

## Film growth and characterization of solution processed MoS<sub>2</sub> semiconductor films for thin film transistors

by

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## Foreword

This thesis is based upon studies and experiments conducted from January 2014 to July 2017 at Evonik Resource Efficiency GmbH, Germany in collaboration with the Department of Physics and Earth Science at Jacobs University Bremen, Germany.

I would like to take this opportunity to express my sincere gratitude to my advisor Prof. Veit Wagner for all the fruitful discussions and the advice in interpreting the results. A special thanks to my supervisor Dr. Marko Marinković for providing me with the EU funded PhD position in MoWSeS project and for the great efforts on tutoring me throughout the whole thesis period. I also would like to express my gratitude to Prof. Thomas Heine and Prof. Ralf Anselmann for being in my dissertation committee and refereeing my PhD thesis. Furthermore, I also thank Dr. Jochen Brendt and Dr. Torsten Balster for all the help with the experiments and interpreting the results. I am grateful to Dr. Duy Vu Pham, Dr. Alexey Merkulov and Dr. Anita Neumann for your countless Q&As during PhD seminar's and your encouragements to persevere.

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## Abstract

A novel wet-chemical synthesis of layered MoS<sub>2</sub> thin films on silicon and sapphire substrate has been achieved. The gap in understanding solution processed MoS<sub>2</sub> deposition needs to be closed to exploit all its excellent properties for low-cost applications. Both top-down and bottom-up approaches such as liquid phase exfoliation (LPE), dip coating, chemical bath deposition (CBD) and spin coating were explored for the synthesis of ultra-thin MoS<sub>2</sub> films from solution phase. In this work, as deposited Mo-precursor thin films were prepared based on the solubility and coating properties of Molybdenum(V) chloride in 1-Methoxy-2-propanol. Subsequent annealing of the deposited amorphous Mo-precursor films in the presence of sulfur and H<sub>2</sub> resulted in the formation of layered MoS<sub>2</sub> films. Highly crystalline films are obtained on sapphire substrates, while inferior quality was obtained on Si/SiO<sub>2</sub>. Generally, improved crystallinity of the deposited films was achieved by increasing the process temperature and performing the post-annealing treatment. Post-annealing at temperatures above 900 °C increased the uniformity of multilayer films, together with the increase of MoS<sub>2</sub> grain size. For charge transport analysis, top-gate top-contact thin film transistors (TFTs) based on these solution processed MoS<sub>2</sub> films were fabricated. Ionic liquid gating of the TFT devices exhibited *n*-type semiconducting behaviour with field-effect mobility as high as 12.07 cm<sup>2</sup>/Vs and  $I_{on}/I_{off}$  ratio ~ 10<sup>6</sup>. While with another precursor even mobility of 16.09 cm<sup>2</sup>/Vs can be achieved. X-ray photoelectron spectroscopy measurements revealed that the films annealed between 900 °C and 980 °C had an average chemical composition of S/Mo  $\sim$  1.84. This simple liquid phase synthesis method with centimeter-scale uniformity and closed films down to  $2 \pm 1$ monolayer is suitable for low-cost preparation. This holds also for other transition metal dichalcogenides thin films in next-generation electronics.

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# **List of Abbreviations and Symbols**

1M2P	1-Methoxy-2-propanol
2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
ATTM	Ammonium tetrathiomolybdate
Ci	Capacitance
CVD	Chemical Vapour Deposition
DEME-TFSI	Diethylmethyl(2-methoxyethyl)ammonium bis
	(trifluoromethylsulfonyl)imide
DMF	Dimethylformamide
EDL	Electric Double Layer
EDLT	Electric Double Layer Transistor
EDX	Energy Dispersive X-ray Analyzer
FET	Field-Effect Transistor
FWHM	Full Width at Half Maxima
HRTEM	High Resolution Transmission Electron Microscopy
IC	Integrated Circuit
Id	Drain Current
IL	Ionic Liquid
IV	Current Voltage
κ	Dimensional Shape Factor/Dielectric Constant
L	Channel Length
LB	Langmuir-Blodgett

MoCl <sub>5</sub>	Molybdenum(V)-Chloride
MX <sub>2</sub>	Transition Metal Dichalcogenide
MOCVD	Metal Organic Chemical Vapour Deposition
MOS	Metal Oxide Semiconductor
$M_{\rm w}$	Molecular Weight
NMP	N-methyl-pyrrolidone
PL	Photoluminescence
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
RPM	Rotation per Minute
RMS	Root Mean Square
SCCM	Standard Cubic Centimeter per Minute
SE	Secondary Electron
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
TFT	Thin Film Transistor
TMD	Transition Metal Dichalcogenide
UV-Vis	Ultraviolet-Visible
Vds	Drain Source Voltage
Vgs	Gate Voltage
$V_{\rm t}$	Threshold Voltage
W	Channel Width
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
μ	Mobility
γ	Disorder Parameter

## **Chapter 1: Introduction**

### **1.1 Motivation**

The current scaling of the device critical size in integrated circuit poses a bottleneck for traditional silicon semiconductors. Therefore, the emergence of novel materials like two-dimensional (2D) transition metal dichalcogenide (TMD) have come into the limelight due to their potential for various range of applications [1–4]. Layered TMDs such as MoS<sub>2</sub>, WS<sub>2</sub>, etc. have a well-defined bandgap with values ranging from 1-2 eV as compared to graphene. Unlike silicon, the ultra-thin body of the TMDs scalable down to monolayer [5] allows for smaller [6], more flexible chips [7] that use less energy. Using these properties, Kis's group demonstrated the first high mobility transistor based on a single 2D layer of semiconducting MoS<sub>2</sub> [1]. This proved that high-quality devices can be made using this class of materials, which resulted in laboratory scale fabrication of high-performance devices such as thin film transistors (TFTs), sensors, photoactive cells, flash memory, etc [8]. Therefore, the development of large-area deposition of TMDs would boost the scalable production of 2D devices, thereby making it economical for the semiconductor industry. Currently, single layered MoS<sub>2</sub> nanosheets or flakes can be obtained by top-down mechanical [9] or chemical exfoliation [10]. The conventional mechanical exfoliation method results in pristine quality nanosheets with lateral size in the range of few millimeter using scotch tape technique on bulk MoS<sub>2</sub> single crystal. While the facile chemical exfoliation method results in MoS<sub>2</sub> nanosheets with lateral size in submicron range due to the schism of nanosheets during exfoliation. Both these approaches result in high-performance devices but restrict the usefulness of TMDs due to the limited size and extreme

difficulty in the spatial arrangement of nanosheets in a commercially viable device. The current state-of-the-art method to synthesize high-quality MoS<sub>2</sub> films by bottomup approach are chemical vapour deposition (CVD) [11], atomic layer deposition (ALD) [12], molecular beam epitaxy (MBE) [13], sputtering [14], etc. which requires vacuum and high-purity precursors rendering it expensive. Furthermore, CVD, ALD and MBE growth of MoS<sub>2</sub> layers using toxic precursors and gases such as Mo(CO)<sub>6</sub> and H<sub>2</sub>S as Mo and S precursors, respectively, is not feasible for industrial processing due to safety hazards. Other methods such as chemical bath deposition [15,16] and hydrothermal synthesis [17] that were reported have restrictions and require further processing to obtain layered nanosheets. Therefore, low-cost wafer-scale synthesis of TMD thin films with high-throughput and high electrical performances is still an open question. In this regard, solution-based techniques such as dip-coating [18-20] and spin-coating [21,22] offer a viable alternative option due to its user-friendliness and low processing cost. In contrast to dip-coating, spin-coating is wafer-scalable, allows precise control of the deposited film thickness through solution concentration or spin speed. Furthermore, it is compatible with the semiconductor manufacturing processes.

### **1.2 Objectives of the Thesis**

Motivated by the importance of realizing the application of 2D TMDs, this PhD work focuses on:

- Systematic investigation of dispersed MoS<sub>2</sub> nanosheets solution with different coating techniques and evaluate the feasibility for large are coating.
- Develop a suitable process for the synthesis of solution processed MoS<sub>2</sub> thin films for large area coating.
- Understand and control the interplay between morphology, defects and electrical properties of the films.
- Fabricate devices e.g. TFT for characterization and demonstration.
- Comparison of wet-chemical and other established MoS<sub>2</sub> deposition methods.

### **1.3 Thesis Organization**

Based on the objectives of this PhD work, the thesis is divided into 7 chapters which are organized as follows:

Chapter 1 provides a short introduction and motivation about this PhD work: select appropriate methods to prepare 2D TMDs for large area coating, characterize the synthesized materials and investigate the electrical properties of TMD TFTs, and lists the aims and problems that need to be elucidated in this PhD work.

Chapter 2 describes the intrinsic properties of 2D TMDs and the basic physics of TFTs. The working principles of various characterization techniques and its connection to 2D TMDs used in this PhD work are introduced: Atomic Force Microscopy, Scanning Electron Microscopy, Transmission Electron Microscopy, Raman Spectroscopy, UV-vis Spectroscopy, X-ray Photoelectron Spectroscopy, X-ray Diffraction and electrical characterization.

Chapter 3 focuses on a systematic study of solution processed MoS<sub>2</sub> using different coating methods and evaluate the feasibility for large are coating. Top-down, solvent-assisted liquid phase exfoliation (LPE) of bulk MoS<sub>2</sub> in various solvents used to prepare 2D MoS<sub>2</sub> nanosheets is investigated. Large area coating of the obtained MoS<sub>2</sub> nanosheets with high crystal quality using dip coating technique is evaluated. Additionally, bottom-up, chemical bath deposition (CBD) of MoS<sub>2</sub> films is studied to improve scalability crucial for device fabrication.

Chapter 4 covers the work on the growth of MoS<sub>2</sub> layers with high crystal quality based on liquid phase precursor. MoS<sub>2</sub> thin films were obtained by sulfurization of spin coated Mo-precursor in an organic solvent on an amorphous substrate. The characterizations of obtained films (size, thickness, crystal structure, etc.) are discussed in detail as well as the deposition mechanism. Furthermore, the influence of the annealing parameters e.g. annealing temperature and environment are discussed in this chapter. Finally, the electrical performance of TFTs based on solution processed MoS<sub>2</sub> film is described.

Chapter 5 presents an improved method to synthesize large area MoS<sub>2</sub> thin films on sapphire substrate using a two-step annealing process. Thickness scaling and film growth on amorphous SiO<sub>2</sub> and c-plane sapphire substrates are studied. Ionic-liquid

(IL) gated TFTs based on MoS<sub>2</sub> films on SiO<sub>2</sub> and sapphire were fabricated to evaluate the film and device properties. IL-gated MoS<sub>2</sub> TFTs with high capacitance and low operating gate voltage helps to overcome charges and trap states at the MoS<sub>2</sub>/substrate interface. Using this approach, the electrical analysis of the devices was carried out to study the intrinsic properties of the MoS<sub>2</sub> films and optimize material synthesis for device fabrication. A model for charge transport in solution processed MoS<sub>2</sub> TFTs is presented. Furthermore, density functional theory (DFT) analysis is used to determine the origin of the MoS<sub>2</sub> film conductivity.

Chapter 6 describes an improved way to synthesize  $MoS_2$  films using air-stable Moprecursor in an organic solvent. This approach allows for ease of handling of the spin coated substrates in the air compared to  $N_2$  environment. The films were characterized and the electrical behaviour was analyzed.

In Chapter 7 a summary of this PhD thesis and an outlook are given.

# Chapter 2: Materials, Methods and Technologies

### 2.1 Transition Metal Dichalcogenides

Graphene was the first 2D material to be analyzed in-depth and studies have shown that their monolayers are stabilized through the development of a ripple structure [23,24]. However, over the past decade, there is significant interest in alternative 2D materials such as transition metal dichalcogenides (TMDs) that have various characteristics and innovative applications. Of these 2D TMDs, a semiconducting 2D material called molybdenum disulphide (MoS<sub>2</sub>) which is earth abundant has gained interest due to its technologically useable optical and electronic characteristics that can pave the path for a new class of optoelectronic and electronic devices.

#### 2.1.1 Structure

The TMDs are materials with the formula MX<sub>2</sub>, where M is a transition metal element from group IV (Ti, Zr, Hf), group V (V, Nb, or Ta) or group VI (Mo, W), and X is a chalcogen (S, Se, or Te). These materials have crystal structures consisting of weakly coupled sandwich layers X–M–X, where an M-atom layer is surrounded within two X layers, and the atoms in layers are hexagonally packed (Figure 2.1a). Adjacent layers are kept together by van der Waals interaction to form the bulk crystal in a variety of polytypes, which differ in stacking orders and metal atom coordination (Figure 2.1b) [25]. In Figure 2.1b the lattice constant *a* is in the range 3.1 to 3.7 Å for different materials. The stacking index c specifies the number of layers in each stacking order, and the interlayer spacing is ~ 6.5 Å. The TMDs have an overall symmetry which is hexagonal or rhombohedral, and the metal atoms have octahedral or trigonal prismatic coordination.



Figure 2.1 Structure of TMD materials: (a) Schematic illustration of a typical MX<sub>2</sub> structure, with the metal atoms (M) in blue and the chalcogen atoms (X) in yellow. (b) Schematics of the structural polytypes: 2H (hexagonal symmetry, trigonal prismatic coordination), 3R (rhombohedral symmetry, trigonal prismatic coordination) and 1T (tetragonal symmetry, octahedral coordination). The metal atoms (M) are grey and the chalcogen atoms (X) are yellow [25].

Unlike graphite, bulk TMDs demonstrate a wide range of polymorphs since an individual MX<sub>2</sub> monolayer containing three layers of atoms (X–M–X), can be in either one of the two phases. The most common polymorphs are 1T, 2H and 3R where the letters stand for trigonal, hexagonal and rhombohedral, respectively, and the numerical digit signifies the number of X–M–X units in the unit cell (represented by *c*). 2H polymorphs exhibit three different polytypes, i.e. different stacking sequences. Depending on the history of its formation a single TMD can be found in multiple polymorphs or polytypes. Geological MoS<sub>2</sub> exhibits 2H phase where the stacking sequence is AbA BaB (the capital and lower case letters denote chalcogen and metal atoms, respectively) while synthetic MoS<sub>2</sub>, often demonstrates 3R phase where the stacking sequence is AbA CaC BcB [26]. In both cases, the metal coordination is trigonal prismatic. Group 4 TMDs such as TiS<sub>2</sub> exhibits 1T phase (metallic) with a

stacking sequence of AbC AbC and octahedral metal coordination. It should be noted that monolayer TMDs exhibit only two polymorphs: trigonal prismatic and octahedral phases. This PhD work is focused on 2H-phase TMDs which is semiconducting and stable.

### **2.1.2 Electrical Properties**

The electronic structure of layered TMDs relies strongly on the transition metal coordination environment and its d-electron count which gives rise to a wide range of electrical properties from insulating to superconducting: insulator (e.g. HfS<sub>2</sub>), semiconductors (e.g. 2H MoS<sub>2</sub> and WS<sub>2</sub>), semi-metal (e.g. WTe<sub>2</sub>), metal (e.g. NbS<sub>2</sub> and VSe<sub>2</sub>) and superconductor (e.g. TaSe<sub>2</sub>). Novoselov et al. [9] first reported on the mobility of mechanically exfoliated layered MoS<sub>2</sub> between 0.5 - 3 cm<sup>2</sup>/Vs with a carrier density in the order of ~ 10<sup>12</sup> cm<sup>-2</sup>. The mobility of MoS<sub>2</sub> increases with the number of layers (1L: 0.03; 2L: 0.07; 3L: 0.17; 4L: 0.22 cm<sup>2</sup>/Vs) [27]. Using high- $\kappa$  dielectric HfO<sub>2</sub> as the dielectric layer, Kis et al. demonstrated the mobility of exfoliated monolayer MoS<sub>2</sub> can be increased to 200 cm<sup>2</sup>/Vs [1]. This pioneering work bolstered the exploration of 2D TMD semiconductors in high performance devices. Recently, Dumcenco et al. [28] measured a field-effect mobility of 43 cm<sup>2</sup>/Vs at high gate voltages from epitaxially grown MoS<sub>2</sub>, similar to the results from CVD MoS<sub>2</sub> [29] and superior to devices based on exfoliated MoS<sub>2</sub> [30].

To gain additional insight into the electronic structure of the TMDs, first principles density functional theory (DFT) was used to calculate their band structures [31]. Figure 2.2 shows the calculated band structures for bulk and few- to monolayer MoS<sub>2</sub>. The bulk MoS<sub>2</sub> is an indirect semiconductor having a bandgap of 1.2 eV with valence band maximum (VBM) at the  $\Gamma$  point and a conduction band minimum (CBM) between the K and  $\Gamma$  points in Brillouin zone. In contrast, monolayer MoS<sub>2</sub> is a direct semiconductor having a bandgap of ~ 1.9 eV with VBM and CBM coinciding at the K point. In both the bulk and monolayer MoS<sub>2</sub>, the VBM and CBM are derived from the hybridization of Mo 4d orbital and S 3p orbital. Other TMDs, such as WS<sub>2</sub> exhibit the same indirect-to-direct transition [31]. The indirect-to-direct bandgap transition obtained going from bulk to monolayer is attributed to quantum confinement effects. The absence of the sp<sub>z</sub> orbital interaction between adjacent MoS<sub>2</sub> layers in monolayer

MoS<sub>2</sub> causes the band gap to widen through quantum confinement effects. This change in orbital hybridization turns monolayer MoS<sub>2</sub> from an indirect-bandgap semiconductor to a direct bandgap semiconductor. This manifested as changes in the optical properties which results in enhanced photoluminescence [32,33], enables optical identification of number of MoS<sub>2</sub> layers [34] and opens the possibility of many optoelectronic applications [35]. With these excellent electrical properties, layered MoS<sub>2</sub> presents itself as a promising candidate for future nanoelectronics.



Figure 2.2 Energy dispersion (energy versus wavevector) development from bulk to monolayer (1L) MoS<sub>2</sub> obtained using DFT. The horizontal dashed red line represents the Fermi level. The green and blue lines represent the conduction and valence band edges, respectively. The lowest energy transition (designated by the solid arrows) is direct (vertical) only in the case of a single layer [31].

### 2.2 Basic Ideas of Thin Film Transistors

#### 2.2.1 Physics of Thin Film Transistors

Thin film transistors (TFTs) are special kind of field effect transistors (FETs), which are commonly used as switching devices in integrated circuits for large area applications. Figure 2.3 illustrates the schematic of a top-gate top-contact TFT consisting of three electrodes, i.e. source, drain and gate.



Figure 2.3 Schematic sketch of a top-gate top-contact TFT.

In this configuration, the semiconducting layer is deposited on the substrate followed by deposition of the source and drain electrodes. Finally, the gate dielectric layer and the gate electrode are deposited on the semiconducting layer between the source and drain electrodes. The semiconducting film thickness is much smaller compared to the channel length (L), i.e. the distance between the source and the drain electrode which contributes to the current flow. The current flow within the semiconducting layer (conductive channel) is controlled by the electric field originating from the voltage  $(V_{gs})$  applied through the gate electrode. Assuming a normally-off (enhancement mode) n-type semiconducting material, the TFT channel conductivity is very low for  $V_{\rm gs}$  < 0 V, i.e. OFF state. When  $V_{\rm gs}$  is larger than the threshold voltage ( $V_{\rm t}$ ), a conductive channel due to electron accumulation is formed at the semiconductor-insulator interface resulting in the ON state. Higher positive  $V_{gs}$  leads to higher channel conductivity. When a small drain-source voltage ( $V_{ds}$ ) is also applied, electrons will flow through the conducting channel which acts as a resistor. The drain current  $(I_d)$  is proportional to the drain voltage  $V_{ds}$  and the range of operation is called linear regime. Assuming an ideal MOS behaviour, the relationship between  $I_d$  and  $V_{ds}$  in the linear regime for an n-channel FET is described by the equation as follows:

$$I_{d} = \frac{W}{L} \mu C_{i} \left( V_{gs} - V_{t} - \frac{1}{2} V_{ds} \right) V_{ds} , V_{ds} \leq V_{gs} - V_{t}$$
 Eq. 2.1

*W* is the channel width and *L* is the channel length.  $C_i$  is the gate capacitance per unit area and  $\mu$  is the mobility which denotes velocity per electric field of charge carriers injected into the semiconductor for  $V_{gs} > V_t$ .

For small *V*<sub>ds</sub>, equation 2.1 can be further simplified to:

$$I_{d} = \frac{W}{L} \mu C_{i} (V_{gs} - V_{t}) V_{ds}, |V_{ds}| << V_{gs} - V_{t}$$
 Eq. 2.2

The linear mobility  $\mu_{lin}$  can be calculated from equation 2.1:

$$\mu_{lin} = \frac{L}{W \cdot V_{ds} \cdot C_i} \cdot \frac{\partial I_d}{\partial V_{gs}} \qquad \qquad Eq. \, 2.3$$

As  $V_{ds}$  increases and equals to  $V_{gs} - V_t$ , the gate induced carrier density in the channel at the drain contact is reduced to zero. This is called pinch-off point. The TFT is said to be in saturation regime where  $I_d$  becomes independent of the applied  $V_{ds}$  as described by the following equation:

$$I_d = \frac{W}{2L} \mu C_i (V_{gs} - V_t)^2, \quad V_{ds} \ge V_{gs} - V_t \qquad Eq. 2.4$$

Figure 2.4a-b shows the output characteristics curve and transfer characteristic curve respectively, of a TFT illustrating the different regimes described above. Hence, quantitative analysis of the measured IV characteristics helps to determine the electrical properties, i.e. mobility, on/off ratio (maximum to minimum  $I_d$  ratio observed in a transfer characteristic usually taken in the linear regime), threshold voltage, channel length dependence effect, etc. of a transistor which is closely linked to the electronic structure of the material. In this PhD work, device performance have been evaluated primarily in the linear regime of operation due to limitations in gate insulator material properties i.e. insulator thickness, chemical reduction, etc.



