SiO₂/Si, pyrolytic carbon (PyC), and quartz substrates as shown in the appendix, Fig.A15. These are applications-oriented substrates frequently used for electronics, electrochemistry, and optics respectively.

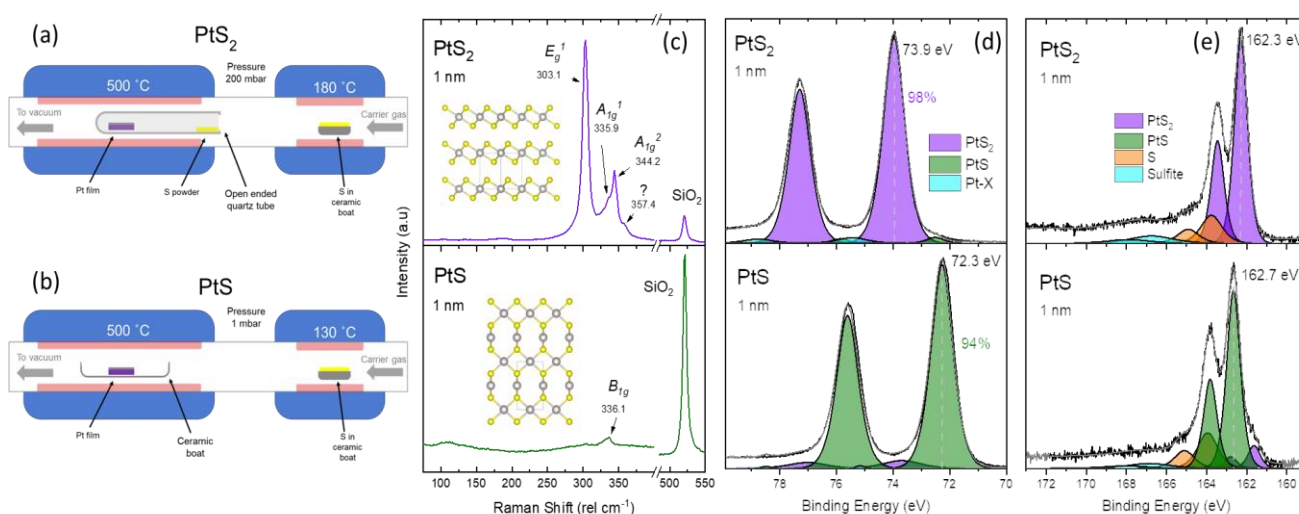


Fig. 6.1 Schematic diagram for the synthesis arrangement for PtS₂ films (a) and PtS films (b). (c) Raman spectra of PtS₂ and PtS films synthesized from a 1 nm Pt film, with an insert showing their atomic

structures (yellow balls represent sulfur atoms, silver balls represent platinum atoms). XPS of the Pt 4f (d) and S 2p (e) core-level regions for PtS₂ and PtS films.

6.3 Raman

Raman spectra of 1 nm PtS₂ and 1 nm PtS, taken using a 532 nm excitation wavelength, are shown in Fig. 6.1(c). PtS₂ has an octahedral (1T) geometry with a hexagonal lattice, and a D_{3d} point group²³², see appendix Fig.A1. Therefore the three primary components to the Raman spectrum of few-layer PtS₂ are the out-of-plane E_g^1 mode at ~ 303 rel cm⁻¹, and the two in-plane modes A_{1g}^1 and A_{1g}^2 at ~ 336 and 344 rel cm⁻¹ respectively.²³² These components are clearly visible in Fig. 6.1(c) alongside an unidentified shoulder at ~ 357 rel cm⁻¹. PtS₂ displays high intensity Raman signals compared to the underlying SiO₂.

The position of these peaks aligns with reports for ~ 2 -3-layer PtS₂²³². The FWHM of the peaks in this spectrum are consistent with those reported for similar growth methods but are significantly broader than those reported for individual mechanically-exfoliated flakes.^{230, 232, 234} While the FWHM of Raman peaks were affected by laser power and the spectral grating, the broadening was comparable to what has been reported for other TMDs when comparing polycrystalline films to large single crystals from CVD.^{118, 238}

To provide a thorough database of characterisation, the Raman spectra of a 5 nm PtS₂ film using three excitation wavelengths (532, 633, and 405 nm) is given in Fig. 6.2. No new modes or significant changes in intensity ratios between the peaks were observed for the different wavelengths.

PtS is a non-layered material with a tetragonal crystal structure, see Fig.A1 in the appendix, and either a $P4_2/mmc$ ^{220, 223} or $P4_2/nmn$ space group.²²⁶ The Raman spectrum of the 1 nm PtS film in Fig.6.1(c) showed a single low intensity peak at ~ 336 rel cm⁻¹. This was consistent with other reports of PtS and was attributed to the Raman-active B_{1g} vibrational mode¹⁸⁰. The 100-150 rel cm⁻¹ region showed a broad background for very thin PtS films, which developed into distinct peaks for thicker films. The Raman spectrum of a 5 nm PtS film acquired with the three different excitation wavelengths is shown in Fig. 6.2. The 532 nm and the 633 nm spectra display several clearly resolved peaks. These spectra are distinct from each other with the 532 nm spectrum being dominated by the B_{1g} peak at ~ 335 rel cm⁻¹ with many lower intensity

peaks across the spectrum. The 633 nm spectrum contains four sharp peaks at approximately 115, 335, 377, and 475 rel cm^{-1} . These various additional peaks in the 532 nm spectrum and the 633 nm Raman of PtS were previously unreported. The disparity in Raman spectra between the excitation energies was likely a result of resonance effects, the additional Raman modes are currently unassigned in literature and should form the basis for further study.

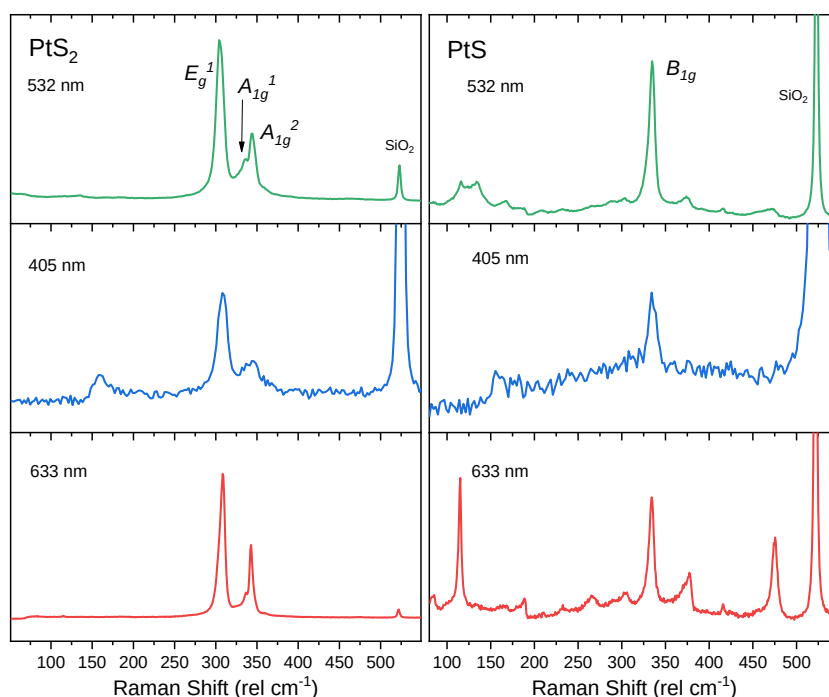


Fig. 6.2. (a) Raman spectra of a 5 nm PtS₂ film using different wavelength Raman lasers. **(b)** Raman spectra of a 5 nm PtS film using different wavelength Raman lasers

6.4 XPS

XPS was used to characterise both of these films as shown in Fig. 6.1(d) and(e). XPS has extreme utility in the characterisation of nanoscale materials as it has very high surface sensitivity, has the ability to differentiate between chemical states, and also allows calculation of stoichiometry amongst other measures. As discussed already throughout the course of this work, the drawback when utilising XPS is the non-trivial nature of interpreting core-level spectra. The data can be complex, leaving significant room for misinterpretation through fitting errors and these uncertainties can be difficult to convey fairly when reporting data. Numerous reports have been published recently in an effort to improve the overall quality of XPS reported

in the literature.^{68, 69} Due to the complicated nature of the XPS of these materials, this section provides a resource to help deconvolute the spectra of platinum-sulfur compounds.

The spectral regions of interest for XPS of platinum sulfides are the Pt 4f and S 2p core-levels. The XPS spectra of the Pt 4f region of 1 nm PtS₂ and PtS films is shown in Fig. 6.1(d). The spectrum for PtS₂ is dominated by a doublet pair corresponding to the Pt(IV) state for PtS₂, with the *Pt 4f*_{7/2} component at 73.9 eV. This accounts for 98% of the Pt atoms measured, indicating the high purity of material obtained. A low-binding energy shoulder with *Pt 4f*_{7/2} at ~72.5 eV is attributed to a Pt(II) state from PtS. The PtS component in the spectrum could potentially be misidentified and assigned as Pt metal due to the relatively small difference in expected binding energy position. While basing peak assignments on literature values of energy position alone has issues,⁷⁶ the symmetric peak shape of the PtS component makes a Pt metal state very unlikely. Low levels of PtS were found to be almost ever present in all of the PtS₂ films synthesised here. A third component with *Pt 4f*_{7/2} at ~75.4 eV is fitted, assignment of this low intensity and broad doublet is difficult and it is provisionally assigned as a Pt-oxide due to the binding energy of the peaks, this aligns with previous interpretations for PtSe₂.¹⁸⁷

Similarly, the Pt 4f spectrum for a PtS film has a doublet with *Pt 4f*_{7/2} at 72.3 eV, this is attributed to Pt(II) from PtS. The PtS component accounts for 94% of the measured Pt atoms. There is also a second doublet with *Pt 4f*_{7/2} at ~73.8 eV is from Pt(IV) in the form of PtS₂.

The S 2p core-level region is significantly more complex and has been frequently oversimplified in the literature.^{88, 180, 212, 237} Similar line-shapes to those shown in this work have been observed but not fitted for the platinum sulfides previously.^{235, 236} The S 2p regions for both platinum sulfides are fitted with four doublets from four chemical states of sulfur. PtS₂ and PtS components are on the low binding energy side with their *S 2p*_{3/2} peaks at 162.3 and 162.7 eV respectively. Elemental sulfur was found on both samples at ~163.8 eV. The fourth component was a consistently low intensity broad peak with *S 2p*_{3/2} at ~166.5 eV. While similar line-shapes have been reported for platinum sulfides previously, there has been little discussion of their origin.⁸³ The most likely chemical state for this broad component is attributed to a S-O species, likely sulfite based on binding energy position.²³⁹ Oxidised sulfur is not commonly observed in XPS for other sulfur TMDs synthesised through similar methods,³⁰ this observation implies that Pt may play a role in the oxidation, or that this broad component might have a different origin.

The overlapping nature of many of the components in both the Pt 4f and the S 2p core-levels increases the possibility for error in each fitting, small changes in relative peak areas can result in large changes in the calculated stoichiometry of the material. In an effort to minimise this error, the stoichiometry values were averaged over several samples (see Fig. 6.3, below) giving S:Pt ratios of 1.87 ± 0.06 for PtS₂ and 0.97 ± 0.09 for PtS. These values are very close to the ideal values, the chalcogen deficiency for PtS₂ potentially indicates that sulfur vacancies are a common defect similar to other TMDs.³²

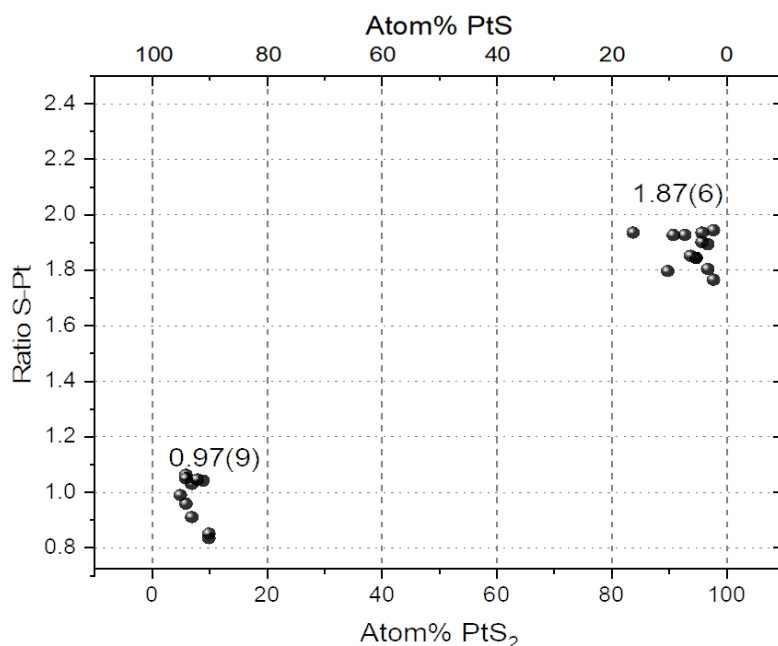


Fig.6.3 Plot of the S-Pt ratio for 24 Pt sulfide films as calculated by comparison of relative XPS peak areas showing the clusters for PtS and PtS₂.