Figure 2.4 Typical (a) output characteristic and (b) transfer characteristic curve of an n-channel FET [36].

### 2.2.2 Structures of Thin Film Transistors

The operating principle of TFTs mainly depends on the relative position of the three electrodes to the semiconducting layer and is used to define the nomenclature of different transistor structures. Figure 2.5 illustrates the types of TFTs: top-gate top-contact, top-gate bottom-contact, bottom-gate top-contact and bottom-gate bottom-contact. Based on the research objective and fabrication conditions, each structure has its merits and demerits. In this PhD work both top-gate top-contact and bottom-gate top-contact TFT configuration has been implemented due to the following advantages: 1) Solution-processed TMD thin films can be effortlessly deposited on the top of the substrate or insulator. 2) Ease of accessibility for characterizing the semiconducting thin film via AFM and optical measurements. 3) Influence of the environment on the device behaviour and stability.



Figure 2.5 Schematic sketch of TFT configurations. (a) Top-gate top-contact, (b) top-gate bottomcontact, (c) bottom-gate top-contact and (d) bottom-gate bottom-contact.

### 2.3 Synthesis of Layered TMDs

Synthesis of high-quality 2D TMDs in a scalable way with uniform properties is vital for translating their new electronic and optical properties into applications. This

section discusses the available techniques for top-down exfoliation from bulk materials and bottom-up synthesis and assesses their relative advantages.

#### 2.3.1 Top-down Methods

Top-down methods allow obtaining mono or few-layers of TMDs from their corresponding bulk materials. The most common top-down method is mechanical exfoliation using Scotch-tape resulting in highest-quality monolayers [9]. These 2D MX<sub>2</sub> samples are perfect for a demonstration of high-performance devices and quantum phenomena [10,25,37,38]. However, mechanical exfoliation is not scalable and has low reproducibility. Another top-down method is thermal ablation where monolayer MoS<sub>2</sub> can be obtained by laser thinning but the use of lasers restricted the scale-up process [39].

The third top-down method is intercalation of TMDs by ionic species [32,40,41] which allows exfoliation of layers in solution. Lithium-based intercalation of TMDs was first demonstrated in 1975 [41], which was later used by Joensen et al. [40] to obtain monolayer MoS<sub>2</sub> with high yield. This involves immersing bulk TMD in a solution of nbutyl lithium for a few days to allow lithium ions to intercalate, followed by exposing the intercalated material to water. The water reacts strongly with the lithium between the layers generating H<sub>2</sub> gas, which causes swelling of the crystal and weakening the interlayer attraction. Additional agitation results in exfoliated nanosheets [32,40] as shown in Figure 2.6a. However, such chemical exfoliation methods also result in monolayers which differ structurally and electronically from the bulk material [32]. In particular, for MoS<sub>2</sub> the lithium intercalation changes the electronic structure of the exfoliated MoS<sub>2</sub> nanosheets from 2H phase (semiconducting) to 1T phase (metallic), while the Mo atom coordination changes from trigonal prismatic to octahedral [5,32]. The 2H-MoS<sub>2</sub> phase can be recovered by annealing at 300°C in an argon atmosphere, thereby restoring the semiconducting bandgap as verified by the photoluminescence measurements [32]. Lithium-based chemical exfoliation has also been demonstrated for various TMDs such as MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub> and SnS<sub>2</sub> [5]. Later electrochemical cells were used to speed up the intercalation process but the flammability of lithium and the requirement of an inert atmosphere limited its use [42].

Alternatively, TMDs can also be exfoliated by liquid phase exfoliation (LPE) using direct sonication (Figure 2.6) in suitable liquids such as organic solvents, mixed

solution of water and ethanol, aqueous surfactant solutions and mixture of polymers in solvents [10,38,43–45]. The exfoliated nanosheets are further stabilized against agglomeration by steric or electrostatic repulsion due to the adsorption of molecules from solution (Figure 2.6c). Solvents such as dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) has been used to obtain nanosheets of layered inorganic compounds, such as MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, NbSe<sub>2</sub>, TaSe<sub>2</sub>, NiTe<sub>2</sub>, MoTe<sub>2</sub>, h-BN and Bi<sub>2</sub>Te<sub>3</sub> [10]. Direct sonication was also used to exfoliate TMDs in an aqueous solution of the surfactant sodium cholate, which also prevents their agglomeration. These techniques rely on the solvent or surfactant to overcome the cohesive force between the adjacent layers. Therefore, the selected solvents must possess surface energies that are comparable to those of the 2D material [38]. The method is easy, but the crucial challenge is to increase the yield of the monolayers while maintaining the lateral dimensions of the exfoliated nanosheets. Sonication causes schism of the nanosheets but with an optimized starting mass, sonication time and centrifugation conditions [46] a yield of moderately large (>1  $\mu$ m) and thin nanosheets can be obtained.



Figure 2.6 Schematic diagram of the liquid phase exfoliation mechanisms. (a) Ion intercalation: Ions (yellow spheres) intercalated between the TMD layers in a solution phase followed by agitation, resulting in an exfoliated dispersion. (b) Ion exchange: Layered materials containing ions (red spheres) between the layers for surface charge neutrality. These ions can be exchanged in a solution phase for larger ions (yellow spheres) which upon agitation results in an exfoliated dispersion. (c) Sonication assisted exfoliation: The layered TMD is sonicated in an appropriate solvent, resulting in exfoliated nanosheets [45].

#### 2.3.2 Bottom-up Methods

Bottom-up methods allow obtaining mono or few-layer TMDs from the molecules or atoms. Chemical preparation of TMDs [15,17] have been initially shown using hydrothermal synthesis and chemical bath deposition, i.e. growth of crystals from an aqueous solution but the film thickness is not conclusively shown to be monolayers.



Figure 2.7 Chemical vapour deposition of TMD layers. (a) Schematic illustration of layered MoS<sub>2</sub> by sulfurization of Mo thin film [47]. (b) The growth of a MoS<sub>2</sub> monolayer from MoO<sub>3</sub> and S powders through a gas-phase reaction [48]. (c) Schematic of atmospheric pressure CVD of MoS<sub>2</sub> layer deposited using MoCl<sub>5</sub> precursor and H<sub>2</sub>S gas [49]. (d) The growth of MoS<sub>2</sub> layers from dip coated precursor by two-step thermolysis on a sapphire and silica substrate [19].

Today the most common method is chemical vapour deposition (CVD) which has been used for synthesising atomically thin MoS<sub>2</sub> films on insulating substrates [19,48,50]. A typical process uses various solid precursors which are heated to elevated temperatures in the presence of sulphur. These include molybdenum metal thin film deposited on a substrate heated with sulphur powder [47,50], MoO<sub>3</sub> and sulphur powder vapourized and co-deposited onto a substrate [48], MoCl<sub>5</sub> and H<sub>2</sub>S gas or

sulphur powder [49,51] and substrates dip-coated in a solution of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> and heated in the presence of argon gas and sulphur [19]. These CVD based methods are illustrated in Figure 2.7. These methods often result in polycrystalline single or fewlayer TMDs with grain size 10-30 nm [48,50,51]. In most of these methods, the final TMD film thickness and quality is dependent on the chamber pressure and concentration or thickness of the initial precursor. Dumcenco et al. demonstrated that by modifying the process, the CVD method can be used for epitaxial growth of singlelayer MoS<sub>2</sub> on micrometer scale [28]. Large-area synthesis of few-layer MoS<sub>2</sub> is of great interest for the preparation of high-performance devices. Therefore, in recent times more sophisticated technology such as MOCVD [11] and ALD [52] with gas phase precursors are used to synthesize large-area, high-quality and well-controlled layered MoS<sub>2</sub> thin films. These CVD studies pave the way for the development and production of other 2D materials with uniform and controllable layer thickness over a large area.

### 2.4 Coating and Deposition of TMDs

Large area uniform coating of layered TMDs can be obtained by various coating methods e.g. dip coating, chemical bath deposition, spin coating, spray coating, inkjet printing and coatings by filtration. Here, we discuss the main coating techniques to produce layered materials.

### 2.4.1 Dip Coating

Dip coating technique is a process where the substrate is immersed in a precursor solution and then withdrawn at constant withdrawal speed under controlled temperature and atmospheric conditions (Figure 2.8). The coating thickness is dependent on the withdrawal speed, by the solid content and the viscosity of the liquid which can be calculated by the Landau-Levich equation [53].

$$h = 0.94 \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}} \qquad \qquad Eq. 2.5$$

where *h* is coating thickness,  $\eta$  is viscosity,  $\gamma_{LV}$  is liquid-vapour surface tension,  $\rho$  is density, *g* is gravity, and *v* is withdrawal velocity. The slower the substrate is withdrawn from the tank the thinner the coating material that will be applied to the substrate.



Figure 2.8 Stages of the dip coating process: dipping of the substrate into the coating solution, wet layer formation by withdrawing the substrate and drying/gelation of the layer by solvent evaporation

The simplicity of this method allows for automation where different sizes of dip tanks can accommodate large-area substrates to be coated. The main drawbacks include light parts tend to float; film thickness varies from top to bottom ("wedge effect") and fatty edges develop on the bottom of the substrate as excess coating drains. The ease of the process allowed Liu et al. [19] and Zeng et al. [20] to synthesize highly crystalline layered MoS<sub>2</sub> by dip coating insulating substrates into a precursor solution of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> followed by annealing in sulphur.

### 2.4.2 Chemical Bath Deposition

Chemical bath deposition (CBD) method is a desirable method for large area deposition of thin films at low cost. The method uses specific chemical reactions to regulate the deposition of a thin film by precipitation. Figure 2.9 shows a typical experiment where a substrate is dipped in an alkaline solution consisting of the metal ion and chalcogenide source. The release of the metal ion can be regulated using a chelating agent. The process requires chalcogen ions (e.g. S<sup>-2</sup>, Se<sup>-2</sup>) in solution along with the low metal ion concentration to produce homogenous precipitation of the thin films on the substrate [54]. Physico-chemical factors such as solubility product, supersaturation, type of precipitation, etc., influences the growth of the deposited film at the substrate surface.


Figure 2.9 Schematic of chemical bath deposition illustrating the dipping of the substrate into the coating solution.

The nucleation on the substrate surface can be initiated by adsorbed cation or anion or impurities on the substrate surface acting as nucleation centers. Further growth takes place by adsorbing additional ions from the alkaline solution resulting in a continuous film. The film growth takes place either by an ion-by-ion condensation or by adsorption of colloidal particles on the substrate surface [55]. However, as the deposition proceeds the concentration of ions decreases thereby resulting in a decrease of the growth rate. The CBD method is simple, low-cost and has been used for large area deposition of nanocrystalline TMDs [15,56,57].

# 2.4.3 Spin Coating

Spin coating can be used to attain uniform thin films on flat substrates. A substantial excess volume of a precursor solution is applied to a substrate using a dispensing syringe in the lid of the spin coater. The substrate is rotated at high speed to spread the solution via centrifugal force homogeneously. Rotation is continued at a constant rate until the desired thickness of the film is realized. The applied solution usually contains a volatile solvent as an ingredient and simultaneously evaporates which dominates the coating thinning behaviour. Apart from the rheology of the solution (solid content and viscosity), the final film thickness is defined by the rotational speed.

The precise control of the constant rotational speed is crucial for homogeneous film formation as well as for wafer to wafer reproducibility.

A separate drying step is often required after the spin coating process to further dry the film without significantly thinning it. This is advantageous for thick films since it requires long drying times to increase the physical stability of the film before handling. Spin coating is extensively used in the semiconductor industry during photolithography, to deposit layers of photoresist about 1-2  $\mu$ m thick. This method can also be used for the fabrication of various thin films on different substrates with thicknesses below 10 nm. The low-cost and wafer scalable properties of spin coating method have also been used for deposition of large-area TMDs using precursor solution [21,22].

This thesis will concentrate on solution processed deposition of MoS<sub>2</sub> films using various facile and low-cost techniques.

# 2.5 Experiment and Characterization Methods

#### 2.5.1 Atomic Force Microscopy (AFM)

The atomic force microscope (AFM) measures the forces between a fine tip and a sample. Figure 2.10 shows the basic concept of an AFM. The sharp tip is attached to the free end of a micromachined cantilever and is brought very close to a surface. Attractive or repulsive forces resulting from interactions between the tip and the surface will cause a positive or negative bending of the cantilever. The bending is detected using a laser beam, which is reflected from the back side of the cantilever and collected in a photodiode. When the laser is displaced vertically there exists a bending due to topography, while if this movement is horizontal, it produces a torsion due to "friction" (lateral force).

AFM measurements were performed to determine the evolution of the TMD surface morphology (topography, roughness, etc.) and the number of layers. For  $MoS_2$ , a monolayer is ~ 0.65 nm, and therefore a 1.95 nm thickness would correspond to a trilayer  $MoS_2$  [1]. In this work, tapping mode AFM (Bruker Dimension 3100) were performed for imaging and investigating film surface morphology.



Figure 2.10 Basic working principle of an AFM.

# 2.5.2 Raman Spectroscopy



Figure 2.11 (a) Elastic & Raman inelastic scattering and (b) schematic diagram of Raman spectrometer.

Raman spectroscopy is widely used to provide a structural fingerprint of material by observing the vibrational and rotational modes. Raman Spectroscopy is based on inelastic scattering (Figure 2.11a) of monochromatic light when it interacts with the phonons in a system causing the energy of the laser light being shifted up or down. There are two kinds of inelastic scattering: Stokes (output energy smaller than input energy) and anti-stokes scattering (output energy larger than input energy). The shift in the energy of the output laser light and the input laser light provides information about the vibrational modes in a material (Figure 2.11b).



Figure 2.12 (a) Schematic drawing of Raman modes for transition metal dichalcogenides. (b) Raman spectra of MoS<sub>2</sub> films and (c) its corresponding frequencies of Raman modes with their difference as a function of layer thickness [58].

Group theory predicts four Raman active modes for 2H-MoS<sub>2</sub> [59,60]: the out-of-plane vibration (c-axis) of S atoms (A<sub>1g</sub>) with a Raman shift of ~408 cm<sup>-1</sup>, the in-plane vibration (basal plane) of Mo and S atoms (E<sup>1</sup><sub>2g</sub>) at ~383 cm<sup>-1</sup>, the in-plane vibration (basal plane) of S atoms (E<sub>1g</sub>) at ~287 cm<sup>-1</sup> and the in-plane vibration (basal plane) of Mo and S atoms (E<sup>2</sup><sub>2g</sub>) at ~ 32 cm<sup>-1</sup> (Figure 2.12a). However, E<sub>1g</sub> mode is forbidden

under back-scattering Raman configuration, while the frequency of  $E^{2}_{2g}$  is relatively low [61]. Therefore, the remaining two Raman modes  $E^{1}_{2g}$  and  $A_{1g}$  exhibiting the highest intensity have been widely studied [58,62]. These Raman modes of MoS<sub>2</sub> are also dependent on the number of layers [58]. As thickness decreases from bulk to monolayer,  $E^{1}_{2g}$  vibration blue shifts and  $A_{1g}$  vibration redshifts (Figure 2.12b-c). These modes shift in the opposite direction due to the influence of the van der Waals interlayer coupling, Coulombic interactions and interlayer stacking [60]. Hence, the Raman spectroscopy can be used to fingerprint various layered TMDs and determine the layer thickness. A detailed discussion can be found in section 4.3.2.

In this work, Raman spectroscopy was performed with 514.5 nm laser excitation with a power of 0.5 mW. The signal was collected through a 50X objective, dispersed with a 1800 g/mm grating, and detected using a charge-coupled device detector cooled in liquid N<sub>2</sub> (Horiba Jobin-Yvon T64000 spectrometer).

# 2.5.3 UV-Visible Spectroscopy

UV-Visible (UV-Vis) spectroscopy was carried out with a Cary 5000 UV-Vis-NIR Spectrophotometer. Figure 2.13a illustrates the schematic drawing of a single beam spectrometer. The light source is a tungsten lamp for the visible range and a deuterium lamp for the ultraviolet light. The light beam is split up using a monochromator grating and a special arrangement of the grid and slit allows the first order interference maximum of a specific wavelength passing through the sample. The photodetector behind the sample collects the signal and sends it to a logic unit for data processing. All UV-Vis measurements in this work were conducted from 300 nm to 900 nm wavelength with a step size of 1 nm.

As an example, a typical UV-Vis absorption spectrum of MoS<sub>2</sub> is shown in Figure 2.13b. The absorption spectra between 400 and 800 nm exhibit the characteristic optical peaks of MoS<sub>2</sub> due to optical transition. The photon energy exceeds the energy value of the band gap in this wavelength range. In an ideal case, this leads to an excitation of the electrons from the valence band into the conduction band. While for a polycrystalline material, electronic states within the band gap would also contribute to the absorption which can cause a red-shift of the optical band gap. The absorption coefficient  $\alpha(\lambda)$  can be calculated using Lambert-Beer law out of the transmission spectra. T denotes transmittance of the film and d the film thickness.





Figure 2.13 (a) Schematic drawing of a UV-Vis Spectrometer and (b) an example UV-Vis spectrum of a MoS<sub>2</sub> thin film on quartz glass.

# 2.5.4 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

Scanning electron microscope (SEM) and transmission electron microscope (TEM) use high energy electron beams to produce images with high magnification. SEM imaging is based on scattered electrons while TEM imaging is based on transmitted electrons. Figure 2.14a and b show the setup of SEM and TEM, respectively, which consists of an electron optical column, vacuum system and electronics. In SEM the electron beam is produced by an electron gun (e.g. tungsten filament) at the top of the microscope which is focused into a fine spot as small as 1 nm in diameter on the sample surface. The interaction of high-energy electron beam with the sample results in various signals including Auger electrons, backscattered electrons, and secondary electrons, as well as X-rays and light (cathodoluminescence). The most frequently used secondary electron (SE) and backscattered electron (BSE) signals using different detectors are mapped as changes in brightness on the image. SE reveals the morphology and topography on samples while BSE provides visual elemental composition and topography in multiphase samples. Furthermore, the X-rays detected using Energy-dispersive X-ray spectroscopy (EDX) provide elemental composition about the sample. Therefore, SEM is used to obtain surface morphology and chemical compositions of samples.



Figure 2.14 Schematic of (a) Scanning electron microscope and (b) Transmission electron microscope.

A TEM (Figure 2.14b), on the other hand, has additional electromagnetic lenses for focusing and deflecting the beam and a high voltage generator for the electron source. The electron beam irradiated from the electron gun passes through a thin sample and these transmitted electrons are collected, focused, and projected on a phosphor screen or a charge coupled device (CCD) camera at the bottom of the column. Additionally, all scattered electrons from the sample are focussed on the back focal plane of the objective lens to obtain the diffraction pattern. Therefore, TEM can be used to analyse crystallinity, shape, size etc. of ultrathin samples. Scanning transmission electron microscope (STEM) combines the working principles of SEM and TEM. Like TEM, STEM requires very thin samples and looks primarily at transmitted electron beam through the sample. Like SEM, the electron beam is finely focused and scanned across the sample in a raster pattern. Furthermore, STEM enables the use of other signals which cannot be spatially correlated in TEM, including secondary electrons, scattered beam electrons, characteristic X-rays and electron energy loss. High-resolution transmission electron microscopy (HRTEM) is an image mode of TEM which uses both the transmitted and the scattered beams to create an interference image. This allows direct imaging of sample atomic structures with high resolution down to 50 pm. In this PhD work, a Zeiss LEO 982 SEM from Fachhochschule Münster, Germany and Titan 80300 kV FEG S/TEM from Trinity College Dublin, Ireland were used to obtain SEM and STEM images.

#### 2.5.5 X-ray Diffraction

X-rays diffraction enable us to probe the crystalline structure of materials and thin films. In this work, the diffraction pattern was obtained from polycrystalline MoS<sub>2</sub> films consisting of numerous ordered crystallites with many random orientations. An X-ray beam irradiated on the sample will be diffracted by crystallites at the lattice planes (d<sub>hkl</sub>) with different orientation in several directions forming a cone of diffracted beam as determined by Bragg's law. Each lattice plane with different dspacing in the crystal results in a Debye-Scherrer cone (rings) diffraction pattern. Therefore, each concentric diffraction rings on the detector plate would correspond to a different crystal plane.



Figure 2.15 Graphical representation of  $\theta$ - $\theta$  scan, goniometer assembly.

The mechanical chassis that makes up the sample holder, detector and the related accessories are referred to as goniometer as shown in Figure 2.15. For  $\theta$ - $\theta$  scan mode, the sample is stationary, the X-ray source moves by the angle  $\theta$  and simultaneously the detector must be rotated by  $\theta$  to capture the diffracted beam by Bragg's law. If the Bragg angle is  $\theta$ , then the angle between the direction of the incident beam and the diffracted beam is 2 $\theta$ . Using Scherrer formula [63] in equation 2.7, the XRD diffractogram can be further analysed to determine the crystallite size where  $\tau$  is the crystallite size,  $\kappa$  is a dimensional shape factor,  $\lambda$  is the wavelength and  $\beta$  is the linewidth.

In this work, X-ray diffraction (X'Pert Pro MPD from PANalytical) in Bragg-Brentano arrangement with  $\theta$ - $\theta$  mode was performed using X-ray tube excitation of 40 kV/40 mA (Cu K<sub>a</sub>).

#### 2.5.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) is a surface sensitive quantitative spectroscopic method to determine the chemical composition and state of the elements present in a material. In XPS, an X-ray beam is generated by irradiating aluminium with an electron beam produced by thermionic emission. XPS spectra are obtained by exposing the sample to a beam of X-rays having specific photon energy of 1486.8 eV while simultaneously measuring the kinetic energy and number of electrons that escape from the sample surface (Figure 2.16). If the absorbed X-ray photon energy  $E_{\text{photon}}$  exceeds the ionization energy of the atom, the electrons will escape having a defined kinetic energy  $E_{\text{kinetic}}$ . If the ionization energy is assumed to be equal to the binding energy, then the kinetic energy is determined by equation 2.8 where  $\varphi$  represents the work function difference dependent on both the spectrometer and the sample material.