6.5 Synthesis Parameters

Naturally, the initial attempt to synthesis the platinum sulfides was through the TAC process which has been used reliably to synthesise MoS₂ and WS₂ in the previous chapters of this thesis, with adjustments to the common variables of synthesis temperature and chalcogenisation time. To encourage complete conversion of the Pt metal film to the sulfide a higher chalcogenisation time of 60 mins, compared to 25 mins for MoS₂ was chosen.

A wide synthesis temperature range of 400–800 °C was examined. Raman and XPS analysis were performed for each of these experiments to characterise and identify the synthesised material.

Synthesis temperatures between 400–600 °C were found to convert thin Pt films to PtS. At 800 °C there was no conversion to the sulfides and due to the weak adhesion of Pt films on SiO₂,^{240, 241} the Pt film beaded up across the surface. A temperature of 400 °C resulted in higher surface contamination from the previously mentioned additional sulfur species and therefore a temperature range of 500–600 °C was found to be the optimal temperature for PtS synthesis.

It was anticipated from the work of Wu *et al.*²³⁴ that increasing the pressure in the system may lead to PtS₂ synthesis. This was first examined using the same procedure optimised for PtS but the vacuum pump was now manually throttled to establish a pressure of ~200 mbar throughout to process. This method yielded no conversion to either platinum sulfide due to a sulfur transport limitation at higher pressure.

With the assistance of Dr Cormac Ó Coileáin and Dr Niall McEvoy this limitation was circumvented by introducing a second local sulfur source. As sulfur powder would normally be quickly removed from the system at temperatures >200 °C, substrates were placed into a 17 mm diameter (2 mm wall) quartz tube with one open end. Sulfur powder was placed inside the entrance of this tube. The tube was then placed into the primary heating zone of the quartz tube furnace with the open side facing into the direction of flow and positioned with the opening near the edge of the main heating zone. The effect of this was to trap a high partial pressure of sulfur in the internal tube. A high operating pressure of ~200 mbar was found to be essential to limit the sulfur transport and ensure trapping inside the internal tube. The trapped sulfurous volume could be seen after synthesis during the cooling stage when the furnace is lifted open to rapidly lower the temperature, as presented in Fig. 6.4.

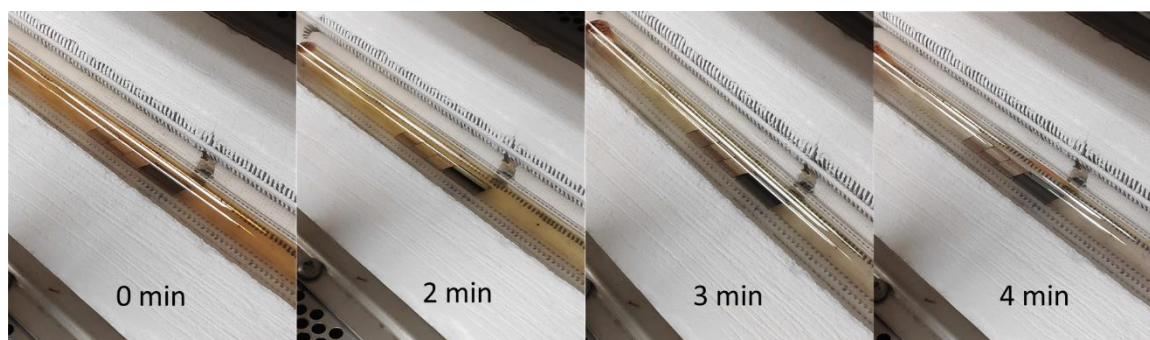


Fig. 6.4. Sequential photographs of the primary heating zone of the furnace during the cooling stage after synthesis of PtS₂.

The temperature of the primary and secondary heating zones in the furnace were varied to optimise the PtS₂ contribution in the synthesised films. 500 °C and 180 °C respectively were found to be the most optimal temperatures but majority PtS₂ films were synthesised for temperatures of 400–600 °C as illustrated in Fig. 6.5, below.

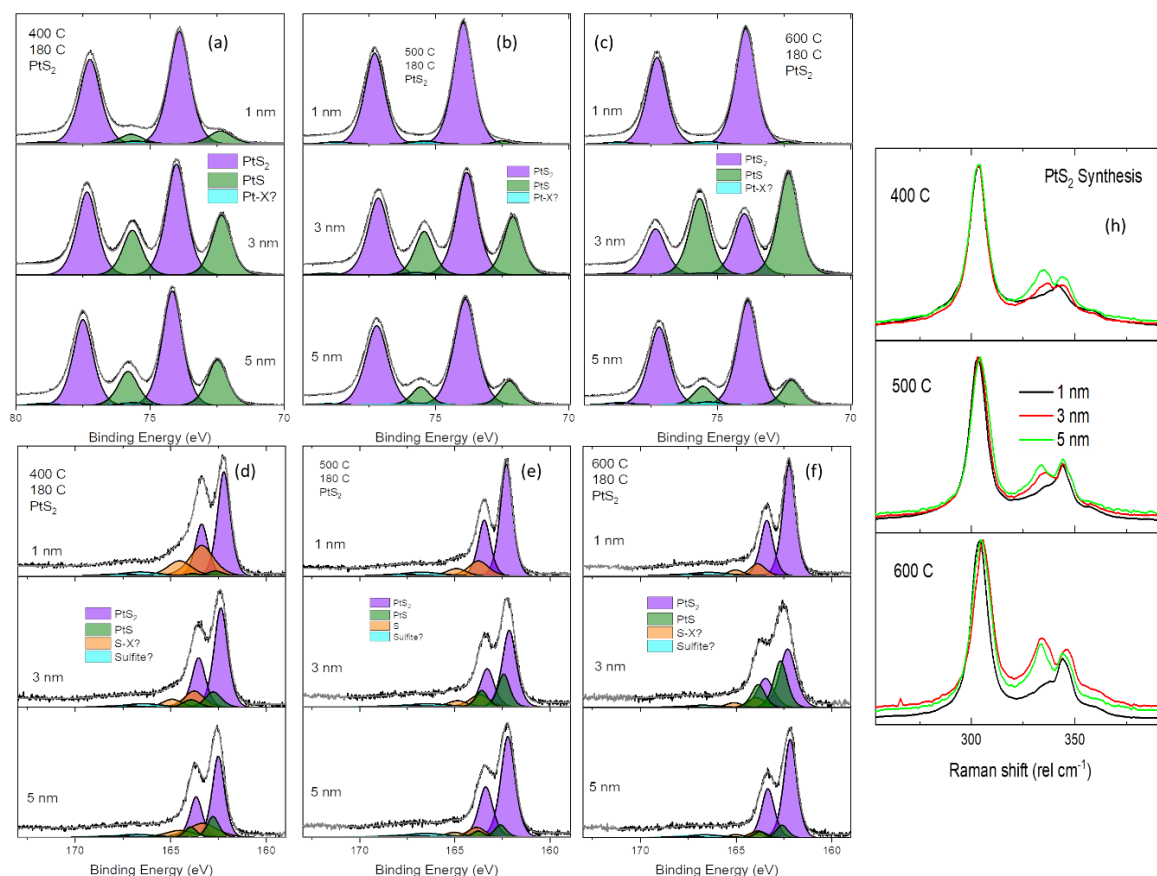


Fig. 6.5. XPS and Raman spectra for three thicknesses of PtS₂ films synthesized at three temperatures. Mo 3d region at (a) 400 °C (b) 500 °C (c) 600 °C. S 2p region at (d) 400 °C (e) 500 °C (f) 600 °C. (h) Raman spectra of the films.

It can be seen in Fig. 6.5 that composite materials (consisting of both PtS and PtS₂) can be readily obtained. A film of both PtS and PtS₂ in approximately equal amounts can be synthesised by lowering the synthesis temperature to 400 °C with a reduced amount of sulfur in the internal tube. The Raman and XPS spectra for this are shown below in Fig. 6.6. Allowing the differences in XPS peak positions from the different chemical states to be more clearly indicated.

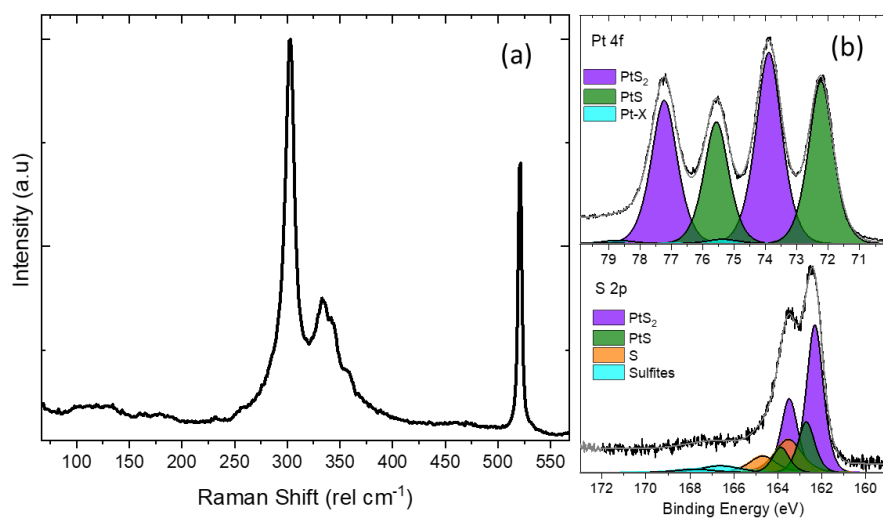


Fig. 6.6. (a) Raman spectra of a mixed PtS₂-PtS film grown at 400 °C. **(b)** XPS Pt 4f and S 2p core-level spectra of the mixed film showing the relevant components of each material

Variations as a result of sample position inside the internal quartz tube were investigated by placing 1 nm Pt films at 6 points along the tube, Fig. 6.7. No significant variance was observed in the XPS or Raman of the films with high purity PtS₂ synthesised at each position. This indicates a roughly uniform environment inside the tube.

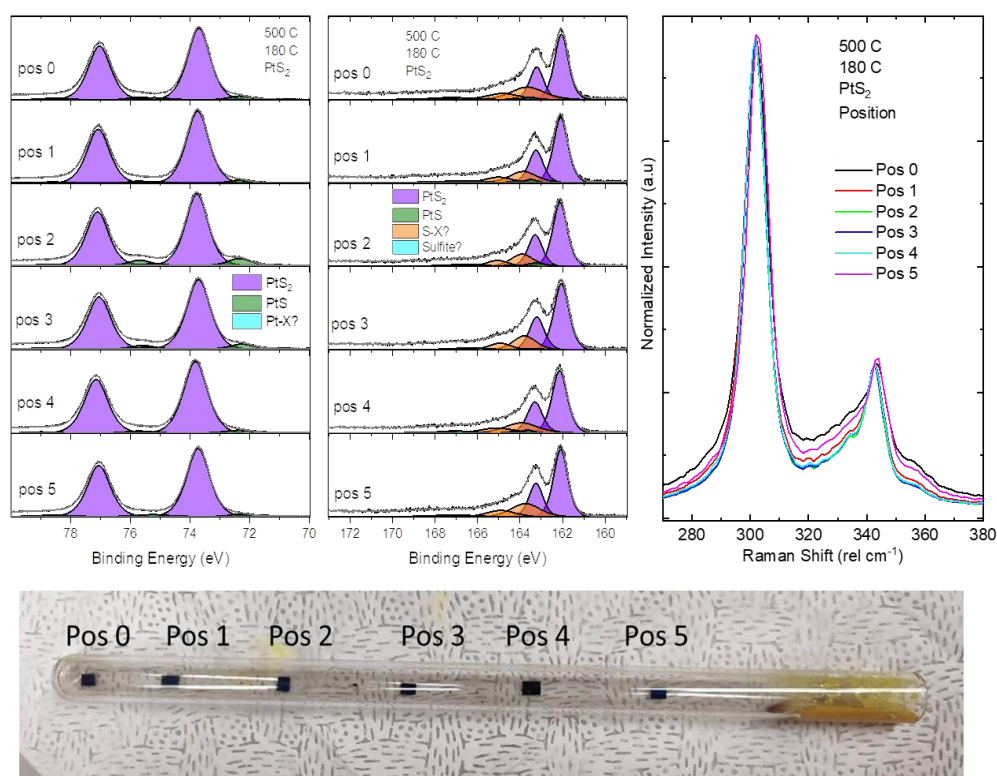


Fig. 6.7. (a) XPS spectra of 1 nm PtS₂ films synthesized along the length of the internal quartz tube. **(b)** Raman spectra of the PtS₂ films. **(c)** Picture of the quartz tube showing the positions of the substrates.