The number of electrons that can escape from a depth of 0 to 10 nm below the sample surface has various kinetic energies depending on the material being analyzed. An electron energy analyzer (hemispherical) is used to distinguish between electrons of different kinetic energies. Only electrons having kinetic energy equal to the passing energy  $E_{\text{pass}}$  traverse a circular trajectory having the same radius as the analyzer sphere will reach the electron detector.

The XPS analysis was carried out using an Omicron UHV XPS analysis system, with photoelectrons excited using a monochromated Al K<sub> $\alpha$ </sub> X-ray source (hv = 1486.6 eV) at a base pressure of 1 × 10<sup>-10</sup> mbar. The spectra were evaluated using Shirley background and a symmetric peak shape defined by a convolution of Gauss and Lorentz peaks for peak fitting.



Figure 2.16 Graphical representation of X-ray photoelectron spectrometer.

# 2.5.7 Electrical Characterization

Electrical characterization of TFTs based on TMD semiconductors can be realized through a wide range of measurement techniques. Current-voltage (IV) characterization is the most common technique to analyze device performance. Therefore, in this PhD work, IV measurements will be the primary electrical characterization technique to determine various electrical parameters of TFTs based on 2D TMDs.

The electrical characterization of TFTs based on solution processed TMDs was mainly performed using an in-house Stala measurement setup which includes a Keithley SourceMeter 2612A, a Keithley SwitchBoard 3700-S and a Stala-Software for measurement and analysis of the output and transfer characteristics. Occasionally, the transistor performance was carried out on a probe station (SÜSS MicroTec) and controlled by a semiconductor device analyzer (Agilent 4156C). The electrical measurements were conducted under nitrogen environment at room temperature.

# Chapter 3: Top-down and Bottom-up synthesis and deposition of MoS<sub>2</sub>

# 3.1 Liquid Phase Exfoliation (LPE) – Top-Down Approach

In this work, three different MoS<sub>2</sub> dispersions in 2-propanol, N-methyl-2-pyrrolidone (NMP) and sodium cholate in water have been used to disperse and fabricate singlelayer and multilayer nanosheets (flakes) to demonstrate large area coating of TMD materials. MoS<sub>2</sub> dispersions in 2-propanol was prepared in-house at Evonik Industries AG while dispersions in NMP and sodium cholate were obtained from Trinity College Dublin.

# **3.1.1 Experimental Procedure**

Commercially available MoS<sub>2</sub> powders were purchased from Sigma-Aldrich and used as supplied. Coleman *et al.* [10] had generated a list of solvents using the Hildebrand solubility parameter and Hansen solubility parameter for exfoliation of TMD materials. An effective solvent must satisfy two conditions. 1) Ability to disperse or suspend the material for a reasonable amount of time and 2) the dispersed material must be very well exfoliated. Hence, 2-propanol, N-methyl-2-pyrrolidone (NMP) and sodium cholate in water were chosen.

It is known that processing parameters such as sonication time and centrifugation rate strongly determine the quality of layered-material dispersions. Improvement in the concentration of the layered-material obtained after centrifugation was realized by partial optimisation of the sonication method, sonication time and centrifugation rate for dispersions of MoS<sub>2</sub> in a solvent. Numerous dispersions were sonicated in round bottom flasks using an ultrasonic bath or point probe (Sonics, VCX 750) for different times. After sonication, the dispersions were centrifuged at different rates, 1500 and 4200 rpm (45 or 60 min). The supernatant was decanted, and the UV-vis spectra was measured (Figure 3.1). The nanosheet dispersion quality was rated by the absorbance per unit length, A/l of the concentration remaining after centrifugation. The most promising dispersions were studied by AFM through drop-casting on silicon wafers to check for evidence of proper exfoliation.



Figure 3.1 Process flow for Liquid phase exfoliation of MoS<sub>2</sub>.

 $MoS_2$  in 2-propanol demonstrated the best dispersion which was sonicated with an initial concentration of 7.5 mg/mL using a point probe, at a nominal power output of 300 W (40% × 750 W) for 24 h. This was followed by centrifugation at 1500 rpm for 45 min (Figure 3.2-3.3).

# **3.1.2 Characterization and Results**

UV-vis spectroscopy was used to evaluate the degree of exfoliation of MoS<sub>2</sub> in 2propanol due to shorter measurement duration. From the Lambert-Beer law ( $A/l = \alpha C$ , where A is absorbance, l is cell length,  $\alpha$  is extinction coefficient and C is concentration), one could calculate the actual concentration (C), from A/l if the extinction coefficient was known. To determine the extinction coefficient [10], dispersions of MoS<sub>2</sub> in 2-propanol were prepared using the optimised processing conditions. Dispersion with an initial concentration of 7.5 mg/mL was sonicated using the point probe (sonic tip) for 24 h, with a nominal power output of 300 W (40% × 750 W). After sonication, the dispersions were allowed to settle for ~ 24 h before centrifuging them at 4200 rpm for 60 min. The top 3/4 of the dispersion was collected by pipette. The UV-vis spectra of each resultant dispersion was recorded. The dispersions were then filtered through porous polyvinylidene fluoride (PVDF) (0.1 µm pore size) membranes of known mass. The membranes were dried and the mass of deposited material measured. This allowed calculating the concentrations (after centrifugation) for MoS<sub>2</sub> in 2-propanol given that the filtered volume was known.

Figure 3.2a illustrates the absorption spectra for  $MoS_2$  in 2-propanol using 25%, 50% and 100% amplitude setting of the point probe (sonic tip). The excitonic peaks at 670 nm and 610 nm [33,64] due to direct transition at the K point demonstrates successful exfoliation of  $MoS_2$  powder into  $MoS_2$  nanosheets (flakes) using 2-Propanol. It is interesting to note the yield of exfoliation for the  $MoS_2$  nanosheets increases with the increasing power of the amplitude. This increase in the concentration of  $MoS_2$  nanosheets results in higher absorbance. However, it was also observed, using higher amplitude power e.g. 100% lead to smaller  $MoS_2$  flakes ~ 50 nm (measured with AFM) due to scission of larger flakes. Hence 40-50% amplitude was taken as the optimised condition.



Figure 3.2 UV-vis-IR spectroscopy of MoS<sub>2</sub> in 2-propanol: Absorption spectra for (a) different amplitudes of point probe (sonic tip) in 24 h and (b) different sonication time with 40% amplitude.

Similarly, Figure 3.2b shows the absorption spectra for  $MoS_2$  in 2-propanol with 24 h, 48 h and 66 h sonication duration of the point probe (sonic tip). Increasing the sonication duration leads to the generation of higher concentration of  $MoS_2$  nanosheets which results in higher absorbance. Therefore, both sonication time and amplitude of the point probe needs to be optimised to obtain monolayers of  $MoS_2$ .



Figure 3.3 (a) Topography image in tapping mode AFM on a drop-casted sample demonstrating the random distribution of MoS<sub>2</sub> nanosheets. (b) Line profile illustrating the successful exfoliation of MoS<sub>2</sub> powder to monolayers (ML).

Unlike UV-vis spectroscopy which can only determine approximately the degree of exfoliation of MoS<sub>2</sub> in 2-propanol, atomic force microscopy (AFM) can accurately measure and verify the formation of monolayers using the LPE technique. Figure 3.3a shows the AFM topography image of a drop-casted sample with MoS<sub>2</sub> nanosheets in 2-propanol. The line profile in Figure 3.3b demonstrates and verifies the formation of MoS<sub>2</sub> monolayers by LPE technique. The MoS<sub>2</sub> nanosheets thicknesses varied from few-layers to monolayer while the lateral size varied from 100 nm to 800 nm. The white regions (Figure 3.3a) denote bulk MoS<sub>2</sub> due to agglomeration of smaller nanosheets.

Figure 3.3a illustrates that the nanosheets are sparsely and randomly distributed over the sample area. However, to form a film (layer), one requires a dense distribution of interconnected MoS<sub>2</sub> nanosheets. To mitigate this problem, multiple drop-casting was performed from 5 to 20 consecutive drop-casts as shown in Figure 3.4. This process leads to a relatively homogeneous distribution of MoS<sub>2</sub> nanosheets and can be used for large area coating of TMD materials as seen in Figure 3.4a-b.

Figure 3.4 also shows that the nanosheets upon drop-casting are randomly distributed over the sample area and this poses a major issue when evaluating the electrical performance of the  $MoS_2$  film since it was not possible to measure any electrical current.



Figure 3.4 SEM image of multiple drop-casting with MoS<sub>2</sub> dispersion for (a) ten consecutive and (b) twenty consecutive rounds.

Experiments were also performed with MoS<sub>2</sub> monolayer dispersed in N-Methyl-2pyrrolidone (NMP) solution (sample obtained from Trinity College Dublin, Ireland). The concentration of the solution was 0.05 mg/mL. However, NMP is toxic and has a high boiling point of 203 °C which lead to a wet surface even after spin coating. Upon annealing, a strong de-wetting effect was observed which resulted in agglomeration of nanosheets. Dip coating also suffers from the same de-wetting effect. Efforts were made to mix the MoS<sub>2</sub> dispersion in NMP with other solvents to solve for the dewetting effect and obtain a homogeneous coating of MoS<sub>2</sub> flakes.

Similarly, MoS<sub>2</sub> monolayer dispersed in water and sodium cholate solution (sample obtained from Trinity College Dublin, Ireland) were tested. Water has a high surface tension value of 70 mN/m at 20 °C which also results in de-wetting and formation of particle agglomeration upon annealing. Removal of sodium cholate (surfactant) can only be obtained by vacuum annealing at 300 °C. Therefore, the above solvent properties limit the use of MoS<sub>2</sub> dispersion in NMP and sodium cholate and are not suitable for spin-coating and dip-coating.

Table 3.1 compares the different solvents used for LPE of MoS<sub>2</sub> nanosheets. 2-propanol is deemed suitable for synthesis of layered MoS<sub>2</sub> nanosheets with reasonable yield. The ease of removal of the 2-propanol solvent by natural evaporation limits the surface contamination of the MoS<sub>2</sub> nanosheets by the solvent, unlike NMP and sodium cholate. LPE results in pristine MoS<sub>2</sub> nanosheets with limited lateral size due to the schism of larger nanosheets upon ultrasonication. Furthermore, uniform deposition of these exfoliated MoS<sub>2</sub> nanosheets into closed films still poses a challenge for electrical performance. To mitigate this issue, dip coating method was explored in the following section.

Solvents	2-propanol	NMP	Sodium Cholate in
			H <sub>2</sub> O
Solution Stability	3-4 weeks	2-3 week	1-2 days
Nanosheet size (µm)	<1	<1	<1
Boiling point (°C)	82.6	203	100
Surface tension (mN/m)	23.00	40.79	70.00
Ease of coating	Yes	No	No

Table 3.1 Comparison of the different solvents used to exfoliate MoS<sub>2</sub> nanosheets

# 3.2 Dip Coating – Bottom-Up Approach

Dip-coating is an ideal method to deposit thin layers from chemical solutions since it is a cost-efficient and waste-free process that is scalable and offers good control over thickness. In this work, commercially available MoS<sub>2</sub> nanosheet dispersion in ethanol and water mixture prepared using co-solvent approach for the exfoliation of layered materials has been used to demonstrate large area coating of TMD materials with dip coating technique. The co-solvent/water mixing ratio gives a surface tension of 22-30 mN/m for exfoliating MoS<sub>2</sub> [65]. Finally, the exfoliated materials are fabricated into thin film via interfacial solution process.

# **3.2.1 Experimental Procedure**

Using the co-solvent method, MoS<sub>2</sub> nanosheet solution exfoliated in Ethanol/water mixture (9:11) was mixed with n-Butanol (1:1). The mixture was added on a DI water (DIW) surface drop-wise and free-standing MoS<sub>2</sub> films were formed (after sufficient amount of materials were added), as n-Butanol (b.p. 117.4 °C) evaporated. The free-standing film on the DIW surface was dip-coated by hexamethyldisilazane (HMDS) vapour treated glass substrate and vacuum annealed at 200 °C for 2 h to remove residual solvent. Scheme of the thin film process is shown in Figure 3.5.



Figure 3.5 (a) Ethanol/water mixed with n-Butanol (1:1). (b) Drop-wise addition to form free-standing MoS<sub>2</sub> film. (c) Film deposition on a silylated glass substrate using dip coating.

# **3.2.2 Characterization and Results**

After dip-coating and annealing, the MoS<sub>2</sub> nanosheets appear to adhere to the glass substrate through physisorption resulting in a change of the glass colour (Figure 3.5c). The optical images in Figure 3.6a-b illustrate that, the MoS<sub>2</sub> nanosheets are homogeneously and randomly distributed over the glass substrate. The main advantage of this method is the MoS<sub>2</sub> nanosheets align in a single plane on the surface of the water without much aggregation. Thus, forming a smooth film (Figure 3.5c) even after dip coating and annealing as observed from the AFM topography images and line profiles in Figure 3.6b-c. This method demonstrated film thicknesses of 10-15 nm (lateral flake size ca. 50 nm) which were verified through AFM and profilometer measurements. However, the deposited films were not completely closed (Figure 3.6a & c) and hence more solution needed to be added to increase the nanosheet density resulting in a closed film. Unfortunately, a further increase in solution resulted in aggregation of the nanosheets rather than a closed film vital for an electrical connection. Thus, dip-coating is not a suitable method for deposition of exfoliated MoS<sub>2</sub> nanosheets.

Langmuir Blodgett (LB) method can be used to overcome this issue by forming a closed film. However, the electrical properties of the deposited MoS<sub>2</sub> films would still be limited due to the high grain to grain contact resistance [66] between the MoS<sub>2</sub> nanosheets.



Figure 3.6 Optical microscope images of the deposited MoS<sub>2</sub> nanosheet film at (a) 50X magnification. AFM image illustrating the (b) line profile, (c) topography and (d) phase contrast of the dip-coated film.

# 3.3 Chemical Bath Deposition – Bottom-Up Approach

Chemical bath deposition (CBD) which is known as solution growth, controlled precipitation, or just chemical deposition, have been employed as a method for the deposition of TMD thin films. It is an analogue, in the liquid phase, of the well-known chemical vapour deposition (CVD) in the gaseous phase. In this work, MoS<sub>2</sub> thin films have been deposited by CBD method on glass and Eagle glass (contains less impurity) substrate using ammonium tetrathiomolybdate, (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub>, as a single source precursor for Mo and S and subjected to annealing at different temperatures and gas environment.

# **3.3.1 Experimental Procedure**

Commercially available (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> powders were purchased from Sigma-Aldrich and used as supplied. 0.2 M (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> solution was prepared in de-ionized water and was mixed with 10 mL of ammonia solution maintained at pH~10 [15]. To this 10 mL of hydrazine monohydrate was added which acts here as a reducing agent. The

hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O) provides the electrons required for reducing the Mo<sup>VI</sup> to Mo<sup>IV</sup> in the (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> precursor (as shown in the chemical reaction below), just like electrochemical depositions where the electrical current supplies them.



Figure 3.7 Schematic illustration of the synthesis of MoS<sub>2</sub> films using chemical bath deposition.

The whole solution ~ 30 ml was stirred well to get a homogeneous solution in a 100 mL Schott bottle as shown in Figure 3.7. A glass substrate was inserted inside, and the bottle was closed with a cap connected to an overpressure valve (~ 0.1 mbar). This prevented an explosion in case of excess pressure build-up upon heating and avoids evaporation of the ammonia from the solution; otherwise the pH of the bulk solution cannot be controlled (Figure 2.9). The bath temperature was maintained at 60 °C for 1 - 4 h (depending on the required thickness). A uniform brown-black thin film was deposited onto the substrate, which was washed in distilled water until heterogeneities and impurities were removed. Finally, the deposited films on different glass substrates were further annealed under atmospheric pressure in N<sub>2</sub> and forming gas (H<sub>2</sub>/N<sub>2</sub>) for 1 h at 450 °C [67]. In case of thick films (>100 nm), after annealing the film exhibited shining metallic lustre.

# **3.3.2 Characterization and Results**

The CBD deposited MoS<sub>2</sub> films were characterized using an optical microscope, AFM, profilometer, scanning electron microscope (SEM) and Raman spectroscopy. The optical image in Figure 3.8a illustrates relative homogeneous deposition of the MoS<sub>2</sub> film on the glass substrate. The main advantage of this method is the MoS<sub>2</sub> films can be grown over a large area ( $\sim$  cm<sup>2</sup>) compared to conventional CVD method ( $\sim$  mm<sup>2</sup>).



Figure 3.8 (a) Optical microscope image of a CBD MoS<sub>2</sub> film after 4 h of deposition and N<sub>2</sub> annealing for 1 h at 450 °C. (b) Film thickness dependence on time for MoS<sub>2</sub> film deposition. (c) Optical microscope image of glass substrates pre-seeded with and without MoS<sub>2</sub> nanosheets.

Figure 3.8b shows the film thickness of the MoS<sub>2</sub> film linearly increases with time as more free ions present in the solution combine to form the nuclei, gets deposited on the substrate. However, after 4 h of deposition, it was observed the growth rate decreases since most of the free ions have already precipitated to form nuclei. Therefore, 4 h was taken as an optimized deposition time for further experiments as it resulted in uniform film deposition. It is also observed that pre-seeding the glass substrates with exfoliated MoS<sub>2</sub> nanosheets from Figure 3.3a affects the number of nucleation site resulting in thicker films as shown in Figure 3.8c.

SEM was used to investigate the surface morphology of the deposited MoS<sub>2</sub> films and to analyse the surface topography, shape, size and distribution of nuclei leading to the film growth. The elemental compositions of the deposited films were determined from the Energy Dispersive X-ray (EDX) measurements.



Figure 3.9 (a) SEM image of MoS<sub>2</sub> reference sample at 3000X magnification. (b) EDX spectra of reference MoS<sub>2</sub> sample.

The SEM image in Figure 3.9a illustrates the flat surface topography of a commercially available MoS<sub>2</sub> crystal used as a reference sample for EDX measurements. The EDX spectra implements a deconvolution algorithm to separate the Mo and S peak as seen in Figure 3.9b. However, as the Mo and S energy spacing is very close, this leads to a slight erroneous quantification of S/Mo  $\sim$  1.75 compared to the ideal case of S/Mo=2 in MoS<sub>2</sub>. Therefore, EDX measurements provide more qualitative analysis and insight compared to quantitative analysis by X-ray photoelectron spectroscopy (XPS) measurements for MoS<sub>2</sub> films.

Figure 3.10a-b shows the surface morphology of films grown for 2 h and 4 h deposition time with pH~10.2 and annealed in N<sub>2</sub> for 1 h at 450 °C. The formation of spheres and needle-like structures acting as nuclei results due to minimization of surface energy. The spheres and needles are scattered and isolated (Figure 3.10a) initially, but with the increase in deposition time they merge to form a relatively closed film (Figure 3.10b). Both samples in Figure 3.10a-b exhibited a S/Mo ratio of 1.5, a value lower than that of the reference sample.

Similarly, experiments were performed by varying pH values. Formation of  $MoS_2$  was possible only with pH ~10. Too low a pH leads to precipitation of amorphous  $MoS_3$ . On the other hand, the samples prepared at too high a pH contain some impurities of  $MoO_2$  due to progressive hydrolysis of  $(NH_4)_2MoS_4$  to oxomolybdate, which reacts further with hydrazine, giving  $MoO_2$ .



Figure 3.10 SEM images of film deposited on glass substrate with (a) 2 h and (b) 4 h deposition time along with pH 10.2 and N<sub>2</sub> annealing at 450 °C for 1 h, and (c) annealed in  $H_2/N_2$  at 450 °C for 1 h with pH 10.2 and 4 h deposition time.

The deposited films were also annealed in  $H_2/N_2$  (1:19) to study the effect of annealing gas environment. Figure 3.10c shows the surface morphology of films grown on a glass substrate with pH~10.2, 4 h deposition time and annealed in  $H_2/N_2$  for 1 h at 450 °C. Compared to Figure 3.10a-b, here only the formation of spheres acting as nuclei is observed, which indicates the annealing gas affects the final morphology of the film formation. The nucleated spheres appear to grow homogeneously without many aggregates and join to form a closed film although it is not ideal for the formation of layered nanosheets. The annealed sample in Figure 3.10c exhibited a S/Mo ratio of 1.73, a value very close to that of the reference sample. Therefore,  $H_2/N_2$  is better suited for annealing of MoS<sub>2</sub> films compared to N<sub>2</sub>. Mainly due to homogeneous growth, a lower percentage of aggregate formation and the better stoichiometric ratio of S/Mo close to the reference sample attributed to the efficient reduction of MoS<sub>3</sub> to MoS<sub>2</sub> in the presence of H<sub>2</sub>.

As seen in the previous figure 3.8b, the CBD film thicknesses were  $\ge$  100 nm and hence scaling is required for thinner ( $\le$  20 nm) large area coating of TMD materials. To

achieve this, the concentration of the (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> precursor solution was reduced to 0.05M. Figure 3.11 illustrates the AFM topography and phase contrast image of a sample deposited with a 0.05M solution. The image shows a complete closed film which was grown having a film thickness of 10 nm and root mean square (RMS) roughness of 0.5 nm which is promising for large area coating. Deposition were also performed at higher precursor concentration (such as 0.1M); however, it resulted in the formation of islands while lower concentration (such as 0.01M) lead to no deposition. Scaling of the MoS<sub>2</sub> films below 10 nm results in the formation of islands or no deposition.



Figure 3.11 AFM image illustrating the (a, c) topography and (b, d) phase contrast of a CBD film in a 60 °C and 80 °C bath with a 0.05M solution, pH 10.15, 4 h deposition time and  $H_2/N_2$  annealing for 1 h at 450 °C.