6.6 Thickness Effect

The thickness dependence of this optimised synthesis procedure was investigated for PtS₂. Raman, XPS spectra, chemical composition data from XPS, and SEM images for 7 thicknesses of PtS₂ films are shown in Fig. 6.8. The Raman spectra for PtS₂ films with increasing Pt film thickness Fig.6.8(a) show only minor changes for the E_g^1 and A_{1g}^2 Raman modes. It is expected from the literature that with increasing thickness the A_{1g}^2 and A_{1g}^1 modes gradually merge, with bulk PtS₂ having only two Raman peaks for the E_g^1 and the A_{1g}^1 ¹⁷⁹. An inconsistent trend was observed due to uniformity issues for thicker films, but it is noteworthy that for films of up to 20 nm starting Pt thickness the two A_{1g} modes are discernible, indicating bulk-like behaviour was not reached. The increasing prominence of what appears to be the A_{1g}^1 at ~334 rel cm⁻¹ is attributed to a convolution of the A_{1g}^1 from PtS₂ and the B_{1g} mode from PtS contamination, this overlap of the Raman modes contributes to the possible errors in identification of the Pt sulfides.

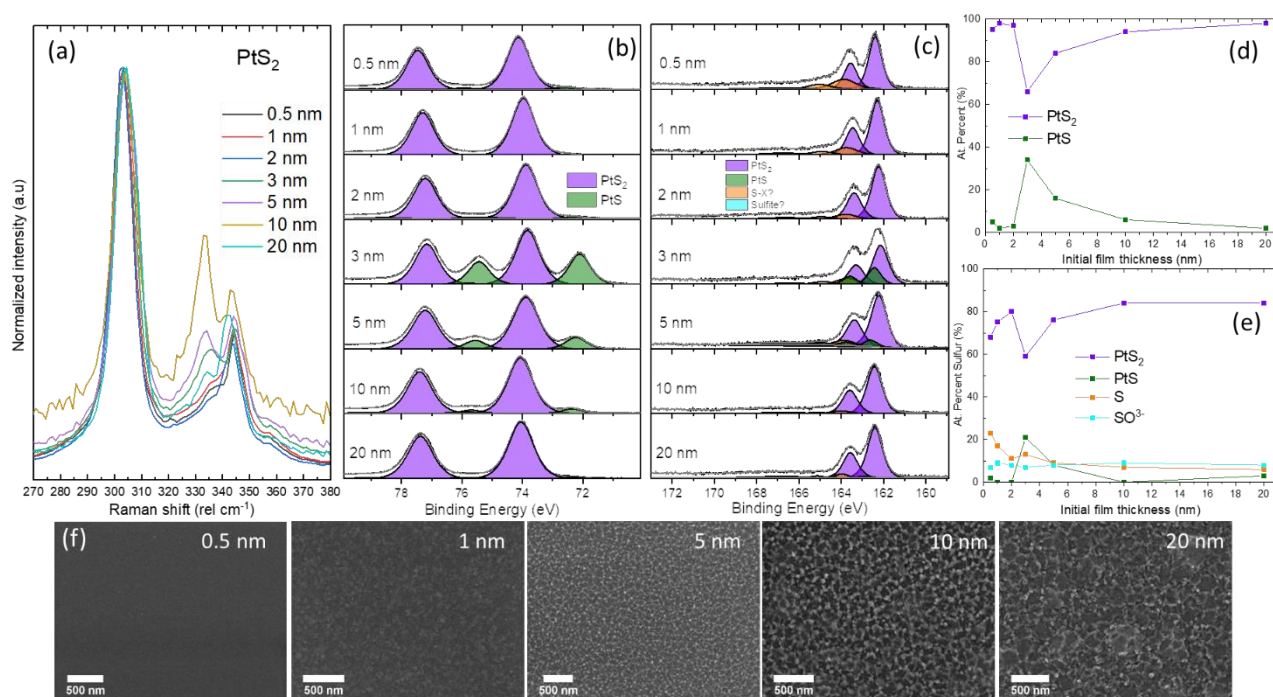


Fig. 6.8. (a) Raman spectra of PtS₂ films of different thickness, normalized to the E_g^1 peak intensity. XPS of the Pt 4f (b) and S 2p (c) core-level regions for PtS₂ films of different thickness. Chemical composition from XPS of the Pt 4f (d) and S 2p (e) XPS regions. (f) SEM images of PtS₂ films of different thickness.

Similarly, to the issues with high synthesis temperatures the weak adhesion of Pt films on SiO₂ was found to effect films of >5 nm starting Pt thickness. These films were prone to bubbling and delaminating from the SiO₂. These effects could potentially be remedied by the use of an adhesion layer between the Pt and the substrate, although common adhesion materials such as Ti may be problematic as they have the potential to sulfurize during synthesis or to leech chalcogen from the platinum sulfide films.¹⁸⁷

XPS spectra for the Pt 4f and S 2p core-level regions PtS₂ films of various thicknesses are shown in Fig. 6.8(b) and(c) with the chemical state composition amassed from XPS for each core-level shown in Fig. 6.8(d) and(e).

The synthesis of PtS₂ was successful at almost all thicknesses examined, with the XPS core-levels of the films showing a consistently high level of PtS₂. The exception were the films synthesised from a starting Pt film of 3 nm. These were consistently observed to poorly convert to PtS₂ with the sample shown here only yielding a 65:35 ratio of PtS₂:PtS. The cause of this peculiarity is not currently understood and merits further study, PtSe₂ thin films have been

shown to change orientation with increasing metal film thickness,⁴⁰ a similar effect could potentially play a role in this system also.

A combination of the shallow measurement depth of XPS and the delamination and/or bubbling of the PtS₂ films, discussed below, results in potentially misleading results from XPS if taken alone. This illustrates why a combination of measurement techniques, as implemented here, with Raman spectroscopy, is the minimum requirement to gain a clear understanding of the entire film's properties and composition.

SEM images of the PtS₂ films are shown in Fig.6.8(f), these images clearly portray the highly polycrystalline nature of the films and how the films visually look similar to other TMD films synthesised through related methods.²⁴² Contrast increases with thickness of the films, individual crystallites on the order of 50–100 nm were visible across the PtS₂ films, with average crystallite size generally increasing with film thickness. While minor changes were observed in film morphology for starting thicknesses less than 5 nm (see also appendix Fig.A16.), this changes substantially over 5 nm, with a combination of effects including the lack of adhesion, expansion of the films, and strain during synthesis resulting in bubbling and delamination for thicker films.

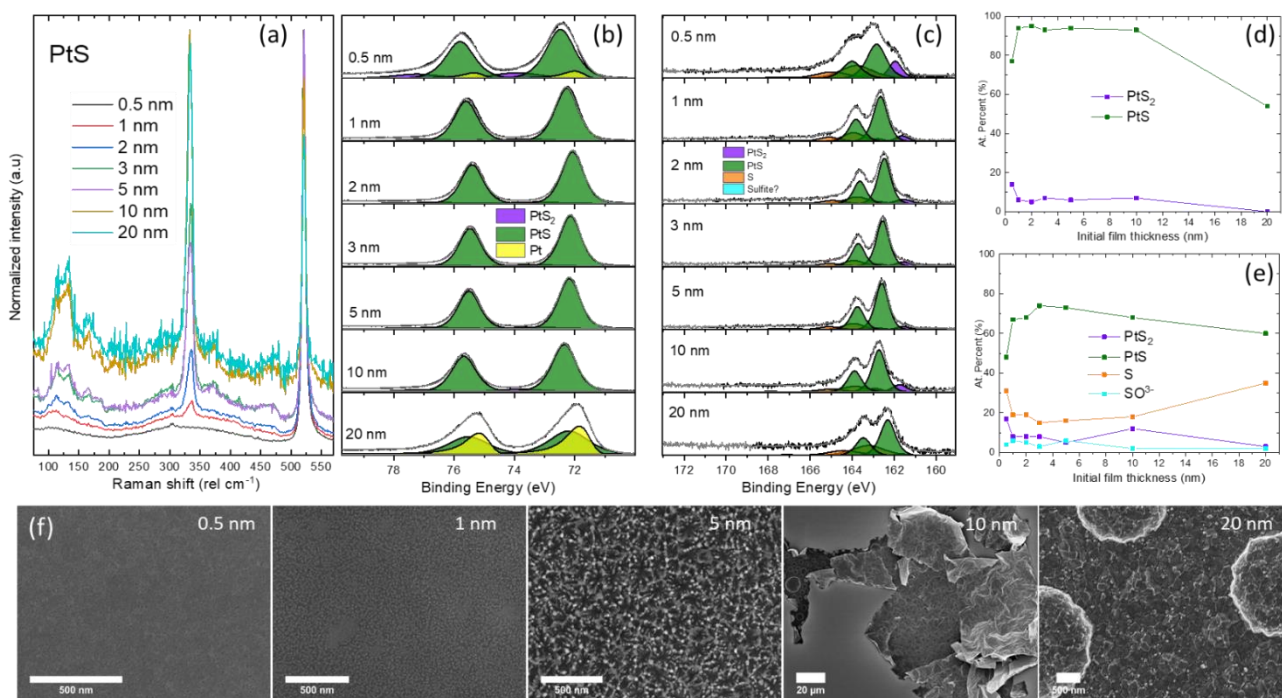


Fig.6. 9. (a) Raman spectra of PtS films of different thickness. XPS of the Pt 4f **(b)** and S 2p **(c)** core-level regions for PtS films of different thickness. Composition of the Pt 4f **(d)** and S 2p **(e)** XPS regions. **(f)** SEM images of PtS films of different thickness.

Similarly, the thickness dependence of PtS films was investigated. The Raman spectra of PtS films are shown in Fig. 6.9(a) to have a strong thickness dependence. Very thin films were seen to show no discernible Raman peaks but have two very broad regions centred at ~ 330 and ~ 100 rel cm^{-1} . As the thickness of the film increased more pronounced modes appeared, first with the B_{1g} at ~ 335 rel cm^{-1} followed by a number of smaller peaks across the spectrum. Two heavily overlapping sharp peaks were seen to develop at ~ 115 and 134 rel cm^{-1} . This work was the first report of these Raman modes and their thickness dependence for PtS, they are currently unassigned.

XPS analysis of the PtS films in Fig. 6.9 (b) and(c) demonstrates the advantage of complementary characterisation with Raman and XPS. While the Raman spectrum from the 0.5 nm film does not show any characteristic PtS Raman modes, in contrast XPS indicates the film is predominantly PtS. Interestingly, there was a small amount of Pt metal present in the 0.5 nm sample indicating that either the film was not fully converted initially or that the film was more prone to degradation upon exposure to ambient conditions. 1–5 nm PtS films provided XPS spectra with high levels of PtS and no Pt metal present. PtS films in this thickness bracket generally showed very similar line shapes, indicating high uniformity. Significant amounts of Pt metal were present for the 20 nm film, this is most likely a result of incomplete conversion for thicker films combined with extensive delamination exposing the lower, unconverted layers. Pt thicknesses >5 nm were very prone to delamination, this can be exacerbated by higher temperatures, increasing the likelihood and degree of delamination.

SEM of the PtS films in Fig. 6.9(f) show relatively uniform films with minimal contrast for an initial 1 nm Pt film. Larger crystallites and an uneven surface appear at ~ 5 nm thickness, with significant bubbling, delamination and folding occurring for thicker films. This was seen clearly in the SEM images for the 10 and 20 nm PtS films.

6.7 Conversion of PtS₂ to PtS: Annealing and PtS₂ stability

The thermally driven transformation of PtS₂ to PtS was analysed at several temperatures using complementary Raman and XPS. Fig. 10 shows the XPS and Raman data for four 1 nm PtS₂ films with post-growth annealing in a quartz tube at 1 mbar under Ar flow for 30 minutes.

Little change occurs when compared to the pristine material (Fig. 6.8), including no reduction of the PtS₂ to PtS for the samples annealed at either 300 or 400 °C, with variations in their PtS content attributed to normal sample-to-sample variation in the starting PtS₂ films.