To study the effect of the bath temperature on the growth and kinetics of the film, the bath temperature was increased from 60 °C to 80 °C. Figure 3.11c-d shows the AFM topography and phase contrast images of a deposition performed at 80 °C. The measured film thickness was 93 nm with an rms roughness of 51 nm. The increase in

temperature leads to faster deposition of ions as nuclei, thereby reducing the deposition time. However, faster deposition of the ions results in island growth rather than layer-by-layer growth required for TMD thin films. Therefore, the optimized bath temperature was taken as 60 °C for future experiments.



Figure 3.12 Raman spectra of MoS<sub>2</sub> films deposited using CBD and dip-coating method on glass substrates.

Figure 3.12 illustrates the Raman spectra obtained for as-deposited MoS<sub>2</sub> films by CBD and dip-coating (exfoliated MoS<sub>2</sub> nanosheets) process on glass substrates. The typical Raman active modes, i.e.  $A_{1g}$  at ~407 cm<sup>-1</sup> and  $E^{1}_{2g}$  at ~382 cm<sup>-1</sup> [58] observed in this spectral range confirms the formation of MoS<sub>2</sub>. MoS<sub>2</sub> films synthesized using CBD approach shows broadening of the line width for both Raman modes implying poor film crystallinity as compared to dip-coated MoS<sub>2</sub> films. The crystallinity of the deposited films can be improved by annealing at elevated temperatures but the scaling of the MoS<sub>2</sub> film thickness below 10 nm poses a bottleneck. Furthermore, process parameters such as pH and annealing gas also strongly affect the MoS<sub>2</sub> film growth apart from precursor concentration and deposition temperature.

# **3.4 Conclusion**

LPE method leads to the formation of pristine  $MoS_2$  nanosheets with limited lateral size due to schism during ultra-sonication while a uniform coating of these nanosheets and the grain to grain contact resistance poses a severe bottleneck using dip coating method. Furthermore, the CBD method results in the formation of thick  $MoS_2$  films with varying surface morphology. Therefore, the above deposition methods pose a severe challenge to the synthesis of layered  $MoS_2$  films (< 10 nm) with a decent lateral size which is essential for the fabrication of electrical devices. Based on the necessity, there is a need to develop a process flow for the synthesis of  $MoS_2$  films using the bottom-up approach with wafer-scale uniformity and controllable thickness.

# Chapter 4: Growth of MoS<sub>2</sub> layers based on liquid phase precursor on Silicon

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# **4.1 Introduction**

In this chapter, a novel route to synthesize MoS<sub>2</sub> films from a precursor solution via spin-coating with excellent layer-to-layer controllability is described [68]. Solubility of Mo-precursor in an appropriate solvent was obtained while having good coating properties essential for thin film formation. Chemical conversion of the as deposited Mo-precursor films on silicon/silicon dioxide substrate to MoS<sub>2</sub> were obtained by annealing in the presence of sulfur. This results in thin MoS<sub>2</sub> films with high uniformity and polycrystallinity with random grain orientation attributed to the amorphous SiO<sub>2</sub> surface of the substrate. Influence of temperature on the morphology, crystallinity and optical properties of the MoS<sub>2</sub> thin film was investigated. The properties of the synthesized MoS<sub>2</sub> films were confirmed by various thin film characterization tools such as Raman spectroscopy, UV-vis spectroscopy, X-ray spectroscopy, X-ray diffraction, atomic force microscopy and scanning/transmission electron microscopy. This facile method allows upscaling to large substrates with controllable film thickness down to 4 nm, which are of interest for low-cost fabrication of electronic devices.

# **4.2 Experiment**

Molybdenum(V)-chloride (50 mg, 99.99%, Sigma Aldrich) was dissolved in 1-Methoxy-2-propanol (1 mL, 99.97%, CG Chemikalien GmbH & Co. KG) solvent and stirred overnight. The solubility of the Mo-precursor in an organic solvent with a hydroxyl functional group (low viscosity alcohol solvents) is studied to obtain thin and uniform films. MoCl<sub>5</sub> being a reactive compound reacts readily with 1-Methoxy-2-propanol, proceeded with chlorine-oxygen interchange and HCl release to form a stable precursor solution [69]. The solution was spin-coated at 3000 rpm for 60 s on highly n-doped Si substrates with 90 nm thick SiO<sub>2</sub> (Si-Mat) to form uniform films over large area (2 x 2 cm<sup>2</sup>). The coated samples were pre-annealed at 150 °C for 10 minutes to evaporate the solvent from the coated film. Both the precursor preparation and preannealing were carried out in nitrogen (N2) environment. Solutions with low Moprecursor concentration and viscosity results in thin, uniform and continuous films with an average pre-annealed film thickness of 5 nm. The samples were then placed in the middle of the tube furnace (Friatec, Al<sub>2</sub>O<sub>3</sub> tube) as shown in Figure 4.1. The temperature gradient is constant over a distance of 30 cm in the middle of the annealing tube along the horizontal axis. Quartz boat holding pure sulfur (4.6 g, 99.9995%, Alfa Aesar) was placed in the upstream near the edge of the furnace. The Al<sub>2</sub>O<sub>3</sub> tube was first purged with Argon (Ar) gas to remove residual air. After purging, the gas flow was changed to 2.4% H<sub>2</sub> in Ar while the furnace temperature was gradually increased from room temperature to target temperature (450 °C, 600 °C, 750 °C or 900 °C) with a heating rate of 50 °C/min. The temperature was maintained at the final temperature for 60 minutes for annealing before cooling down to room temperature in presence of Ar.

The deposited films were characterized by different techniques as described in section 2.5 to observe morphology and crystalline structures and to investigate film composition, optical properties and crystallinity. TEM cross-section was obtained by using a focused ion beam (FIB, Carl Zeiss Auriga). The lamella was welded onto an omniprobe grid for further ion milling with Nanomill at 500 eV (after plasma cleaning the sample). The planar view was obtained by using the Nitto blue tape (BT-150E-CM, Nitto Denko Corporation) to peel off the MoS<sub>2</sub> from the SiO<sub>2</sub> substrate and transferred directly onto a lacey carbon film copper TEM grid. Geological reference MoS<sub>2</sub> single

crystal was purchased from SPI supplies and used as a reference for characterization of obtained MoS<sub>2</sub> films.



Figure 4.1 Schematic illustration of the synthesis of MoS<sub>2</sub> thin films from liquid phase.

# 4.3 Results and Discussion

# 4.3.1 Formation of MoS<sub>2</sub> Films from Soluble Molybdenum Precursor

# 4.3.1.1 Film Formation Under Different Atmospheric Conditions

A crucial step in the production of homogenous and uniform MoS<sub>2</sub> films is the deposition environment of the Mo-precursor solution onto the Si/SiO<sub>2</sub> substrate. This step involves the spin-coating and the pre-annealing process as shown in Figure 4.1. Figure 4.2a-c shows the surface morphology of Mo-precursor films spin-coated and pre-annealed in ambient air, spin-coated in N<sub>2</sub> and pre-annealed in ambient air and spin-coated and pre-annealed in N<sub>2</sub> environment, respectively. It is evident that Figure 4.1b-c demonstrates better film uniformity compared to Figure 4.1a which suffers from the formation of pin-holes over the entire film surface. Processing the Mo-precursor solution derived from highly reactive MoCl<sub>5</sub> in air causes the as-deposited film to react readily with moisture resulting in pin-holes, inhomogeneity and increased rms roughness (3 nm) as seen in Figure 4.2d. While samples spin-coated and annealed in N<sub>2</sub> exhibited no pin-holes with an rms roughness of ~ 1 nm. Therefore, all future depositions involving spin-coating and pre-annealing of Mo-precursor solution were carried out in N<sub>2</sub> environment.



#### Inertenvironment

#### Reactivity of MoCl<sub>5</sub>



Figure 4.2 Optical image of Mo-precursor films deposited on Si/SiO<sub>2</sub> substrate by (a) spin-coating and pre-annealing in air, (b) spin-coating in N<sub>2</sub> and pre-annealing in air and (c) spin-coating and pre-annealing in N<sub>2</sub>. (d) AFM topography of Mo-precursor film synthesized by spin-coating and pre-annealing in air.

#### 4.3.1.2 Growth Mechanism of MoS<sub>2</sub> Nanocrystals During Annealing

The as-deposited Mo-precursor film is subsequently reduced in Ar/H<sub>2</sub> environment followed by sulfurization through diffusion resulting in the formation of MoS<sub>2</sub> (Figure 4.1). The hydrogen assists in the removal of all impurities arising from the solvent while the high vapour pressure of sulfur helps sulfur atoms to diffuse into the reduced Mo-precursor. Sulfurization of the reduced Mo-precursor results in the formation of both MoS<sub>2</sub> and MoS<sub>3</sub>. MoS<sub>3</sub> can be further reduced to stochiometric MoS<sub>2</sub> at elevated temperatures [67] such as 900 °C in a reducing environment as shown in Figure 4.3.





In contrast, processing in the absence of  $H_2$  with Ar and sulfur environment at 900 °C resulted in a poor Mo:S atomic ratio ~ 1:2.94 attributed to excess diffusion of sulfur. Therefore,  $H_2$  plays a vital role in the film formation as unreduced impurities would impede the sulfur diffusion and are suspected to interrupt the crystal structure and degrade the electrical properties of the MoS<sub>2</sub>. Besides, the reducing environment inhibits further oxidation of the synthesized film.

The reduction in H<sub>2</sub> and sulfurization of the Mo-precursor film are temperature driven process. Therefore, in the following section, the effect of annealing temperature on the growth and formation of MoS<sub>2</sub> films will be investigated.

# 4.3.2 Influence of Temperature on Morphological and Optical Properties of MoS<sub>2</sub>

The SEM images in Figure 4.4a-c illustrates the surface morphology of the as deposited  $MoS_2$  films having film thickness 27 nm under different annealing temperatures ranging from 450 °C to 900 °C.



Figure 4.4 SEM planar views of solution processed MoS<sub>2</sub> films fabricated at different annealing temperatures (a) 450 °C–600 °C; (b) 750 °C and (c) 900 °C. (d) Film thickness and root mean square roughness dependence on precursor concentration for samples annealed at 900 °C. Inset illustrates the AFM topography of a 4 nm thick film.

The samples annealed at 450 °C and 600 °C (Figure 4.4a) did not exhibit any changes in surface morphology due to its amorphous nature. However, annealing at higher temperatures, formation of crystalline grain was observed, as seen in 750 °C (Figure 4.4b) and 900 °C (Figure 4.4c). The crystalline grains/platelets size increased with higher annealing temperatures. The grains/platelets appear to be randomly oriented most likely due to the amorphous nature of the SiO<sub>2</sub> substrate, i.e. absence of commensurability of the SiO<sub>2</sub> with MoS<sub>2</sub> lattice. The MoS<sub>2</sub> film thickness of 27 nm were further scaled down through serial dilution of the precursor solution to obtain thinner MoS<sub>2</sub> films. Figure 2d shows the film thickness and root mean square (rms) roughness dependence on precursor concentration. The film thickness scales linearly with precursor concentration and below 30 mg/mL all films demonstrated a rms roughness less than 1 nm. The films appeared to be homogenous and without pinholes for 4 nm thick films (average pre-annealed film thickness of 5 nm) as seen from the inset AFM topography image in Figure 4.4d. Scaling below 4 nm results in the formation of pinholes and agglomerates due to minimization of film surface energy, i.e. absence of interaction/wettability between the crystalline film and amorphous substrate. To shed more light on the film growth, crystallinity and to understand the layer formation, TEM studies were performed.

Figure 4.5 illustrates the optical images of  $MoS_2$  with different film thicknesses processed at 900 °C. The films appear to be homogeneous over the entire substrate (except the edges) and thickness scales almost linearly as shown in Figure 4.4d. The difference in  $MoS_2$  film colour is based on achieving a contrast between reflected light from SiO<sub>2</sub> and the blank substrate, which strongly depends on the thickness of SiO<sub>2</sub> and the wavelength of incident light [34]. This allows direct visualization of ultra-thin  $MoS_2$  films deposited on SiO<sub>2</sub>/Si with optimized SiO<sub>2</sub> thickness of 90 nm or 270 nm.



Figure 4.5 Optical images of different thicknesses of MoS<sub>2</sub> films which were prepared by wet-chemical process.



Figure 4.6 TEM analyses of fabricated MoS<sub>2</sub> films annealed at 750 °C: (a) the cross-section TEM image, (b) planar view reveals no distinct grain boundaries and (c) shows its diffraction pattern. MoS<sub>2</sub> films annealed at 900 °C revealed (d) uniformity in the interlayer spacing with (e) distinct grain boundaries and (f) the diffraction pattern taken from the planar view (e).

TEM analyses done on the wafer scale synthesis [22,70] shows perfect crystal structure with uniform layers with an interlayer spacing of about 0.65 nm. In this work, chemically synthesized MoS<sub>2</sub> films annealed at 750 °C exhibited crystalline structures, however the random crystal orientation of the layers formed showed varying interlayer spacing ranging from 0.62 to 0.68 nm (Figure 4.6a). The film showed formation of sulfur clusters (bright white spots) as could be seen in Figure 4.6b. This was verified by STEM-EDX and HRTEM measurements. HRTEM of the clusters showed d-spacing of about 0.33 nm which does not match with any MoS<sub>2</sub> lattice parameters. Point EDX acquired from the clusters revealed presence of sulfur and no distinct grain boundaries were observed for samples annealed at 750 °C. Figure 4.6c shows the corresponding diffraction pattern of Figure 4.6b proving the film to be polycrystalline. However, when the sample is annealed at 900 °C the MoS<sub>2</sub> layers exhibits significantly improved crystal orientation having around 30 layers with a

film shows clear grain boundaries (in the range of 30-120 nm), rather than sulfur cluster formation as observed after annealing at 750 °C. Figure 4.6f exhibits corresponding diffraction pattern of the region shown in Figure 4.6e. Although the diffraction pattern still shows poly-crystallinity caused by random grain orientation or intra-grain dislocations [71,72], it is worth noting that the quality of the film has been much improved due to the formation of larger grain size and absence of sulfur clusters. The observation of spots in the diffraction pattern (Figure 4.6f) demonstrates that the crystallinity of the film is improved with higher annealing temperature compared to Figure 4.6c. MoS<sub>2</sub> film processed at 900 °C is highly continuous compared to film annealed at lower temperatures with each grain exhibiting layered crystalline structure on the substrate and only interrupted by grain boundaries.

The reduction of the Mo-precursor in Ar/H<sub>2</sub> followed by sulfurization through diffusion leads to the formation of MoS<sub>2</sub> (Figure 4.3). The formation of sulfur clusters at 750 °C implies the temperature is not high enough that the sulfur can sublimate out of the cluster due to higher sulfur vapour pressure inside the annealing chamber. Thereby, resulting in a two-phase system with non-homogeneous randomly distributed smaller grains (Figure 4.6a-b). The diffusion of sulfur can also be impeded if the Mo-precursor is not properly reduced in Ar/H<sub>2</sub> at 750 °C. This issue is mitigated by annealing at 900 °C resulting in no sulfur clusters (Figure 4.6e). This implies that elevated temperature is essential for the diffusion of sulfur and subsequent formation of uniform MoS<sub>2</sub> film (Figure 4.6d).

Formation of MoS<sub>2</sub> films through solution phase processing were investigated by optical characterizations such as Raman and UV-visible spectroscopy. Raman spectroscopy is a reliable tool to probe the presence of thin TMD films as phonon frequencies are sensitive to the materials being studied. Raman spectra on asdeposited MoS<sub>2</sub> thin films as well as geological MoS<sub>2</sub> crystal were collected for comparisons. Figure 4.7a shows the Raman spectra obtained for 27 nm as-deposited MoS<sub>2</sub> films on SiO<sub>2</sub> substrate under different annealing temperatures.

Three typical Raman active modes are observed in this spectral range: the out-of-plane vibration (c-axis) of S atoms ( $A_{1g}$ ) with a Raman shift of ~408 cm<sup>-1</sup>, and the in-plane vibration (basal plane) of Mo and S atoms ( $E^{1}_{2g}$ ) at ~383 cm<sup>-1</sup> and the in-plane vibration (basal plane) of S atoms ( $E_{1g}$ ) at ~287 cm<sup>-1</sup> [58]. Group theory predicts four



Raman active modes for 2H-MoS<sub>2</sub> [59]. However, only three Raman active modes are observed due to the lower measuring limit of the spectrometer.

Figure 4.7 Optical characterization of fabricated MoS<sub>2</sub> thin films. (a) Raman spectra of MoS<sub>2</sub> films and (b) FWHM of A<sub>1g</sub> and E<sup>1</sup><sub>2g</sub> vibrating modes obtained after annealing process at different temperatures. UV–Vis absorption spectra of MoS<sub>2</sub> thin films (c) after annealing at different temperatures by keeping film thickness constant with 27 nm thick film and (d) annealed at 900 °C for different film thicknesses. Inset graph shows the energy of the A exciton peak (extracted from the absorption spectra in the main curve) as a function of average film thickness.

Due to film thicknesses beyond 5 monolayers obtained from this solution process, the typical  $\Delta \omega$  separation between  $A_{1g}$  and  $E^{1}_{2g}$  modes for very thin MoS<sub>2</sub> films could not be observed [58]. In Figure 4.7a, the lower growth temperatures (450 °C and 600 °C) exhibited lower peak intensity ratio of  $E^{1}_{2g}/A_{1g}$  (attributed to weak  $E^{1}_{2g}$  peak intensity) compared to the bulk geological MoS<sub>2</sub> crystal. Similar behaviour was reported in CVD [50] process and is indicative of low crystallinity and structural film property. In samples grown at 750 °C, the overall peak intensity ratio was increased but was still lower than the bulk geological MoS<sub>2</sub>. The samples synthesized at a higher temperature as 900 °C, showed similar peak intensity ratio, but with 1.6 times

intensity higher than samples at 750 °C. This implies that the crystallinity of the films is significantly improved, and a higher growth temperature is crucial for the formation of high-quality MoS<sub>2</sub>.

It is also observed that the Raman peak intensities for  $E^{1}_{2g}$  and  $A_{1g}$  are different for the solution processed MoS<sub>2</sub> and bulk geological MoS<sub>2</sub>. Since the in-planar vibration ( $E^{1}_{2g}$ ) is dependent on the nanoscale and random orientation of the grains in the processed MoS<sub>2</sub> (Figure 4.4c and 4.6e). Thus, exhibiting a lower intensity compared to geological bulk MoS<sub>2</sub>. This is further verified by the SEM image of geological bulk MoS<sub>2</sub> where the grain size is much larger, typically in the range of few microns or more.

In addition, the intensity ratio of  $E_{12g}^{1}/A_{1g}$  mode can be used as an indicator of doping levels [73] which implies that our synthesized MoS<sub>2</sub> is more doped than the geological MoS<sub>2</sub> crystal counterpart since the  $A_{1g}$  mode is broader in the synthesized film. The suggested doping in our films could be presumably due to an increased concentration of sulfur content. It should be noted that the intensity ratio of  $E_{2g}^{1}/A_{1g}$  is a cumulative effect of doping and crystallinity as deconvolution is not possible. Figure 4.7b presents the full width at half maxima (FWHM) for both Raman modes as a function of annealing temperature. The FWHM decreases with increase in temperature which indicates an increase in crystallinity of the film. The MoS<sub>2</sub> films formed at 900 °C with layer thickness of more than 8 monolayers, the bulk-like inner layers will dominate the Raman intensity, resulting in reduced line width. The FWHM of the Raman modes at 900 °C almost reaches the reference value of geological MoS<sub>2</sub> crystal (FHWM  $A_{1g} \sim 1.97$ cm<sup>-1</sup> and FHWM  $E_{2g}^{1} \sim 1.7$  cm<sup>-1</sup>). The difference is attributed to the polycrystalline nature of the films with numerous grain boundaries and defects.

UV-visible absorption spectroscopy was performed to study the optical characteristics of the large area synthesized MoS<sub>2</sub> films for different annealing temperatures and film thicknesses on SiO<sub>2</sub> substrates. Figure 4.7c illustrates the absorption spectra for a 27 nm thick MoS<sub>2</sub> film under various annealing conditions. As-deposited and annealed samples at 450 °C and 600 °C exhibited no clear absorption peak. This indicates the absence of the formation of MoS<sub>2</sub> film at temperatures below 600 °C as the film is still amorphous (Figure 4.4a). However, samples annealed at 750 °C and 900 °C exhibited absorption peaks with the later demonstrating distinct peaks due to better crystallinity. The absorption spectra (Figure 4.7c) in the region 400-800 nm exhibit
the characteristic optical peaks of bulk MoS<sub>2</sub> due to optical transition between dorbitals [64]. The spectrum shows the typical A and B peaks at 685 nm (1.81 eV) and 629 nm (1.97 eV) respectively, due to band edge excitons demonstrating high optical quality of the films [10,33,74]. Furthermore, one also observe C and D peaks at 451 nm (2.75 eV) [75] and 408 nm (3.04 eV) respectively, corresponding to interband transitions from the occupied dz<sup>2</sup> orbital to unoccupied dxy,  $x^2-y^2$  and dxz, yz orbitals [76]. Figure 4.7d shows the absorption spectra of MoS<sub>2</sub> films annealed at 900 °C with different film thicknesses from 4 nm to 27 nm. A blue shift in the A (Figure 4.7d inset graph) and B excitonic peaks are observed as the film thickness scales from 27 nm to 4 nm due to confinement effect [32].