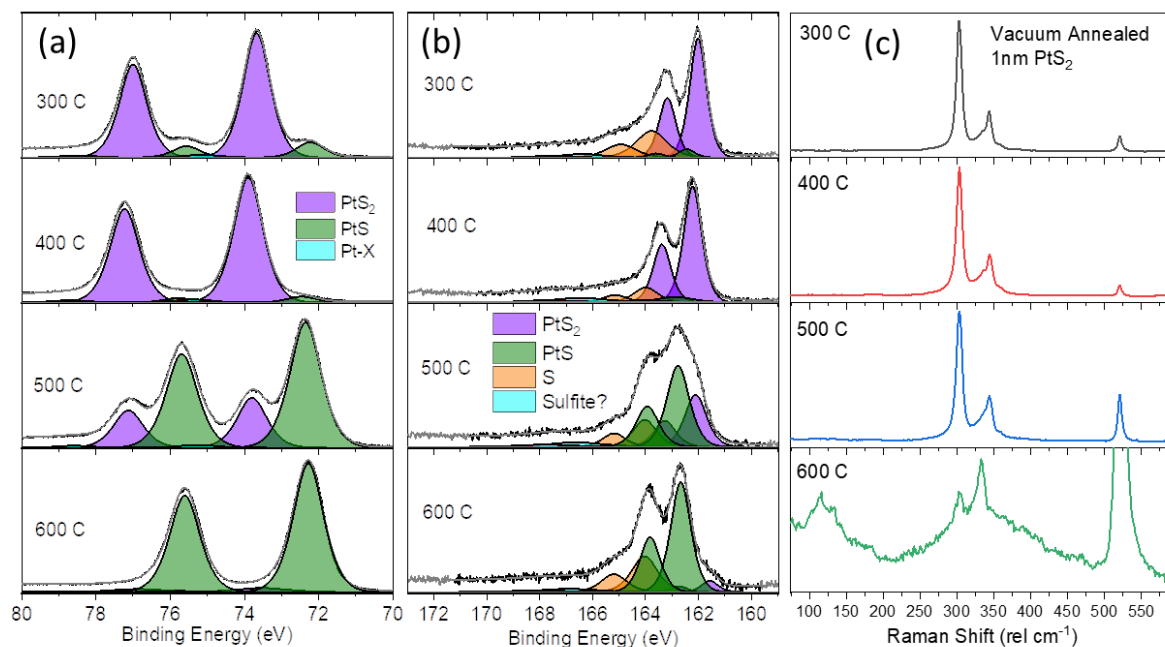


Fig. 6.10. XPS of the Pt 4f (a) and S 2p (b) core-level regions for 1 nm PtS₂ films after annealing at various temperatures. (a) Raman spectra of 1 nm PtS₂ films after annealing at various temperatures

500 °C annealing results in majority conversion of the PtS₂ film into PtS with a 27:73 ratio of PtS₂:PtS. Despite the large majority of PtS in the film, the Raman spectrum is only slightly altered from that of pure PtS₂, this is a potentially major factor in mischaracterisation of Pt sulfide films. The disparity is a result of the Raman signal for PtS₂ being significantly more intense than that of PtS, illustrating that Raman alone is not a reliable technique for characterisation of these materials.

This may explain the discrepancy with the results of Wu *et al.* who reported the reversible conversion of the Pt sulfides: Annealing at 525 °C converting PtS₂ into PtS, while annealing at 450 °C in a sulfur vapour converts PtS into PtS₂, both were characterised using only Raman spectroscopy.²³⁴

Annealing at 600 °C yielded an XPS spectrum in Fig. 6.10(a) with 95% PtS with a corresponding pronounced change in the Raman spectrum Fig. 6.10(c), the characteristic PtS Raman mode at ~336 rel cm⁻¹ and the broad modes between 100-150 rel cm⁻¹ were all visible. A remnant of PtS₂ Raman signal was still visible with the E_g^1 at ~300 rel cm⁻¹, further indicating

the imbalance in their Raman signal intensity. While stability at 400 °C is significant for a few-layer material this should be seen as an upper limit for thermal stability of PtS₂ in an anaerobic environment. The thermal stability is a potentially important factor when considering the compatibility of materials in device fabrication.

6.8 Conclusions

In this chapter efficient methods to synthesise polycrystalline thin films of both PtS₂ and PtS were demonstrated. The non-layered material PtS was synthesised using a standard TAC style process at 500 °C. The layered TMD PtS₂ required a high partial pressure of sulfur to be synthesised and so a modified process using a second open-ended internal quartz tube was used to effectively trap sulfur vapours in proximity to the Pt substrates. This internal tube method enabled high purity (98%) films of PtS₂ to be synthesised at 500 °C.

The limited literature characterisations for thin films of PtS and PtS₂ were considerably expanded upon with fitted XPS spectra revealing the components responsible for the complex peak structures often seen for the platinum sulfides. Both materials were shown to almost always contain a proportion of the other material, particularly PtS₂ containing PtS. Unlike other sulfur TMDs, the S 2p core-level region revealed persistent elemental sulfur contamination and a consistent broad feature at ~167 eV which was tentatively attributed to sulfite.

Raman spectra for both high-purity platinum sulfides were examined over several thicknesses using three excitation laser lines, this enabled the respective Raman peaks to be clearly allocated to each material, which is important as they often exist as a mixture in literature. Substantial variations in the number and proportion of Raman modes in PtS using different excitation energies were found, indicating a resonant Raman effect with 633 nm (1.96 eV) excitation.

Thermal processability limits for thin films of PtS₂ were examined and shown to result in gradual conversion to PtS for anaerobic annealing over 400 °C.

While PtS₂ and PtS have been frequently confused in literature, the high purity synthesis methods and the complementary characterisations presented here with XPS and Raman allows the two materials to be unambiguously distinguished from one another.

7 -Conclusions

In this thesis the synthesis, fundamental chemistry, and extensive characterisation of several 2D TMDs were examined and developed. Firstly, particular focus was given to XPS of TMDs, with the intention of forming a transparent understanding of the analysis of their spectra. The well-known utility of XPS leads to its prevalence in TMD characterisation. However, proficient measurement and interpretation of XPS data are complex tasks with significant room for error and misinterpretation. A feature of modern TMD research is often the need for multiple different complex characterisation techniques, the variety and complexity of these techniques increases the opportunity for errors to be published into the literature, where they may proliferate uncritically. An undue pressure can then be placed onto a limited panel of reviewers to have a broad and comprehensive expertise across a large field of techniques that would allow them to correct any and all errors.

Secondly, TMDs were synthesised and examined with a variety of methods and in many chemical environments to provide information about their core properties, chemical reactivity, and synthesis methods. Moreover, these materials were examined to bridge gaps in the literature by investigating 2D TMD materials in not just pristine forms, but across a range of states while prioritising refined characterisation of the material with detailed discussion and analysis.

In Chapter 3, high-quality, largely monolayer crystals of MoS₂ were synthesised on SiO₂ using the ‘microreactor’ CVD method. CVD methods are seen as the most scalable methods to produce large areas of highly-crystalline TMDs for potential use in applications for example advanced electronics. While CVD synthesis of monolayer MoS₂ has been commonly achievable for several years, there remains significant issues with repeatability, crystallinity, coverage, and properties such as electrical and photoluminescence. The inherent variability of this method generated diverse samples with a range of crystal formations, e.g. isolated single-crystal monolayers, various types of grain boundaries, stitched monolayer films, and terraced multiple-layer regions. These various crystal arrangements were synthesised directly on electronics-compatible substrates enabling many aspects of mono- and few-layer MoS₂ to be examined.

Mapping Raman and PL spectroscopies were used to examine the individual layers of CVD MoS₂ crystals. Layer number and crystal quality metrics were determined by evaluating many CVD MoS₂ samples. CVD monolayers grown on SiO₂ were found to have an average Raman

mode separation of 20.9 cm^{-1} . This synthesis method was found to generate large numbers of MoS_2 monolayers with high-quality, mechanically-exfoliated equivalent PL. A relation between the FWHM of the *A* exciton and the relative intensity of the *B* exciton was used to benchmark PL for monolayer MoS_2 samples. These results demonstrate the utility of this method to produce high-quality individual crystals of monolayer MoS_2 , but also clearly illustrate the need for improvements in coverage, repeatability, and standard metrics for validation and comparison in the literature.

Having explored and verified the synthesis and common characterisation methods of CVD monolayer MoS_2 , in Chapter 4 the effects of NH_3 plasma on mono- and few-layer CVD-grown MoS_2 were reported. Methods to functionalise, alter, or tune the properties of TMDs are becoming of greater importance as applications focused research becomes more common. The inability to “dope” 2D materials in a similar way to traditional silicon electronics has encouraged exploration of an array of methods to tune their properties. Plasma based treatments offer an interesting route due to the large supply of process gases, and the ability to adjust the chemical reactivity and physical etching behaviour of the plasma. XPS analysis established that NH_3 plasma treatment resulted in the controllable formation of covalent bonds between Mo and N atoms, by substitutional doping of nitrogen atoms into the MoS_2 lattice with removal of sulfur atoms, with monolayer alloys of $\text{MoS}_{0.5}\text{N}_{1.1}$ realised. Analysis also served to clarify the XPS features attributed to nitrogen doping of MoS_2 , these components have been frequently confused in the literature.

NH_3 plasma treatment was found to have a pronounced impact on the PL emitted from monolayer MoS_2 , shifting the PL energy in a tuneable and stable manner. Shifts in the MoS_2 PL peak to over 2 eV (620 nm) were demonstrated, representing a $\sim 200\text{ meV}$ (70 nm) shift.

The extreme surface sensitivity of this plasma process was observed using Raman analysis. Bilayers of MoS_2 were found to transition to monolayer-like Raman signal after plasma treatment, indicating that the top-most layer is predominantly affected. Low-frequency Raman spectroscopy was used to confirm decoupling of the bilayer stack of MoS_2 .

The substantial morphology changes were examined with AFM and SEM, it was found NH_3 plasma caused tears along crystalline directions across the MoS_2 surface. These tears gradually rolled into nanoscrolls, creating roughly uniform fields of mixed molybdenum sulfur-nitride MoS_xN_y nanoscrolls over the surface. The significant changes to chemical composition, spectroscopic properties, and morphology of the MoS_2 with increasing NH_3 plasma treatment

serve to show the necessity of using a multitude of characterisation methods to gain a more complete understanding of 2D TMD materials and their reaction to functionalisation methods. The utility of plasma methods to alter the properties of 2D TMDs in a tuneable manner is further reinforced here and merits further study.

The frequency and severity of some common errors or misinterpretations of TMD XPS data in the literature was discussed to illustrate the need for, and to echo experts calling for several improvements to the measurement, fitting, interpretation, and presentation of XPS data. To this end Chapter 5 set out a coherent methodology to understand and fit the XPS spectra of a wide range of TMDs. Ten transition metal chalcogenides were synthesised through conversion of pre-deposited metal films on SiO₂ using the versatile TAC method. These included the sulfides, selenides, and tellurides of Mo, W, and Pt, together these encompass the vast majority of materials studied in modern TMD literature. Raman spectroscopy, using multiple excitation wavelengths, was presented alongside the XPS analysis to both verify and improve the overall analysis of each material.

To expand on the utility of this data as a resource, the stability of each TMD film was also examined and compared through measurement of their degradation over several ambient annealing steps up to 400 °C. This provided a trend of evolving XPS and Raman spectra for each material, which were used to improve the accuracy and confidence of the XPS fitting. Disparities between the Raman and XPS spectra highlighted the risks of using a single characterisation method and demonstrated differences in their surface and material sensitivities. The library of spectra with increasing anneal temperatures allowed for an approximate ambient stability scale to be concluded. In terms of chalcogen, the stability in decreasing order went sulfides > selenides > tellurides. In terms of transition metal, in decreasing order of stability was platinum > tungsten > molybdenum. Paradoxically it was found that PtS₂, which this scale would indicate is the most stable, is in fact the least stable of the TMDs studied. The cause of this instability was examined in Chapter 6.

Unlike most TMD materials, PtS₂ exhibits a more stable monosulfide, PtS, which is preferentially formed in most scenarios. In Chapter 6, synthesis methods and the characterisation of the two closely linked platinum sulfide materials were explored. Recently TMDs using Group 10 TMs (e.g. PtSe₂) have risen to prominence as being worthy of deeper study. PtS₂ has as-of-yet been one of the lesser studied TMDs, a significant aspect of this is likely the more complicated and obscure synthesis requirements. To resolve this issue efficient

methods to synthesise high-purity polycrystalline thin films of both the non-layered PtS and the layered PtS₂ were developed using TAC methods here. Both a higher system pressure and partial-pressure of sulfur vapour were determined to be essential for favouring PtS₂ synthesis over PtS.

The limited literature characterisations for thin films of PtS and PtS₂ were considerably expanded upon with layer thickness and excitation dependant Raman spectra presented and fitted XPS spectra revealing the components responsible for the often-complex spectra seen for the platinum sulfides.

While PtS₂ and PtS have frequently been confused for one another in both historical and modern literature, the high purity synthesis methods and the complementary characterisations presented here allow the two materials to be unambiguously distinguished from one another. This work providing further insight and methodology into the synthesis of both platinum sulfides, can be seen as a follow up study to the initial research synthesising both materials by one of the fathers of Irish chemistry, Edmund Davy in 1812.

Overall, the information presented in this thesis demonstrated methods to synthesise a variety of 2D TMDs including high-quality monolayers of MoS₂, and thin films of high-purity PtS₂. By prioritising the reliable characterisation of the materials, a wide array of complementary characterisation data has been assembled for the most common TMDs across multiple chemical environments. Common issues within the literature regarding the characterisation of the TMDs, primarily with XPS, were exhibited in detail to provide a transparent understanding of the issues and steps to remedy them. While the focus of the 2D materials research community progresses towards applications of these novel materials, the fundamental characterisation issues discussed here show the continued need for both fundamental studies and clear educational content in the literature regarding characterisation of 2D TMD materials.

Taken as a whole, this thesis expands the knowledge of these materials, the methods to synthesise them, and the ability to characterise them.

8 -Bibliography

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9 -Appendix

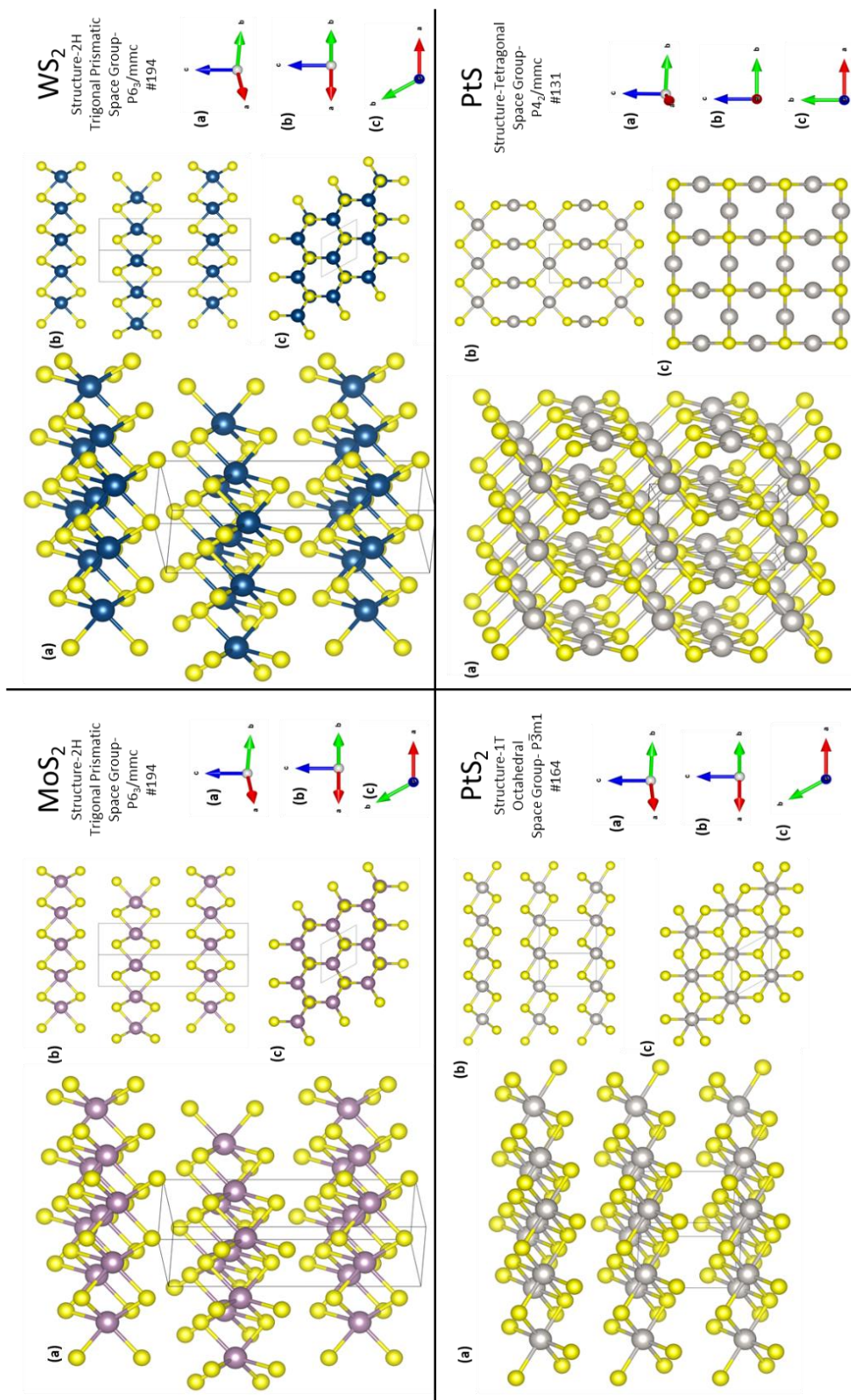


Fig.A1 Structural figures for MoS₂, WS₂, PtS₂, and PtS.