# $\label{eq:4.3.3} \mbox{ Influence of Temperature on Crystallinity and Chemical Composition of $MoS_2$} \label{eq:4.3.3}$

X-ray diffraction measurements of the MoS<sub>2</sub> films verifies the trends evident from the Raman spectra. Figure 4.8a illustrates the  $\theta$ - $\theta$  scans of MoS<sub>2</sub> films annealed at temperatures ranging from 450 °C to 900 °C, bare Si/SiO<sub>2</sub> and for geological bulk MoS<sub>2</sub>. In addition, reference peak positions (20) in dark cyan colour for 2H-MoS<sub>2</sub> powder is provided for comparison. The reference bulk MoS<sub>2</sub> crystal shows sharp (002), (004) and (006) diffraction peaks at  $2\theta = 14.4^{\circ}$ ,  $29.1^{\circ}$  and  $44.2^{\circ}$ , respectively. The diffractogram for the sample annealed at 450 °C showed no clear diffraction peaks, while the lowest order peak (002) at  $2\theta = 14.4^{\circ}$  was barely visible for sample annealed at 600 °C. This implies, that the annealed films are still amorphous, complementing reports for lower temperature growth of MoS<sub>2</sub> on SiO<sub>2</sub> [50]. The very sharp diffraction peaks in the diffractogram is attributed to the underlying crystalline silicon substrate. Sample annealed at 750 °C demonstrates a distinct (002) peak, while the higher order peaks (004) and (006), are slightly visible thereby suggesting, that a higher annealing temperature to improve the crystallinity of the films. As expected, for the sample, annealed at 900 °C, higher order peaks were evident signifying long-range crystalline order. Therefore, this demonstrates that the films structural quality and crystal orientation of the MoS<sub>2</sub> improves with increasing temperatures. The (002), (004) and (006) diffraction peaks at  $2\theta = 14.4^{\circ}$ , 29.1° and 44.2° correspond to an average d = 6.15 Å, the distance between two MoS<sub>2</sub> layers in 2H structure which is also reported in the literature [26,77]. The FWHM of the diffraction peaks helps us to determine the crystallite size in the film using the Scherrer equation [63]. Since the (002) peak exhibited the highest intensity, it was utilized to calculate the crystallite size. Samples annealed at 750 °C and 900 °C demonstrated a crystallite size of 18 nm and 30 nm respectively, as an effective thickness of the grains in the direction perpendicular to the diffraction plane (002). The increase in crystallite size further re-iterates the need for higher processing temperature to form MoS<sub>2</sub> with larger grains.



Figure 4.8 (a) X-ray diffraction spectra for samples annealed at different temperatures from 450 °C to 900 °C, bulk MoS<sub>2</sub> and silicon substrate. XPS spectra of fabricated MoS<sub>2</sub> film on Si/SiO<sub>2</sub> substrate annealed at 900 °C: (b) and (c) corresponds to the binding energy of Mo 3d and S 2s, and S 2p core levels respectively.

XPS was conducted to explore the stoichiometry of MoS<sub>2</sub> film grown on Si/SiO<sub>2</sub> substrate. Figure 4.8b-c exhibits Mo 3d, S 2s, and S 2p core level spectra. The spectra were evaluated using Shirley background and a symmetric peak shape defined by a convolution of Gauss and Lorentz peaks for peak fitting. The binding energies for Mo  $3d_{5/2}$  and S  $2p_{3/2}$  were found to be at 228.3 eV and 162 eV respectively, which agrees well with the XPS conducted by Brown et al. [78]. Samples annealed at 750 °C resulted in a low Mo/S atomic ratio (1:2.5) due to presence of two-phase system, i.e. stoichiometric MoS<sub>2</sub> and sulfur clusters in the film (Figure 4.6b). On the contrary,

samples annealed at 900 °C demonstrated an improved chemical composition of Mo:S  $\sim 1:2.13$  from the spectra. This indicates the sulfur concentration is 6.5% higher in the fabricated films, in comparison to ideal 1:2 stoichiometry. The presence of excess sulfur can give rise to point defects (e.g. Mo-vacancies, S-interstitials, anti-sites) in the MoS<sub>2</sub> film as reported earlier [79,80]. Point defects such as sulfur S<sub>1</sub> interstitials and S<sub>Mo</sub>, S2<sub>Mo</sub> anti-sites with low formation energy under S-rich conditions resulted in localized states in the band gap close to the valence band. Thus, the occurrence of these localized states due to excess sulfur [81] could affect the electrical properties of the solution processed MoS<sub>2</sub> films.



#### 4.3.4 Electrical Performance of Bottom-Gated MoS<sub>2</sub> TFT

Figure 4.9 Electrical characterizations of  $MoS_2$  TFTs. (a) Schematic of the bottom-gated  $MoS_2$  TFTs. (b) Output ( $I_d - V_{ds}$ ) characteristics of a 6 nm thick  $MoS_2$  sample for different applied gate bias  $V_{gs}$ . (c) Drainsource current  $I_d$  dependence on gate-to-source applied voltage  $V_{gs}$  with a constant drain-to-source applied voltage  $V_{ds} = -45$  V.

The electrical transport properties of solution processed MoS<sub>2</sub> films were further investigated by fabricating MoS<sub>2</sub> TFT devices with gold source and drain contacts as

shown in Figure 4.9a. Device characterization was performed with a channel width (W) of 10,000  $\mu$ m and channel length (L) of 255  $\mu$ m to obtain the current-voltage (I-V) curves. The transfer and output I-V characteristics of a 6 nm thick MoS<sub>2</sub> TFT are shown in Figure 4.9b and 4.9c, respectively. Figure 4.9b shows the output characteristics (drain current, *I*<sub>d</sub> as a function of applied drain-to-source voltage, *V*<sub>ds</sub>) of a TFT for different applied gate-to-source voltage (*V*<sub>gs</sub>).

The linear regime of transistor operation ( $V_{ds} > -5V$ ) in the output characteristics suggests the absence of a significant barrier for charge carrier injection. From the curve, the linear field-effect mobility ( $\mu_{FE}$ ) can be determined by using equation 2.2

$$\mu_{FE} = \frac{dI_{\rm d}}{dV_{\rm ds}} \cdot \frac{L}{WC_{\rm ox}} \cdot \frac{1}{V_{\rm gs} - V_{\rm t}} \qquad Eq. \ 4.1$$

where  $C_{ox} = 38.36 \text{ nF/cm}^2$ , is the capacitance of the SiO<sub>2</sub> layer and V<sub>t</sub>, is the threshold voltage. Fabricated devices with MoS<sub>2</sub> films deposited from solution phase exhibited mobilities of 0.03 cm<sup>2</sup>/Vs for  $V_{gs} = -50$  V and V<sub>t</sub> = -10.13 V. The rather low mobility value is within the typical range which was previously reported for CVD grown MoS<sub>2</sub> films having numerous grains [6,9,48,50]. The obtained mobility value is also in good agreement with devices based on liquid phase exfoliated MoS<sub>2</sub> by Lee et al [82].

The low mobility is mainly attributed to the random crystalline orientation of MoS<sub>2</sub> grains as shown in the STEM image in Figure 4.6e. The formation of numerous grain boundaries and grain to grain contact results in high resistance for the transport of charged carriers, unlike single-crystalline films. This explanation is supported by Dumcenco et al., who had demonstrated a potential drop across grain boundary of two merged MoS<sub>2</sub> single crystals indicating the presence of an electrically resistive grain boundary [28]. Furthermore, other defects such as impurities, point defects (vacancies, anti-sites, etc.) cause localized states near the defects which can act as scattering and trapping centers [79]. All these effects significantly reduce the mobility in the MoS<sub>2</sub> film. The mobility can be improved using a high-k dielectric (e.g. HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) [30,83] and a c-plane sapphire [28] substrate for optimized growth of MoS<sub>2</sub> films.

Figure 4.9c shows the transfer characteristics ( $I_d$  vs  $V_{gs}$ ) of the device measured for  $V_{ds}$  = -45 V and L = 255 µm. Compared to geological MoS<sub>2</sub> crystal which shows *n*-type semiconductor properties, solution processed MoS<sub>2</sub> film from this work exhibit *p*-type semiconductor behaviour. The high "OFF" state current is mainly attributed to current passing through the bulk of crystal [84] apart from the crystal defects.



Figure 4.10 Electrical characterization of MoS<sub>2</sub> TFTs. (a) Cross-section and top view of the MoS<sub>2</sub> TFTs illustrating the TLM layout and (b) TLM analysis and its corresponding R<sub>sh</sub> and R<sub>c</sub>W for fabricated 6 nm MoS<sub>2</sub> film.

Using the transmission line method (TLM) structure as shown in Figure 4.10a, the normalized contact resistance of  $45.9 \pm 22.1 \text{ k}\Omega$ -cm and the sheet resistance of  $11.8 \pm 3.7 \text{ M}\Omega$  at  $V_{gs} = -50 \text{ V}$  for the 6 nm thick polycrystalline MoS<sub>2</sub> film (Figure 4.10b) was calculated. The high sheet resistance of the film due to randomly distributed grain to grain contacts affects the electrical transport due to scattering across grain boundaries and leads to lower mobility. Transistor switching behaviour was observed for devices with MoS<sub>2</sub> film thicknesses thinner than 9 nm, while devices with thicker films showed a resistor-like I-V characteristic. Higher film thicknesses contain more pathways for the current to go and the gate voltage is not able to deplete the conducting channel due to the carriers generated by defects.

The electrical behaviour of fabricated TFT devices is strongly determined by the Metal/MoS<sub>2</sub> contact, MoS<sub>2</sub> film and MoS<sub>2</sub>/SiO<sub>2</sub> interface. In this work, Au (work function ~ 5.1 eV) has been used as a source-drain contact for MoS<sub>2</sub> (~ 4.7 eV), which is reported to result in *n*-type behaviour [85,86]. However, the TFT exhibits a *p*-type behaviour which implies the influence of metal/MoS<sub>2</sub> interface is not the dominating factor. Point defects [79] (vacancies, anti-sites, etc.) in the MoS<sub>2</sub> films can result in localized states which adversely affects the transport. It has been reported from experiments that local variation in defects and impurities concentration leads to spatial variation in MoS<sub>2</sub> properties. McDonnell et al. demonstrated MoS<sub>2</sub> with defect

concentration <1% exhibited n-type behaviour (S vacancy or Mo excess), and *p*-type behaviour can be observed for 5% and more of defects due to excess S (anti-sites, interstitials) [87]. The excess sulfur leads to lower binding energies (B.E.) of the Mo 3d and S 2p. Our solution processed MoS<sub>2</sub> films exhibit 8.5% excess S than stoichiometric MoS<sub>2</sub>. In addition, the binding energy of the latter peaks in the XPS spectra is also lower compared to the spectra from CVD grown *n*-type MoS<sub>2</sub> films. As indicated in the XPS spectra, the MoS<sub>2</sub> films have excess sulfur in the MoS<sub>2</sub>, which determines the electrical transport and results in *p*-type conducting behaviour.



Figure 4.11 Density of states (DoS) of a 4-layer MoS<sub>2</sub> film on (a) defect-free SiO<sub>2</sub> substrate and on (b) defective SiO<sub>2</sub> substrate obtained using DFT analysis.

Another reason for the observed *p*-type behaviour could be the presence of localized trap states (immobile ionic charges, oxygen dangling bonds or foreign impurities) at the MoS<sub>2</sub>/SiO<sub>2</sub> interface as reported by Dolui et al. [88]. These trap states pin the Fermi-level of the MoS<sub>2</sub>/SiO<sub>2</sub> system just below the valence band maxima as shown in Figure 4.11b. In this work, high annealing temperatures of 900 °C can lead to formation of oxygen dangling bonds at the MoS<sub>2</sub>/SiO<sub>2</sub> interface. It should be noted, that the *p*-type behaviour of MoS<sub>2</sub> films on SiO<sub>2</sub> as reported earlier using various, different synthesis techniques [50,89,90] seems to have the excess sulfur in common. Moreover, the substrate/MoS<sub>2</sub> interface during the growth conditions determine the conducting behaviour of the MoS<sub>2</sub> film.

# **4.4 Conclusion**

In summary, this novel approach demonstrated fabrication of large area, solution processed MoS<sub>2</sub> films using a combination of spin-coating for Mo-precursor and high temperature annealing in the presence of sulfur. The fabrication process allows uniform growth of MoS<sub>2</sub> films with controllable film thickness over the whole substrate. Raman spectra, AFM topography and HR-STEM images indicate the fabricated MoS<sub>2</sub> are of high crystallinity with a 2H-MoS<sub>2</sub> structure. The film is polycrystalline in nature with each grain having a highly crystalline layered structure. The stoichiometry and crystallinity of the MoS<sub>2</sub> film are strongly dependent on the annealing temperature attributed to the reduction of Mo-precursor and sulfur diffusion. The electrical measurement of bottom-gate top-contact transistors exhibited a dominant *p*-type semiconductor behaviour with a current on/off ratio of  $10^2$  and field effect mobility of 0.03 cm<sup>2</sup>/Vs. Electrical performance of the obtained TFTs is attributed to excess sulfur and the polycrystalline nature of the MoS<sub>2</sub> film. The presented low-cost, non-vacuum and facile synthesis method is suitable for preparation of large area transition metal dichalcogenide thin films for various applications.

# Chapter 5: EDLTs fabricated based on solution processed MoS<sub>2</sub> on sapphire

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# **5.1 Introduction**

In this chapter, an improved method to synthesize layered MoS<sub>2</sub> thin films based on solution processed precursor via spin-coating is presented. A unique two-step annealing process was performed for the chemical conversion of the as-deposited Moprecursor films to MoS<sub>2</sub> in the presence of sulfur followed by post-annealing treatment. This results in an improved crystallinity, uniformity of the multi-layered films together with an increase of the MoS<sub>2</sub> grain size. Furthermore, the growth of MoS<sub>2</sub> films using bottom-up approach is also strongly dependent on the substrate choice, e.g. Si/SiO<sub>2</sub> and sapphire substrate attributed to the crystallinity of substrate. This is verified by the electrical performance of ionic liquid (IL) gated TFTs based on MoS<sub>2</sub> layers grown on different substrates with different annealing conditions. ILgated MoS<sub>2</sub> TFT devices exhibited *n*-type semiconducting behaviour with a high current on/off ratio and competitive mobility. Density functional theory (DFT) analysis demonstrates the *n*-type response is attributed to the intercalation of excess molybdenum atoms between the MoS<sub>2</sub> layers by acting as donors. Our findings show the film morphology, crystallinity, chemical composition and electrical performance are dictated by the MoS<sub>2</sub> film formation under various processing condition. The

proposed route provides an alternative method for low-cost and scalable production of MoS<sub>2</sub> thin films via a wet-chemical approach.

# **5.2 Experiment**

#### 5.2.1 MoS<sub>2</sub> Films Preparation

Molybdenum(V)-chloride (12.5 mg, 99.99%, Sigma Aldrich) was dissolved in 1-Methoxy-2-propanol (1 mL, 99.97%, CG Chemikalien GmbH & Co. KG) solvent and stirred overnight to form a stable precursor solution. The solution was spin-coated at 3000 rpm for 60 s on (a) silicon substrates (highly n-doped) with 90 nm thick SiO<sub>2</sub> (Si-Mat) and (b) c-plane (0001) sapphire substrates (99.998%, Siegert Wafer GmbH) to form uniform films over a large area  $(2 \times 2 \text{ cm}^2)$ . The substrates were cleaned in an ultrasonic bath using a mixture of acetone and isopropanol (1:1), and pure isopropanol for 2 and 10 minutes, respectively followed by rinsing with deionized water. The substrates were then dried with nitrogen (N<sub>2</sub>) and baked on a hot plate at 120 °C for 5 minutes before exposing them to UV-Ozone for 10 minutes before each experiment. This pre-treatment results in a hydrophilic surface which promotes improved coating behaviour. The coated samples were then pre-annealed at 150 °C for 10 minutes to remove the residual solvent from the coated film. Both the precursor solution preparation and pre-annealing were carried out in N<sub>2</sub> environment. The coated samples and a quartz boat holding pure sulfur (4.6 g, 99.9995%, Alfa Aesar) were then placed in the middle and near the edge (upstream) of the tube furnace (Friatec, Al<sub>2</sub>O<sub>3</sub> tube), respectively as shown in Figure 5.1. After purging the Al<sub>2</sub>O<sub>3</sub> tube with Argon (Ar) gas, the gas flow was changed to 2.4% H<sub>2</sub> in Ar while the furnace temperature was gradually increased from room temperature to target temperature (900 °C or 980 °C) with a heating rate of 50 °C/min. The temperature was maintained at the final annealing temperature for 60 minutes before cooling down to room temperature in the presence of Ar. The experimental procedure used for synthesizing MoS<sub>2</sub> thin films from Mo-precursors is detailed in our previous work [68]. Finally, post-annealing treatment was performed on the sulfurized films covered with blank sapphire or Si substrates (Figure 5.1) at 980 °C for 60 minutes in Ar gas only to avoid unwanted reduction of the sulfur in the presence of H<sub>2</sub>.



Figure 5.1 Schematic illustration of the synthesis of MoS<sub>2</sub> films from liquid phase using two-step annealing.

#### 5.2.2 Characterization of MoS<sub>2</sub> Films

The deposited films were characterized by different techniques described in section 2.5 to observe morphology and crystalline structures and to investigate film composition and crystallinity. Using a scalpel, the film surface was scratched to determine the film thickness using AFM. The TEM planar view was obtained by using the Nitto blue tape (BT-150E-CM, Nitto Denko Corporation) to peel off the MoS<sub>2</sub> from the sapphire substrate and transferred directly onto a lacey carbon film copper TEM grid. Geological MoS<sub>2</sub> single crystal was purchased from SPI supplies and used as a reference for characterization of synthesized MoS<sub>2</sub> films.

# 5.2.3 Fabrication of IL-gated MoS<sub>2</sub> TFTs

*Preparation of IL gel*: The IL N, N-Diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI, 98.5%, Mw = 426.40, Sigma Aldrich) has a electrochemical window of about 6.5 V (cathodic limit -3.0 V, anodic limit +3.5 V), viscosity of 120 mPa-s at 20 °C and ionic conductivity of 2.62 mS/cm [91]. The large electrochemical window allows DEME-TFSI to be used commonly in electric double layer transistors (EDLTs) for superior electrostatic charge accumulation. The

host polymer for the IL gel dielectric Poly(vinylidene fluoride-co-hexafluoropropylene (PVDF-HFP, Mw ~ 400000, Sigma Aldrich) provides DEME-TFSI with a polymeric matrix to stabilize the ions. For the fabrication of the IL gel tape as shown in Figure 5.2a, DEME-TFSI was mixed with PVDF-HFP pellets dissolved in acetone (99.5 %, Sigma Aldrich) with a ratio of 1:2:10. The mixture was kept stirring on the hot plate at 70 °C for 1 h, prior to spin-coating at 1000 rpm for 60 s on a hexamethyldisilazane (HMDS) treated Si/SiO<sub>2</sub> substrates ( $2 \times 2 \text{ cm}^2$ ). The IL gel coated substrates as shown in Figure 5.2a were then annealed at 90 °C in a vacuum oven overnight to remove residual solvents and moisture. This prevents the formation of chemically reactive protons and hydroxyls through the electrolysis of water [92]. The thickness of the obtained IL gel determined by profilometry is ~ 4 µm. The prepared IL gel samples were stored inside the glove box or vacuum oven at room temperature.



Figure 5.2 (a) Schematic illustration of the synthesis of ionic liquid gel tape. (b) Optical image of ILgated MoS<sub>2</sub> transistor fabricated on sapphire and Si substrates.

*Fabrication of IL-gated device*: Top-gate top-contact IL-gated TFTs based on solution processed MoS<sub>2</sub> thin films were fabricated with the IL gel tape on sapphire and Si/SiO<sub>2</sub> substrates as shown in Figure 5.2b. Firstly, 40 nm thick gold was deposited by e-beam evaporation using a shadow mask to define source and drain contacts for the transistor layout. Gold contacts were chosen due to chemical inertness and noble properties. Secondly, a square IL gel tape was cut by a razor and placed on top of the

MoS<sub>2</sub> film with the source and drain contacts. Finally, a 1 mm thick gold film (cut-off from a gold sputter target) was placed on top the IL gel as the top-gate electrode. This process of "cut and stick" IL gels as high capacitance gate dielectrics is a modification of a process developed by Lee et al. [93]. The transistor performance was carried out on a probe station (SÜSS MicroTec) and controlled by an in-house Stala measurement setup described in section 2.5.7.

### 5.2.4 Theoretical Calculation of MoS<sub>2</sub> Films

First-principle electronic structure calculations were carried out within the framework of density-functional theory (DFT), using plane-wave basis set and projector-augmented wave formalism (PAW) [94], as implemented in Quantum ESPRESSO package [95]. The exchange and correlation effects were treated with the generalized-gradient (GGA) approximation of Perdew, Becke and Ernzerhof (PBE) [96]. The energy cutoffs of 60 Ry and 600 Ry were used for wave-function and charge-density expansion, respectively. All structures were relaxed with the threshold of 0.02 eV/Å for atomic forces and 0.5 kbar for stresses. Brillouin zone of pristine MoS<sub>2</sub> unit cell was sampled with a  $12 \times 12 \times 4$  uniform k-mesh, while the k-meshes for the supercells used in defect study were scaled accordingly (e.g. a  $6 \times 6 \times 4$  k-mesh was used for a  $2 \times 2 \times 1$  supercell). In addition, the semi-empirical potential of Grimme [97] was used to account for the dispersion corrections.

# **5.3 Results and Discussion**

# 5.3.1 Growth of MoS<sub>2</sub> Films on Sapphire and its Comparison to Silicon Substrate

The SEM images in Figure 5.3a-d illustrates the surface morphology of the synthesized MoS<sub>2</sub> thin films on Si and sapphire substrates having different film thicknesses under 900 °C annealing temperature. MoS<sub>2</sub> films grown on Si substrates (Figure 5.3a-b) shows the formation of crystalline grains [68] that are randomly oriented most likely due to the amorphous nature of the SiO<sub>2</sub> substrate (absence of commensurability of the SiO<sub>2</sub> with MoS<sub>2</sub> lattice) and low surface energy of SiO<sub>2</sub> surface (287 mJ/m<sup>2</sup>) [98,99]. This leads to the formation of grain boundaries and pinholes in 6 nm thick films (Figure 5.3a, prepared from 12.5 mg/mL) and further thickness scaling down to 3 nm (Figure 5.3b, prepared from 6.25 mg/mL) results in formation of randomly

distributed MoS<sub>2</sub> islands. Thereby restricting the usefulness of our solution processed MoS<sub>2</sub> films grown on Si substrates due to limited thickness scaling and extreme difficulty in the spatial arrangement of crystalline grains in a commercially viable device.



Figure 5.3 Surface morphology of the as-deposited MoS<sub>2</sub> films from liquid phase. SEM images of MoS<sub>2</sub> films grown on silicon and sapphire substrates for (a, b) 6nm and (c, d) 3 nm film thickness. AFM images of 6 nm MoS<sub>2</sub> films on (e) amorphous silicon dioxide wafer and (f) c-plane sapphire crystalline substrate.

This implies the substrate plays a crucial role in the bottom-up growth of crystalline MoS<sub>2</sub> films from the liquid phase. To mitigate this issue, MoS<sub>2</sub> thin films were synthesized on c-plane (0001) sapphire substrates due to commensurability of the sapphire lattice with MoS<sub>2</sub> which exhibits a small lattice mismatch of 0.4% [100]. Unlike SiO<sub>2</sub>/Si substrates, the sapphire has a higher surface energy ( $638 \text{ mJ/m}^2$ ). Thus, MoS<sub>2</sub> grown thin films on the sapphire substrate exhibited the defect-free growth and less number of grain boundaries, as well as lower stress and strain stored at the interface due to the comparable thermal expansion coefficient between MoS<sub>2</sub> films and sapphire substrate [98,99]. This favours surface wettability when forming continuous and flat films which probably enhances the crystallinity along the c-axis orientation. Figure 5.3c-d illustrates the surface morphology of synthesized MoS<sub>2</sub> thin films grown on sapphire substrates which shows improved film formation, polycrystalline in nature for varying film thicknesses. Since the contrast in SEM images indicates variation in topography, i.e. different numbers of stacked layers in a layered structure, it confirms that the as-deposited MoS<sub>2</sub> film (Figure 5.3d) consists of region with some thicker and thinner layers. The small white (AFM topography) particles in Figure 5.3d were analyzed by Raman spectroscopy, and most probably represent delaminated MoS<sub>2</sub> films due to stress or weakened interaction with the sapphire under high thermal budget. These were observed only for films thinner than 4 nm.

AFM measurements were performed to shed more light on the surface morphology of the chemically synthesized MoS<sub>2</sub> films on different substrates, i.e. amorphous and crystalline. Figure 5.3e-f illustrates the AFM topography images obtained from 6 nm thick MoS<sub>2</sub> films grown on Si and sapphire respectively when annealed at 900 °C. Films synthesized on amorphous Si (Figure 5.3e) and crystalline sapphire substrates (Figure 5.3f) demonstrated an root mean square (rms) roughness of 1.143 nm and 0.485 nm, respectively. The higher film roughness on the SiO<sub>2</sub> substrate is attributed to the low surface energy of SiO<sub>2</sub> surface and its poorer surface wettability than in the case of the sapphire substrate. Therefore, scaling below 4 nm on Si substrate poses a bottleneck which results in the formation of pinholes and agglomerates due to minimization of film surface energy compared to sapphire.

#### 5.3.2 Size, Thickness, Crystal Quality and Influence of Post-Thermal Treatment

The improved film growth on sapphire allowed us to scale the film thickness further down to 1 - 3 monolayers (ML). This was obtained through successive dilution of the Mo-precursor solution from 12.5 mg/mL to 3.125 mg/mL. In addition, the effect of annealing temperature and post-annealing treatment on the ultra-thin MoS<sub>2</sub> films on sapphire was investigated.



Figure 5.4 AFM topography of MoS<sub>2</sub> films processed on sapphire at (a) 900 °C, (b) 980 °C and (c) 900 °C with an additional post-annealing at 980 °C. Corresponding section profile of MoS<sub>2</sub> on sapphire annealed at (d) 900 °C, (e) 980 °C and (f) 900 °C with an additional post-annealing at 980 °C.

Figure 5.4a-b illustrates the AFM topography of MoS<sub>2</sub> films processed on sapphire with 3.125 mg/mL precursor solution at 900 °C, 980 °C and 900 °C with an additional postannealing treatment at 980 °C respectively. MoS<sub>2</sub> film synthesized at 900 °C (Figure 5.4a) shows the formation of homogeneously distributed numerous small grains. These films exhibit an average film thickness of ~ 2.43 nm (Figure 5.4d) with an rms roughness of 0.27 nm. MoS<sub>2</sub> film processed at a higher annealing temperature of 980 °C (Figure 5.4b) demonstrated the formation of larger grains attributed to the cohesion of smaller grains resulting in improved crystallinity. The obtained section profile (Figure 5.4e) from Figure 5.4b shows the formation of both monolayer (~ 0.63 nm) and bilayer (~ 1.25 nm) MoS<sub>2</sub> with an average film thickness of ~ 1.47 nm. However, a significant portion of the MoS<sub>2</sub> film is also desorbed from the surface due to the high annealing temperature thereby, exposing the underlying sapphire substrate. To mitigate this issue, annealing of the MoS<sub>2</sub> at 900 °C followed by additional post-annealing treatment at 980 °C to minimize surface desorption of MoS<sub>2</sub> film was performed. Figure 5.4c shows the topography of MoS<sub>2</sub> films with improved surface coverage and larger grains. The grains in these films form a connected channel which is essential for fabrication of MoS<sub>2</sub> TFTs. These films also show the formation of both monolayer (~ 0.68 nm) and bilayer (~ 1.32 nm), in addition to trilayer (~ 2.07 nm) MoS<sub>2</sub> as shown in the section profile in Figure 5.4f.

This shows the MoS<sub>2</sub> film thickness and rms roughness dependence on different annealing temperatures at 900 °C, 980 °C and 900 °C with additional post-annealing treatment at 980 °C. The latter two exhibited lower film thicknesses due to the formation of one to three-layer MoS<sub>2</sub>. Lowest film thickness (1.47 nm) and roughness (0.205 nm) was observed for 980 °C annealed films due to desorption of the film. In contrast, post-anneal treated samples showed slight higher roughness (0.242 nm) owing to the formation of tiny MoS<sub>2</sub> particles as shown in Figure 5.3d and Figure 5.4c. Similar behaviour was exhibited by MoS<sub>2</sub> films grown on Si substrates with an increase in grain size through the cohesion of smaller grains as the annealing temperature was increased from 900°C to 980 °C. Post-annealing treatment of these films resulted in lower roughness with improved crystallinity. To delineate the MoS<sub>2</sub> film growth, crystallinity and to understand the layer formation on sapphire, TEM studies were performed.

MoS<sub>2</sub> crystal structure and layer uniformity can be assessed by TEM analyses as reported e.g. for CVD wafer scale synthesis [11,47,49]. In this work, chemically synthesized MoS<sub>2</sub> films on sapphire annealed at 900 °C exhibited crystalline structures when viewed from the top (Figure 5.5a) as verified by the TEM analyses. Higher magnification of the film (Figure 5.5b) shows the formation of uniform crystalline layers only interrupted by grain boundaries. Figure 5.5c illustrates the corresponding diffraction pattern of Figure 5.5b verifying the film to be poly-crystalline attributed to grain orientation or intra-grain dislocations [71,72]. The distinct bright spots in the diffraction pattern (Figure 5.5c) demonstrates the high crystallinity of the film on sapphire due to the formation of larger grain size as compared to silicon [68].

Sapphire, therefore, provides the ideal condition for bottom-up growth of solution processed layered MoS<sub>2</sub> films.



Figure 5.5 TEM analysis of MoS<sub>2</sub> film grown on sapphire processed at 900 °C. (a, b) Planar view reveals distinct grains and boundaries, and (c) shows its diffraction pattern. (d) X-ray diffraction spectra of MoS<sub>2</sub> films for different annealing process, bulk MoS<sub>2</sub> and sapphire substrate.

The crystallinity of these wet chemical processed MoS<sub>2</sub> films on sapphire under different annealing temperatures were further investigated by X-ray diffraction measurements. Figure 5.5d illustrates the  $\theta$ - $\theta$  scans of 27 nm thick MoS<sub>2</sub> films annealed at 900 °C, 980 °C, 900 °C with an additional post-annealing treatment at 980 °C, bare sapphire and for geological bulk MoS<sub>2</sub> crystal. Additionally, reference peak positions (2 $\theta$ ) in dark cyan colour for 2H-MoS<sub>2</sub> powder is provided for comparison. The reference bulk MoS<sub>2</sub> crystal exhibits sharp (002), (004) and (006) diffraction peaks at 2 $\theta$  = 14.4°, 29.1° and 44.2°, respectively. The diffractogram for the sample annealed at 900 °C demonstrates a distinct (002) peak at 2 $\theta$  = 14.4°, while higher order peaks (004) and (006) are barely visible thereby suggesting, that a higher annealing temperature to improve the crystallinity of the films. As expected, sample annealed at 980 °C show a sharp (002) peak with improved line width, though the higher order peaks are slightly visible indicating, the absence of long-range crystalline

order. In contrast, samples processed at 900 °C with an additional post-annealing treatment at 980 °C exhibit higher order peaks indicating long-range crystalline order. Thereby, improving the MoS<sub>2</sub> film structural quality and crystal orientation. The very sharp diffraction peaks in the diffractogram are due to the underlying crystalline sapphire substrate.

An average distance of 6.15 Å between two MoS<sub>2</sub> layers in a 2H structure was calculated from the (002), (004) and (006) diffraction peaks at  $2\theta = 14.4^{\circ}$ , 29.1° and 44.2°, similar to reports found in the literature [26,77]. Using Scherrer equation [63], the crystallite size in the film from the line width of the diffraction peaks was determined. The (002) peak with the highest intensity was utilized to calculate the crystallite size. Samples annealed at 900 °C, 980 °C, 900 °C with an additional post-annealing treatment at 980 °C demonstrated a crystallite size of 11 nm, 18 nm and 32 nm, respectively, as an effective thickness of the grains in the direction perpendicular to the diffraction plane (002). The increase in crystallite size further re-iterates that the two-step annealing process significantly improves the film crystallinity thus forming MoS<sub>2</sub> with larger grains.

Formation and elemental composition of the as-grown continuous MoS<sub>2</sub> films obtained through solution phase processing under various annealing temperatures were further investigated by Raman, and X-ray photoelectron spectroscopy (XPS), respectively. Raman spectra of as-deposited MoS<sub>2</sub> thin films as well as geological MoS<sub>2</sub> crystal were collected for comparisons. Figure 5.6a shows the Raman spectra obtained from asdeposited MoS<sub>2</sub> films with varying thicknesses (3.125, 6.25 and 12.5 mg/mL Moprecursor solution) on sapphire substrate using two-step annealing process. Though group theory predicts four Raman active modes for 2H-MoS<sub>2</sub> [59], only two typical Raman active modes are observed in this spectral range: the out-of-plane vibration (caxis) of S atoms (A<sub>1g</sub>) with a Raman shift of ~407 cm<sup>-1</sup> and the in-plane vibration (basal plane) of Mo and S atoms (E<sup>1</sup><sub>2g</sub>) at ~383.6 cm<sup>-1</sup> [58]. This confirms the formation of semiconducting 2H-MoS<sub>2</sub> layers.



Figure 5.6 Optical characterization of fabricated MoS<sub>2</sub> thin films. (a) Raman spectra of varying film thicknesses of MoS<sub>2</sub> with two-step annealing process. (b) Raman spectra of MoS<sub>2</sub> films and (c) FWHM of A<sub>1g</sub> and E<sup>1</sup><sub>2g</sub> vibrating modes obtained after different annealing temperatures and process. XPS spectra of fabricated MoS<sub>2</sub> film on sapphire substrate processed at 900 °C with an additional postannealing at 980 °C: (d) and (e) corresponds to the binding energy of Mo 3d and S 2s, and S 2p core levels respectively.

Figure 5.6a also illustrates the blue-shift and red-shift for  $E_{2g}^{1}$  and  $A_{1g}$  modes respectively, with scaling of the film thickness which also results in a weaker signal. The separation  $\Delta \omega$  between  $A_{1g}$  and  $E_{2g}^{1}$  modes (shown in the inset table) corresponds to the number of layers in the MoS<sub>2</sub> film [58]. Due to the formation of mono to trilayer films (Figure 5.4b-c) obtained from this solution process, the typical  $\Delta \omega = 23.7 \text{ cm}^{-1}$ separation for 1.5 nm thin MoS<sub>2</sub> films could be observed. Moreover, MoS<sub>2</sub> films with thickness  $\geq 4$  nm behave as bulk like the reference geological MoS<sub>2</sub> crystal. Figure 5.6b shows the Raman spectra obtained from as-deposited MoS<sub>2</sub> films (3.125 mg/mL Moprecursor solution) under different annealing temperatures. The lower growth temperatures (900 °C) exhibited a lower peak intensity of  $E^{1}_{2g}$  and  $A_{1g}$  attributed to relatively low crystallinity and structural film property compared to the bulk geological MoS<sub>2</sub> crystal [50]. While solution processed MoS<sub>2</sub> films synthesized on SiO<sub>2</sub> substrate demonstrated even lower peak intensity [68]. In samples processed at 980 °C, the overall peak intensity was increased but was still lower than the bulk geological MoS<sub>2</sub>. Whereas samples grown at 900 °C with an additional post-annealing treatment at 980 °C, showed 1.2 times higher intensity than samples only annealed at 980 °C. This improvement in the crystallinity of the films with higher post-annealing temperature is essential for the formation of high-quality MoS<sub>2</sub>.

The in-plane vibration  $(E^{1}_{2g})$  is dependent on the nanoscale and random orientation of the grains in the film (Figure 5.3d and 5.5a). Thus, demonstrating a lower Raman peak intensity compared to geological MoS<sub>2</sub> crystal, where the grain size is much larger, typically in the range of few microns or more.

Figure 5.6c presents the full width at half maxima (FWHM) for both Raman modes as a function of annealing temperature. The FWHM decreases with increase in temperature attributed to the improved crystallinity of the film. Thus, the MoS<sub>2</sub> films formed after post annealing treatment at 980 °C with layer thickness  $\leq$  3 monolayers, demonstrated reduced line width owing to a higher degree of order and crystallinity also seen in Figure 4d. The improved FWHM with post annealing treatment reduces the gap to the reference value of geological MoS<sub>2</sub> crystal (FWHM A<sub>1g</sub> ~ 1.97 cm<sup>-1</sup> and FWHM E<sup>1</sup><sub>2g</sub> ~ 1.7 cm<sup>-1</sup>). The remaining difference is ascribed to the polycrystalline nature of the films with grain boundaries and defects. Additionally, the broader line width of the A<sub>1g</sub> mode from the samples can also be used as an indicator of doping levels [73] which indicates that our synthesized MoS<sub>2</sub> is more doped than the geological MoS<sub>2</sub> crystal counterpart. This could presumably be due to an excess or deficit of sulfur and molybdenum content. Eventually, the intensity ratio of E<sup>1</sup><sub>2g</sub>/A<sub>1g</sub> is a convolution of doping and crystallinity of the film.

XPS was conducted to explore the chemical bonding state and stoichiometry of MoS<sub>2</sub> film grown on sapphire substrate. Figure 5.6d-e exhibits Mo 3d, S 2s, and S 2p core level spectra which were evaluated using Shirley background and a symmetric peak shape defined by a convolution of Gauss and Lorentz peaks for peak fitting. The spectra reveal the existence of Mo<sup>4+</sup> peaks at 229.7 eV ( $3d_{5/2}$ ) and 232.8 eV ( $3d_{3/2}$ ), and S<sup>2-</sup> peaks at 162.5 eV (2p<sub>3/2</sub>) and 163.7 eV (2p<sub>1/2</sub>). These binding energies are similar to the reported values for MoS<sub>2</sub> crystals [78,101,102]. The absence of a peak at ~ 236 eV, which corresponds to the  $Mo^{6+}$  (3d<sub>3/2</sub>), signifies that Mo oxidation is negligible [102]. Similarly, no S 2p peak was observed between 168 and 170 eV, indicating that the sulfur atoms are also not oxidized. These results indicate that the synthesized MoS<sub>2</sub> layers were composed only of Mo and S species. Samples annealed in Ar/H<sub>2</sub> and sulfur environment at 900 °C, 980 °C and 900 °C with an additional postannealing treatment at 980 °C demonstrated a chemical composition of Mo:S ~ 1:1.91, 1:1.76 and 1:1.85, respectively. The poor chemical composition of 980 °C annealed samples is attributed to the partial desorption of the sulfur at high temperatures as seen in Figure 3b. It is also observed that the sulfur concentration is 7.5% lower in the post-anneal treated films, in comparison to ideal 1:2 stoichiometry. This can give rise to regions with point defects which are either sulfur-deficient (S-vacancies Vs) or molybdenum-rich (Mo-interstitials Moi, anti-sites Mos) in the MoS<sub>2</sub> film as reported earlier [79,80,87]. These point defects with low formation energy under Mo-rich conditions results in localized states close to the conduction band. They can act as scattering and trapping centers which could affect the electrical properties of the solution processed MoS<sub>2</sub> films.

In contrast, processing in the absence of H<sub>2</sub> with Ar and sulfur environment at 900 °C resulted in a poor Mo:S atomic ratio ~ 1:2.94 attributed to excess diffusion of sulfur. The presence of H<sub>2</sub> coupled with the high-temperature annealing aids in the reduction of Mo-precursor and controlled sulfurization of the reduced film (Figure 5.1). In addition, the reducing environment inhibits further oxidation of the synthesized film (Figure 5.6d-e). Therefore, H<sub>2</sub> plays a vital role in the film formation as unreduced impurities are suspected to interrupt the crystal structure and degrade the electrical properties of the MoS<sub>2</sub>.

#### 5.3.3 Electrical Characterization of IL-gated MoS<sub>2</sub> TFTs

After the growth and characterization of the MoS<sub>2</sub> films with different annealing conditions on sapphire substrates, their electrical performance was evaluated by fabricating top-gate top-contact IL-gated TFTs based on solution processed MoS<sub>2</sub> films.



Figure 5.7 (a) Schematic cross-section diagram of top-gate top-contact IL-gated MoS<sub>2</sub> TFT illustrating the formation electric double layer under applied positive gate bias. (b) Optical image of the fabricated IL-gated MoS<sub>2</sub> TFT on sapphire substrate. (c) Time dependence of *I*<sub>d</sub> for transistor with pure IL under applied gate bias. (d) Time dependence of *I*<sub>d</sub> for IL-gated MoS<sub>2</sub> TFT under applied gate bias. (e) Output curve of IL-gated MoS<sub>2</sub> TFT with two-step annealing process. (f) Transfer curve of IL-gated MoS<sub>2</sub> TFT processed at 900 °C, 980 °C and 900 °C with an additional post-annealing at 980 °C.

Figure 5.7a shows the schematic view of the IL-gated TFT with DEME-TFSI as the dielectric layer for superior electrostatic charge accumulation [103]. DEME-TFSI has been commonly used to study the electrical properties of exfoliated MoS<sub>2</sub> nanosheets [84,91]. Unlike conventional transistors, most EDLTs require a voltage sweep rate < 50 mV/s for ionic diffusion in response to the bias voltage. The slow accumulation of high-density carriers limits the switching performances of EDLTs and hence unlikely to be used directly in industrial applications. In contrast, the relatively high dielectric constant [104] of ILs might improve device performance as observed with HfO<sub>2</sub> [30] and Al<sub>2</sub>O<sub>3</sub> [83]. Therefore, IL gating of TFTs based on solution processed MoS<sub>2</sub> presents an interesting yet unexplored avenue of research.

To comprehend the effect of IL gel on the electronic properties of the channel, an ILgated TFT without MoS<sub>2</sub> layer was fabricated and its electrical characteristics were measured as shown in Figure 5.7c. As expected, this transistor with only IL gel as the active layer demonstrated no flow of current through the IL gel with applied gate-tosource voltage ( $V_{gs}$ ) during device operation. This is attributed to the absence of conductive paths within the IL gel resulting in an insulating behaviour. The gate voltage ( $V_{gs}$ ) induced behaviour of the IL gel is demonstrated with a time dependence measurement as shown in Figure 5.7d for an IL-gated TFT with MoS<sub>2</sub> (Figure 5.7a-b) as can be seen from the current transient. The transistor was operated with a duty cycle of 50% and period 200 s. With  $V_{gs} = 0$  V (gate off), no device current (Id) was observed while  $V_{gs} = +3$  V (gate on) exhibited an increase in  $I_d$  due to the accumulation of induced charges in MoS<sub>2</sub>. The drain current  $I_d$  reaches a steady state in ~ 50 s thereby demonstrating the IL gel can endure a maximum  $V_{gs}$  sweep rate of 60 mV/s. Therefore, for all future measurements, a lower  $V_{gs}$  sweep rate of 25 mV/s was used.

Figure 5.7e shows the output characteristics of a post-annealing treated MoS<sub>2</sub>.  $I_d$  as a function of applied drain-to-source voltage ( $V_{ds}$ ) of an IL-gated TFT for different applied  $V_{gs}$  is plotted. The linear regime of transistor operation ( $V_{ds} < 0.1$  V) in the output characteristics suggests the absence of a significant barrier for charge carrier injection. The current  $I_d$  distinctly increases as  $V_{ds}$  increases for a positive  $V_{gs}$ , exhibiting an *n*-type semiconducting behaviour which is also observed in naturally grown MoS<sub>2</sub> crystal [105]. No current saturation is observed since the device operates

in the linear regime. The total resistance calculated from the slope of the output characteristics in the low-bias region ( $V_{ds} < 0.1 \text{ V}$ ) is 0.727 m $\Omega/\Box$  at  $V_{gs} = 3 \text{ V}$  for the IL-gate configuration. Thereby, indicating IL-induced Schottky barrier thinning which significantly reduces the contact resistance resulting in increased current  $I_d$  [106].