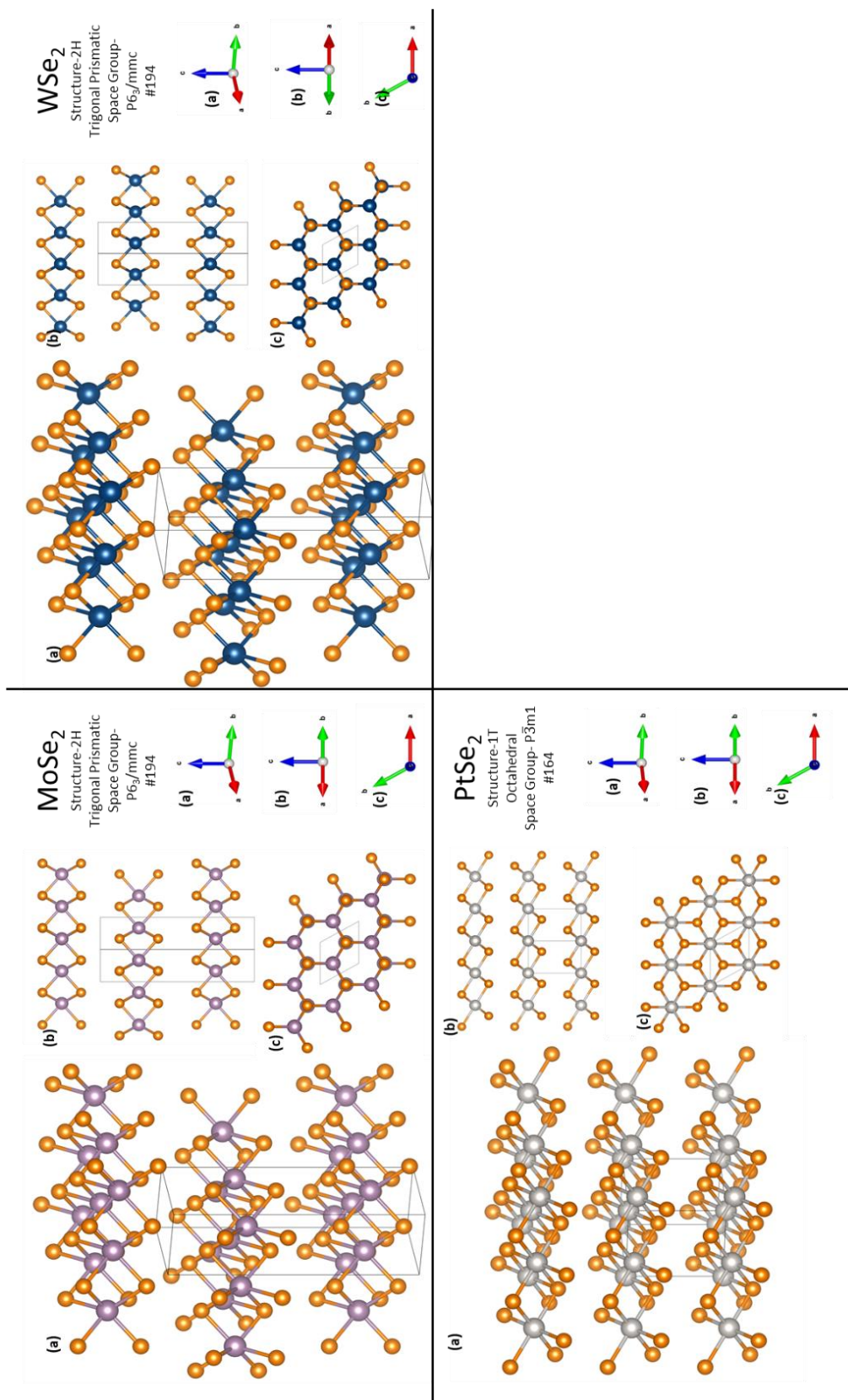


Fig.A2 Structural figures for MoSe₂, WSe₂, PtSe₂

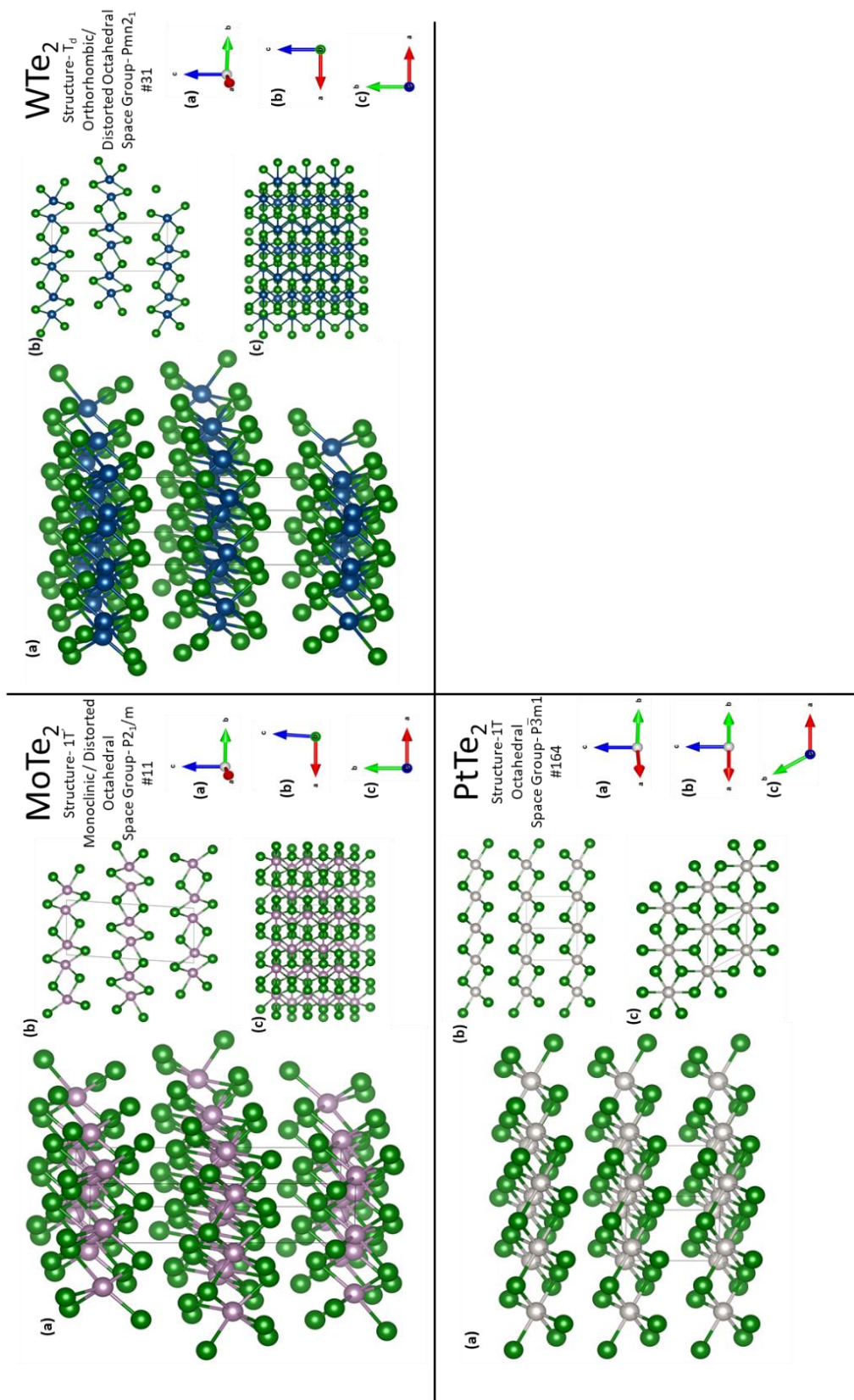


Fig.A3 Structural figures for MoTe₂, WTe₂, PtTe₂

1 H Hydrogen 2.2																		2 He Helium					
3 Li Lithium 0.98	4 Be Beryllium 1.57																	5 B Boron 2.04	6 C Carbon 2.55	7 N Nitrogen 3.04	8 O Oxygen 3.44	9 F Fluorine 3.98	10 Ne Neon
11 Na Sodium 0.93	12 Mg Magnesium 1.31																	13 Al Aluminum 1.61	14 Si Silicon 1.9	15 P Phosphorus 2.19	16 S Sulfur 2.58	17 Cl Chlorine 3.16	18 Ar Argon
19 K Potassium 0.82	20 Ca Calcium 1	21 Sc Scandium 1.36	22 Ti Titanium 1.54	23 V Vanadium 1.63	24 Cr Chromium 1.66	25 Mn Manganese 1.55	26 Fe Iron 1.83	27 Co Cobalt 1.88	28 Ni Nickel 1.91	29 Cu Copper 1.9	30 Zn Zinc 1.65	31 Ga Gallium 1.81	32 Ge Germanium 2.01	33 As Arsenic 2.18	34 Se Selenium 2.55	35 Br Bromine 2.96	36 Kr Krypton 3						
37 Rb Rubidium 0.82	38 Sr Strontium 0.95	39 Y Yttrium 1.22	40 Zr Zirconium 1.33	41 Nb Niobium 1.6	42 Mo Molybdenum 2.16	43 Tc Technetium 1.9	44 Ru Ruthenium 2.2	45 Rh Rhodium 2.28	46 Pd Palladium 2.2	47 Ag Silver 1.93	48 Cd Cadmium 1.69	49 In Indium 1.78	50 Sn Tin 1.96	51 Sb Antimony 2.05	52 Te Tellurium 2.1	53 I Iodine 2.66	54 Xe Xenon 2.6						
55 Cs Cesium 0.79	56 Ba Barium 0.89	*	72 Hf Hafnium 1.3	73 Ta Tantalum 1.5	74 W Tungsten 2.36	75 Re Rhenium 1.9	76 Os Osmium 2.2	77 Ir Iridium 2.2	78 Pt Platinum 2.28	79 Au Gold 2.54	80 Hg Mercury 2	81 Tl Thallium 1.62	82 Pb Lead 2.33	83 Bi Bismuth 2.02	84 Po Polonium 2	85 At Astatine 2.2	86 Rn Radon						
87 Fr Francium 0.7	88 Ra Radium 0.9	**	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Mc Moscovium	116 Lv Livermorium	117 Ts Tennessine	118 Og Oganesson						
		*	57 La Lanthanum 1.1	58 Ce Cerium 1.12	59 Pr Praseodymium	60 Nd Neodymium 1.14	61 Pm Promethium	62 Sm Samarium 1.17	63 Eu Europium	64 Gd Gadolinium 1.2	65 Tb Terbium	66 Dy Dysprosium 1.22	67 Ho Holmium 1.23	68 Er Erbium 1.24	69 Tm Thulium 1.25	70 Yb Ytterbium	71 Lu Lutetium 1.27						
		**	89 Ac Actinium 1.1	90 Th Thorium 1.3	91 Pa Protactinium 1.5	92 U Uranium 1.38	93 Np Neptunium 1.36	94 Pu Plutonium 1.28	95 Am Americium 1.3	96 Cm Curium 1.3	97 Bk Berkelium 1.3	98 Cf Californium 1.3	99 Es Einsteinium 1.3	100 Fm Fermium 1.3	101 Md Mendelevium 1.3	102 No Nobelium 1.3	103 Lr Lawrencium 1.3						

Fig.A4 Periodic table of the elements with their electronegativity on the Pauling scale shown. (Periodic Table of Elements, National Center for Biotechnology Information, <https://pubchem.ncbi.nlm.nih.gov/periodic-table/#view=table&property=Electronegativity> , Dec. 31, 2020)

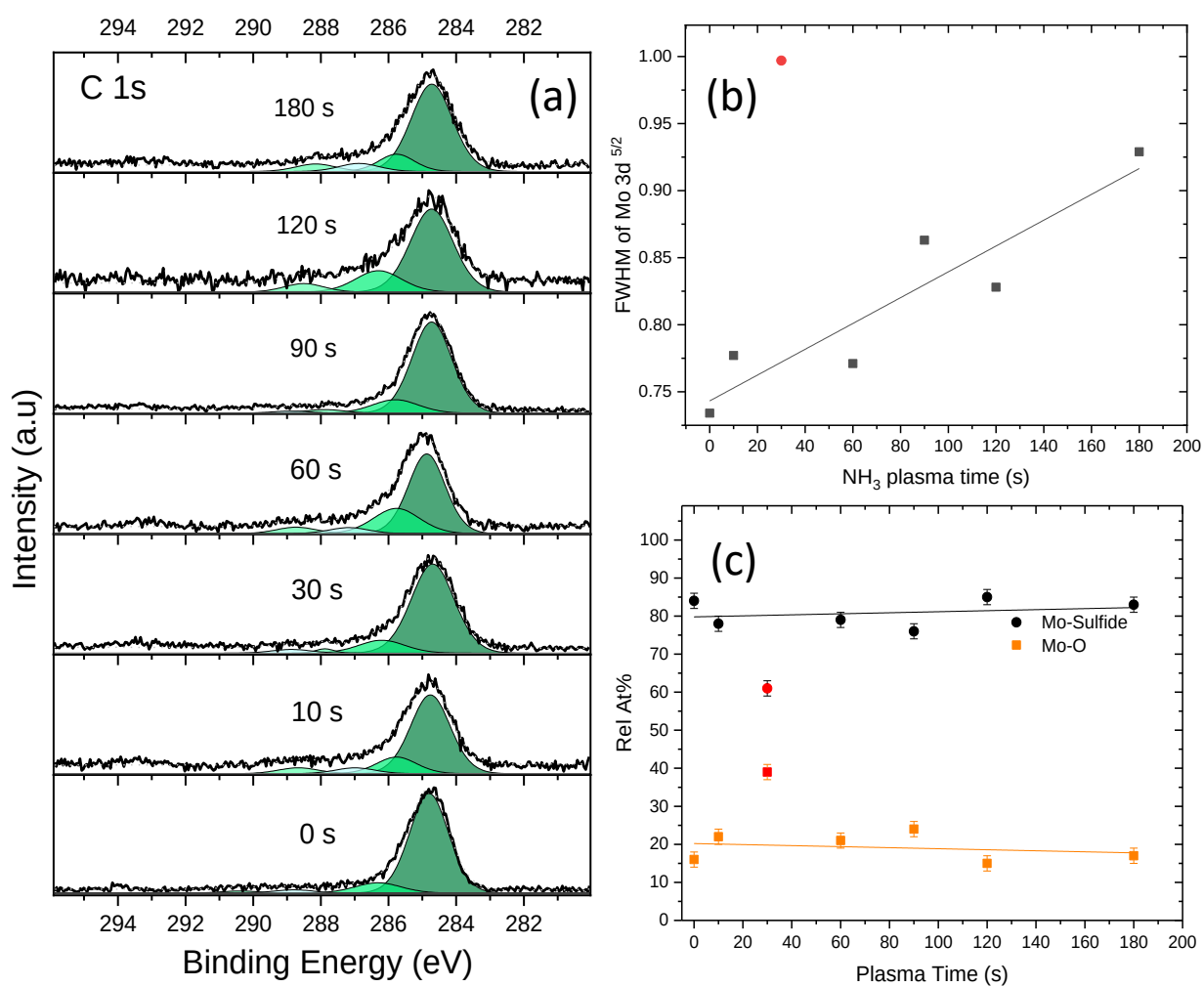


Fig. A5 (a) charge corrected C 1s core-level spectra of MoS₂ after NH₃ plasma (b) Graph of the FWHM of the Mo 3d_{5/2} Mo⁴⁺ peak with NH₃ plasma treatment time, with linear fit excluding the outlier at 30 s. (c) Graph of the relative atomic percentages of the Mo 3d sulfide and oxide components with plasma treatment time, with linear fit excluding the outlier at 30 s.

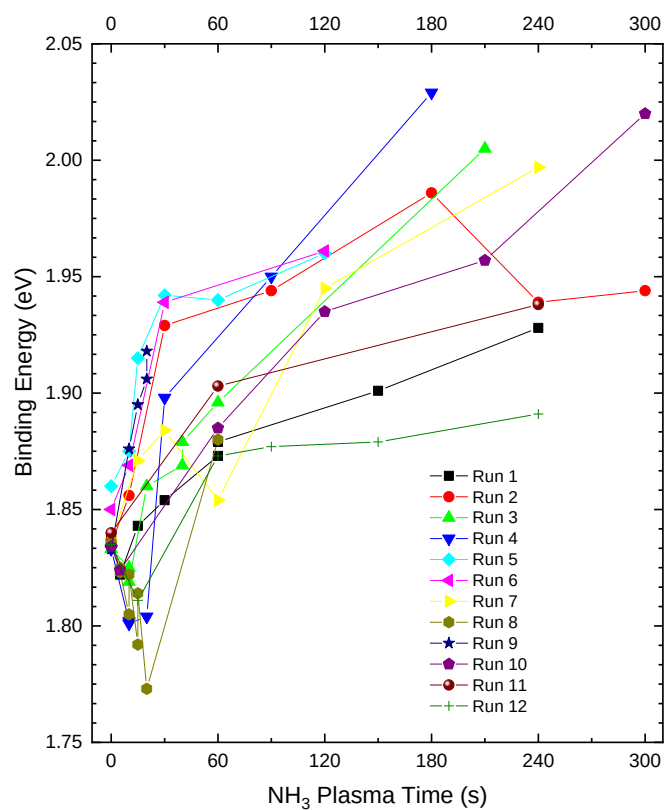


Fig. A6 Plot of the PL peak position for monolayer MoS₂ for 76 samples from 12 separate sets of MoS₂ samples after various amounts of NH₃ plasma

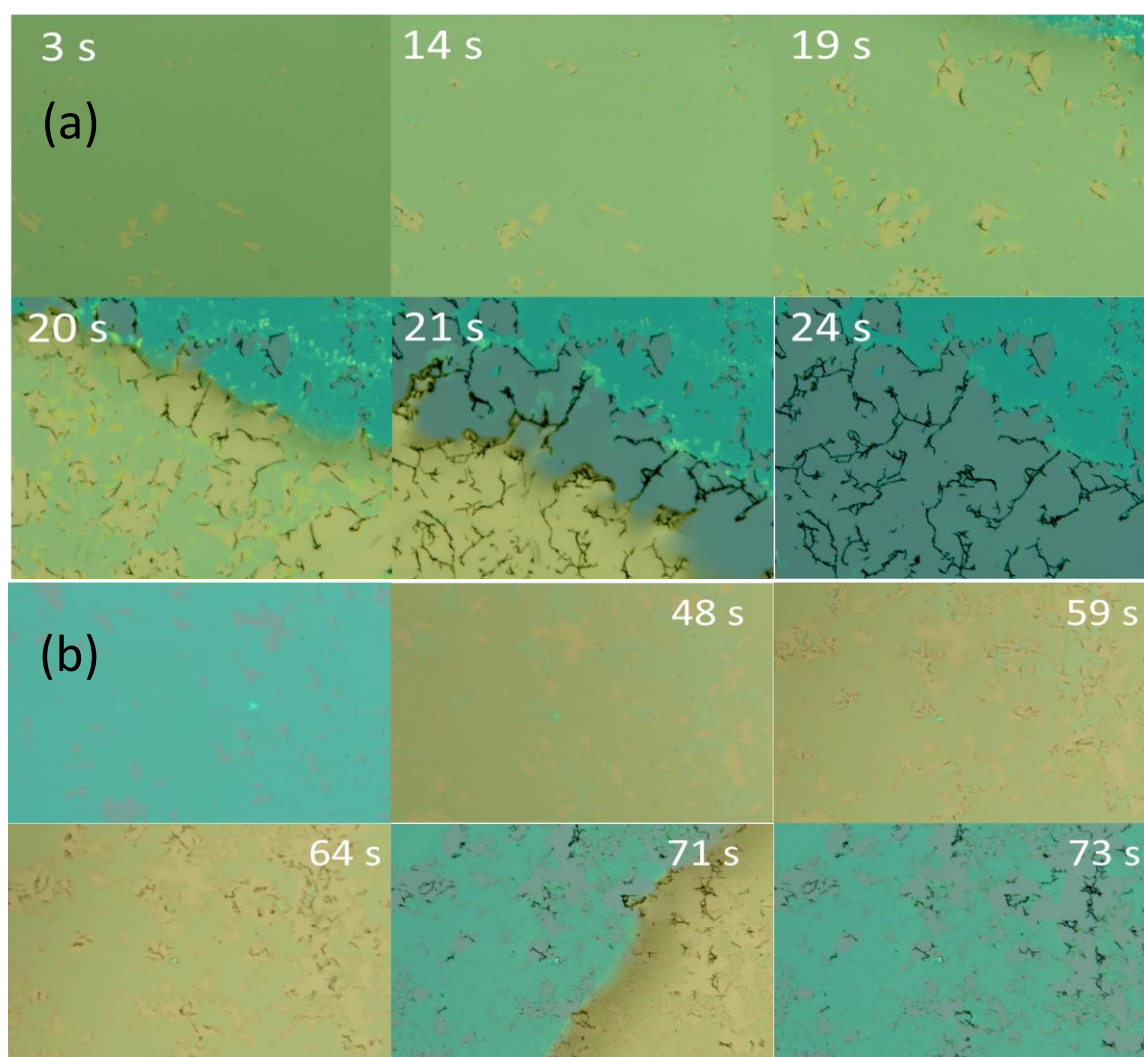


Fig. A7 Optical microscopy images of MoS₂ **(a)** Pristine MoS₂ with methanol evaporating on the surface **(b)** MoS₂ with 30s NH₃ plasma with methanol evaporating on the surface