Figure 5.7f shows the transfer characteristics ( $I_d$  versus  $V_{gs}$ ) of IL-gated TFTs on MoS<sub>2</sub> processed at 900 °C, 980 °C and 900 °C with additional post-annealing treatment at 980 °C on sapphire substrate measured at a drain-source voltage  $V_{ds}$  of 0.25 V. Among the different annealing temperatures, MoS<sub>2</sub> films synthesized at 900 °C with additional post-annealing treatment at 980 °C demonstrated the highest  $I_d$ . This is attributable to improved crystallinity, enhanced grain size and surface coverage with reduced voids as seen in Figure 3c and Figure 4d. At  $V_{gs}$  = -3 V, the MoS<sub>2</sub> channel of the IL-gated TFT was turned off with an OFF-state  $I_d \sim 1.99 \times 10^{-9}$  A while the ON-state current  $I_d$  at  $V_{gs}$  = +3 V was ~ 1.65 × 10<sup>-3</sup> A, thus yielding an on/off current ratio ~ 8.29 × 10<sup>5</sup>. As  $V_{gs}$  increases from -3 V to +3 V, the channel conductance rises from 0.008 µS to 6600 µS, implying modulation of the Fermi level within the band gap. It is also observed the device operates in the linear regime from which the linear field-effect mobility of the IL-gated TFT can be determined by using the formula from equation 2.3 [107]

$$\boldsymbol{\mu}_{lin} = \left(\frac{L}{WC_{IL}}\right) \left(\frac{1}{V_{ds}} \cdot \frac{\Delta I_d}{\Delta V_{gs}}\right) \qquad Eq. \ 5.1$$

where  $V_{ds}$  is the drain-source voltage (0.25 V); L is the channel length (55 µm) and W is the gated channel width (5000 µm). The IL gate capacitance  $C_{IL} = \varepsilon_0 \varepsilon_{IL}/d$  (6.42 µF/cm<sup>2</sup>) was obtained using  $\varepsilon_0 = 8.854 \times 10^{-12}$  F/m;  $\varepsilon_{IL} = 14.5$ , dielectric constant of DEME-TFSI and d ~ 2 nm, electrostatic screening thickness in the IL, which agree with values reported in the literature [103,104,108]. Fabricated devices with post-annealing treated MoS<sub>2</sub> films deposited from solution phase exhibited field-effect mobility ~ 12.07 cm<sup>2</sup>/Vs for  $V_{gs} = +3$  V. This device mobility is 1 – 2 orders of magnitude higher than the typical range for most of the previously reported wetchemically synthesized [22,70,85,109] and exfoliated [66,82,110] MoS<sub>2</sub>, and CVD grown [19,50,81,102] MoS<sub>2</sub> films containing numerous grains. It is worth to note that the device performance of our polycrystalline MoS<sub>2</sub> film is comparable with the devices prepared from mechanical exfoliation of single crystal MoS<sub>2</sub> [105,111]. This information is summarised in Table 5.1.

		Field-effect		
Serial #	Deposition method	mobility	Ion/Ioff ratio	Reference
		$(cm^2/Vs)$		
1	solution processed	12.07	~ <b>10</b> <sup>6</sup>	this work
2	vacuum filtration	0.117	-	[82]
3	spray-coating	10-4	$\sim 10^{2}$	[66]
4	exfoliation	0.423	$\sim 10^{2}$	[110]
5	dip-coating - CVD	4.7	$\sim 10^{5}$	[19]
6	e-beam - CVD	0.004 - 0.04	-	[50]
7	sputtering - CVD	0.20	$4 \times 10^2$	[81]
8	e-beam - CVD	0.8	$\sim 10^{5}$	[102]
9	wet-chemical	0.24	$\sim 10^4$	[22]
10	wet-chemical	0.1	$\sim 10^{2}$	[70]
11	wet-chemical	0.4	$\sim 10^{6}$	[85]
12	CVD	43	$\sim 10^{7}$	[28]
13	exfoliation	15	$\sim 10^{5}$	[105]
14	exfoliation	313	$\sim 10^{7}$	[111]

#### Table 5.1 Comparison of different MoS<sub>2</sub> based FETs.

The threshold voltage ( $V_t$ ) is determined by linear extrapolation method to ~ 1.05 V for post-anneal treated samples. By using the equation  $n_{2D} = C_{IL}(V_{gs} - V_t)/q$ , the electron carrier density is 7.82 × 10<sup>13</sup> cm<sup>-2</sup> at  $V_{gs}$  = +3 V, consistent with results reported in the literature [91]. Figure 5.7f also shows that our IL-gated MoS<sub>2</sub> channel is in a non-conductive state at  $V_{gs} < V_t$ , which may be attributed to a higher concentration of negative than positive ions adsorbed near MoS<sub>2</sub>. The increase in  $I_d$  with  $V_{gs} > V_t$ , causes accumulation of higher positive ions on the MoS<sub>2</sub> surface which leads to the formation of a conducting channel with increased electron charge carrier density in the MoS<sub>2</sub>. This formation of the EDL (~2 nm) significantly reduces the contact Schottky barrier thickness through strong band bending near the metal-semiconductor contacts [91]. Wang et al. [104] demonstrated that the transport mechanism in IL-gated MoS<sub>2</sub> transistors is characterized by Schottky emission at the

metal –  $MoS_2$  interface. Additionally, the high- $\kappa$  IL provides better screening which minimizes scattering from charged impurities and results in improved conductivity and mobility.

Annealing conditions	Field-effect mobility (cm²/Vs)	Ion/Ioff ratio	
900 °C (Ar+H <sub>2</sub> )	3.37	~ 104	
980 °C (Ar+H <sub>2</sub> )	6.01	~ 105	
900 °C (Ar+H₂) w/ 980 °C (Ar)	12.07	~ 10 <sup>6</sup>	

 Table 5.2 Comparison of IL-gated MoS<sub>2</sub> TFTs with various annealing process fabricated on sapphire substrate.

Table 5.2 compares the field-effect mobility and  $I_{on/off}$  ratio of our chemically synthesized IL-gated MoS<sub>2</sub> device on sapphire substrate under different annealing temperatures. Samples annealed at 900 °C and 980 °C exhibited lower mobility attributed to the formation of random crystalline orientation of MoS<sub>2</sub> grains (Figure 5.4a and Figure 5.5b) and voids (Figure 5.4b), respectively. The formation of numerous grain boundaries and grain to grain contact results in high resistance for the transport of charged carriers, unlike single crystalline films [28]. In addition, these samples demonstrated poor  $I_{on/off}$  ratio mainly due to the relatively large "OFF" state current passing through the bulk of the crystal [84]. This was also observed for IL-gated TFTs based on MoS<sub>2</sub> grown on Si/SiO<sub>2</sub> substrate (Figure 5.8 and Table 5.3). All these effects significantly reduce the mobility in the MoS<sub>2</sub> film.

Based on our analysis above, the superior electrical performance of the IL-gated  $MoS_2$  TFTs may be attributed to three factors: (1) The two-step annealing of the  $MoS_2$  film results in improved crystallinity, enhanced grain size and uniform surface coverage with reduced voids. (2) Thickness scaling and improved  $MoS_2$  film growth on sapphire due to lattice commensurability. (3) High- $\kappa$  IL reduces the Schottky barrier thickness and scattering from charged impurities through screening.



Figure 5.8 Electrical measurements of 6 nm thick MoS<sub>2</sub> films processed on a SiO<sub>2</sub> substrate. (a) Transfer curve and (b) output curve of IL-gated MoS<sub>2</sub> TFT with a two-step annealing process.

Annealing conditions	Field-effect mobility (cm²/Vs)	Ion/Ioff ratio	
900 °C (Ar+H₂) w/ 980 °C (Ar)	2.27	~ 104	

 Table 5.3 Electrical performance of IL-gated MoS2 TFTs with a two-step annealing process fabricated on

 SiO2 substrate.

#### 5.3.3.1 Modeling of Transport Properties

Vissenberg Matters (VM) model [112] is used to calculate the TFT charge carrier mobility from the measured IV data. The VM model is based on a percolation hopping in an exponentially distributed tail of localized DOS which can explain the  $V_{gs}$  (or charge carrier density) dependent mobility observed in semiconductors. Using the standard TFT model according to gradual channel approximation with gate voltage dependent mobility and bulk resistance parallel to the TFT, the current  $I_{ds}$  can be written as:

$$I_{ds} = \frac{W}{L} C_{IL} \frac{\mu}{V_{aa}^{\gamma}(\gamma+2)} \left[ max(\mathbf{0}, V_{gs} - V_t)^{\gamma+2} - max(\mathbf{0}, V_{gs} - V_t - V_{ds})^{\gamma+2} \right] + \frac{V_{ds}}{R_{bulk}} Eq. 5.2$$
 where

Where the  $\mu'$  is the VM mobility that changes with gate field with the power exponent  $\gamma$ ,  $V_{aa}$  is a fixed parameter chosen during the VM modelling such that the pre-factor  $\mu$  yields the VM mobility at  $V_{aa} = V_{gs} - V_t$ . For this reason, the pre-factor  $\mu$  is always associated with a particular effective gate voltage  $V_{gs} - V_t$ . It is evident larger the  $\gamma$ 

exponent; the larger is the channel energetic disorder. R<sub>bulk</sub> is the bulk resistance to account for the OFF current in the device.



Figure 5.9 Electrical measurements of IL-gated MoS<sub>2</sub> TFTs with two-step annealing process fabricated on (a) sapphire and (b) SiO<sub>2</sub> substrate. TFT IV data (blue open circles) measured at 300 K. Gate voltage dependent fit (Equation 5.2, red curve) is used to reproduce the measured data.

Annealing conditions	Substrate	MoS₂ thickness (nm)	γ	V <sub>t</sub> (V)	μ (cm²/Vs)	R <sub>bulk</sub> (MΩ)	I <sub>ON</sub> /I <sub>OFF</sub> ratio
900 °C (Ar+H <sub>2</sub> ) w/ 980 °C (Ar)	Sapphire	1.2 ± 0.65	0.26	1.05	5.32	1.25 x 10 <sup>2</sup>	~ 10 <sup>6</sup>
900 °C (Ar+H <sub>2</sub> ) w/ 980 °C (Ar)	Si/SiO <sub>2</sub>	6	0.22	1.70	1.49	9.00	~ 104

Table 5.4 Comparison of fitting parameters (with  $V_{aa} = 1$  V) obtained from the transfer curve for ILgated MoS<sub>2</sub> TFTs fabricated on different substrates.

Figure 5.9a-b illustrates the transfer curves for IL-gated MoS<sub>2</sub> TFTs synthesized on sapphire and SiO<sub>2</sub> substrates with a two-step annealing process. The hysteresis in the I-V curve (blue open circles) is attributed to the slow mobility of the ions [84] which is dependent on the applied  $V_{gs}$  sweep rate (25 mV/s). Smaller hysteresis could be realized with a lower  $V_{gs}$  sweep rate. However, a lower sweep rate will expose the device under high  $V_{gs}$  for a longer time, which would increase the possibility of a chemical reaction. Except for the hysteresis, the features in the transfer curve are consistent in the forward and backward sweep of  $V_{gs}$ .

Using equation 5.2 and 5.3 (with  $V_{aa} = 1$  V) on the measured I-V data, a numerically fitted transfer characteristic curve (red line) was obtained with good agreement. Table

5.3 shows all the calculated fitting parameters. The power exponent  $\gamma$  disorder is similar for both substrates but the  $V_t$  is higher for Si/SiO<sub>2</sub> presumably due to the increased surface roughness of MoS<sub>2</sub>. This affects the uniform accumulation of ions on the surface and thereby the charged carrier concentration in the channel. TFTs fabricated on sapphire demonstrated higher mobility and R<sub>bulk</sub> attributed to the uniform growth of ultra-thin MoS<sub>2</sub> films with low defect density which lead to a high  $I_{on/off}$  ratio ~ 10<sup>6</sup>. While the Si/SO<sub>2</sub> is plagued by the poor  $I_{on/off}$  ratio due to high "OFF" state current (low R<sub>bulk</sub>) flowing through the MoS<sub>2</sub> film. This is mainly due to the limited scaling of MoS<sub>2</sub> film thickness on Si/SiO<sub>2</sub> till 6 nm. In addition, the presence of any conducting defects such as aromatic carbons from the organic solvent and Moclusters could also affect the "OFF" state current.

Interestingly, MoS<sub>2</sub> films synthesized on Si/SiO<sub>2</sub> substrate demonstrated both *p*-type and *n*-type conduction with bottom-gate top-contact geometry (Figure 4.9c) and topgate top-contact geometry (Figure 5.9b), respectively. The type of conduction of a MoS<sub>2</sub> TFT is significantly affected by Metal/MoS<sub>2</sub> contact and MoS<sub>2</sub>/SiO<sub>2</sub> interface. In this work, Au was used as source/drain contact, which is reported to result in *n*-type behaviour. However, the TFT in Figure 4.9c displays *p*-type behaviour which means that the influence of MoS<sub>2</sub>/SiO<sub>2</sub> interface dominates, attributed to oxygen dangling bonds at the SiO<sub>2</sub> surface [88]. Therefore, to analyze the intrinsic property of as grown MoS<sub>2</sub>, EDLTs were fabricated which can avoid the influence of defect and disorders from MoS<sub>2</sub>/SiO<sub>2</sub> interface. The *n*-type behaviour observed in Figure 5.9b confirms that the previous *p*-type conduction of MoS<sub>2</sub> transistors originated from MoS<sub>2</sub>/SiO<sub>2</sub> interface.

#### 5.3.3.2 DFT Analysis of Synthesized MoS<sub>2</sub> films

To gain a deeper insight to the possible origin of the observed *n*-type behaviour, Vladimir Bačić from Jacobs University performed DFT calculations on bulk MoS<sub>2</sub> with two types of defects: (i) Mo atoms intercalated between the layers (Figure 5.10b), and (ii) S vacancies.



Figure 5.10 Side view of (a) pristine MoS<sub>2</sub> layer and (b) MoS<sub>2</sub> layer with intercalated Mo defect.



Figure 5.11 Bandstructure and DoS of MoS<sub>2</sub> with intercalated Mo atoms (middle and right figure on each of the four sub-panels) for various Mo:S atomic ratios: (a) Mo<sub>1.03125</sub>S<sub>2</sub>, (b) Mo<sub>1.05555</sub>S<sub>2</sub>, (c) Mo<sub>1.0625</sub>S<sub>2</sub> and (d) Mo<sub>1.08333</sub>S<sub>2</sub>. For comparison, bandstructures of the pristine MoS<sub>2</sub> (calculated for the corresponding supercell) are also shown (left figure on each subpanel). Since for each defect concentration different (supercell) cell was used, the bandstructures of pristine MoS<sub>2</sub> differ accordingly.

As mentioned before, the measured stoichiometry is most likely caused by defects clustering into "islands", while in the bulk of our film the stoichiometry (and the

structure) is closer to the pristine  $MoS_2$ . Therefore, the Mo:S ratio of ranged from  $\sim 1.85$  to  $\sim 1.94$  in our calculations (calculations on systems with lower defect concentrations were not possible due to limited computational resources).

It can be seen from Figure 5.11, intercalation of Mo atoms results in forming narrow filled bands in the band gap of pristine MoS<sub>2</sub> and shifting the Fermi level towards the CBM, which is a typical example of *n*-type doping. In the case of S vacancies, the situation is essentially reversed: the mid-gap states are empty and the Fermi level is shifted towards the VBM, showing the typical *p*-type behaviour. Similar results were reported for S vacancies in MoS<sub>2</sub> monolayer [113].

Despite the shortcoming of the DFT method in that it generally predicts wrong band gaps, our findings are qualitatively correct and conclude that the observed *n*-type behaviour is very likely caused by intercalated Mo atoms (rather than S vacancies). However, further research is needed to resolve this issue, and plan to approach it with more sophisticated (i.e. beyond-DFT) methods in the future.

# **5.4 Conclusion**

In summary, a solution based route for the fabrication of large area  $MoS_2$  thin films ( $\leq$ 3ML) on sapphire substrate using two-step annealing process has been demonstrated. The synthetic approach is simple and scalable with controllable film thickness over the whole substrate. Thickness scaling and improved film growth are attributed to the lattice commensurability, higher surface energy and better surface wettability of the cplane sapphire with MoS<sub>2</sub>, unlike amorphous SiO<sub>2</sub> substrate. AFM topography, Raman and XRD spectra indicate two-step annealing approach improved film crystallinity, enhanced grain size and surface coverage with reduced voids. The electrical behaviour of top-gate top-contact IL-gated TFT exhibit an *n*-type semiconductor behaviour with a high  $I_{on/off}$  ratio ~ 10<sup>6</sup> and field-effect mobility of ~ 12.07 cm<sup>2</sup>/Vs. Furthermore, DFT calculation shows that the *n*-type behaviour in the synthesized films originates from the intercalation of molybdenum atoms between the MoS<sub>2</sub> layers forming narrow filled band states close to the CBM. This is the first-time high mobility solution processed MoS<sub>2</sub> thin films on sapphire with centimeter-scale uniformity has been achieved which paves the way for the low-cost synthesis of large area 2D TMD thin films for various applications.

# **Chapter 6:** Growth of MoS<sub>2</sub> layers based on air-stable Mo-precursor

# 6.1 Introduction

The current state-of-the-art chemical vapour deposition (CVD) process is scalable but expensive and therefore low-cost wet-chemical synthesis methods such as dip-coating [20] and spin-coating [22,68,70] have gained impetus for synthesis of 2D TMDs. However, these scalable deposition methods use precursor solutions based on ammonium tetrathiomolybdate [20,22,70] or molybdenum(V) chloride [68] which decomposes over time [114] or reacts readily with moisture [69] respectively, thereby affecting the precursor film formation.

This chapter presents an improved method to synthesize layered MoS<sub>2</sub> thin films based on air stable Mo-precursor for solution phase deposition via spin-coating. The unique two-step annealing process results in an improved crystallinity, uniformity of the multi-layered films with an overall increase of the MoS<sub>2</sub> grain size. This is verified by the electrical performance of ionic liquid (IL) gated TFTs based on MoS<sub>2</sub> layers grown on sapphire substrates. IL-gated MoS<sub>2</sub> TFT devices exhibited *n*-type semiconducting behaviour with a high current on/off ratio and competitive mobility. Our findings show the MoS<sub>2</sub> film formation dictates the film morphology, crystallinity, chemical composition and electrical performance under various processing condition. The proposed route provides an alternative method for low-cost production of largearea MoS<sub>2</sub> thin films under atmospheric conditions via a wet-chemical approach.

# **6.2 Experiment**

## 6.2.1 MoS<sub>2</sub> Films Preparation

Bis(acetylacetonato)dioxomolybdenum(VI) (100 mg, 99.99%, Sigma Aldrich) was dissolved in 1-Methoxy-2-propanol (1 mL, 99.97%, CG Chemikalien GmbH & Co. KG) solvent and stirred overnight to form a stable precursor solution. The solution was spin-coated at 3000 rpm for 60 s on c-plane (0001) sapphire substrates (99.998%, Siegert Wafer GmbH) to form uniform films over a large area (2 x 2 cm<sup>2</sup>) under atmospheric conditions. The substrate cleaning and pre-treatment procedure are the same as in Chapter 5.



Figure 6.1 Schematic illustration of the synthesis of MoS<sub>2</sub> films from liquid phase using two-step annealing under atmospheric conditions.

The coated samples were then pre-annealed at 150 °C for 10 minutes to remove the residual solvent from the coated film. Both the precursor solution preparation and pre-annealing were carried out in an ambient environment. The coated samples and a quartz boat holding pure sulfur (4.6 g, 99.9995%, Alfa Aesar) were then placed in the middle and near the edge (upstream) of the tube furnace (Friatec, Al<sub>2</sub>O<sub>3</sub> tube), respectively as shown in Figure 6.1. After purging the Al<sub>2</sub>O<sub>3</sub> tube with Argon (Ar) gas,

the gas flow was changed to 2.4%  $H_2$  in Ar while the furnace temperature was gradually increased from room temperature to target temperature (900 °C or 980 °C) with a heating rate of 50 °C/min. The temperature was maintained at the final annealing temperature for 60 minutes before cooling down to room temperature in the presence of Ar. Finally, post-annealing treatment was performed on the sulfurized films covered with blank sapphire at 980 °C for 60 minutes in Ar gas only to avoid unwanted reduction of the sulfur in the presence of H<sub>2</sub>.

# 6.2.2 Characterization of MoS<sub>2</sub> films

The deposited films were characterized by different techniques defined in section 2.5 to observe morphology and crystalline structures and to investigate film composition and crystallinity. Using a scalpel, the film surface was scratched to determine the film thickness using AFM. Geological MoS<sub>2</sub> single crystal purchased from SPI supplies was used as a reference for the characterization of synthesized MoS<sub>2</sub> films.

# 6.2.3 Fabrication of IL-gated MoS<sub>2</sub> TFTs

*Preparation of IL gel*: Experimental procedure as described in section 5.2.3. *Fabrication of IL-gated device*: Top-gate top-contact IL-gated TFTs based on solution processed MoS<sub>2</sub> thin films were fabricated with the IL gel tape on sapphire substrates (Figure 6.2) using the experimental procedure described in section 5.2.3.



Figure 6.2 Optical image of an IL-gated MoS<sub>2</sub> transistor fabricated on sapphire substrate.