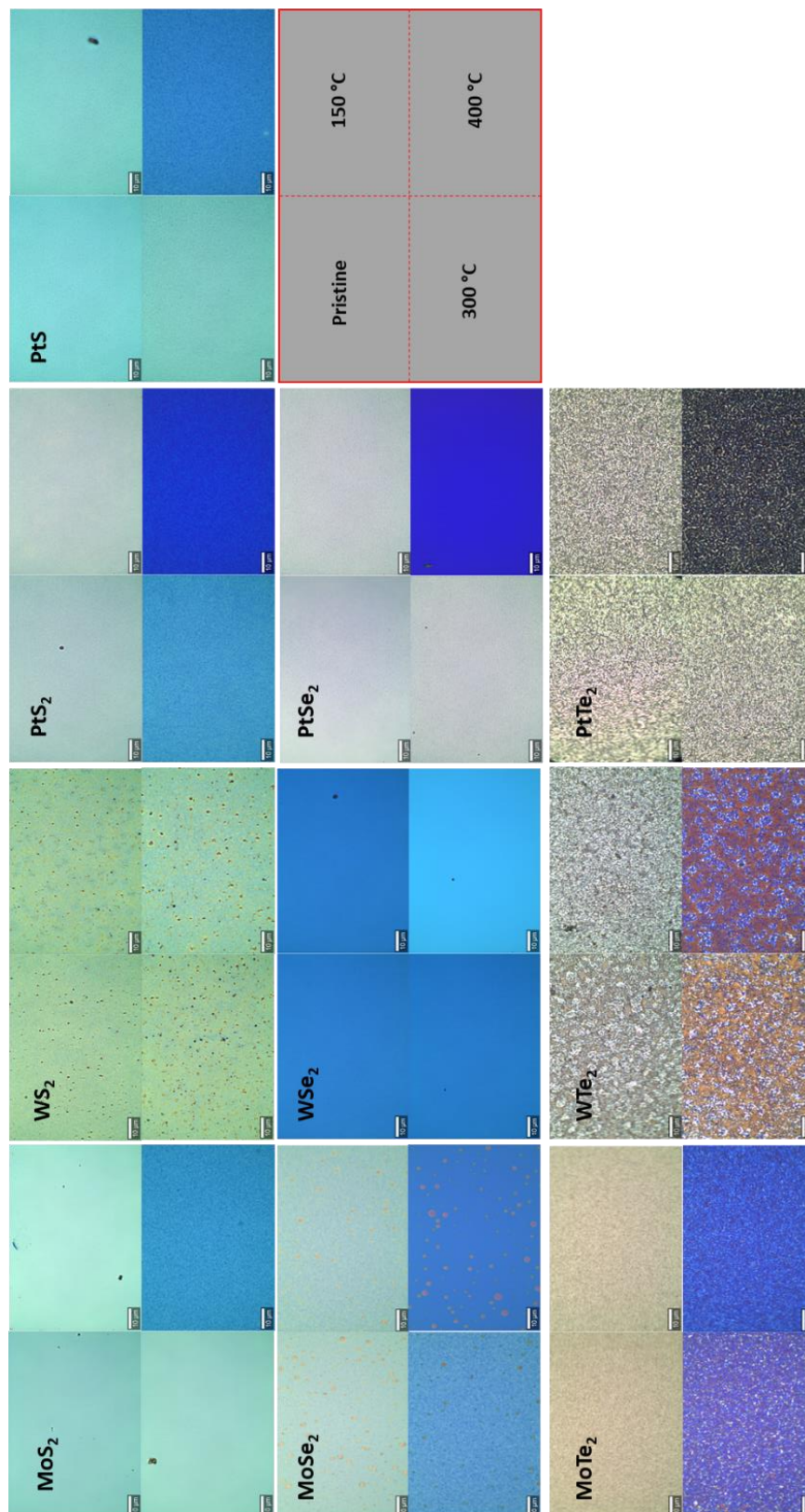


Fig.A8 Optical microscope images of the films after the various anneals (through the Raman)

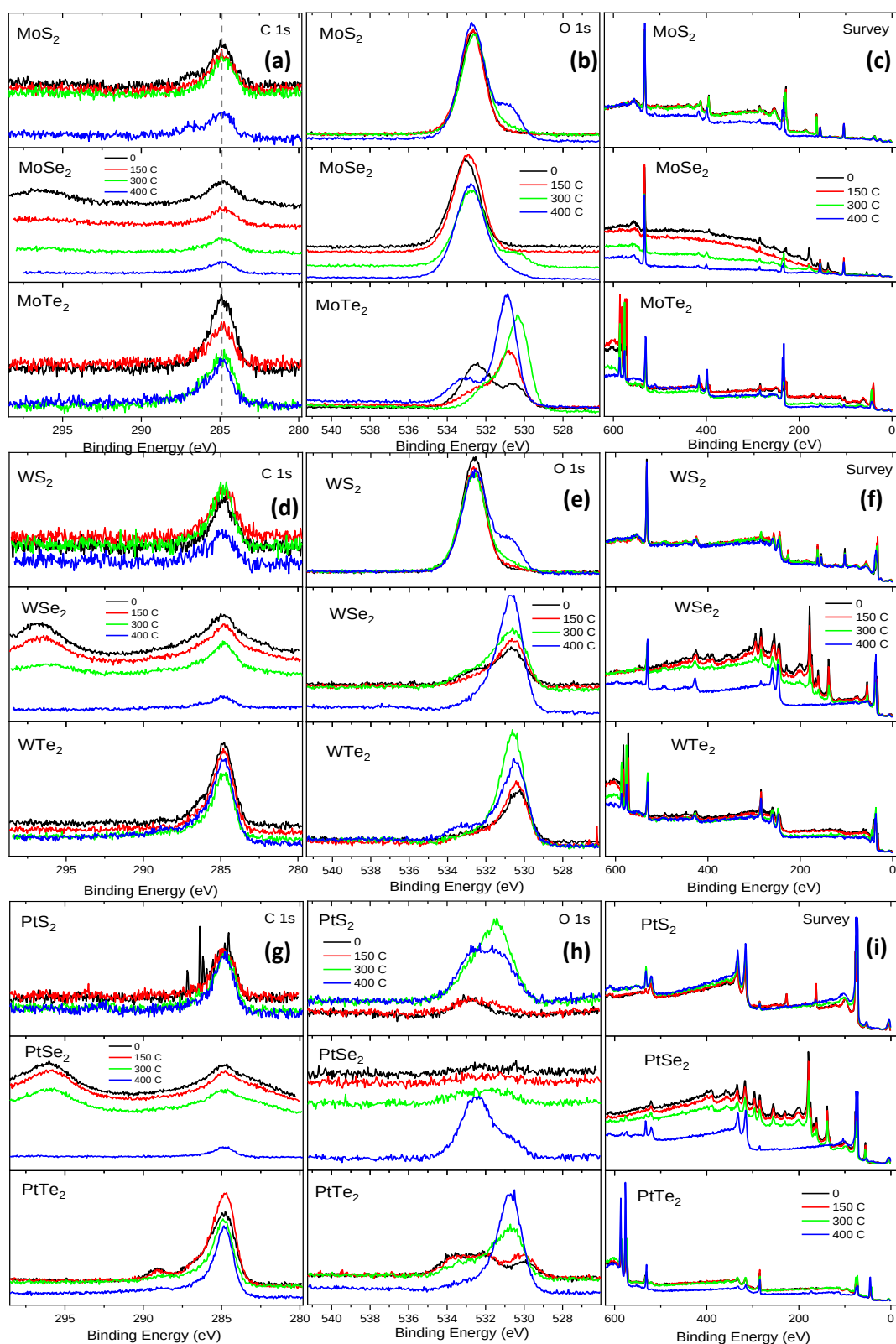


Fig.A9 The accompanying XPS spectra for the TMDs measured here at each anneal temperature. C 1s, O 1s, and Survey XPS data for the Mo TMDs (a–c), W TMDs (d–f), and Pt TMDs (g–i)

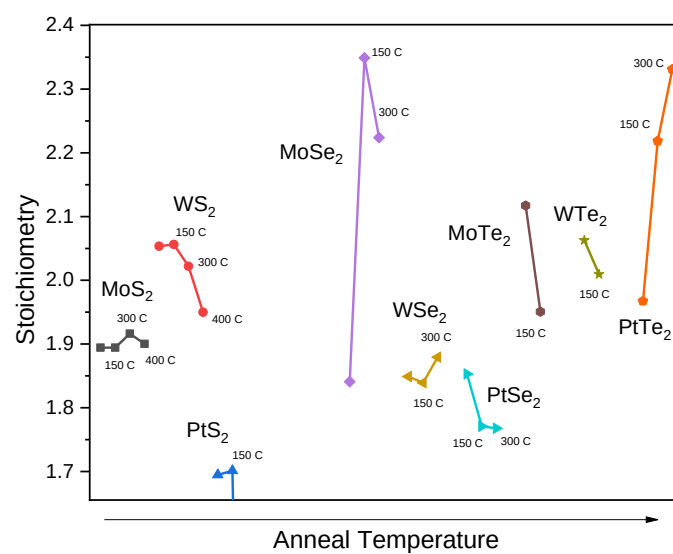


Fig.A10 Stoichiometry data from all of the samples.

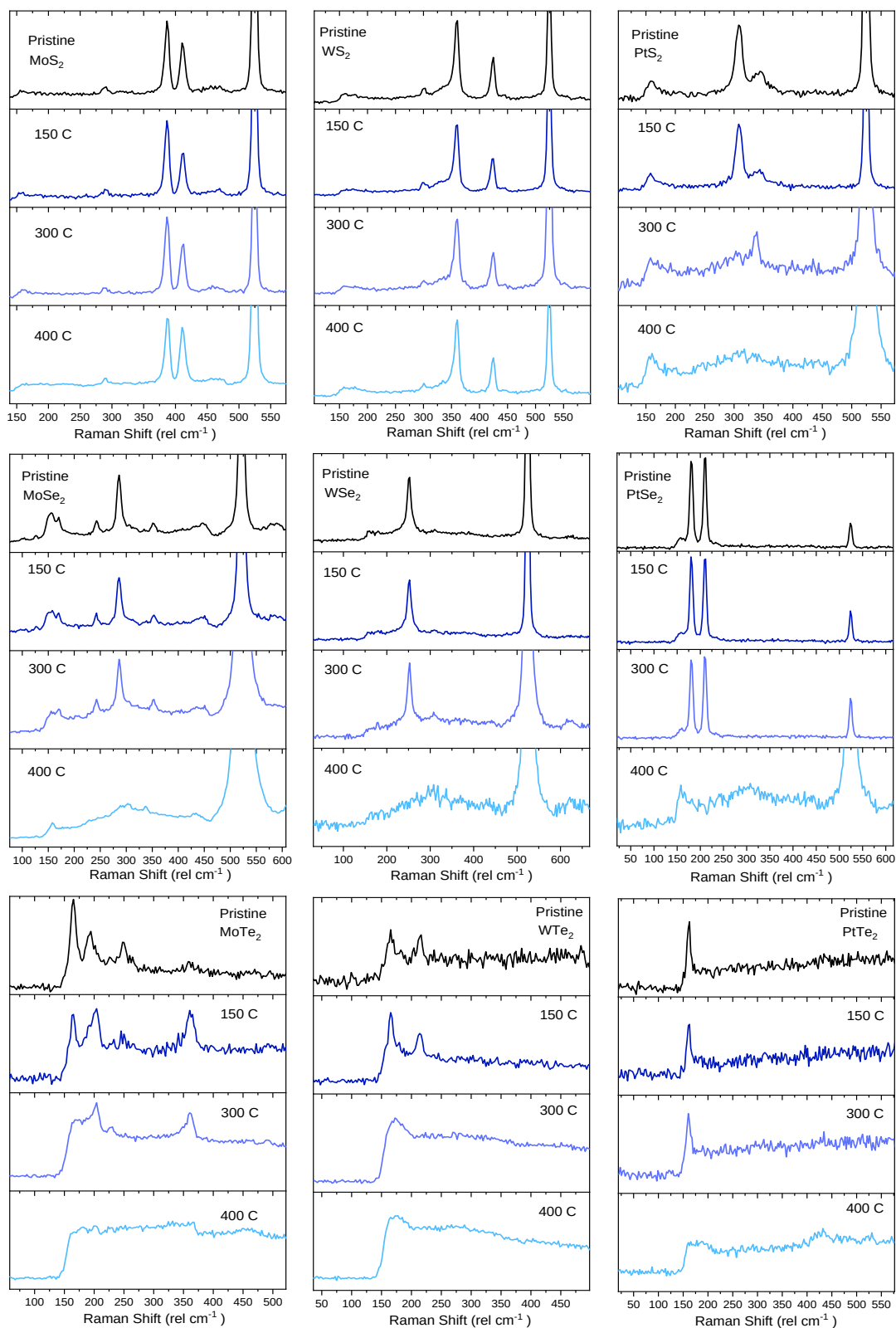


Fig.A12 405 nm excitation Raman spectra of the nine TMD films pre- and post-anneal at three temperatures.

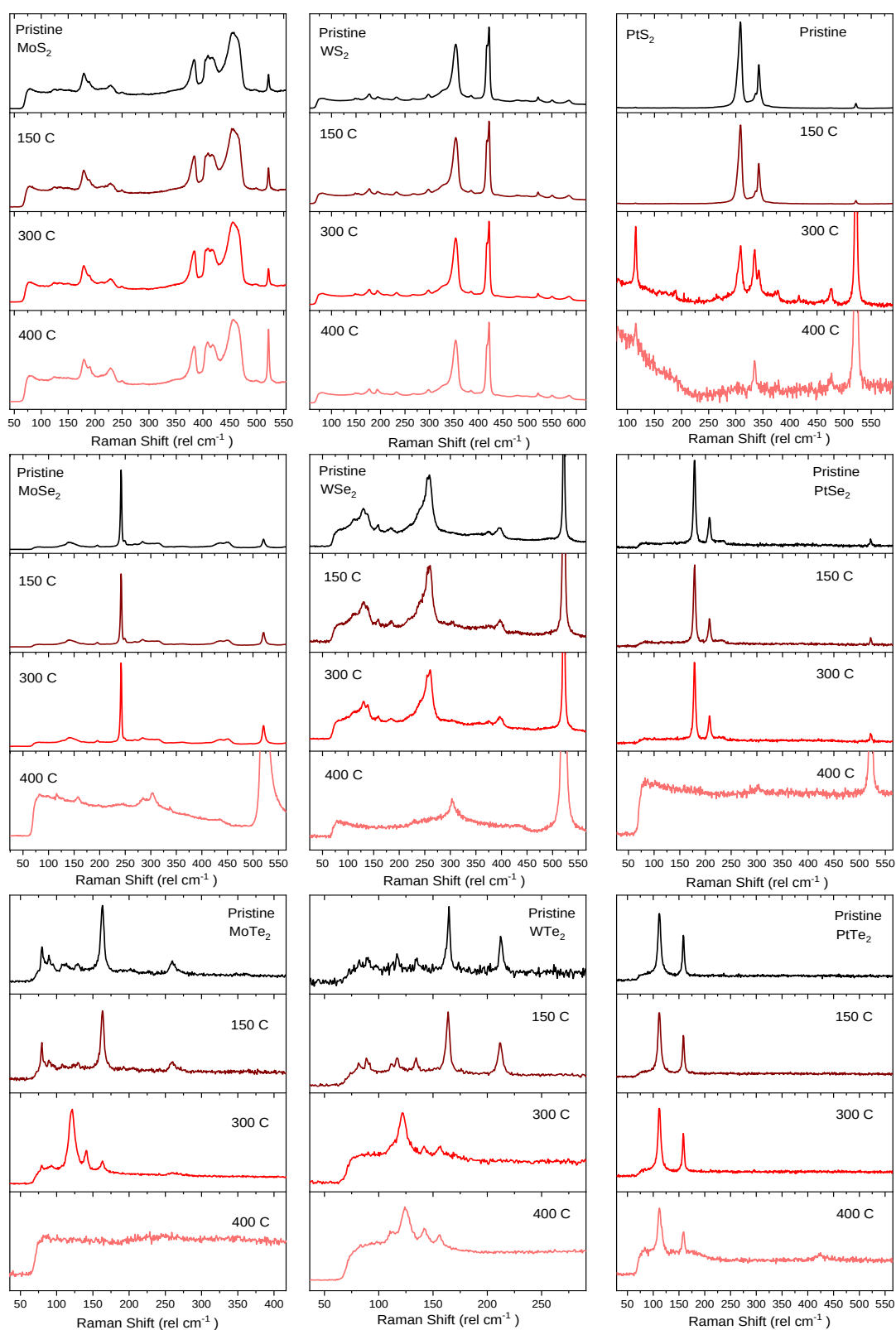


Fig.A13 633 nm excitation Raman spectra of the nine TMD films pre- and post-anneal at three temperatures.

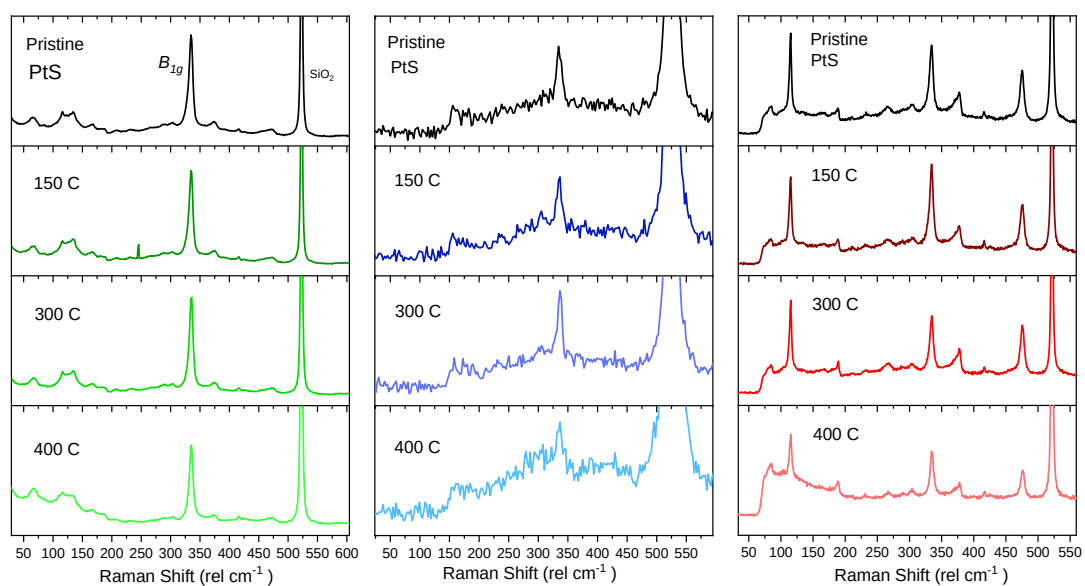


Fig.A14 Raman spectra of PtS with 532, 405, and 633 nm excitation energy, pre- and post-anneal at three temperatures.

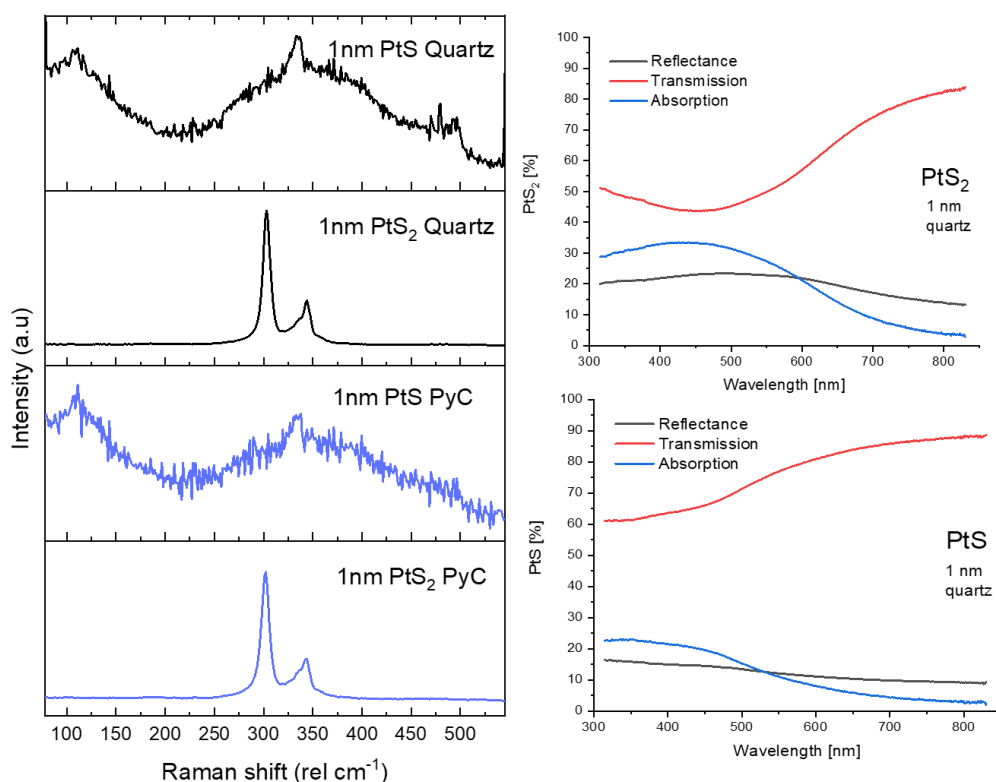


Fig. A15. (a) Raman spectra of 1 nm PtS₂ and PtS films synthesized on quartz and PyC substrates acquired with 532 nm excitation. **(b)** Optical spectra measured for platinum sulfide films synthesized on quartz.

Fig.A15(a) shows Raman spectra which indicate the successful synthesis of PtS and PtS₂ on quartz and pyrolytic carbon (PyC) substrates.

1 nm PtS₂ and PtS films were deposited on quartz substrates to investigate their optical properties. Fig.A1(b) shows reflectance, transmission and absorption spectra for both films between 314-830 nm. The PtS₂ film shows relatively uniform reflectivity across the range at ~20%. An absorption maximum was seen of 34% at ~440 nm while being >70% transparent for wavelengths greater then ~680 nm. The PtS film has lower, but also roughly uniform, reflectivity of ~15%. PtS also shows consistently lower absorption across the range with a maximum of 23% at ~350 nm and >70% transmission for wavelengths >490 nm. The measurements were taken using a UV-vis spectrophotometer with an integrating sphere attachment (Perkin Elmer LAMBDA 650). A lens system was used to collect the spectrum of a 1 mm diameter area. The total diffuse transmission and specular and diffuse reflection were measured. The difference between these two measurements was used to calculate the absorption of the films.

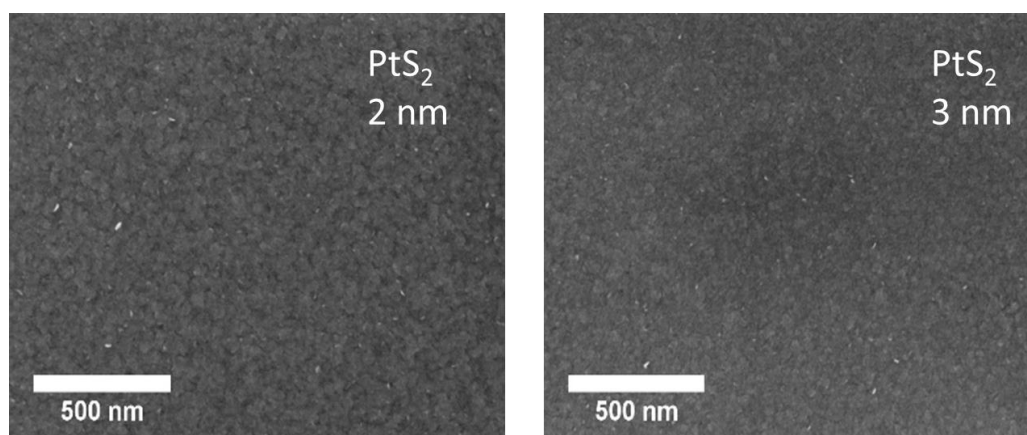


Fig. A16. SEM images of PtS₂ films synthesized from 2 and 3 nm Pt films.