# **6.3 Results and Discussion**

# 6.3.1 Characterization of MoS<sub>2</sub> Films from air-stable Molybdenum Precursor



Figure 6.3 AFM topography of MoS<sub>2</sub> films processed on sapphire at (a, c) 900 °C and (b, d) 900 °C with an additional post-annealing at 980 °C. Corresponding section profile of MoS<sub>2</sub> on sapphire annealed at (e) 900 °C and (f) 900 °C with an additional post-annealing at 980 °C.
AFM measurements were performed to shed light on the surface morphology of the chemically synthesized MoS<sub>2</sub> films on sapphire substrates annealed at 900 °C and 900 °C with an additional post-annealing treatment at 980 °C. Figure 6.3a-d illustrates the AFM topography images of MoS<sub>2</sub> films prepared from 100 mg/mL Mo-precursor solution under different annealing conditions. Films synthesized at 900 °C demonstrated a film thickness of 2.29 nm (Figure 6.3a and e) and a rms roughness of 0.471 nm (Figure 6.3c). The surface morphology of the synthesized films shows the formation of randomly distributed single-layer MoS<sub>2</sub> islands which could adversely affect the electrical performance of an IL-gated TFT. To mitigate this issue, MoS<sub>2</sub> thin films were synthesized with a two-step annealing process. This resulted in a thinner film and lower rms roughness of 1.71 nm (Figure 6.3b and f) and 0.231 nm (Figure 6.3d), respectively. The topography of MoS<sub>2</sub> films (Figure 6.3d) shows improved surface coverage and larger grains attributed to the cohesion of the smaller grains upon post-annealing treatment. It is also observed, that the growth of the MoS<sub>2</sub> film is aligned to the substrate step edges due to miscut of the sapphire surface, similar to reports found in the literature [28]. The formation of a connected channel is crucial for fabrication of MoS<sub>2</sub> TFTs. However, these films occasionally show the formation of monolayer ( $\sim 0.72$  nm) MoS<sub>2</sub> as shown in the section profile in Figure 6.3f. Thus, postannealing treatment of these films resulted in lower roughness with improved crystallinity. To delineate the MoS<sub>2</sub> film growth, crystallinity and to understand the layer formation on sapphire, XRD and Raman studies were performed.

X-ray diffraction measurements further investigated the crystallinity of these solution processed MoS<sub>2</sub> films on sapphire under different annealing temperatures. Figure 6.4a illustrates the  $\theta$ - $\theta$  scans of 25 nm thick MoS<sub>2</sub> films annealed at 900 °C, 900 °C with an additional post-annealing treatment at 980 °C, bare sapphire and for geological bulk MoS<sub>2</sub> crystal. Additionally, reference peak positions (2 $\theta$ ) in dark cyan colour for 2H-MoS<sub>2</sub> powder is provided for comparison. The reference bulk MoS<sub>2</sub> crystal exhibits sharp (002), (004) and (006) diffraction peaks at 2 $\theta$  = 14.4°, 29.1° and 44.2°, respectively. The diffractogram for the sample annealed at 900 °C demonstrates a distinct (002) peak at 2 $\theta$  = 14.4°, while higher order peaks (004) and (006) are barely visible thereby suggesting, that a higher annealing temperature to improve the crystallinity of the films. As expected, samples processed with two-step annealing treatment show a sharp (002) peak with improved line width and higher order peaks were evident, indicating long-range crystalline order. Thereby, improving the MoS<sub>2</sub> film structural quality and crystal orientation. The very fine diffraction peaks in the diffractogram are due to the underlying crystalline sapphire substrate.



Figure 6.4 Optical characterization of fabricated MoS<sub>2</sub> thin films. (a) X-ray diffraction spectra of MoS<sub>2</sub> films for different annealing process, bulk MoS<sub>2</sub> and sapphire substrate. (b) Raman spectra of MoS<sub>2</sub> films obtained after different annealing temperatures and process.

An average distance of 6.17 Å between two  $MoS_2$  layers in a 2H structure was calculated from the (002), (004) and (006) diffraction peaks. Using Scherrer equation (*Eq. 2.3*) [63], samples annealed at 900 °C and 900 °C with additional post-annealing treatment at 980 °C demonstrated a crystallite size of 9 nm and 31 nm respectively, as an effective thickness of the grains in the direction perpendicular to the diffraction plane (002). The increase in crystallite size demonstrates that the two-step annealing process significantly improves the film crystallinity and promotes the formation of larger grains.

Formation of MoS<sub>2</sub> films through solution phase processing under various annealing temperatures was further investigated by Raman spectroscopy. Raman spectra of asdeposited MoS<sub>2</sub> thin films as well as geological MoS<sub>2</sub> crystal were collected for comparisons. Figure 6.4b shows the Raman spectra obtained from as-deposited MoS<sub>2</sub> films (100 mg/mL Mo-precursor solution) on sapphire substrate under different annealing temperatures. Two typical Raman active modes are observed in this spectral range: the out-of-plane vibration (c-axis) of S atoms (A<sub>1g</sub>) with a Raman shift of ~407 cm<sup>-1</sup> and the in-plane vibration (basal plane) of Mo and S atoms (E<sup>1</sup><sub>2g</sub>) at ~383.3 cm<sup>-1</sup> [58]. This confirms the formation of semiconducting 2H-MoS<sub>2</sub> layers. Furthermore, the reduced separation  $\Delta \omega = 23.7 \text{ cm}^{-1}$  (compared to 25 cm<sup>-1</sup> for bulk MoS<sub>2</sub>) between A<sub>1g</sub> and E<sup>1</sup><sub>2g</sub> modes indicates formation of thin MoS<sub>2</sub> films [58]. In Figure 6.4b, the lower growth temperatures (900 °C) exhibited lower peak intensity of E<sup>1</sup><sub>2g</sub> and A<sub>1g</sub> attributed to relatively low crystallinity and structural film property compared to the bulk geological MoS<sub>2</sub> crystal [50]. While samples grown at 900 °C with an additional post-annealing treatment at 980 °C, demonstrated 1.3 times higher intensity than samples only annealed at 900 °C. Thus, Raman measurements verify the trends evident from the X-ray diffraction spectra that higher post-annealing temperature is vital for the formation of high-quality MoS<sub>2</sub> films.



Figure 6.5 XPS spectra of fabricated MoS<sub>2</sub> film on sapphire substrate processed at 900 °C with additional post-annealing at 980 °C: (a) and (b) corresponds to the binding energy of Mo 3d and S 2s, and S 2p core levels respectively.

XPS was conducted to explore the chemical bonding state and stoichiometry of MoS<sub>2</sub> film grown on sapphire substrate. Figure 6.5a-b exhibits Mo 3d, S 2s, and S 2p core level spectra which were evaluated using Shirley background and a symmetric peak shape defined by a convolution of Gauss and Lorentz peaks for peak fitting. The spectra reveal the existence of Mo<sup>4+</sup> peaks at 229.7 eV (3d<sub>5/2</sub>) and 232.8 eV (3d<sub>3/2</sub>), and S<sup>2-</sup> peaks at 162.5 eV (2p<sub>3/2</sub>) and 163.7 eV (2p<sub>1/2</sub>). These binding energies are similar to the reported values for MoS<sub>2</sub> crystals [78,101,102]. The absence of Mo<sup>6+</sup> (3d<sub>3/2</sub>) peak at 236 eV and S 2p peak between 168 and 170 eV signifies that the level of oxidation is negligible and the synthesized MoS<sub>2</sub> layers were composed only of Mo and S species. Samples annealed in Ar/H<sub>2</sub> and sulfur environment at 900 °C and 900 °C with an additional post-annealing treatment at 980 °C demonstrated a chemical composition of Mo:S ~ 1:1.94 and 1:1.87, respectively. It is observed that the sulfur

concentration is 6.5% lower in the post-anneal treated films, in comparison to ideal 1:2 stoichiometry. This can give rise to regions with point defects [79,80,87] in the MoS<sub>2</sub> film which can act as scattering and trapping centers thereby affecting the electrical properties of the solution processed MoS<sub>2</sub> films.

#### 6.3.2 Electrical Performance of IL-gated MoS<sub>2</sub> TFT

The electrical performance of the MoS<sub>2</sub> thin films with different annealing conditions on sapphire substrates was evaluated by fabricating top-gate top-contact IL-gated TFTs as shown in Figure 6.2. The device was operated in the linear regime to avoid chemical reaction by exceeding the electrochemical window of the IL. Figure 6.6a shows the transfer characteristics ( $I_d$  versus  $V_{gs}$ ) of IL-gated TFTs on MoS<sub>2</sub> processed at 900 °C and 900 °C with an additional post-annealing treatment at 980 °C on sapphire substrate measured at a drain-source voltage V<sub>ds</sub> of 0.25 V (channel length 155 μm). MoS<sub>2</sub> films synthesized with two-step annealing treatment demonstrated the highest  $I_{d}$ . This is attributable to improved crystallinity, enhanced grain size and surface coverage with reduced voids as seen in Figure 6.3d and Figure 6.4a. Unlike post-anneal treated samples, annealing at 900 °C demonstrated higher threshold voltage ( $V_t$ ) attributed to the rough morphology (Figure 6.3c) of the MoS<sub>2</sub> film which results in higher accumulation of ions on the MoS<sub>2</sub> surface to form a closed channel. Figure 6.6b illustrates the measured and fitted transfer characteristics (channel length 55  $\mu$ m) of a two-step annealed MoS<sub>2</sub> layer. The IL-gated TFT exhibited an OFF-state  $I_d$ ~  $4.65 \times 10^{-8}$  A ( $V_{gs}$  = -3 V) and an ON-state current  $I_d$  ~  $2.68 \times 10^{-3}$  A ( $V_{gs}$  = +3 V), thus yielding an on/off current ratio  $\sim 5.96 \times 10^4$ . Fabricated devices with post-annealing treated MoS<sub>2</sub> films exhibited *n*-type behaviour with field-effect mobility  $\sim$ 16.09 cm<sup>2</sup>/Vs for  $V_{gs}$  = +3 V calculated using equation 5.1 with IL gate capacitance  $C_{IL}$  =  $6.42 \mu F/cm^2$ . This device mobility is comparable to the results obtained in Chapter 5 and is 1 - 2 orders of magnitude higher than the typical range for most of the previously reported wet-chemically synthesized, exfoliated MoS<sub>2</sub> and CVD grown MoS<sub>2</sub> films containing numerous grains. Thus, Bis(acetylacetonato)dioxomolybdenum(VI) precursor (air-stable) can be a good substitute for the reactive Molybdenum(V)chloride precursor (stable in an inert environment) used in the synthesis of MoS<sub>2</sub> films.



Figure 6.6 Electrical measurements of IL-gated MoS<sub>2</sub> TFTs. (a) Transfer curve (L=155 μm) of MoS<sub>2</sub> processed at 900 °C and 900 °C with an additional post-annealing at 980 °C. (b) Transfer curve (L=55 μm) of MoS<sub>2</sub> with two-step annealing process. TFT IV data (blue open circles) measured at 300 K. Gate voltage dependent fit (Equation 5.2, red curve) is used to reproduce the measured data. (c) Output curve of IL-gated MoS<sub>2</sub> TFT with two-step annealing process.

Annealing conditions	Substrate	MoS <sub>2</sub> thickness (nm)	γ	V <sub>t</sub> (V)	μ (cm²/Vs)	R <sub>bulk</sub> (MΩ)	Ion/Ioff ratio
900 °C (Ar+H <sub>2</sub> ) w/ 980 °C (Ar)	Sapphire	1.2 ± 0.65	0.48	1.08	7.56	5.50	~ 104

Table 6.1 Fitting parameters (with  $V_{aa} = 1 V$ ) obtained from the transfer curve for IL-gated MoS<sub>2</sub> TFTswith a two-step annealing process.

Using equation 5.2 and 5.3 (with  $V_{aa} = 1$  V) on the measured I-V data, a numerically fitted transfer characteristic curve (red line) was obtained with good agreement. Table 6.1 shows all the calculated fitting parameters. It is observed the device exhibits poor  $I_{on/off}$  ratio due to high "OFF" state current (low R<sub>bulk</sub>) flowing through the MoS<sub>2</sub> film. This can be attributed to the presence of any conducting defects such as aromatic

carbons from the organic solvent and Mo-clusters which could affect the "OFF" state current.

Figure 6.6c shows the output characteristics of a post-annealing treated MoS<sub>2</sub>.  $I_d$  as a function of applied drain-to-source voltage ( $V_{ds}$ ) of an IL-gated TFT for different applied  $V_{gs}$  is plotted. The linear regime of transistor operation ( $V_{ds} < 0.1$  V) in the output characteristics suggests the absence of a significant barrier for charge carrier injection. The current  $I_d$  distinctly increases as  $V_{ds}$  increases for a positive  $V_{gs}$ , exhibiting an *n*-type semiconducting behaviour which is also observed in naturally grown MoS<sub>2</sub> crystal [105].

#### **6.4 Conclusion**

In this chapter, a solution based route is developed to prepare large-area MoS<sub>2</sub> films ( $\leq$  3ML) with excellent layer-to-layer controllability by simple sulfurization of spincoated air-stable Mo-precursor (Bis(acetylacetonato)dioxomolybdenum(VI)) in an organic solvent. AFM topography, Raman and XRD spectra indicate two-step annealing approach improved film crystallinity, enhanced grain size and surface coverage with reduced voids. The electrical behaviour of top-gate top-contact IL-gated TFT exhibit an *n*-type semiconductor behaviour with a  $I_{on/off}$  ratio ~ 10<sup>4</sup> and field-effect mobility of ~ 16.09 cm<sup>2</sup>/Vs. IL-gating provides an effective route to understand the properties of the synthesized MoS<sub>2</sub> film and assist in optimizing the material synthesis. Further investigations need to be done for more quantitative analysis. The simple wetchemical synthesis is promising to realize centimeter-scale uniformity MoS<sub>2</sub> thin film for device fabrication.

## **Chapter 7: Conclusions and Outlook**

The focus of this thesis is on synthesis, device fabrication, physical and electrical characterization of solution processed layered MoS<sub>2</sub> semiconductors to pave the way for commercializing modern electronic devices made of 2D materials. Two different wet-chemical methods were explored, i.e. top-down and bottom-up approach to synthesize MoS<sub>2</sub> nanosheets and films for low-cost scalable deposition.

Chapter 3 focuses on solvent-assisted liquid phase exfoliation (LPE) of bulk MoS<sub>2</sub> in NMP, sodium cholate and 2-propanol to achieve dispersion of MoS<sub>2</sub> nanosheets with high yield. Removal of residual solvents from the MoS<sub>2</sub> nanosheets such as NMP (high boiling point) and sodium cholate (thermal treatment) posed a challenge and therefore 2-propanol was chosen for its ease of use. The MoS<sub>2</sub> nanosheets thicknesses varied from few-layers to monolayer while the lateral size varied from 100-800 nm. The reduced lateral size is attributed to schism during ultra-sonication. Also, the uniform coating of these nanosheets coupled with the grain-to-grain contact resistance poses a severe bottleneck when using dip-coating method aiming for device fabrication based on coating techniques. Furthermore, the CBD method leads to the formation of thick MoS<sub>2</sub> films (>10 nm) with varying surface morphology and poor crystallinity. Therefore, the above synthesis methods (LPE and CBD) although low-cost and scalable are not suitable for the synthesis of large-area layered MoS<sub>2</sub> films (<10 nm) crucial for device fabrication.

To mitigate the above issue, a novel route to synthesize large-area MoS<sub>2</sub> films based on liquid phase Mo-precursor was developed using the bottom-up approach as described in Chapter 4. Simple sulfurization of a spin-coated formulation (MoCl<sub>5</sub> in 1M2P) on SiO<sub>2</sub> substrate resulted in uniform growth of MoS<sub>2</sub> films with layer-to-layer controllability. The synthesized films were polycrystalline with 2H-MoS<sub>2</sub> structure. The stoichiometry and crystallinity of the MoS<sub>2</sub> film are strongly dependent on the annealing temperature attributed to the reduction of Mo-precursor and sulfur diffusion. Electrical measurement of bottom-gate top-contact transistors exhibited a dominant *p*-type semiconductor behaviour with a current on/off ratio of  $10^2$  and field effect mobility of  $0.03 \text{ cm}^2/\text{Vs}$ . The poor device electrical performance is attributed to excess sulfur and the polycrystalline nature of the MoS<sub>2</sub> film. This low-cost, non-vacuum and scalable wet-chemical approach is suitable also for preparation other 2D TMDs thin films.

Chapter 5 presents an improved method to synthesize large area  $MoS_2$  thin films ( $\leq$ 3ML) on sapphire substrate using a two-step annealing process. This results in an improved crystallinity, uniformity (surface coverage with reduced voids) of the multilayered films together with an increase of the MoS<sub>2</sub> grain size. Thickness scaling and improved film growth are attributed to the lattice commensurability, higher surface energy and better surface wettability of the c-plane sapphire with MoS<sub>2</sub>, unlike amorphous SiO<sub>2</sub> substrate. The above improvements are translated into a superior electrical performance of top-gate top-contact IL-gated TFT exhibiting an *n*-type semiconductor behaviour with a high  $I_{on/off}$  ratio ~ 10<sup>6</sup> and field-effect mobility of ~ 12.07 cm<sup>2</sup>/Vs. IL-gating provided an effective strategy to study the intrinsic properties of the synthesized MoS<sub>2</sub>. Additionally, interface effects of MoS<sub>2</sub>/substrate and thickness dependence were discussed to comprehend the properties of MoS<sub>2</sub>. DFT calculation shows that the *n*-type behaviour in the synthesized films originates from the intercalation of molybdenum atoms between the MoS<sub>2</sub> layers forming narrow filled band states close to the CBM. This is the first-time, high mobility solution processed MoS<sub>2</sub> thin films on sapphire with centimeter-scale uniformity has been achieved. This paves the way for the low-cost synthesis of large area 2D TMD thin films.

Using the same synthesis method, a study on air-stable Mo-precursor (Bis(acetylacetonato)dioxomolybdenum(VI)) in an organic solvent is described in Chapter 6. MoS<sub>2</sub> films demonstrated improved film crystallinity, enhanced grain size and surface coverage with reduced voids. The electrical behaviour of top-gate top-contact IL-gated TFT exhibit an *n*-type semiconductor behaviour with a  $I_{on/off}$  ratio ~ 10<sup>4</sup> and field-effect mobility of ~ 16.09 cm<sup>2</sup>/Vs which confirm the excellent quality of MoS<sub>2</sub> film. This approach allows for ease of handling of the spin-coated substrates in the air compared to N<sub>2</sub> environment. Further investigations need to be done for more quantitative analysis.

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# **List of Publications**

#### **Journal Contributions**

**Francis Oliver Vinay Gomes**, Anuj Pokle, Marko Marinkovic, Torsten Balster, Meghan Canavan, Karsten Fleischer, Ralf Anselmann, Valeria Nicolosi and Veit Wagner, Influence of temperature on morphological and optical properties of MoS<sub>2</sub> layers as grown based on solution processed precursor, Thin Solid Films. 645 (2018) 38–44. doi: 10.1016/j.tsf.2017.10.022.

**Francis Oliver Vinay Gomes**, Anuj Pokle, Marko Marinkovic, Torsten Balster, Ralf Anselmann, Valeria Nicolosi and Veit Wagner, High mobility solution processed MoS<sub>2</sub> thin film transistors, Solid-State Electronics. 158 (2019) 75–84. doi: 10.1016/j.sse.2019.05.011.

### **Conference Contributions**

Xiaoling Zeng, **Francis Oliver Vinay Gomes**, Marlis Ortel, Marko Marinkovic, Jochen Brendt and Veit Wagner. Poster: Solution Processed and Exfoliated MoS<sub>2</sub> Nanosheets. Flatlands beyond graphene 2014, Dublin, Ireland, July 9-11, 2014.

**Francis Oliver Vinay Gomes**, Marko Marinkovic, Jochen Brendt, Torsten Balster and Veit Wagner. Poster: Deposition and growth of solution processed MoS<sub>2</sub> films, Flatlands beyond graphene 2015, Tel Aviv, Israel, July 7-9, 2015.

**Francis Oliver Vinay Gomes**, Marko Marinkovic, Jochen Brendt, Torsten Balster and Veit Wagner. Oral presentation: Novel deposition approach of semiconducting MoS<sub>2</sub> thin films and their application for electronic devices. Frühjahrstagung der Deutsche Physikalische Gesellschaft (DPG), Regensburg, Germany, March 6-11, 2016.

**Francis Oliver Vinay Gomes**, Marko Marinkovic, Jochen Brendt, Torsten Balster and Veit Wagner. Poster: *P*-type MoS<sub>2</sub> thin film transistors fabricated from liquid phase. Flatlands beyond graphene 2016, Bled, Slovenia, July 5-8, 2016.

**Francis Oliver Vinay Gomes**, Anuj Pokle, Marko Marinkovic, Jochen Brendt, Torsten Balster, Valeria Nicolosi, Ralf Anselmann, and Veit Wagner. Poster: Liquid phase synthesis of MoS<sub>2</sub> thin films and its thin film transistor applications, MRS Fall 2016 Meeting, Boston, United States, November 27-December 2, 2016.

**Francis Oliver Vinay Gomes**, Xiaoling Zeng, Marko Marinkovic, Torsten Balster and Veit Wagner. Oral presentation: Ionic Liquid Gating of Solution Processed MoS<sub>2</sub> Thin Film Transistors. Frühjahrstagung der Deutsche Physikalische Gesellschaft (DPG), Dresden, Germany, March 19-24, 2017.

Talha Nisar, Torsten Balster, **Francis Oliver Vinay Gomes** and Veit Wagner. Oral presentation: Novel deposition approach of MoS<sub>2</sub> thin films for hydrogen evolution reaction. Frühjahrstagung der Deutsche Physikalische Gesellschaft (DPG), Regensburg, Germany, March 31-April 5, 2019.